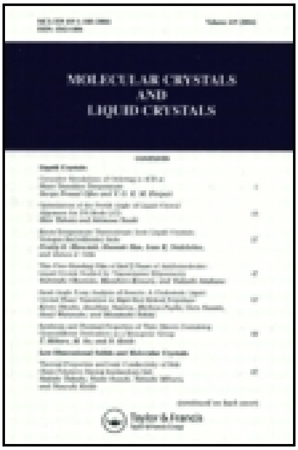

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The Phase-Structural Transitions in Liquid Crystalline Alkoxycyanobiphenyls and The Kinetics of Nitroxides Formation

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THE PHASE-STRUCTURAL TRANSITIONS IN LIQUID CRYSTALLINE ALKOXYCYANOBIPHENYLS AND THE KINETICS OF NITROXIDES FORMATION

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Abstract The kinetics of photoinduced nitroxides formation has been studied by ESR in mesogenic alkoxycyanobiphenyls 6OCB, 7OCB, 8OCB and their mixtures in temperature range 173-383 K. The nitroxide formation effectively takes place in isotropic, nematic,smectic and solid states of the systems. The reaction kinetics is sensitive to the phase structure on the molecular level.

The chemical reactions in liquid crystals have been intensively studied[1-5] due to a unique combination of orientational and in some cases translational ordering of molecules with their high mobility. The spread of applications of optoelectronic devices based on liquid crystals causes great interest in physicochemical investigations of liquid crystalline compositions and in chemical reactions occurring in them in a wide temperature range.

The kinetics of the model process of di-(tert-butyl) nitroxide formation upon the photolysis of 2-methyl-2-nitrosopropane:

$$tC_4H_9NO \xrightleftharpoons[\Delta]{h\nu\ (\lambda > 650\ \mathrm{nm})} [tC_4H_9{}^{\bullet}\uparrow + \uparrow{}^{\bullet}NO] \dashrightarrow tC_4H_9{}^{\bullet} + NO$$

$$tC_4H_9{}^{\bullet} + tC_4H_9NO \xrightarrow{k_T} tC_4H_9-N(O^{\bullet})-tC_4H_9$$

has been studied by ESR* in mesogenic alkoxycyanobiphenyls 6OCB, 7OCB, 8OCB and their mixtures 1:1, 3:7, 7:3 w/w in the temperature range of 173-383 K. The

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*) The experimental conditions can be found in[1].

reaction of nitroxide formation effectively takes place in isotropic, nematic, smectic and solid states of the systems.

The kinetics of nitroxide formation has been found to be sensitive to the structural organization c the medium and to the changes of molecular mobility within the systems. The temperature dependence of the initial reaction rate (W_0,relative units) in 8OCB liquid crystal is given as an example in Figure 1.In addition to nematic phase this compound shows also low temperature smectic S_A-phase.

A monotonous decrease of W_0-values was observed in isotropic and nematic phases at cooling. This correlate with monotonous decrease of the nitroxide tumbling mobility. The W_0-value droped abruptly at the nematic-smectic phase transition. The reaction rate in smectic phase within the experimental accuracy did not depend on temperature (Figure 1). The ESR spectrum in this phase appearedto be the superposition of the di-(tert-butyl)nitroxide radical spectra typical for nematic (ordered) and isotropic (disordered) phases. It is probable that in this particular case there occurs an incorporation of nitrosocompound and the reaction product into the ordered smectic layeres,formed by rigid biphenyl fragments, and into practically isotropic interlayer area, formed by mobile hydrocarbone chains. The mobility of nitrosocompound molecules and nitroxides in the ordered rigid part of smectic layers is lower. This results in a certain decrease of the process rate. Distribution of nitrosocompound molecules over the areas with different ordering determines the kinetics of nitroxide formation in smectic phase.

In supercooled state of the liquid crystalline

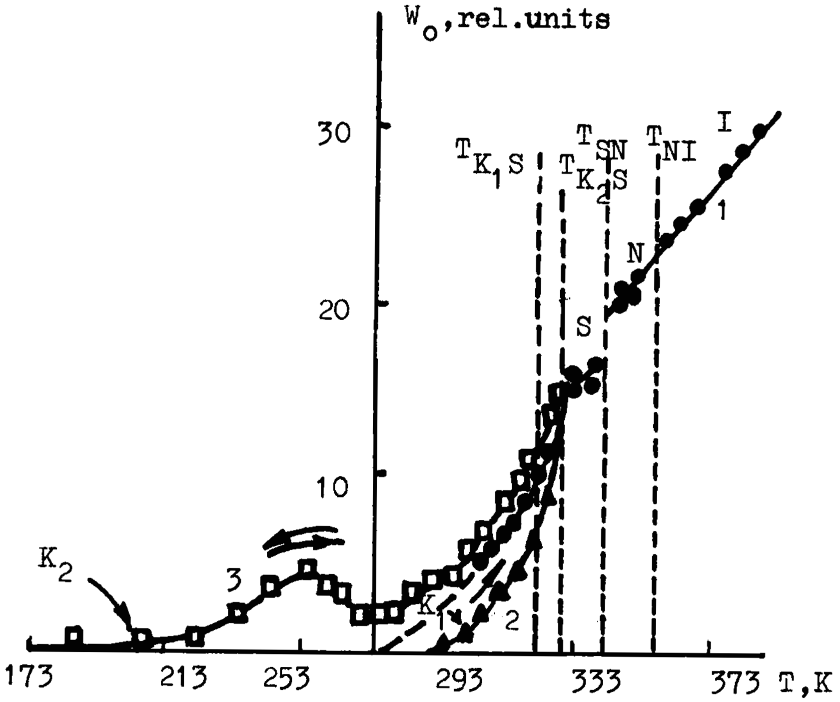

FIGURE 1. Temperarture dependences of initial nitroxides formation rate W_o during photolysis of 2-methyl-2-nitrosopropane in 8OCB: 1 - in isotropic, nematic, smectic and supercooled states; 2 - in solid K_1-phase; 3 - in solid K_2-phase.

system the decrease in W_o-values with the lowering of the temperature became more rapid. While in the case of isotropic and nematic phases the experimental activation energy of nitroxide formation process equaled 11 kJ/mole , in supercooled state the experimental activation energy was about 40 kJ/mole. Similar values were found for the activation energy of rotational mobility of nitroxides in isotropic and nematic phases. The study of photoinduced nitroxide formation in different low temperature solid modifications of 8OCB, obtained under various crystallization conditions showed that the reaction kinetics was sensitive to the variations in microstructure and in the local ordering of the molecules. The W_0-values in K_1-phase, obtained from isotropic state by fast crystallization of the system upon cooling droped abruptly with the temperature decrease and equaled practically zero at 295 K. In K_2-phase, obtained by isothermal crystallization of the supercooled system, the nitroxide formation rate differed from zero down to 223 K and its temperature dependence was a complicated one(Figure 1).

It has been found by DTA-method that 7OCB and 8OCB liquid crystals in mixtures form continuoussolid solutions.[6] The differences in the nitroxide formation kinetics in comparison with individual compounds in K_1-phase can be attributed to the influence of additional free volume in the investigating systems which appears probably as a result of different lengths of alkyl chains. For these mixtures the sharp increase of W_0-values in 253-263 K temperature range was observed, which we connect with the phase structure transformation.

It has been shown that under definite conditions the mixtures of polar liquid crystals form the reentrant phases[7]. We have studied the kinetics of photoinduced nitroxides formation in 6OCB-8OCB mixtures (3:7 w/w). Cooling of this mixture from the nematic state to 318 K led to marked decrease in W_0-values and complex ESR spectra of nitroxides, which can be considered as a superposition of the ESR- spectra. Such ESR-spectra were observed for reaction in 8OCB in smectic S_A-phase. The cooling of the system up to 280 K was accompanied by typical for nematic state of the system ordnary triplet structure of nitroxide ESR-spectra. The observed W_0-values in this phase could be obtained by extrapolation of the reaction rate temperature dependence measured in nematic phase.

Thus the kinetics of nitroxides formation has been found to be sensitive to the phase structure of liquid crystalline systems and to the type of local molecular ordering and can be used for probing the phase-structural transitions.

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