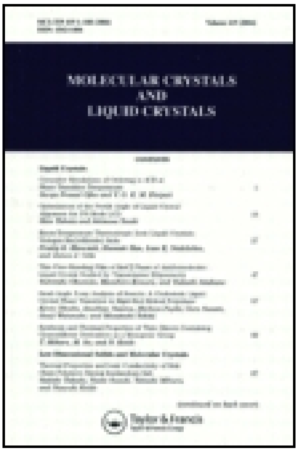

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Low Temperature Solid States of Mesogenic Alkyl- and Alkoxy-Cyanobiphenyls and Nitroxide Formation Kinetics

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LOW TEMPERATURE SOLID STATES OF MESOGENIC ALKYL- AND ALKOXY-CYANOBIPHENYLS AND NITROXIDE FORMATION KINETICS

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Abstract. Four low temperature solid states of long chain alkyl- and alkoxycyanobiphenyls(n= 5-8) have been obtained by special crystallization technique. The peculiarities of local molecular ordering and molecular dynamics in these phases are discussed on the basis of DTA- and kinetic data. Thermal behavior and molecular dynamic properties of liquid crystalline systems at low temperatures are of great interest. Lowering the temperature led to stabilization.

Solid state polymorphism is a particular feature of mesogenic compounds[1]. The variety of molecular organization in liquid crystalline mesophases of long chain alkyl- and alkoxycyanobiphenyls is closely connected with their solid phase structures.

It has been shown by DTA-method that mesogenic alkylcyanobiphenyls: C_5H_{11}-C_6H_4-C_6H_4-CN (5CB)
C_8H_{17}-C_6H_4-C_6H_4-CN (8CB)
and alkoxycyanobiphenyls: $C_7H_{15}O$-C_6H_4-C_6H_4-CN (7OCB)
$C_8H_{17}O$-C_6H_4-C_6H_4-CN (8OCB)
form at low temperature four solid states: glass-like and three crystal phases. Using some special methods:

- -fast cooling (up to 1000K/min)
- -cooling of the samples and maintaining at constant temperature
- -slow cooling (~1K/min) of the sample
- -isothermal crystallization
- -directional crystallization

TABLE 1 (continuation).

5OCB	nematic(N)		N→ I	342	0.38
	crystal.K1	Direct crystallization with initiation at 298K and thermal treatment at 324K	K1 →N K1 →K2	324	14.3
	crystal K1'	Direct crystallization with initiation at 298K and therm. treatment at 323K	K1' →N K1' →K2	322.5	14.4
	crystal.K2	Isothermal crystallization at 305K	K2 →N	320	25.7
	crystal K2'	Isothermal crystallization at 299K	K2' →N K2' →K2	300	11.8
	crystal.K3	Freezing in liquid nitrogen and heating up to temp. 245.5K	K3 →K1 K3 →K1' K3 →K2	245.5	-8.6
	crystal K1	Freezing in liq. nitrogen heating up to temps above 223K	K1 →N	322	27.6
	crystal K2	Isotermal crystallization at 308 K	K2 →N	321	27.1
	crystal K3	Freezing in liq. nitrogen.	K3 →K1		-0.55

transformed by heating to stable crystal forms. Heating of nonstable crystal phase K3 of 5OCB up to 246K led to the mixture of three more stable crystal phases K1, K1', K2.

Isothermal crystallization of all studied mesogenic cyanobiphenyls allowed us to obtain additional crystal phases. Isothermal crystallization of 5CB at 268-273K led to K2 and K3 crystal phases formation with equal probabilities. Crystallization rates were $0.72*10^{-3}$cm/s for K2-phase and $2.9*10^{-3}$cm/s for K3-phase. K2 is stable for a long time and ΔH-value of its melting process is almost equal to the value for stable K1-phase melting. K3-phase of 5CB was less stable and slowly transformed to K1-phase.

Isothermal crystallization of alkoxycyanobiphenyls 5OCB

TABLE 1 (continuation).

5OCB	nematic(N)		N→ I	342	0.38
	crystal.K1	Direct crystallization with initiation at 298K and thermal treatment at 324K	K1 →N K1 →K2	324	14.3
	crystal K1'	Direct crystallization with initiation at 298K and therm. treatment at 323K	K1' →N K1' →K2	322.5	14.4
	crystal.K2	Isothermal crystallization at 305K	K2 →N	320	25.7
	crystal K2'	Isothermal crystallization at 299K	K2' →N K2' →K2	300	11.8
	crystal.K3	Freezing in liquid nitrogen and heating up to temp. 245.5K	K3 →K1 K3 →K1' K3 →K2	245.5	-8.6
	crystal K1	Freezing in liq. nitrogen heating up to temps above 223K	K1 →N	322	27.6
	crystal K2	Isotermal crystallization at 308 K	K2 →N	321	27.1
	crystal K3	Freezing in liq. nitrogen.	K3 →K1		-0.55

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Isothermal crystallization of alkoxycyanobiphenyls 5OCB (at 303K), 7OCB (at 308K) and 8OCB (at 309K) led to K2 - crystal phase formation. Melting temperature for this phase is lower than the melting temperature for K1 - crystal phase.

The relative stability of K1, K2 - crystal phases of alkoxycyanobiphenyls changes according to the length of alkyl chain.

For liquid crystal 5OCB, K2 - crystal phase is the most stable at temperatures which are lower than the melting point. The ΔH-value of its melting process is almost two times greater than for K1(K1')-phase. Under maintaining of K2-phase at temperatures lower than the melting temperature the transition K2 ⟶ K1(K1') has been observed. For both liquid crystals 7OCB and 8OCB K1 and K2 crystal phases are stable and we don't observe transformations within few months. For liquid crystal 8OCB K1 - crystal phase is more stable, under ordinary temperatures the whole transformation from K2-phase to K1-phase occures during several hours. ΔH-values for K1 and K2- crystal phases of 7OCB and 8OCB are almost equal and are close to the value for 5OCB.

This fact can be discussed in view of pecularities in the K1 and K2 crystal structures. It was shown for liquid crystal 8OCB[3-5] that K1- crystal phase was formed by monomeric cyanobiphenyl units.

Crystallografic data for K2-phase of 5OCB[6] indicate the dimeric layered structure of this phase. The increase of alkyl chain length led to weakening of the dipole-dipole interactions between the monomer molecules according to the fact that molecular size increases upon maintaining of molecular dipole moment. Due to this effect the stability of the dimeric structures decreased.

The kinetics of model photoinduced nitroxide formation process:

$$t\text{-}C_4H_9NO \underset{\Delta}{\overset{h\nu(\lambda>650nm)}{\rightleftarrows}} [t\text{-}C_4H_9^{\bullet}+NO\ ] \xrightarrow{-NO} t\text{-}C_4H_9^{\bullet}$$

$$t\text{-}C_4H_9NO+t\text{-}C_4H_9^{\bullet} \longrightarrow t\text{-}C_4H_9N(O)^{\bullet}\text{-}t\text{-}C_4H_9$$

was investigated by ESR-method in different low temperature solid states of cyanobiphenyls. It has been shown that the kinetics of this process is determined by the relation of probabilities of the primary radical pair to recombine, their reorientation and escape to the volume. It reflects the percularities of the local molecular ordering and molecular dynamics of the media[7].

Special investigation by DTA-method has shown that in all the cases the guest component (2-methyl-2-nitrosopropane) and the host component (cyanobiphenyl) formed the solid solution structure. Nitrosomolecules can be included in the host crystal structure of cyanobiphenyls, forming a combined crystal structure. Thus the kinetic data obtained give us the information on the internal molecular dynamics and local molecular ordering of the cyanobiphenyl matrix.

In glass-like states of 5CB, 8CB and 5OCB obtained by fast cooling of liquid crystalline system, the quantum yield of nitroxides (ϕ) is negligible. This reflects the strong inhibition of tumbling and translational diffusion process in this phase.

In all the crystal states ϕ-value differs from zero in a wide temperature range down to the temperatures wich are about 100-150K lower than the melting points of cyanobiphenyls. This fact correlates with the maintaining of high tumbling mobility of nitroxide spin probe in this temperature range. In the case of nonstable crystal phases (K3) obtained by fast freezing of liquid crystalline samples (7OCB, 8OCB) or by crystallization of frozen samples upon their heating (5OCB, 5CB) ϕ-values are significantly lower than the values for the methastable (K2) and stable (K1) phases. Probably, it is connected with the partially glass-like character of these phases with lower molecular mobility. It seems that slow molecular motions are the main condition of these nonstable phases existence.

Heating of the samples accompanied by rising of the molecular mobility led to their rapid transformation to more stable crystal phases. This phase transition is accompanied by a sharp increase in nitroxides yield. So one can see the hysteresis phenomenon for the ϕ-values of nitroxides formation in mesogenic cyanobiphenyls at low temperatures. Temperature dependent ϕ-values in different low temperature solid state cyanobiphenyls is shown in Figure 1.

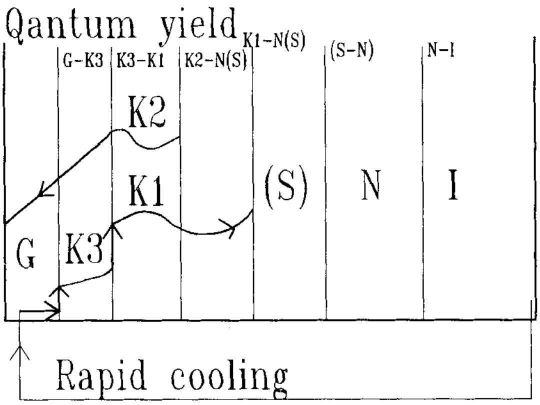

FIGURE 1 Temperature dependent ϕ-values in the low temperature solid states of cyanobiphenyls.

The ϕ-values for stable (K1) and methastable (K2) phases are close with the ϕ-values of investigated liquid phase cyanobiphenyls. We connected this fact with the high ordering of these crystal phases. This fact leads to preferential localization of guest nitrosocompound molecules between highly mobile hidrocarbon chains of alkyl and alkoxy substituents. The mobility of flexible hydrocarbon chain is not coupled with the self-diffusion of cyanobiphenyl molecules and high molecular mobility in this region maintains to rather low temperatures. In this case introduction of rather small guest molecules doesn't cause significant distortions and strain in the layered crystal structures formed by rigid aromatic cores of host molecules. Lowering of the temperature led to the intensification of this tendency and to the selforganization of the structure of solid solution of nitrosocompound in cyanobiphenyl matrix.

This process competes with the ordinary molecular mobility of the system decrease during lowering of the temperature. This fact leads to the existence of maxima in temperature dependent ϕ-values for K2 and K1 crystal phases.

It is of interest to note that for all three alkoxycyanobiphenyls studied we have the following sequence: $\phi(K2)>\phi(K1)>\phi(K3)$. This fact shows that similar crystal phases (stable, methastable or nonstable) of these mesogens have similar elements. It is in agreement with the principle of corresponding states for solid phases of mesogens[1,2]. This fact confirms by the X-ray diffraction and fluorescence spectroscopy wich show all K1-crystall phases of investigated alkoxycyanobiphenyls to be formed by monomers[3-5] or linear dimers with monomer units being in contact only by CN-groups. These structural units can form a tightly packed layered structure with conformational ordering of hydrocarbon chains. So the molecular mobility and the essiciancy of nitroxides formation in these phases are small.

The K2-phases have been obtained by crystallization of highly dimerized supercooled nematic or smectic states of mesogenic cyanobiphenyls. K2-Phases of investigated cyanobiphenyls[6] are formed by dimers with overlapping of aromatic biphenyl fragments. In this case the dimeric packing in layers is less close and the molecular mobility is higher. According to this fact the yield of nitroxides in K2-phases is higher than in K1-phases of alkoxycyanobiphenyls at the corresponding temperatures.

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