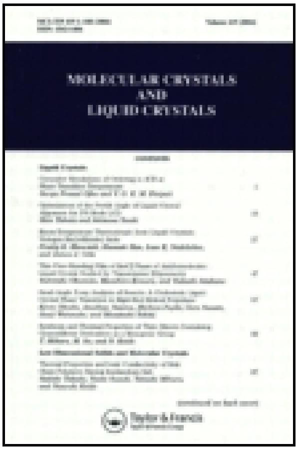

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Glass Forming Nematic-Discotic Oligomesogens

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GLASS FORMING NEMATIC-DISCOTIC OLIGOMESOGENS

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New star-like oligomers are presented characterized by the chemical linkage of a defined number of disc-shaped multialkynylbenzene moieties via a central linking unit. The compounds exhibit a nematic mesophase which can be quenched into a glassy state. The molecular orientation of the discotic oligomesogens on rubbed polyimide layers has been investigated.

Keywords: alignment control; LC-glasses; liquid crystalline multiyne oligomers

INTRODUCTION

Discotic liquid crystals mainly are composed of a flat or nearly flat rigid central core substituted with several peripheral long flexible chains [1]. Several types of mesophases formed by those disc-shaped molecules have been identified including nematic-discotic (N_D), nematic-columnar (N_{Col}) and various columnar (Col) phases with the columns being organized on a two-dimensional lattice [2].

Furthermore, it has become apparent that manipulations and even inductions of columnar liquid crystalline phases can be achieved with binary mixtures of complementary compounds which, for example, form hydrogen bonds [3] or charge-transfer complexes [4,5].

However, compared with investigations regarding the relation between molecular structure and liquid crystalline bulk properties, only little is known regarding surface-assisted molecular orientation control of

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disc-shaped compounds. Examples that have been reported so far include the use of mechanically rubbed polymers [6], the photoalignment technique [7] and Langmuir-Blodgett (LB) films [8].

We have previously shown that benzene centred radial multiynes substituted with just one terminal polar group form monolayers at the air/water with the flat aromatic planes oriented perpendicular to the surface [9,10]. The edge-on orientation is preserved during the formation of periodical multilayers by the LB technique [11]. More recently we reported on orientational control of low molar mass nematic-discotic pentaalkynylbenzene derivatives by placing the compounds on photoirradiated thin films of an azobenzene polymer [12,13].

A problem regarding long-term stability of the oriented films, however, may arise from the tendency of the monomers to crystallize upon cooling to room temperature. To avoid crystallization we followed the concept to combine mesogenic properties with glass forming tendencies by linking chemically a defined number of anisometric molecular sub-units. We present here star-like oligomers with three flat multiyne moieties grafted to a central linking unit via flexible spacers.

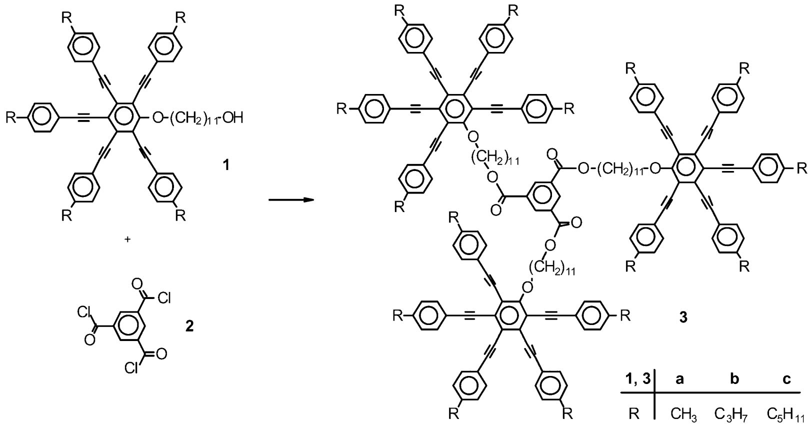
EXPERIMENTAL

Texture observations were made with an Olympus polarizing microscope fitted with a Linkam TMH/S 600 hot stage in conjunction with a Linkam TP 92 control unit. Photo micrographs were obtained with an Olympus OM-4 Ti system camera. Calorimetric investigations were performed with a Netzsch DSC 204 Phoenix. Determination of pre-tilt angles of oriented oligomer films were performed in transmission by the crystal rotation method [14,15] along the rubbing direction of polyimide orientation layer.

RESULTS AND DISCUSSION

Synthesis

The synthesis of the new pentayne trimers **3** was carried out starting from the hydroxy substituted radial pentaalkynylbenzene derivatives **1** (Scheme 1). The pentaynes **1a** and **1c** have already been described previously [16,17]. The newly synthesized fivefold propyl modified member **1b** was prepared by five-fold Palladium catalysed C,C-coupling of 11-(pentabromophenoxy)undecan-1-ol with 4-propylphenylacetylene according to the method given in ref. 17. The star-shaped oligomers **3** with three multiyne groups linked to a central benzene ring via ester bonds were obtained by reaction of compounds **1** with 1,3,5-benzenetricarbonyl



SCHEME 1 Synthesis of the star-like trimeric pentaynes **13**.

trichloride **2** in the presence of pyridine and catalytic amounts of 4-N, N-dimethylaminopyridine.

All oligomers **3** showed IR and ^{1}H NMR spectra in accordance with their supposed structures. No impurities, i.e. traces of diesters, could be detected by NMR spectroscopy.

Thermal Properties

The hydroxy substituted pentaalkynes **1a-c** exhibit an enantiotropic nematic-discotic (N_D) mesophase within the temperature range given in Table 1. The compounds are crystalline at room temperature like it is most

TABLE 1 Phase Transition Temperatures (°C) of the Low Molar Mass Pentaalkynylbenzene Derivatives **1** and of the Multiyne Oligomers **3** (DSC 2nd Heating at 10 K/min); Transition Enthalpies (kJ/mol) in Parenthesis; Monotropic Phase Transitions in Square Brackets

Compound	R	T_g	T_m	T_i
1a	CH_3	–	171.6 (43.9)	226.6 (0.5)
1b	C_3H_7	–	90.0 (19.3)	135.5 (0.1)
1c	C_5H_{11}	–	67.0 (25.8)	94.2 (0.2)
3a	CH_3	–	–	173.6 (68.4)
		–	[148.0 (28.9)]	[172.9 (0.4)]
3b	C_3H_7	24.0	66.1 (8.88)	141.9 (0.6)
3c	C_5H_{11}	– 12.4	–	23.6 (4.7)

T_g: glass transition; T_m: transition from the crystalline state to the liquid crystalline phase; T_i: transition to the isotropic phase.

frequently found for low molar mass thermotropic liquid crystals. The melting as well as the isotropization temperatures decrease with increasing chain length of the five peripheral alkyl chains.

The star-like multiyne oligomers **3** exhibit Schlieren textures between crossed polarizers on cooling from the isotropic melts. These optical textures are characteristic for a nematic-discotic but also for a nematic columnar (N_{Col}) liquid crystalline phase. X-ray investigations are currently in progress to determine the phase type in detail. The thermal fluctuations within the mesophases are typical for mesogenic monomers rather than for polymeric liquid crystals.

However, contrary to the appropriate monomer **1a** the methyl substituted member **3a** exhibits only a monotropic mesophase on cooling form the isotropic liquid. Increasing the chain length of the peripheral alkyl substituents leads to enantiotropic mesomorphism in case of the higher homologues **3b,c**.

Furthermore, the liquid crystalline phases of **3b** and **3c** can be quenched into a glassy state. The glass transition as well as the isotropization temperature are very low for compound **3c**. Above T_g, for the propyl substituted star-shaped multiyne **3b** an endotherm is detectable by DSC at 51°C which is due to thermally induced crystallization. The endotherm is followed by re-melting to the mesophase before the transition to the isotropic phase occurs. However, without thermal treatment we found the anisotropic glassy state to be stable for several months.

Alignment Behaviour

Spin-coating films of the star-shaped pentayne oligomer **3b** with a thickness of 1 μm were prepared on glass substrates provided with a rubbed polyimide orientation layer. The films were heated above the clearing temperature followed by slow cooling to the mesophase. After annealing within the mesophase for a few minutes the films were cooled down to room temperature. In accordance with the thermal bulk properties no crystallization occurs during the cooling.

To elucidate if the thermal treatment along with the polyimide alignment layer gives rise to a three-dimensional orientation, birefringence measurements of the glassy films were performed as a function of incident angle of probing light from the surface normal.

Asymmetrical plots of the optical phase difference were found (Fig. 1) which indicate a tilted alignment of the disc-shaped groups. The average pre-tilt angle of the planes of the flat aromatic pentaalkynylbenzene cores was estimated to be approximately 14° relative to the substrate surface. It seems likely that the tilt angles continuously alter in order to minimize the free energy at the outermost film/air interface [7,12].

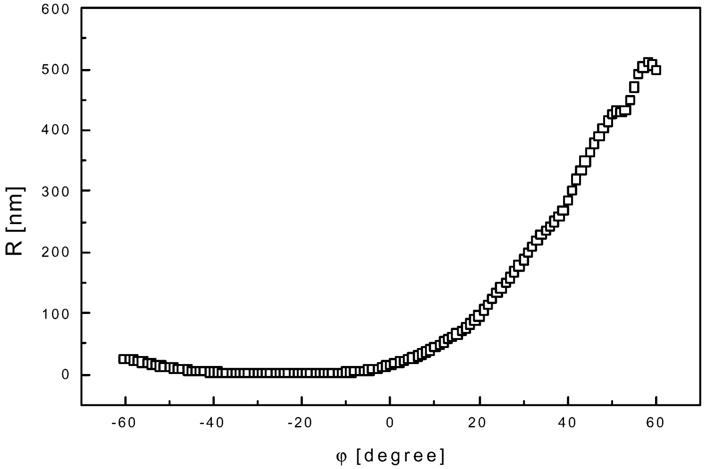


FIGURE 1 Optical phase difference (R) of a glassy film of the oligomer **3b** as a function of incident angle of probing light (φ) after annealing on top of a polyimide orientation layer (measured along the rubbing direction of the polyimide).

CONCLUSIONS

First members of a new family of oligomeric star-like mesogens were prepared by linking covalently a defined number of rather flat pentaalkynylbenzene units to a central benzene moiety via flexible alkyl spacers. The oligomers exhibit a nematic (N_D or N_{Col}) mesophase. In certain cases LC-glasses are formed upon cooling. Thin films of the oligomers were prepared on top of rubbed polyimide orientation layers by spin coating from solution. Annealing these films within the liquid crystalline phase leads to a tilted orientation of the planes of the aromatic cores.

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