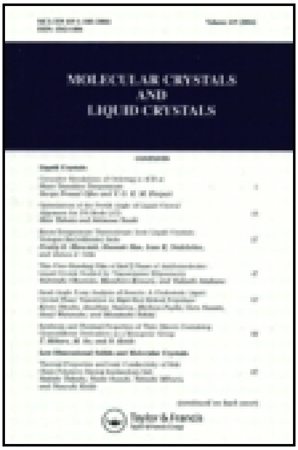

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"CAGE EFFECT" IN REACTIONS OF FREE RADICALS FORMATION AND RECOMBINATION IN NEMATIC AND CHOLESTERIC LIQUID CRYSTALS

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Abstracts The kinetics of free radical formation during thermal decomposition of AIBN and free radical recombination in nematic 5CB-5OCB mixtures and cholesteric ChOl-ChPel mixtures has been studied. The effect of orientational order of the systems on probabilities of radical escape and their recombination has been found.

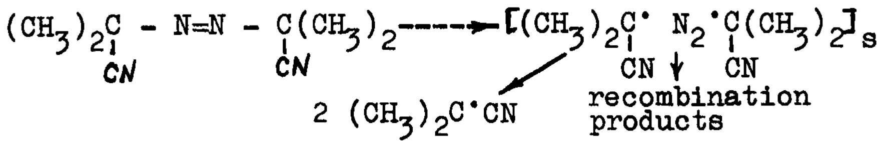
The investigation of free radicals reactions in liquid crystalline systems is of interest in particular in respect of searching ways of effective chemical stabilization of liquid crystalline materials. The problem is especialy acute for a number of nematic and cholesteric liquid crystals.[1,2]

The kinetics of free radicals formation in orientationaly ordered media has been studied for an example of thermal decomposition of azoisobutane acid dinitril (AIBN), which is widely used as free radical processes initiator[3] in nematic system based on 4-pentyl-4'-cyanobiphenyl (5CB) and 4-pentyloxy-4'-cyanobiphenyl(5OCB) mixtures and in cholesteric system based on cholesteryl oleate (ChOl) and cholesteryl pelargonate (ChPel) mixtures. The amount of free radicals in the sample volume was registrated by expenditure of stable 2,2,6,6-tetramethyl-4-piperidine-N-oxyl (TEMPO) which had been used in this case as a "counter" of active radicals.

The initial rate of cyanisopropyl radical formation in the nematic system 5CB/5OCB (60/40%) is shown in

Figure 1.vs temperature. The temperature decrease led to the phase transition of the system from isotropic state to nematic one and was accompanied by decrease of radical formation rate. The experimental activation energies for the process actually coincided in isotropic phase E_a=29,6±0.5 and in nematic E_a=31.0±0.5 kcal/mole. The transition from isotropic state to nematic one can be realized also by varying the composition of liquid crystalline system. As an example Figure 2 presents data on the kinetics of cyanisopropyl radicals formation as a result of AIBN thermal decomposition at 40°C in 5CB/5OCB mixtures. The change of alkoxycompound component from 18 to 22 % caused the transition from isotropic to orientationally ordered nematic phase and was accompanied by sharp change of process rate. The viscosity of the system practically did not change in this case. Mesophase disappearance, which has been caused by isotropic solvent (i.e. benzene) addition, also led to the pronounced decrease of free radicals formation rate in the case of nematic system and in the case of cholesteric one. Table 1 shows free radicals yield in mesophase and isotropic media calculated from data obtained.

The rate of AIBN thermal decomposition is known to be actually independent on solvent nature[4] and can be considered as almost constant at given temperature. Data obtained indicate therefore that the system transition from isotropic state to orientationally ordered one results in the decrease of primary radicals escape into the volume due to the increase of their heminate recombination probability:



$$(CH_3)_2\underset{CN}{C} - N{=}N - \underset{CN}{C}(CH_3)_2 \longrightarrow [(CH_3)_2\underset{CN}{C}^{\cdot}\ N_2\ {}^{\cdot}\underset{CN}{C}(CH_3)_2]_s \to 2\ (CH_3)_2C^{\cdot}CN;\quad \downarrow \text{recombination products}$$

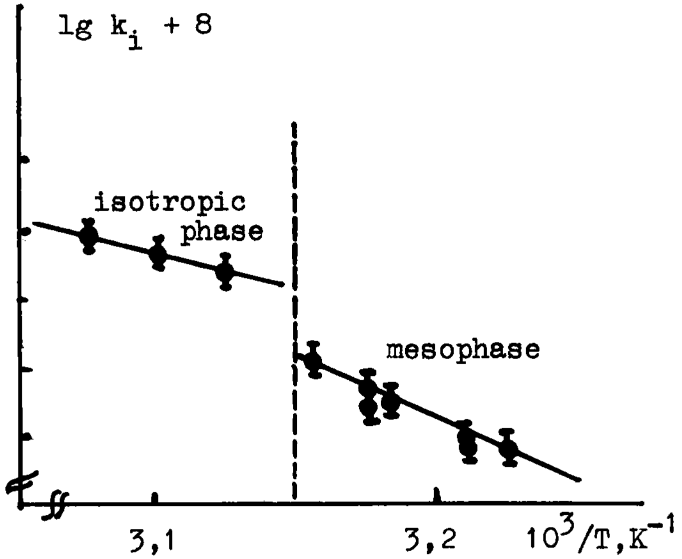


FIGURE 1. The initial rate constant of free radical formation during AIBN thermal decomposition in 5CB/5OCB mixture (60/40%) ([AIBN] =2.8·10^{-2}mol /l) vs temperature.

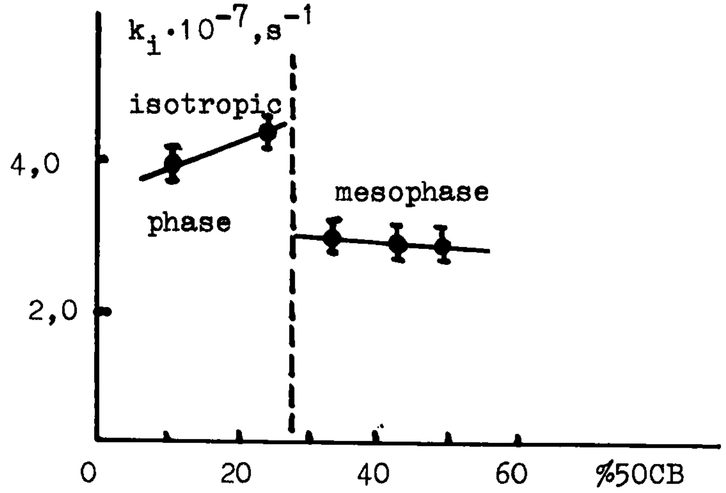


FIGURE 2. The initial rate constant of free radical formation during AIBN thermal decomposition in 5CB/5OCB mixture vs its composition, T=40°C, [AIBN]=2.8.10^{-2}mol /l.

TABLE 1 The values of cage effect(e) for free radical generation during thermal decomposition of AIBN and lauryl peroxide in different media, T=40°C.

Initiator	System	e isotropic	 mesophase
AIBN	Benzene	0.62	-
AIBN	5CB/5OCB	0.33	0.25*
AIBN	5CB/5OCB	0.39	0.25**
AIBN	5CB/5OCB	0.33	0.20***
lauryl peroxide	ChPel/ChOl	0.36	0.28

*introduction benzene additives

**variation in major components content

***extrapolation of temperature dependence

We have considered the influence of media orientational ordering directly on active radicals reaction kinetics for an example of peroxyl radical recombination, those formed during the process of cholesterol derivatives oxidation initiated by lauryl peroxide:

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_6} \text{products}$$

Process rate was determined using chemiluminescent method by oxygen afteraction.[5] Obtained values of recombination rate constant (k_6,l/mol·s) are presented in Table 2. Accuracy in k_6-values determination was ±10%.

TABLE 2 Recombination rate constant values of peroxide radicals(k_6) in ChPel/ChOl mixtures of different composition.([In]=$2.6\cdot10^{-2}$mol/l,T=47°C).

Composition ChPel/ChOl,%	Phase state	$k_6\cdot10^3$,l/mol·s
15/85	isotropic	1.5
60/40	mesophase	3.5

The data presented show that the transition of the system from isotropic to cholesteric phase with local order similar to nematic one is accompanied by sharp growth of recombination rate. Mesophase disappearence as a result of isotropic chlorbenzene adding in the ChOl/ChPel system(40/60%) caused the k_6-values decrease from $3.5\cdot10^{-3}$ l/mol·s to $1.5\cdot10^{-3}$ l/mol·s. The latter value has been obtained by extrapolation of recombination rate constant values for different benzene concentrations in the system to its zero concentration and characterizes k_6-value in isotropic state of the system. The transition from isotropic state to mesophase in this case also caused the increase of probability of radicals recombination most likely to their orientational ordering.

Thus the data obtained demonstrate the effect of orientational order changes achieved as by temperature changes, as by varying liquid crystalline system composition, on free radicals formation and recombination reactions, which represent the key stages in chain oxidation reactions.

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