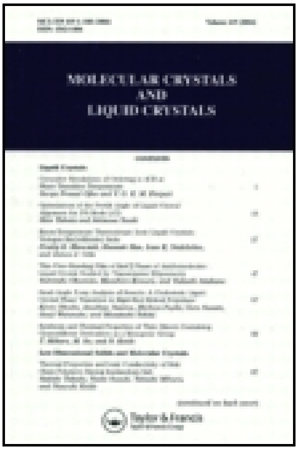

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Hydrogen-Bonded Block Mesogens with Fluorinated Molecular Fragments

Dietmar Janietz [a] & Alexandra Kohlmeier [a]
[a] Fraunhofer Institute for Applied Polymer Research, Potsdam-Golm, Germany

To cite this article: Dietmar Janietz & Alexandra Kohlmeier (2009): Hydrogen-Bonded Block Mesogens with Fluorinated Molecular Fragments, Molecular Crystals and Liquid Crystals, 509:1, 39/[781]-46/[788]

To link to this article: http://dx.doi.org/10.1080/15421400903051069

Mol. Cryst. Liq. Cryst., Vol. 509, pp. 39/[781]–46/[788], 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903051069

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Hydrogen-Bonded Block Mesogens with Fluorinated Molecular Fragments

Dietmar Janietz and Alexandra Kohlmeier
Fraunhofer Institute for Applied Polymer Research, Potsdam-Golm, Germany

An alkoxyphenyl substituted melamine derivative has been investigated in binary mixtures with a two-chain semiperfluorinated benzoic acid. The two components are non-liquid crystalline in their own right. Equimolar mixtures of the melamine with the complementary benzoic acid form discrete hydrogen-bonded heterodimers. The dimeric supermolecules exhibit an induced rectangular columnar mesophase with two-dimensional c2mm lattice symmetry. The columnar phase represents a ribbon phase resulting from the collapse of smectic bilayers. Docking of two or three equivalents of the two-chain benzoic acid to the melamine core leads to the induction of hexagonal columnar mesophases.

Keywords: columnar phases; hydrogen bonding; mesophase induction; nanosegregation

INTRODUCTION

The formation of thermotropic and lyotropic liquid crystalline phases mainly results from nanoscale segregation of incompatible moleculer segments [1,2]. Thereby, the mesophase morphologies, lamellar, columnar or cubic, are predominantly determined by the volume fractions of the chemically distinct molecular fragments such as rigid/flexible or polar/nonpolar which separate into different subspaces.

The intramolecular contrast can be reinforced if a lipophilic chain is replaced by a perfluorinated segment. (Semi)perfluorinated molecular

This work was supported by the Land Brandenburg, Germany and the Fonds der Chemischen Industrie. We are very grateful to B. Smarsly for the kind support in performing X-ray measurements at the Max Planck Institute of Colloids and Interfaces, Potsdam-Golm, Germany.

Address correspondence to Dietmar Janietz, Fraunhofer Institute for Applied Polymer Research, Geiselbergstr. 69, Potsdam-Golm D-14513, Germany. E-mail: dietmar.janietz@iap.fraunhofer.de; dietmar.janietz@iap.fhg.de

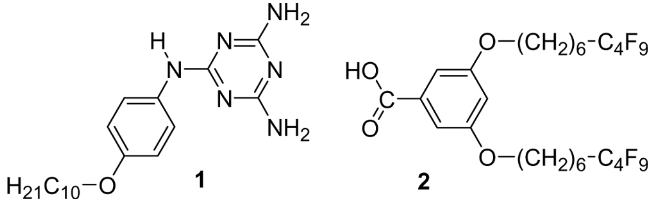
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FIGURE 1 Chemical structures of the decyloxyphenyl substituted melamine **1** and of the semiperfluorinated benzoic acid **2**.

fragments have been successfully introduced into calamitic [3], discotic [4] and polycatenar [5] mesogens as well as in liquid crystals without a pronounced anisometric molecular shape such as taper-shaped [6] and tetrahedral [7] compounds. It could be shown that the fluorophobic effect may lead to a significant stabilization and even to modifications of smectic, columnar and cubic mesophases.

A powerful tool towards designing highly organised soft matter arises from strong cohesive forces such as hydrogen bonding between identical or complementary molecules [8]. For example, mesomorphic complexes have been reported emerging from double-hydrogen bonding of 2,6-diacylaminopyridines with aromatic carboxylic acids [9,10] and of amino substituted 1,3,5-triazine derivatives with benzoic acids grafted either with lipophilic alkyl tails [11,12] or with semiperfluorinated chains [13–15].

We report here on mesophase inductions by combining molecular recognition between two complementary molecular species and fluorophobic effect. We present mesomorphic structure formation of the alkoxyphenyl substituted melamine derivative **1** in mixtures with the two-chain semiperfluorinated benzoic acid **2** (Fig. 1). The two components are non-liquid crystalline by themselves.

EXPERIMENTAL

The decyloxyphenyl substituted melamine **1** was prepared by reaction of 6-chloro-2,4-diamino-1,3,5-triazine with 4-decyloxyaniline. The two-fold semiperfluorinated benzoic acid **2** was obtained by etherification of methyl 3,5-dihydroxybenzoate with 1-bromo-1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecane [16] in the presence of potassium carbonate followed by alkaline ester cleavage. The binary mixed systems of the arylmelamine **1** with the benzoic acid **2** were prepared by dissolving the components separately in THF, combining the solutions and evaporating the solvent. Further investigations were performed after annealing the samples in the isotropic state. Texture observations were made using an Olympus BHS polarizing microscope in conjunction with a Linkam TMH/S 600 hot stage and a Linkam TP 92 control unit. Photo micrographs were obtained with an Olympus E20 digital mirror reflex camera. Calorimetric investigations were performed with a Netzsch DSC 200. The X-ray studies (CuK_α) were carried out with a Nenius PDS 120 (Bruker) equipped with a detector from Inel.

RESULTS AND DISCUSSION

The phase transition temperatures of the aryl modified melamine derivative **1**, of the semiperfluorinated benzoic acid **2** and of binary mixed systems **1**/**2** are collected in Table 1. The pure compounds **1** and **2** show a direct transition from the crystalline state to the isotropic liquid. Each investigated binary mixture **1**/**2** displays an enantiotropic mesophase. The clearing temperatures are higher than the melting temperature of the pure carboxylic acid **2**. The mixtures show a strong tendency towards supercooling. The isotropization temperature is lower for the 1:2 complex in comparison to the 1:1 mixed system. A further decrease of the clearing temperature is observed for the mixture containing three equivalents of the acid **2**.

Fernlike optical textures develop on cooling the equimolar composition of the triazine **1** with the two-chain acid **2** from the isotropic liquid which collate to form spherulitic textures (Fig. 2). The mesophase textures of the investigated (1:2) and (1:3) compositions are identical and can be characterized by the observation of large homeotropic aligned regions containing birefringent filaments (Fig. 3). Therefore, it seems that the mixtures exhibit different mesophases depending on the molar content of the semiperfluorinated acid.

TABLE 1 Phase Transition Temperatures (°C) of the Pure Compounds **1** and **2** and of Binary Mixtures of the Melamine **1** with the Complementary Semiperfluorinated Benzoic Acid **2** (DSC 2nd Heating; Phase Transition Enthalpies (kJ/mol) in Parenthesis)

Sample	Transition temperatures					Lattice constants (Å)
1	Cr	206.0			I	
2	Cr	58.8			I	
(1:1) **1/2**	Cr	–	Col_r	108.3 (2.2)	I	$a = 65.1$, $b = 71.1$
(1:2) **1/2**	Cr	−37.0 (1.7)	Col_h	83.1 (2.8)	I	$a_{hex} = 38.5$
(1:3) **1/2**	Cr	–	Col_h	73.3 (4.3)	I	$a_{hex} = 40.3$

Cr: crystalline; Col_r: rectangular columnar; Col_h: hexagonal columnar; I: isotropic.

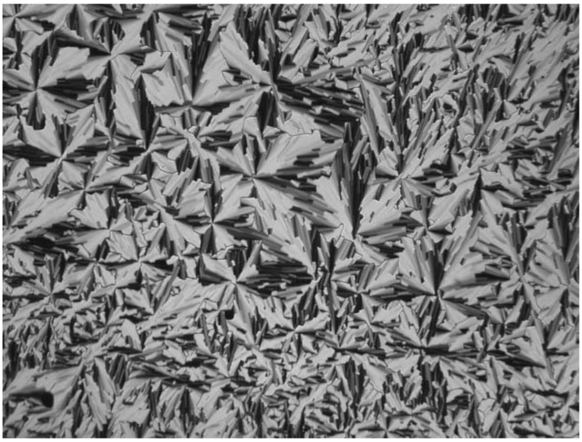

FIGURE 2 Optical texture of the induced mesophase of the equimolar composition **1**/**2** between crossed polarizers.

Figure 4 displays the wide angle X-ray diffractogram obtained for the mesophase of the equimolar **1**/**2** mixture. The small angle reflections can be indexed on the basis of a two-dimensional rectangular unit cell with a centered *c2* mm lattice symmetry. The lattice parameters are $a = 65.1\,\text{Å}$ and $b = 71.1\,\text{Å}$.

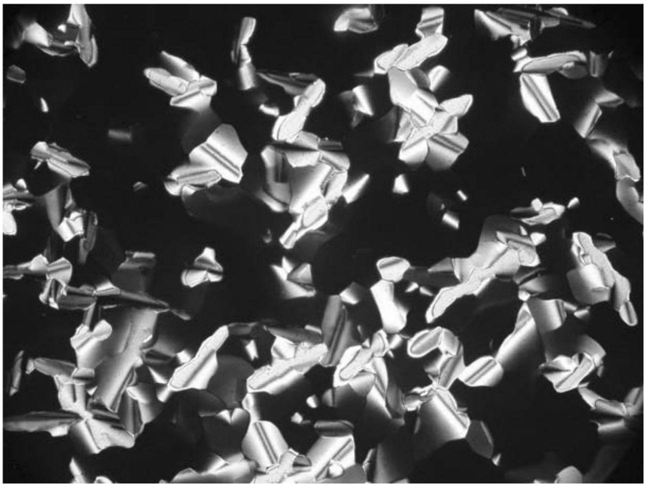

FIGURE 3 Microphotograph of the columnar mesophase of the melamine **1** in mixture with two equivalents of the benzoic acid **2** between crossed polarizers.

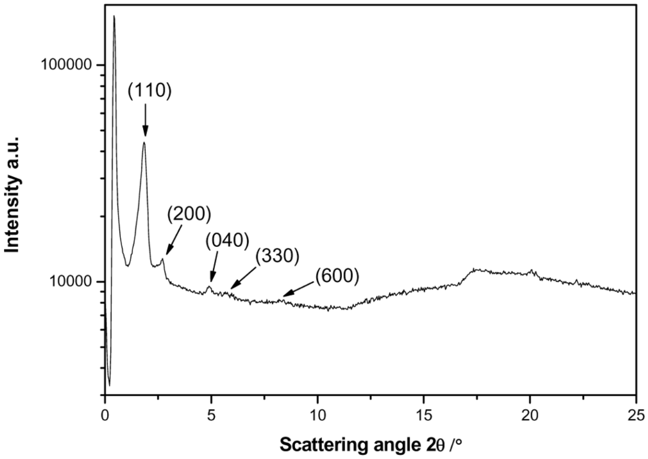

FIGURE 4 Wide angle X-ray diffractogramm for the rectangular columnar phase of the equimolar complex of the triazine **1** with the benzoic acid **2**.

The WAXS diffractogram for the (1:2) **1**/**2** complex is given in Figure 5. The X-ray diffraction pattern of the mesophase of the mixed system **1**/**2** at a 1:2 molar ratio exhibits three sharp reflections in the small angle region and a diffuse halo in the wide angle region. The ratio of positions of the reflections is 1:$3^{1/2}$:2, proving the existence of a hexagonal columnar (Col_h) mesophase. The hexagonal

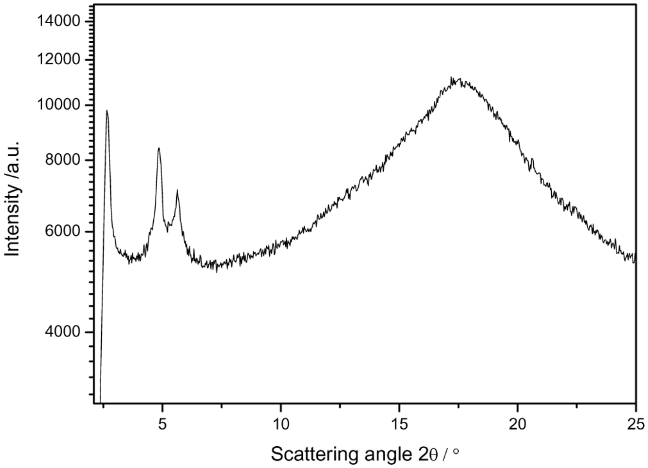

FIGURE 5 Wide angle X-ray diffractogram obtained for the Col_h phase of the (1:2) mixture **1**/**2**.

lattice constants a_{hex} for the mixtures of the melamine **1** with two and three acid equivalents are given in Table 1.

IR-spectroscopic investigations previously have proven that association of phenyl substituted diamino-1,3,5-triazines with complementary benzoic acids is related to double-hydrogen bonding between the nitrogen heterocycle substituted with two exocyclic primary amino groups and the carboxylic group of the acid [13]. Thereby, in equimolar compositions, preferentially heterodimers are formed with a rod-like shape of the polar H-bonded core [13,15]. Hence, it is reasonable to suggest that docking of one equivalent of the benzoic acid **2** to the melamine heterocycle **1** preferably occurs opposite from the bulky phenyl group leading to heterodimeric supermolecules **1**/**2** with a pronounced rod-like core geometry as well.

The linear pre-organization of the extended hydrogen-bonded cores should enable sufficiently strong attractive interactions to favour a parallel organization. As it is evident from CPK models the length of H-bonded dimers **1**/**2** amounts to approximately 45 Å considering almost stretched conformations of the flexible alkyl segments. The lattice parameter *b* matches nearly twice the molecular length. Therefore, it is most likely that hydrogen-bonded bilayer aggregates are present in the rectangular lattice.

The cross sectional area of the terminal semiperfluorinated chains exceeds the cross-section of the closely aligned central H-bonded aromatic and the lipophilic regions. The smectic bilayers should break up into infinite ribbon-like segments with curved interfaces due to the different space filling of the fluoroaliphatic and aromatic regions.

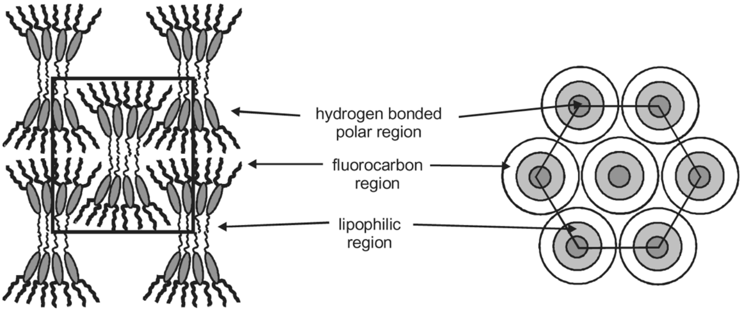

FIGURE 6 Schematic presentation of the induced mesophases of the mixed systems **1**/**2**. Left: rectangular columnar phase (*c2* mm lattice symmetry) of the 1:1 complex; Right: hexagonal columnar phase (two-dimensional *p6* mm space group) of the 1:2 and 1:3 complexes.

The ribbon-like aggregates organize to a columnar mesophase on a two-dimensional rectangular lattice (Fig. 6).

The proposed ribbon model seems reasonable since it enables the segregation of fluorophilic and lipophilic moieties into separate regions whereby the parallel organization of the polar H-bonded cores is maintained.

CPK models reveal that docking of two or three molecules of the semiperfluorinated benzoic acid **2** at the melamine core leads to H-bonded associates with a pronounced circular geometry. Cylindrical aggregates are formed that consist of three distinct molecular regions, the polar hydrogen-bonded aromatic region located in the centre surrounded by the lipophilic alkyl segments and, finally, the fluorinated blocks distributed arround the cylindrical core region. The parallel alignment of these aggregates leads to the two-dimensional hexagonal lattice symmetry (Fig. 6).

The diameter of the (1:3) mixture of the melamine **1** and the acid **2**, for example, evaluated from the CPK model amounts to approximately 44 Å. This value is in excellent agreement with the hexagonal lattice constant (40 Å) determined by X-ray diffraction.

CONCLUSIONS

The hydrogen-bonded complexes of the alkoxyphenylmelamine with the complementary semiperfluorinated benzoic acid can be considered as non-covalent analogues of block mesogens composed of three different and incompatible molecular segments. Docking of one equivalent of the acid preferentially leads to heterodimers with elongated aromatic cores. Microsegregation along with the linear pre-organization of the extended H-bonded polar segments favours a parallel bilayer-like arrangement. However, the stabilization of layered mesophases is in competition with the disturbance provided by the different space requirements of the fluorinated and lipophilic molecular blocks. A bilayer ribbon phase with two-dimensional *c2* mm plain group is formed.

A further approach towards controlling the molecular topology arises from the molar content of the acid. Hydrogen-bonding with two or three acid molecules defines a cylindrical molecular geometry of the melamine/benzoic acid associates which, consequently, organize to hexagonal columnar mesophases.

Hence, the cooperative interplay of hydrogen bonding, nanoscale segregation of incompatible molecular block and controlling the interface curvature of assembled aggregates by the volume fractions of molecular fragments segregated in different sub-spaces accounts for tailoring the mesophase morphologies of the complementary molecular species.

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