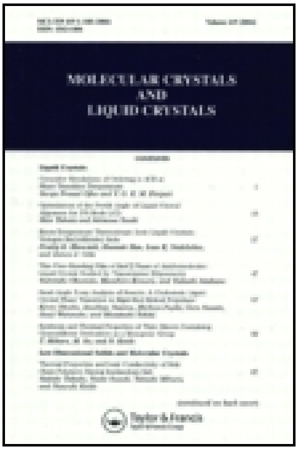

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Synthesis and Properties of Liquid-Crystalline Polymers with Laterally and Terminally Linked Mesogenic Units

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Synthesis and Properties of Liquid-Crystalline Polymers with Laterally and Terminally Linked Mesogenic Units

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Within the class of dimesogenic liquid-crystalline polymers, series of new LC-polyesters with laterally and terminally linked mesogenic units were synthesized. The mesogenic moieties perpendicularly arranged to the main chain are endowed either with identical or with unequal wing groups. Depending on the wing group and the spacer length, the polyesters can form monotropic or enantiotropic nematic and smectic phases. These polymers were subjected to characterization studies using optical microscopy, differential scanning calorimetry and X-ray diffraction techniques. The phase behavior is compared with that of combined and cross-shaped polymeric mesogens.

Keywords: structures of dimesogenic LC-polymers, combined LC-polymers, lateral fixation of mesogens, equal or unequal substituents

INTRODUCTION

In recent years the dependence of the thermotropic behavior and the phase structure upon the molecular architecture of polymeric liquid crystals has been the subject of much attention. One of the possible routes to vary the chemical structure of liquid-crystalline polymers concerns the way of incorporation of mesogenic constituents into the macromolecules. Derived from the classical main chain and comb-like liquid-crystalline polymers with rod-like mesogens, some novel types of LC-polymers have recently been described.[1,2] With respect to the type and structure of mesophases, dimesogenic LC-polymers are of special interest (Scheme 1). Polysiloxanes with paired mesogens of the same or different chemical structure (A)[3] have been intensively investigated by X-ray studies.[4] The attachment of the paired mesogenic groups to the flexible main chain favors smectic phases and a microphase separation within the smectic layers.[5]

Another way to incorporate different mesogenic units led to combined main-

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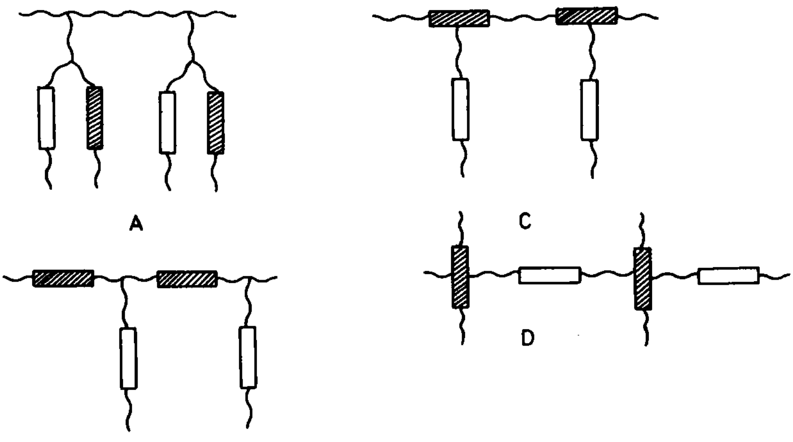


Scheme 1

chain/side-group polymers (B,C)[1,6] Whereas polyesters of type B form predominately smectic phases,[1] the connection of azobenzene side groups directly to the polyester main-chain mesogens (C) yields products having broad nematic phases.[6] X-ray diffraction provided indications for a parallel arrangement of main chain and side group mesogens for both types of polymers.[6]

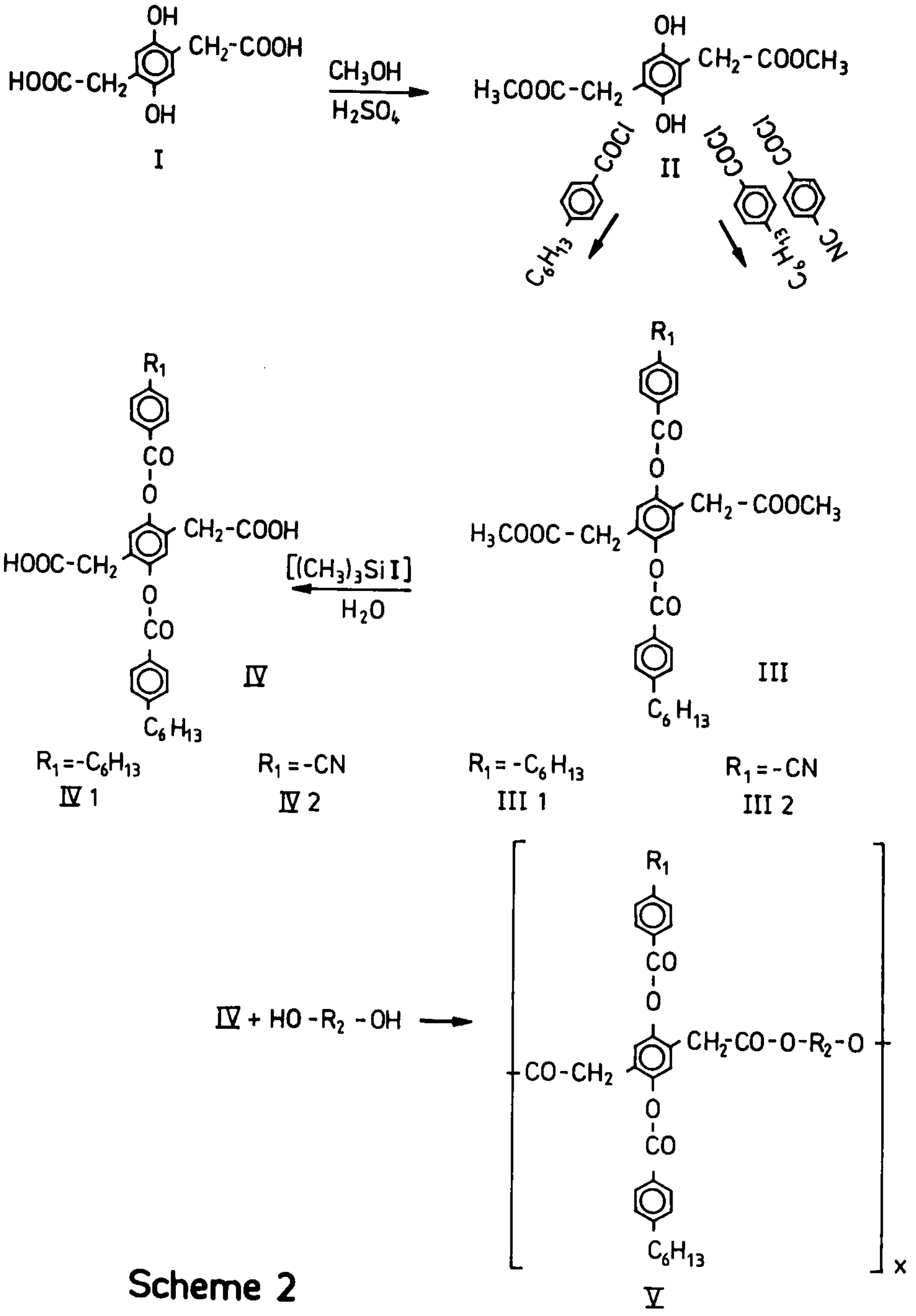
In this paper we report on the synthesis of a series of polymers with laterally and terminally linked mesogenic moieties (D) according to an idea of Ringsdorf *et al.*[7] Similar co-operative synthetic work is done in the Mainz group.[8] Generally, our special interest in the field is to study the influence of a systematic variation of the spacer length on the phase behavior as well as on the structural and dynamic properties of the mesophases. Furthermore, the role of different structural elements in the main chain and the effect of a polar terminal substituent one-sided linked to the mesogenic unit crossing the backbone are also subjects of our attention.

EXPERIMENTAL

Preparation of polyesters with the lateral fixation of mesogens into the main chain is described in Scheme 2.

In order to obtain 2,5-bis-(4-*n*-hexylbenzoyloxy)-1,4-benzenediacetic acid (IV 1) and 2-(4-cyanobenzoyloxy)-5-(4-*n*-hexylbenzoyloxy)-1,4-benzenediacetic acid (IV 2) the preparation of dimethyl 2,5-dihydroxy-1,4-benzenediacetate (II) was necessary. Reaction of the hydroquinone derivative II with 4-*n*-hexylbenzoyl chloride or 4-*n*-hexylbenzoyl chloride and 4-cyanobenzoyl chloride led to the compounds III 1 and III 2. The selective cleavage of the methylesters III 1 and III 2 yielded the mesogenic dicarboxylic acids IV 1 and IV 2. Polyesters V 1–30 were prepared by solution-polycondensation of the dicarboxylic acid IV 1 or IV 2 with various diols.

Thermal properties of the polyesters were studied using a polarizing microscope


I
CH3OH
H2SO4
II
C6H13-C6H4-COCl
NC-C6H4-COCl
III
[(CH3)3SiI]
H2O
IV
R1 = -C6H13
IV 1
R1 = -CN
IV 2
R1 = -C6H13
III 1
R1 = -CN
III 2
IV + HO-R2-OH
V
x

Scheme 2

fitted with a heating stage. Furthermore, the transition temperatures were checked by DSC. In some cases, the observed liquid-crystalline phases were metastable with respect to the crystalline solids. Due to the high viscosity of the molten samples, an annealing for at least several hours below the clearing temperature was necessary to decide whether the mesophases were stable or not.

The molecular weights were determined in 1,2-dichloro ethane by vapor pressure osmometry (Fa. Knauer). In the case of cyano-substituted polyesters, the molecular weights were mostly beyond the detection limit of the applied method. This is probably due to molecular association in solution.

To identify the mesophases, X-ray patterns of unoriented samples and melt-drawn oriented fibres using Ni-filtered CuK_α-radiation were recorded by a flat film camera.

RESULTS AND DISCUSSION

The properties of the synthesized polyesters are summarized in Table I.

The mesophase behavior of the polymers described in this paper (type D) is characterized by the preferential formation of nematic phases. Only some of the unsymmetrically substituted polyesters (R_1 = CN) show nematic and smectic phases. The strong tendency to form nematic phases is in agreement with the behavior of combined polymers consisting of rigid rod or semiflexible main chain polyesters with lateral mesogenic groups (type C).[6] Also main-chain polyesters with cross-shaped mesogens[2] exhibit only nematic phases. Generally, the perpendicular arrangement and a certain lateral stress of mesogenic units being constituent parts of a main chain seem to promote the formation of nematic mesophases.

Table I indicates that polyesters with two identical wing groups (R_1 = C_6H_{13}) show monotropic nematic phases. This behavior has been proved by means of DSC and polarizing microscopy. In Figure 1 as an example the DSC curves of polyester V 2 are shown. Symmetrical polyesters with long spacers (n = 11; V 6 and V 18) do not show liquid-crystalline phases.

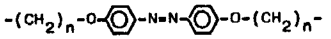
In contrast to this behavior the unsymmetrical products (R_1 = CN) are distinguished by the existence of stable nematic mesophases with exception of polymers V 9 and V 12. Obviously, this stability is increased by replacement of biphenyl by azobenzene in the main chain. Some of the unsymmetrically substituted polyesters form nematic and smectic mesophases (V 9, V 11, V 12, V 21, V 23, V 24). As one typical example, the behavior of polyester V 21 measured by DSC is shown in Figure 2. Polymers obtained by lateral fixation of mesogens via spacers without mesogenic units in the main chain (V 25–V 30) do not show liquid-crystalline behavior.

In accordance with similar types of combined polyesters, the clearing as well as the glass temperatures generally increase as the main chain spacer becomes shorter. Furthermore, the well known even–odd effect with respect to the spacer length (n) is observed.

On cooling below the clearing temperature, the microscopic samples of isotropic melts became birefringent, and no specific textures could be observed immediately. After annealing close to the transition temperature typical marbled textures ap-

TABLE I

Phase transition temperatures and molecular weights of the synthesized polyesters (g = glassy, cr = crystalline, s_C = smectic C, s_A = smectic A, *n* = nematic, is = isotropic)

Polymer	R_1	R_2	n	Phase transition temperatures in °C	M_n
V 1	$-C_6H_{13}$		2	cr (g 42 n 113 is) 151 is	8 800
V 2	$-C_6H_{13}$		3	cr (g 30 n 60 is) 97 is	7 400
V 3	$-C_6H_{13}$		4	cr (g 24 n 105 is) 114 is	6 200
V 4	$-C_6H_{13}$		5	cr (g 23 n 64 is) 98 is	7 900
V 5	$-C_6H_{13}$		6	cr (g 26 n 102 is) 115 is	11 400
V 6	$-C_6H_{13}$		11	cr 99 is	10 200
V 7	-CN		2	g 66 n 157 is	
V 8	-CN		3	g 55 n 95 is	
V 9	-CN		4	cr (g 60 s_A 78 n 147 is)147 is	
V 10	-CN		5	g 40 n 95 is	
V 11	-CN		6	g 51 s_A 102 n 123 is	
V 12	-CN		11	cr (g 33 s_C 71 n 83 is) 83 is	
V 13	$-C_6H_{13}$		2	cr (g 49 n 133 is) 149 is	5 200
V 14	$-C_6H_{13}$		3	cr (g 39 n 92 is) 114 is	8 000
V 15	$-C_6H_{13}$		4	cr (g 32 n 132 is) 140 is	9 100
V 16	$-C_6H_{13}$		5	cr (g 27 n 98 is) 116 is	10 200
V 17	$-C_6H_{13}$		6	cr (g 29 n 120 is) 120 is	11 100
V 18	$-C_6H_{13}$		11	cr 122 is	10 500
V 19	-CN		2	g 68 n 179 (dec.) is	
V 20	-CN		3	g 59 n 122 is	
V 21	-CN		4	cr (g 63 s_A 110 n 160 is)135 n 160 is	
V 22	-CN		5	g 49 n 117 is	
V 23	-CN		6	g 50 s_A 101 n 137 is	
V 24	-CN		11	g 36 s_C 47 n 91 is	
V 25	$-C_6H_{13}$		2	cr 104 is	
V 26	$-C_6H_{13}$	$-(CH_2)_n-$	5	cr 51 is	
V 27	$-C_6H_{13}$		6	cr 84 is	
V 28	$-C_6H_{13}$		12	cr 105 is	
V 29	-CN		5	g 29 is	
V 30	-CN		6	g 22 is	

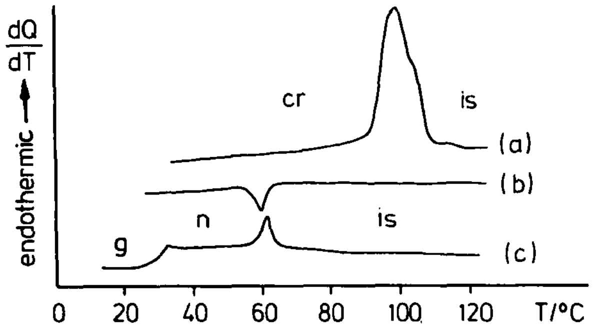


FIGURE 1 DSC curves of polyester V 2 (heating/cooling rate: 8°C/min). (a): Heating after annealing at 80°C (20 h). (b): Cooling from the isotropic melt. (c): Heating immediately after cooling from the isotropic melt.

peared. By applying pressure in the LC-phase the polyesters show a tendency to form homogeneous textures.

The X-ray diffraction pattern found for specimen of our polymers (V 2, V 3, V 9) are typical for a nematic phase. Besides the diffuse outer reflexion corresponding to mean lateral distance of about 5 Å a diffuse scattering at small angles $\theta \approx 2°$ can be observed. The later one is changed into an interference with a sharp profile indicating the appearance of smectic phases. Smectic A phases have been observed in the case of polyesters V 9, V 11, V 21, V 23 whereas smectic C phases have been found in the case of samples V 12 and V 24.

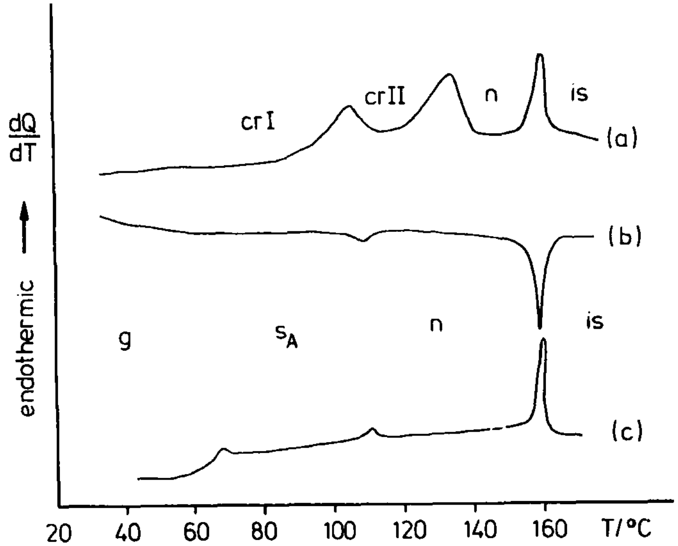


FIGURE 2 DSC curves of polyester V 21 (heating/cooling rate: 8°C/min). (a): Heating after annealing at 80°C (20 h). (b): Cooling from the isotropic melt. (c): Heating immediately after cooling from the isotropic melt.

More detailed X-ray investigations, dielectric measurements and conoscopic observations to characterize this new type of LC-polymers are in progress.

MATERIALS

2,5-Dihydroxy-1,4-benzenediacetic acid (I)

It was synthesized according to literature procedures.[9]

Dimethyl 2,5-dihydroxy-1,4-benzenediacetate (II)

Nine g 2,5-dihydroxy-1,4-benzenediacetic acid were dissolved in 200 ml of methanol. After addition of 5.4 ml of conc. H_2SO_4 the mixture was stirred and refluxed for 5 h. After filtration the residue was recrystallized from methanol; m.p. 218°C (dec.). Yield: 90%.

Dimethyl 2,5-bis (4-*n*-hexylbenzoyloxy)-1,4-benzenediacetate (III 1)

Dimethyl 2,5-dihydroxy-1,4-benzenediacetate (II) was esterified with 4-*n*-hexylbenzoyl chloride following the procedure described by Einhorn.[10] The crude product was recrystallized from methanol; m.p. 79°C. Yield: 79%.

Dimethyl 2-(4-cyanobenzoyloxy)-5-(4-*n*-hexylbenzoyloxy)-1,4-benzenediacetate (III 2)

Compound III 2 was synthesized in two steps applying the Einhorn method.[10] In the first step dimethyl 2-(hydroxy)-5-(4-*n*-hexylbenzoyloxy)-1,4-benzenediacetate was prepared by esterification of II with 4-*n*-hexylbenzoyl chloride. The intermediary product was recrystallized from *n*-heptan; m.p. 82–83°C. Yield: 52%. Esterification of the intermediary product with 4-cyanobenzoyl chloride led to compound III 2. The product was recrystallized from methanol; m.p. 107°C (metastable), 129°C (stable). Yield: 85%.

2,5-Bis-(4-*n*-hexylbenzoyloxy)-1,4-benzenediacetic acid (IV 1) and 2-(4-cyanobenzoyloxy)-5-(4-*n*-hexylbenzoyloxy)-1,4-benzenediacetic acid (IV 2)

The selective cleavage of the methylester groups was achieved following a procedure described by Olah *et al.*[11] 0.0166 mol of the methylester III 1 or III 2 and 0.166 mol of anhydrous NaI were dissolved in 200 ml of dry acetonitrile. The stirred solution was heated to 80°C and 0.166 mol of $(CH_3)_3SiCl$ were added dropwise under dry nitrogen. The mixture was heated under reflux with stirring for 125 h and protected from atmospheric moisture and oxygen by flushing the apparatus with dry nitrogen. After the completion of the cleavage the mixture was cooled down and diluted with 800 ml of water. After filtration the crude acids were recrystallized from methanol. IV 1; m.p. 225°C (dec.). Yield: 90%. IV 2; m.p. 205°C. Yield: 80%.

4,4'-Dihydroxyazobenzene

The preparation was carried out in a way recommended by Willstätter.[12] The crude product was recrystallized from ethanol/water (vol. ratio 1:3); m.p. 217°C (dec.). Yield: 28%.

4,4'-Bis (ω-hydroxyalkyloxy)azobenzenes and 4,4'-bis(ω-hydroxyalkyloxy)biphenyls

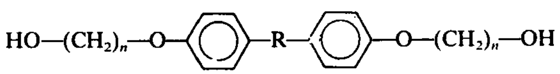
The preparation of the compounds was carried out in two ways:

Procedure A. A stirred mixture of 0.01 mol of 4,4'-dihydroxybiphenyl or 4,4'-dihydroxyazobenzene, 0.03 mol of ω-halogenalcohol, 0.04 mol of KOH, and a catalytic amount of KI in 50 ml of ethanol/water (vol. ratio 1:1) was refluxed for 50 h. The reaction mixture was cooled down to room temperature and 50 ml of water were added. After filtration the precipitate was washed several times with hot 1 *n* KOH and recrystallized from butyl acetate. In this manner the etherification with 2-bromoethanol, 3-bromo-1-propanol, 6-chloro-1-hexanol, and 11-bromo-1-undecanol was carried out.

Procedure B. 4-Bromo-1-butanol and 5-chloro-1-pentanol could not be used for etherification directly due to preferential formation of tetrahydrofuran and tetrahydropyran, respectively. For this reason the etherification with 4-bromobutyl benzoate and 5-chloroamyl acetate (prepared from tetrahydrofuran and tetrahydropyran, respectively) was carried out under anhydrous conditions. 0.01 Mol of 4,4'-dihydroxybiphenyl or 4,4'-dihydroxyazobenzene, 0.022 mol of the halogen derivative, 0.025 mol of anhydrous K_2CO_3, 35 ml of dry acetone, and a catalytic amount of KI were refluxed for 40 h. After removing the acetone 0.13 mol of KOH dissolved in 50 ml of ethanol/water (vol. ratio 1:1) were added and the saponification of the benzoates or acetates was completed by stirring and refluxing of the mixtures.

TABLE II

Melting temperatures and yields of the synthesized diols with mesogenic groups



n	R	Melting temperatures in °C	Yield in %	Procedure
2	—	211	65	A
3	—	205	38	A
4	—	196	73	B
5	—	180	31	B
6	—	170	67	A
11	—	160	90	A
2	—N=N—	205	58	A
3	—N=N—	177	51	A
4	—N=N—	174	82	B
5	—N=N—	153	30	B
6	—N=N—	147	41	A
11	—N=N—	145	61	A

After 5 h the reaction mixtures were cooled down to room temperature and filtered. The residues were recrystallized from butyl acetate.

The data of the diols containing mesogenic units are presented in Table II.

Polyesters V 1–30; general procedure. A mixture of 0.00166 mol of the dicarboxylic acid (IV 1 or IV 2), 0.00166 mol of a diol, and a catalytic amount of *p*-toluenesulfonic acid (30 mg) was suspended in 30 ml of anhydrous 1,2-dichloroethane and heated under reflux in a Soxhlet-extractor for 70 h. After 2–4 h the mixture became homogeneous. The water formed during esterification was adsorbed on "Zeosorb A3" placed in the Soxhlet tube. The polyesters were precipitated several times in a 20-fold volume of methanol and dried in vacuum at 80°C. Yields: 58–85%.

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