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MESOGENIC LOW MOLECULAR AND POLYMERIC HYDRAZIDES. I. SYNTHESIS

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ABSTRACT

Synthesis and characterization of new mesogenic N,N′-bis[3,4,5-tris(alkoxy)benzoyl]hydrazides are described. Polyhydrazides, containing the tris(alkoxy)benzoylhydrazide unit in the main chain have been prepared by polycondensation of a monoacylhydrazide and an acid chloride component. Three well defined model compounds with different substitution pattern of the aromatic core have been obtained. Phase transition temperatures and transition enthalpies of all compounds, determined by DSC-measurements, are given.

INTRODUCTION

Main chain liquid crystal polymers (MCLCPs), exhibiting discotic mesophases are of considerable interest because of their mechanical and optical properties. Incorporation of classical discotic mesogens, consisting of rigid aromatic cores with six or more flexible side chains, into a polymeric backbone can only be accompanied by functionalisation of two of the side chains [1-8]. Columnar mesomorphism can be obtained without using disk-shaped mesogenes, if an oriented interaction is present, prefering disk-shaped geometries of the aggregates by self-organization. As known since a long time, intermolecular hydrogen bonding is able to cause the formation of liquid crystalline phases [e.g.: 9 - 18]. In a recent study it was shown, that the combination of flexible alkoxy chains and amidic hydrogen bonds can lead

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to a new class of columnar mesogens, the "three chain" primary benzamides [19]. The aim of this work is the synthesis of new polyhydrazides, exhibiting columnar mesomorphism. In the first part of this study, synthesis, spectroscopic characterisation and phase-behaviour of the synthesized alkoxybenzoylhydrazides are reported. Detailed investigations of the columnar mesophases will be given in an subsequent paper.

MATERIALS

1. Alkoxybenzoylhydrazides

N,N'-bis[3,4,5-tris(alkoxy)benzoylhydrazides ("three chain" hydrazides, **2**, FIGURE I) can be obtained by addition of hydrazine hydrate [18] to a solution of the corresponding 3,4,5-tris(alkoxy)benzoic acid chloride **1** in dry 1,4-dioxane. Homologous alkoxybenzoylhydrazides were synthesized with the chain lengths n = 3-12 and 14.

2. Monomers

In the first step, two of the phenolic hydroxy groups of commercial available gallic acid methyl ester (FIGURE II, **3**) are protected by using diphenyldichlormethane, as described by L. Jurd [20]. The obtained product **4** is converted into the bis-ester **5** by condensation with 1,10-dibromodecane. The protective groups are removed by boron trichloride in dry methylene chloride. In a subsequent step the phenolic hydroxy groups of **6** are alkylated and the key-intermediate for the monomer-synthesis, 1,10-bis[3',4'-bis(alkoxy)-1'-carboxymethoxy-phenyl-5'-oxy]decane, **7**, is obtained. Bis-ester **7** can be treated further in two ways: First, the two ester groups are saponificated with ethanolic potassium hydoxide solution and the resulting carbonic acid is directly converted into the corresponding bis[acid chloride] **8**. Addition of hydrazine hydrate and n-pentanol to bis-ester **7** leads to the formation of the bis[monoacylhydrazine] **9**. Monomers **8** and **9** were synthesized with propyloxy- and hexyloxy-chains (propyloxy: **8a**, **9a** / hexyloxy: **8b**, **9b**).

3. Model compounds

Model compounds **11a** and **11b**, being the "twins" of hydrazides **2** (FIGURE IIIa) are simply obtained by the N,N'-dimethylaminopyridine catalyzed reaction of **9** with 3,4,5-tris(decyloxy)benzoic acid chloride **10** in dry tetrahydrofurane. For the synthesis of model compound **15**, two additional steps are necessary (FIGURE IIIb). Analogous to the synthesis of **5** from **4** (comp. FIGURE II), two mols of 4-hydroxy-benzoic acid methyl ester **12** are coupled via a decamethylenedioxy bridge. After that, the "one-chain bis ester" **13** is hydrazinolyzed to the 1,10-bis[1'-carboxyhydrazyl-phenyl-4'-oxy]decane **14**. From this, model compound **15** is received by simple addition of acid chloride **10**.

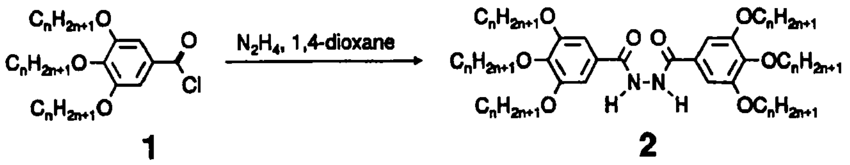

FIGURE I

Synthesis of N,N′-bis[3,4,5-tris(alkoxy)benzoyl]hydrazides, 2

(2a: n = 3 - 2k: n = 12, 2l: n 14)

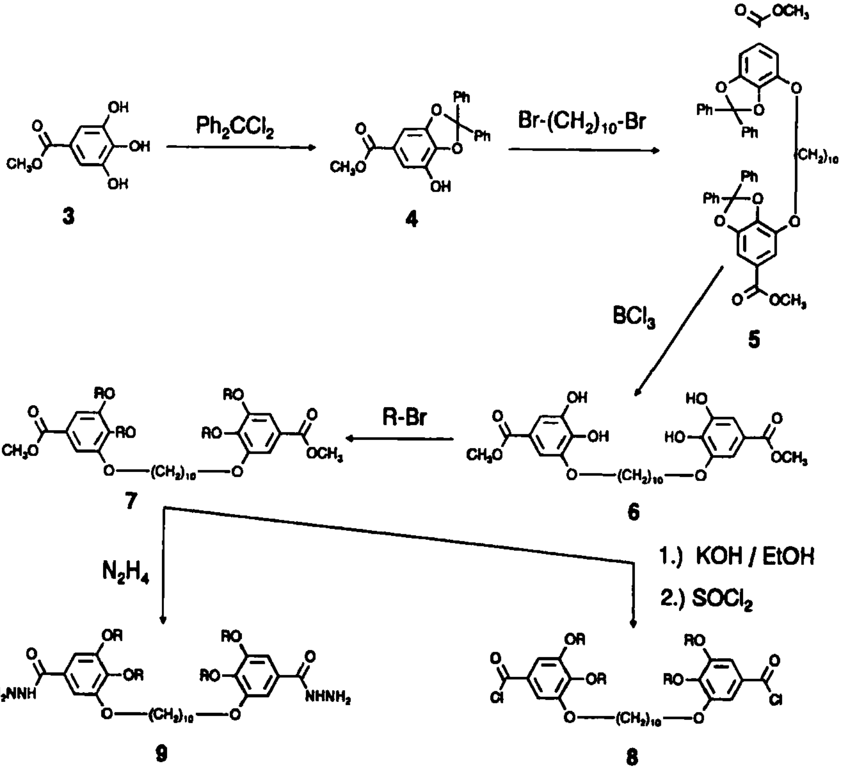

FIGURE II

Synthesis of monomers 8 and 9

(R = C_nH_{2n+1}: 7a, 8a, 9a: n = 3, 7b, 8b, 9b: n = 6)

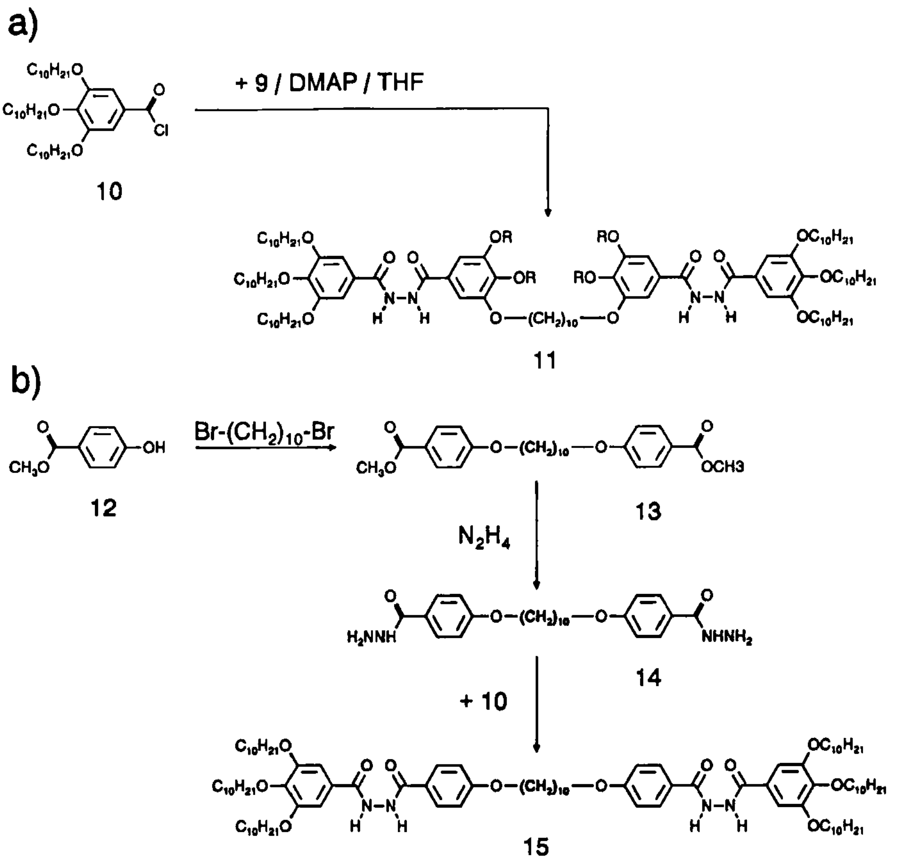

FIGURE III

Synthesis of model compounds 11 and 15

(IIIa: R=C_nH_{2n+1}, n = 3 : 11a, n = 6 : 11b)

4. Poly(alkoxybenzoylhydrazides)

Polymer synthesis, via polycondensation (FIGURE IV), was performed by mixing a solution of a bis(monoacylhydrazine) monomer (9 or 14) with a solution of the bis(acid chloride) 8. The degree of polymerisation was controlled via the stoechiometric ratio of {acid chloride : hydrazide}. In every case, an excess of hydrazide component was used to obtain polymers with defined hydrazide end groups. Additionally, the excess of hydrazide groups should prevent crosslinking,

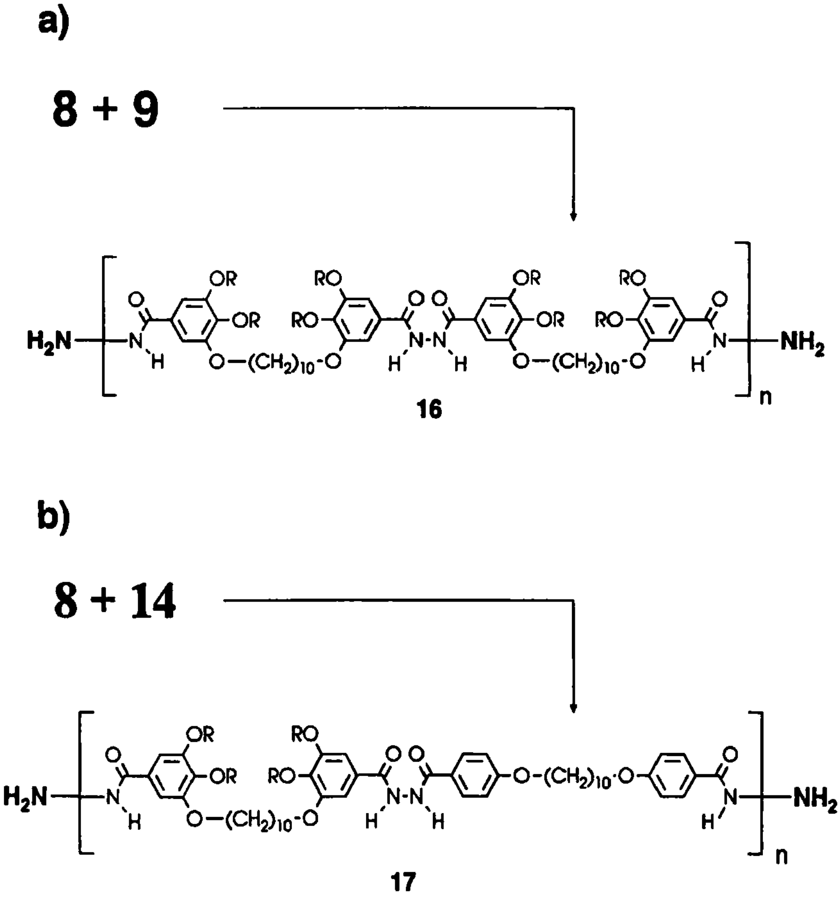

FIGURE IV

Synthesis of poly[alkoxy)benzoyl] hydrazides 16 and 17

(IVa und IVb: R = C_nH_{2n+1}, 16a: n = 3, 16b: n = 6, 17: n = 6) caused by reaction of acid chloride groups with N,N'-bisacyl-hydrazide groups in the polymeric main chain.

Two types of poly(alkoxybenzoylhydrazides) were prepared (cf. TABLE II). Polymers **16** are homopolymers, containing only the structural unit of the "three chain" hydrazide **2** in their main chain (**16a** bearing propyloxy-, **16b** hexyloxy-chains). Samples **16a**-1,2 and **16b**-1 - **16b**-4 are polymers with different molecular weights, obtained by runs with various stoechiometric ratios.

In contrast to this, polymeric compounds **17** are copolymers, composed of "three chain/one chain" hydrazide units.

METHODS

For DSC measurements, a PERKIN-ELMER DSC 7 unit was used. Infrared spectra were taken from a BIORAD FTS-40 spectrophotometer, ^{1}H-NMR (250 MHz) and ^{13}C-NMR (63 MHz) spectra from a BRUKER AC250 model. Mass spectra were obtained from a VARIAN MAT 312 spectrometer. SEC measurement were performed with a WATERS Modell 590, containing four Polymer Laboratories columns (50, 100, 1000 and 5000 nm pore size, 30.5 cm length)

RESULTS AND DISCUSSION

The thermal behaviour of all compounds was investigated by DSC measurements and additionally by polarizing microscopy. The results are summarized in TABLE I (low molecular compounds) and TABLE II (polymers). All the investigated tris-(alkoxy)benzoylhydrazides **2** and model compounds **11b** exhibit enantiotropic mesomorphism. The clearing temperatures of **2** and **11b** are in the range between 140 ^{O}C and 210 ^{O}C, showing the stability of the mesophase. In the series of compound **2**, clearing temperatures decrease with increasing length of the alkoxy chains. The values of the clearing enthalpies are rather high ($10 < \Delta H_C < 15$ kJ/mol), indicating a highly ordered mesophase. Compound **11a** is monotropic, because the propyloxy chains attached to the central part of the molecule are perhaps too short to guaranty optimal space filling. From this, it is not surprising, that the mesophase stability of model compound **15** ($T_C = 115$ ^{O}C, $\Delta H_C = 4$ kJ/mol), bearing a lower number of alkoxy chains, is the poorest one of all investigated substances.

Polymeric compounds **16** exhibit mesomorphic states, with transition temperatures depending on the length of the alkoxy chains and the molecular weight. In all cases, the propyloxy-chains containing materials show higher clearing temperatures then the polymers with hexyloxy chains (compare TABLE II). The poly[(propyloxy)-benzoylhydrazide] **16a**-2 shows a very poor solubility and cannot be characterized properly. In contrast to the common behaviour that the transition temperatures

TABLE I

Transition temperatures and enthalpies of N,N′-bis[3,4,5-tris(alkoxy)benzoyl]-hydrazides (2a - 2l) and model compounds (11a, 11b, 15)

Compound	C_2		C_1		M		I
2a (n = 3)	•	183.5 (2.0)(a)	•	199.5 (17.2)	•	209.0 (13.8)	•
2b (n = 4)	•	147.5 (31.9)(a)	•	163.0 (13.8)	•	199.0 (13.1)	•
2c (n = 5)			•	147.9 (18.3)	•	185.0 (10.8)	•
2d (n = 6)			•	141.0 (15.3)	•	176.0 (11.5)	•
2e (n = 7)			•	143.0 (14.1)	•	165.0 (10.0)	•
2f (n = 8)			•	139.0 (12.3)	•	141.4 (12.3)	•
2g (n = 9)			•	143.5 (14.1)	•	158.5 (14.5)	•
2h (n = 10)	•	81.5 (69.8)	•	148.0 (14.4)	•	154.5 (14.4)	•
2i (n = 11)			•	149.0 (14.8)	•	151.0 (14.5)	•
2k (n = 12)	•	6.0 (19.2)	•	143.2 (29.6)(b)	•	150.5	•
2l (n = 14)	•	31.7 (31.1)	•	140.0 (30.4)(b)	•	141.0	•
11a (n = 3)			•	148.0 (41.6)	•	[147.0 (14.9)]	•
11b (n = 6)			•		•	141.0 (13.7)	•
15			•	126.0(78.6)(a)	•	115.0 (4.0)(c)	•

C_1 and C_2 : crystalline phases, M : mesophase, I : isotropic phase, heating rate: 10 K/min, transition temperatures in °C, in brackets: transition enthalpies in kJ/mol, (a) first heating only, (b) summarized melting and clearing enthalpy, (c) monotropic with respect to the crystalline virgin phase, [···] monotropic phase

increase with increasing molecular weight till a constant value [24], the clearing temperatures of polymers **16b**-1 - **16b**-5 decrease with increasing molecular weight. In the range of $M_n \approx 10000$ g/mol, a lower limiting value of $T_c \approx 145$ °C is reached.

It is assumed, that this dependence is caused by a sterical hindrance due to the next-neighbours in the polymeric back bone. Additionally, end group effects can not be excluded.

TABLE II

Molecular weights and transition temperatures of investigated poly[(alkoxy)benzoylhydrazides] (16 and 17)

Polymer	n	M_n	M_w	T_g	T_c
16a-1	(n = 3)	2730	6610	175	193
16a-2	(n = 3)	----(a)	----(a)	154	196
16b-1	(n = 6)	3590	5460	116	154
16b-2	(n = 6)	3650	7630	118	154
16b-3	(n = 6)	3790	7980	115	153
16b-4	(n = 6)	6940	14320	110	151
16b-5(b)	(n = 6)	14880	20220	105	147
17	(n = 6)	2600	----(c)	100	----

M_n, M_w in g/mol: SEC values, T_g : glass transition temperature, T_c : clearing temperature, temperatures in °C, heating rate : 10 K/min, (a) sample insoluble, (b) high molecular fraction from 16b-4, (c) not determined

In accordance with literature [24], polymers 16a and 16b exhibit higher clearing temperatures and more stable mesophases than their model compounds 11a and 11b. Furthermore all polymeric compounds don't show any crystalline phases but only glass transitions.

Polymer 17, containing the substitution pattern of compound 15, is not a liquid crystal, it seems that the disturbation caused by the polymeric back bone is too strong for the occurance of a mesophase in this system.

The results of the thermal investigations demonstrate clearly, that skillful combination of amidic hydrogen bonding and flexible alkyl chains can be used to produce new low- and highmolecular mesogenic compounds. Investigations on the mesophase structure in the hydrazide systems will be published in a subsequent paper.

EXPERIMENTAL SECTION

N,N'-bis[3,4,5-tris(alkoxy)benzoyl]hydrazides (2):

Different alkoxybenzoylhydrazides, FIGURE I, were synthesized by addition of 2 mmol of hydrazine hydrate to a solution of the corresponding acid chloride 1 [21] in 1,4-dioxane (2 mmol/20 ml). After stirring at room temperature over night, water (100 ml) was added, the white precipitate was filtered off and purified by column chromatography (silica gel, hexane/ethyl acetate). Finally, the compounds were freeze-dried from a benzene solution. Characterization for 2a:

Yield: 0.86 g, 73% of theory

IR (KBr-pellet): 3342, 2964, 2939, 2877, 1688, 1647, 1620, 1585, 1492, 1332, 1213, cm^{-1}

^{1}H-NMR ($CDCl_3$), d = 0.95 (T, 18H), 1.75 (M, 12H), 3.98 (M, 12H),7.05 (S, 2H), 9.55 (D, 2H)

^{13}C-NMR ($CDCl_3$), d= 10.4, 22.6, 23.5, 70.6, 74.9, 105.8, 125.8, 141.8, 153.0, 165.4

MS: m/z = 588, 279; 237, 195, 153 , 125

3-hydroxy-4,5-diphenylmethylenedioxy-benzoic acid methyl ester (4):

Synthesis was carried out according to L. Jurd [20].

1,10-bis[(3',4'-diphenylmethylendioxy)-1'-carboxyethoxyphenyl-5'-oxy]decane (5):

In analogy to literature [23] a suspension of 1.8 g (6 mmol) 1,10-dibromodecane, 5.6 g (16 mmol) of 4, 2.75 g (20 mmol) potassium carbonate, 1 g potassium iodide and 100 ml cyclohexanone was heated to reflux for 5 hours. After filtration, the solvent was removed and the residue taken up with 100 ml of chloroform. The organic phase was washed with sodium hydroxide solution (10 M) and water. Methanol was added until precipitation started, then the crystallisation was completed at 0 °C.

Yield: 4.11 g, 82% of theory

IR(KBr-pellet): 2982, 2940, 2873, 2855, 1709, 1633, 1605, 1512, 1494, 1431, 1300, 1248, 1204, 1117, 1020, 993, 873, 806, 779, 767, 758, 640 cm^{-1}

^{1}H-NMR ($CDCl_3$), d = 1.10 (T, 6H), 1.35 (6H, M), 1.79 (M, 4H), 3.83 (S, 6H), 4.13 (T, 4H), 7.2-7.45 (M, 16H), 7.55 (M. 8H)

MS: m/z = 862, 817, 785, 500, 362, 285, 167, 105

1,10-bis[3',4'-dihydroxy-1'-carboxyethoxy-phenyl-5'-oxy]decane (6):

According to literature [22] 5.0 g (6 mmol) freeze-dried 5, dissolved in 80 ml of anhydrous methylene chloride, were cooled to -68 °C. 17 ml of a 1 M solution of borontrichloride in methylene chloride was added dropwise, causing an intensive red colour. After addition, the mixture was allowed to warm up to 20 °C. The reaction was stopped by addition of 20 ml methanol and the solvent was evaporated. To remove the boric acid, the following procedure was repeated three times: 50 ml of methanol were added, gently heated and evaporated under reduced pressure. Then, the oily residue was washed with 100 ml of hot hexane and recrystallized twice from methanol.

Yield: 2.32 g, 76% of theory

IR (KBr-pellet): 3400, 2942, 2926, 2873, 2854, 1690, 1610, 1516, 1465, 1442, 1371, 1311, 1217, 1084, 1026, 770 cm^{-1}

^{1}H-NMR ($CDCl_3$), d = 1.35 (M+T, 18H), 1.79 (M, 4H), 3.05 (Q, 4H), 4.05 (T, 4H), 5.5 (S, 2H), 5.9 (S, 2H) 7.15 (D, 2H), 7.33 (D, 2H)

1,10-bis[3',4'-bis(alkoxy)-1'-carboxyethoxy-phenyl-3,5'-oxy]decane (**7**)
O-alkylation was obtained in analogy to the synthesis of **5**. After evaporation of the solvent, the residue was directly recrystalized from a methanol/ethanol mixture.

1,10-bis[3',4'-bis(propyloxy)-1'-carboxyethoxy-phenyl-5'-oxy]decan (**7a**)
Yield: 3.11 g, 77% of theory
IR (KBr-pellet): 2936, 2876, 2856, 1721, 1587, 1496, 1464, 1433, 1387, 1334, 1242, 1217, 1120, 1013, 960 , 764 cm^{-1}
^{1}H-NMR ($CDCl_3$), d = 0.88 (M, 12H), 1.1 - 1.4 (M, 12H), 1.45 (D, 6H), 1.75 (M, 12H), 3.05 (Q, 4H), 4.0 (T, 12H), 7.22 (S, 4H)
MS: m/z = 674, 600, 558, 184

1,10-bis[3',4'-bis(hexyloxy)-1'-carboxyhydroxy-phenyl-5'-oxy]decane (**7b**)
Yield: 4.91 g, 97% of theory
IR (KBr-pellet): 2951, 2922, 1714, 1587, 1503, 1466, 1429, 1392, 1367, 1333, 1253, 1220, 1126, 1113, 1037, 763 cm^{-1}
^{1}H-NMR ($CDCl_3$), d = 0.88 (T, 12H), 1.1 - 1.4 (M, 44H), 1.45 (D, 6H), 1.75 (M, 12H), 3.05 (Q, 4H), 4.0 (T, 12H), 7.22 (S, 4H)

1,10-bis[3',4'-bis(alkoxy)-1'-carboxychloryl-phenyl-5'-oxy]decane (**8**)
To a boiling solution of 5 g **7** in 70 ml ethanol, 30 ml of 12 M potassium hydroxide solution was added. After heating for 4 hours, the mixture was given into 100 ml of water and acidified with hydrochloric acid (12 M). The precipitate was filtered off and dried in vacuo.The dry acid was mixed with 50 ml of thionyl chloride and heated to reflux for 4 hours. After evaporation of the reagent, the crude acid chloride was purified by recrystallisation from absolutely dry (P_4O_{10}) acetone.

1,10-bis[3',4'-bis(propyloxy)-1'-carboxychloryl-phenyl-5"-oxy]decane (**8a**)
Yield: 4.90 g , 97% of theory
Characterization was performed from the intermediate acid only:
IR (KBr-pellet): 3435, 2953, 2930, 2870, 2856, 2660, 1686, 1587, 1503, 1467,1433, 1391, 1330, 1275, 1228, 1103, 959,949, 700 cm^{-1}
^{1}H-NMR ($CDCl_3$), d= 0.88 (T, 12H), 1.3 (M, 8H), 1.45 (D, 12H), 1.75 (M,12H), 3.95 (T, 12H), 7.15 (S, 4H)
^{13}C-NMR (DMSO-d_6), d= 13.97/14.03, 22.5 - 30.2, 31.5/31.7, 69.1,73.5, 108.5, 123.8, 143.1, 152.8, 172.1

1,10-bis[3',4'-bis(hexyloxy)-1'-carboxyhydroxy-phenyl-5'-oxy]decane (**8b**)
Yield. 4.90 g, 97% of theory

Characterization was performed from the intermediate acid only:

IR (KBr-pellet): 3435, 2953, 2930, 2870, 2856, 2660, 1686, 1587, 1505, 1466, 1431, 1385, 1332,1273, 1227, 1125 cm^{-1}

^{1}H-NMR (CDCl$_3$), d= 0.88 (T, 12H), 1.3 (M, 44H), 1.45 (D, 12H), 1.75 (M,12H), 3.95 (T, 12H, a-CH), 7.15 (S, 4H)

^{13}C-NMR (DMSO-d$_6$), d= 13.97/14.05, 22.4- 30.1, 31.3/31.9, 69.3,73.4, 108.1, 123.6, 143.5, 152.8, 172.3

1,10-bis[3',4'-bis(alkyloxy)-1'-carboxyhydrazyl-phenyl-5'-oxy]decane (9)

A mixture of 5 g bis-ester 7, 20 ml n-pentanol and 20 ml hydrazine hydrate was heated to reflux for 3 hours. After addition of 60 ml methanol the solution was cooled to 0^{o}C over night, the resulting white slurry was filtered off, washed with methanol and recrystallized from a methanol/ethanol mixture. Just before use for synthesis, the monoacylhydrazide was freeze-dried from a benzene solution.

1,10-bis[3',4'-bis(propyloxy)-1'-carboxyhydrazyl-phenyl-5'-oxy]decane (9a)

Yield: 4.74 g, 95% of theory

IR(KBr-pellet): 3290, 2962, 2936, 2876, 2853, 1635, 1581,1579, 1496, 1467, 1425, 1388, 1342, 1240, 1124, 959 cm^{-1}

^{1}H-NMR (CDCl$_3$), d= 1.21 (M, 12H), 1.5 (S, 8H), 1.74 (M, 12H), 1.95 (M, 12H), 2.83 (S, 2H), 3.98 (T, 12H), 6.95 (S, 4H), 8.9 (S, 1H)

1,10-bis[3',4'-bis(hexyloxy)-1'-carboxyhydrazyl-phenyl-5'-oxy]decane (9b)

Yield: 4.35 g, 87% of theory

IR (KBr-pellet): 3265, 2954, 2926, 2870, 2853, 1629, 1581, 1521, 1496, 1344, 1242, 1125 cm^{-1}

^{1}H-NMR (CDCl$_3$), d = 0.88 (T, 12H), 1.3 (M, 28H), 1.4 (M, 12H),1.75 (M, 12H), 2.83 (S, 3H, 3.98 (T, 12H), 6.95 (S, 4H)

MS: m/z = 842, 811,727, 611, 391, 306, 237, 153

1,10-bis[4'5'-bis(alkoxy)-1'-carboxy-N-(N'-3",4",5"-tris(decyloxy)enzoyl)-hydrazylphenyl-3'-oxy]decane (11)

To a solution of 1.1 mmol bis-monoacylhydrazide 9 and 0.19 g (1.5 mmol) N,N'-dimethyl-aminopyridine in 20 ml dry THF, 0.62 g (1 mmol) of acid chloride 1 (n = 10), dissolved in 10 ml dry THF, was added dropwise. Further treatment is the same as described for the synthesis of 2.

1,10-bis[4'5'-bis(propyloxy)-1'-carboxy-N-(N'-3",4",5"-tris(decyloxy)benzoyl)-hydrazyl-phenyl-3'-oxy]decane, 2[3HZ-3,3,5], (11a)

Yield: 1.63 g, 90% of theory

IR (KBr-pellet): 3240, 2957, 2924, 2854, 1687, 1645, 1585, 1493, 1487, 1427, 1334,1215, 1119, 960, 856, 747 cm^{-1}

^{1}H-NMR (CDCl$_3$), d = 0.85 (T, 18H), 1.0 (M,12H), 1.24 (M, 80H), 1.38 (M, 16H), 1.70 (M, 24H), 3.95 (M, 24H), 7.07 (S, 5H), 7.11 (S, 2H), 9.90/9.99 (M, 4H)

^{13}C-NMR (CDCl$_3$), d= 10.0, 14.0 , 22.6 - 31.9, 68.9/69.1/70.6/73.4/74.9,105.6, 125.8, 141.7, 153.1, 165.3

1,10-bis[4'5'-bis(hexyloxy)-1'-carboxy-N-(N'-3",4",5"-tris(decyloxy)-benzoyl)-hydrazylphenyl-3'-oxy]decane, 2[3HZ-6,6,5] (11b)

Yield: 1.71 g, 86% of theory

IR (KBr-pellet): 3249, 2955, 2926, 2870, 2855, 1686, 1645, 1584, 1491, 1468, 1427,1335, 1217, 1115, 960, 856, 747 cm^{-1}

^{1}H-NMR (CDCl$_3$), d = 0.85 (T, 30H),1.24 (M, 96H), 1.38 (M, 24H),1.70 (M, 24H), 3.95 (M, 24H), 7.07 (S, 5H), 7.11 (S, 2H), 9.90/9.99 (M, 4H)

^{13}C-NMR (CDCl$_3$), d= 13.96, 14.05, 22.6 - 31.9, 69.1, 73.4, 105.7, 125.7, 141.74, 153.1, 165.3

1,10-bis[1'-carboxymethoxy-phenyl-4'-oxy]decane (13)

Compound 13 was obtained from 4-hydroxy-benzoic acid methyl ester (12) and 1,10-dibromodecane as described for the synthesis of 5.

Yield: 9.3 g, 69% of theory

IR (KBr-pellet):2930, 2870, 2857, 1721, 1606, 1436, 1331, 1283, 1253, 1222, 1170, 1123,669 cm^{-1}

^{1}H-NMR (CDCl$_3$), d = 1.35 (M, 12H), 1.43 (M, 4H), 3.85 (S, 6H), 3.98 (M, 5H), 6.85 (D, 2H), 7.95 (D, 2H)

1,10-bis[1'-carboxyhydrazyl-phenyl-4'-oxy]decane (14)

Compound 14 was prepared by hydrazinolysis of bis-ester 13, as described for synthesis of 9.

Yield: 4.40 g, 87.0% of theory

IR (KBr-pellet): 3334, 3268, 3074, 2940, 2920, 2875, 2850, 1661, 1603, 1570, 1549, 1474, 1464, 1392, 1339, 1302, 1250, 1170, 1111, 1043, 847 cm^{-1}

MS: m/z = 442, 411, 259, 121

1,10-bis[1'-carboxy-N-(N'-3",4",5"-tris(decyloxy)benzoyl)hydrazyl-phenyl-4'-oxy]decane, (15)

Model compound 15 was obtained by N-acylation of bis(monoacylhydrazine) 14 with acid chloride 10, as described for the synthesis of 11.

Yield: 1.11 g, 84% of theory

IR (KBr-pellet): 3183, 2953, 2922, 2852, 1636, 1608, 1581, 1570, 1516, 1491, 1467, 1456, 1429, 1389, 1339, 1296, 1257, 1184, 1119, 841 cm^{-1}

^{1}H-NMR (CDCl$_3$), d = 0.85 (T, 18H),1.25 (M, 80H), 1.45(M, 16H),1.75 (M, 16H), 3.95 (M, 16H), 6.82 (D, 4H),7.05 (S, 4H), 7.75 (D, 4H), 9.8 (M, 4H)

^{13}C-NMR (CDCl$_3$), d= 14.0, 22.6 - 31.9, 66.2, 69.3, 73.4, 106.1, 114.3, 123.5, 126.0, 129.3,142.0, 153.1, 162.4, 165.1/165.3

MS: m/z = 1587, 1586, 1442, 1423, 1283, 1159, 965, 630, 590, 573, 450, 433, 310, 170

***polycondensation* (16, 17)**

0.5 mmol monoacylhydrazine component (9 or 14) and calculated amounts of bis(acid chloride) 8 for desired stoechiometric ratios were treated as described for the synthesis of model compounds 11 and 15. The polymers were isolated and purificed by precipitation in cold methanole, acidified with hydrochloric acid.

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REFERENCES

[1] M. Werth, H. W. Spiess, Makromol. Chem., Rapid. Commun. **14**, 329 (1993)

[2] V. Percec, C. G. Cho, C. Pugh, D. Tomazos, Macromolecules **25**, 1164 (1992)

[3] T. S. Hsu, B. Hueser, T. Pakula, H. W. Spiess, M. Stamm, Makromol. Chem. **191**, 1597 (1990)

[4] W. Kranig, B. Hueser, H. W. Spiess, W. Kreuder, H. Ringsdorf, H. Zimmermann, Adv. Mater. **2**, 36 (1990)

[5] H. Ringsdorf, P. Tschirner, O. Schönherr, J. H. Wendorff, Makromol. Chem. **186**, 431 (1987)

[6] O. Herrmann-Schönherr, J. H. Wendorff, W. Kreuder, H. Ringsdorf, Makromol. Chem., Rapid. Commun. **7**, 97 (1986)

[7] G. Wenz, Makromol. Chem., Rapid. Commun. **6**, 677 (1985)

[8] D. Demus, H. Demus and H. Zaschke, "Flüssige Kristalle in Tabellen", VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1974

[9] J. D. Bunning, J. E. Lydon, C. Eaborn, P. M. Jackson, J. W. Goodby , G.W. Gray, J. Chem. Soc., Faraday Trans. 1, **78**, 713 (1982)

[10] S. Diele, E. Geissler, H.-M. Vorbrodt, H. Zaschke, Mol. Cryst. Liq. Cryst., **102**, 181 (1984)

[11] G. A. Jeffrey, Acc. Chem. Res., **19** 168 (1986)

[12] G. Lattermann, G. Staufer, Liquid Crystals **4**, 347 (1989)

[13] K. Praefke, A. M. Levelut, B. Kohne, A. Eckert, Liquid Crystals **6**, 263 (1989)

[14] C. Tschierske, G. Brezesinski, F. Kuschel, H. Zaschke, Mol. Cryst. Liq. Cryst. Lett. **6** 139 (1989)

[15] H. A. van Doren, R. van der Geest, R. M. Kelloy, H. Wynberg, Rec. Trav. Chim. Pays-Bas **109** 197 (1990)

[16] V. Vill, B. Sauerbrei, H. Fischer, J. Thiem, Liquid Crystals **11**, 949 (1992)

[17] D. Demus, A. Gloza, H. Hartung, A. Hauser, I. Rapthel, A. Wiegeleben, Cryst. Res. Technol. **16** 1445 (1981)

[18] H. Schubert, J. Hauschild, D. Demus, S. Hoffmann, Z. Chem. **18**, 256 (1978)

[19] U. Beginn, G. Lattermann, Mol. Cryst. Liq. Cryst. **241**, 215 (1994)

[20] L. Jurd, J. Am. Chem. Soc. **81**, 4606 (1959)

[21] J. Malthete, A.-M. Levelut, Nguyen Huu Tinh, J. Phys. Lett., Paris, **46**, L875 (1985)

[22] S. Schmidt, Dissertation, p. 57f, Bayreuth 1993

[23] C. Lin, H. Ringsdorf, M. Ebert, R. Kleppinger, J. H. Wendorff, Liquid Crystals **5**, 1841 (1989)

[24] H. Finkelmann, Angew. Chem. **99**, 840 (1987)