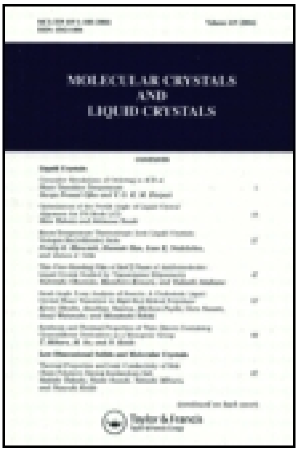

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 27 Oct 2006.

To cite this article: V. A. Batyuk , Yu. N. Morosoy , T. I. Shabatina & G. B. Sergeev (1992): Photoinduced Formation of Nitroxides in Partially Disordered Solid Phases of Plastic and Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 211:1, 407-413

To link to this article: http://dx.doi.org/10.1080/10587259208025841

Mol. Cryst. Liq. Cryst. 1992, Vol. 211, pp. 407–413
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Printed in the United States of America

PHOTOINDUCED FORMATION OF NITROXIDES IN PARTIALLY DISORDERED SOLID PHASES OF PLASTIC AND LIQUID CRYSTALS

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(*Received September 14, 1991*)

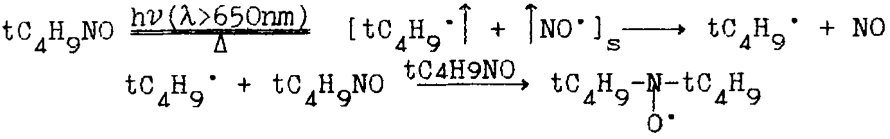
Abstract. The kinetic features of photoinduced nitroxide formation from 2-methyl-2-nitroso-propane in a number of plastic crystals (PC: cyclohexane, cyclohexanone, cyclohexanol, 1,1,1-trichlorethane, tert-butylchloride, tert-butylamine) and liquid crystals (LC: 5CB;5OCB;7OCB;8OCB) have been studied by ESR at low temperatures.

It was shown that in crystal phases of LC's and in complete ordered phases of PC's the nitroxide formation quantum yields differ from zero even at temperatures which are 100-150K lower than melting points of the systems. The kinetic consequences of some orientational and positional degrees of freedom are discussed.

Keywords: nitroxides, plastic crystal, liquid crystal, electron paramagnetic resonance, photolysis

The solid phases of liquid crystals (LC's) and plastic crystals (PC's) are of great interest due to partial orientational or positional molecular disordering. The different molecular organization of the solid states in this cases must have pronounced effects on reaction kinetics.

The photoinduced process of di-tert-butylnitroxide radical formation



$$tC_4H_9NO \xrightarrow[\Delta]{h\nu(\lambda>650nm)} [tC_4H_9^{\cdot}\uparrow + \uparrow NO^{\cdot}]_s \longrightarrow tC_4H_9^{\cdot} + NO$$

$$tC_4H_9^{\cdot} + tC_4H_9NO \xrightarrow{tC4H9NO} tC_4H_9-\underset{\underset{O^{\cdot}}{|}}{N}-tC_4H_9$$

in a number of LC's and PC's was chosen as an object of investigation. The LC cyanobiphenyls : 4-n-pentyl-4'-cyanobiphenyl (5CB), 4-n-pentyloxy-4'-cyanobiphenyl (5OCB), 4-n-heptyloxy-4'-cyanobiphenyl (7OCB), 4-n-octyloxy-4'-cyanobiphenyl (8OCB) and PC's: cyclohexane, cyclohexanone, cyclohexanol, CCl_3CH_3, t-C_4H_9Cl, t-$C_4H_9NH_2$ were used as reaction media.

The kinetics of model processes were studied by ESR. The samples before photolysis were vacuum treated to eliminate oxygen.The ESR spectra obtained were used for estimation of the di-tert-butyl-nitroxide radicals' rotational reorientation frequency (ν_r).[1] The phase diagrams of "2-methyl-2-nitrosopropane - host (LC or PC)" systems were constructed on the basis of the samples' thermograms obtained with the help of sensitive equipment constructed in our laboratory. Examples of the temperature dependence of φ vs. T and ν_r vs. T in different solid states of 5OCB, cyclohexane and CCl_3CH_3 are given in Figs. 1 and 2 (see also Figs.3-6 for other results).

The analysis of obtained "nitrosocompound - host" phase diagrams has shown that nitrosocompound molecules are incorporated in "host" crystal lattices both by substitution type (in PC's) and by incorporation type (in LC's). The formation of the reaction product di-tert-butylnitroxide is possible only if some rotational or translational mobility remains in the solid phase[2,3].

In LC glassy phases φ was practically equal to zero. In crystalline phases of LC's and incomplete ordered phases of PC's, φ differs from zero even at temperatures 100-150K lower than the melting points (Tm) of the systems. Some of the characteristics of the temperature dependences of φ and ν_r in different solid states of LC's and PC's are given below.

The diffusion of tert-butyl radicals and NO molecular radicals occurs in the crystalline phases of PC's by several different mechanisms. Thus far, as the tert-butyl radicals have the same dimensions as the matrix molecules, their translational displacement are provided by matrix self-diffusion mechanisms. The small NO size allows its incorporation into octahedral holes of PC face-centered cubic lattices without remarkable lattice distortion; thus NO diffusion may occur between interstices. At low temperatures the NO diffusion gives the basic contribution to the geminal radical pair's [$tC_4H_9^{\bullet}$+ $NO^{\bullet}$] separation and the consequent nitroxide formation. The convergence of activation energies corresponding to the φ decrease with temperature (15.1±3.0 kJ/mol) and matrix self-diffusion (42 kJ/mol measured by NMR)[4] in the high-temperature orientationally disordered crystalline phase of cyclohexane provide additional evidence for this statement.

Matrix	Crystal phase	Tm,K	Tss,K	Type of φ – T curve	Tmax,K φ – T curve
5CB	K1 (stable)	295	–	extrem.	243
	K2 (metast.)	288	–	extrem.	258
	K3 (metast.)	282	–	extrem.	258
5OCB	K1 (metast.)	324	–	extrem.	243
	K2 (stable)	320	–	extrem.	243
	K2' (metast.)	300	–	––	–
	K3 (unstable)	–	246.5	monoton.	–
7OCB	K1 (stable)	324	–	extrem.	243
	K2 (metast.)	322	–	extrem.	243
	K3 (unstable)	–	223	monoton.	–
8OCB	K1 (stable)	325	–	extrem.	243
	K2 (metast.)	317	–	extrem.	243
	K3 (unstable)	–	223	monoton.	–
cyclo-hexane	K1 (stable)	280	–	monoton.	–
	K2 (stable)	–	187	extrem.	173
cyclo-hexanone	K1 (stable)	230	–	monoton.	–
	K2 (stable)	–	221	monoton.	–
cyclo-hexanol	K1 (stable)	306	–	monoton.	–
CH_3CCl_3	K1 (stable)	242.5	–	extrem.	230
	K2 (stable)	–	230	monoton.	–
$tC_4H_9NH_2$	K1 (stable)	205	–	monoton.	–
	K2 (stable)	–	201	extrem.	200
	K3 (stable)	–	197.5	monoton.	–
tC_4H_9Cl	K1 (stable)	245.	–	monoton.	–
	K2 (stable)	–	210	monoton.	–
	K3 (stable)	–	180	––	–

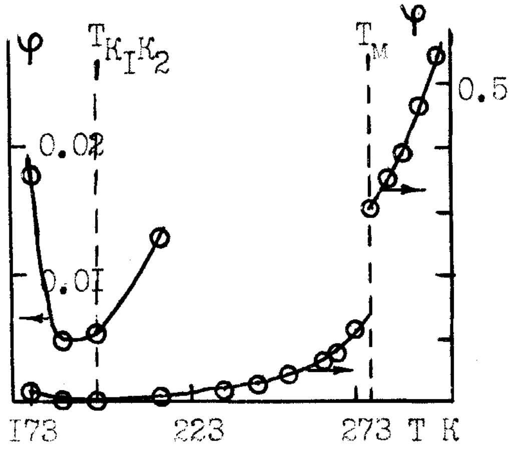


FIGURE 1. Temperature dependence of quantum yield of di-tert-butylnitroxides (φ) during photolysis of 2-methyl-2-nitrosopropane in cyclohexane.

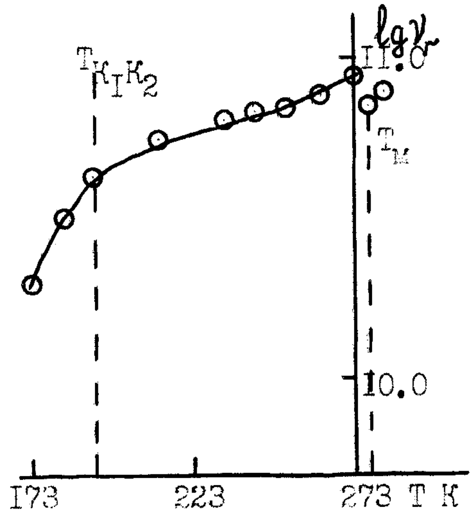


FIGURE 2. Temperature dependence of rotational reorientational frequency of di-tert-butylnitroxides (ν_r) in cyclohexane.

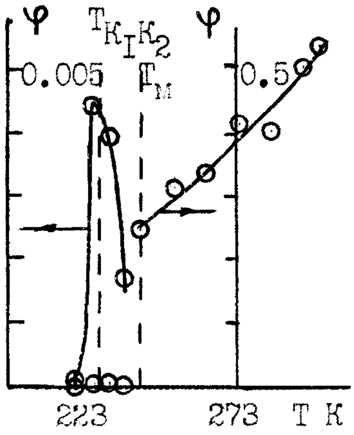


FIGURE 3. Temperature dependence of quantum yield of di-tert-butylnitroxides (φ) during photolysis of 2-methyl- 2 - nitrosopropane in 1,1,1-trichlorethane.

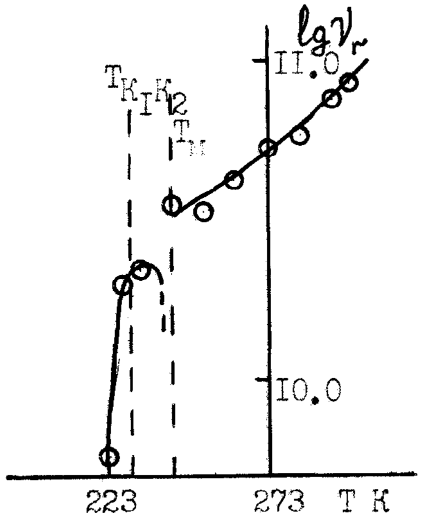


FIGURE 4. Temperature dependence of rotational reorientational frequency of di-tert-butylnitroxides (ν_r) in 1,1,1-trichlorethane.

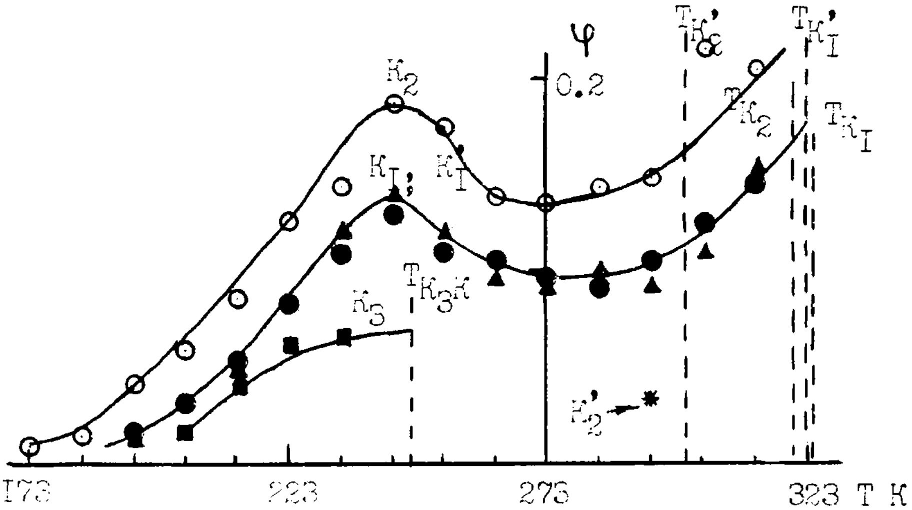


FIGURE 5. Temperature dependence of quantum yield of di-tert-butylnitroxides (φ) during photolysis of 2-methyl-2-nitrosopropane in 4-n-pentyloxy-4'-cyanobiphenyl.

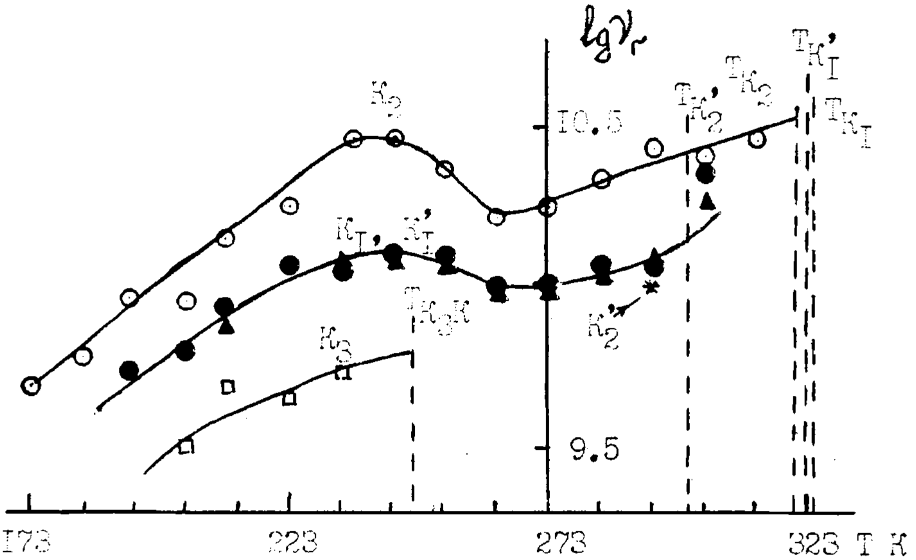


FIGURE 6. Temperature dependence of rotational reorientation frequency of di-tert-butylnitroxides (ν_r) in 4-n-pentyloxy-4'-cyanobiphenyl.

The rotational reorientation of nitroxides is influenced by rotational reorientation of matrix molecules. (Nitroxides rotational reorientation activation energy appeared equal to 5.2±1.9 kJ/mole for the high-temperature orientationally-disordered phase of cyclohexane and almost equal to the rotational reorientation activation energy of cyclohexane molecules - 6.4 kJ/mole[4].)

In low-temperature phases of PC's, some degree of molecular mobility due to motion of some atomic groups in molecules (for instance rotation of methyl groups in 1,1,1-trichlorethane and conformational rearrangements of cyclohexane ring) is maintained, and assists in the formation of nitroxides to some small extent.

For unstable crystalline phases of LC's, φ and ν_r are lower than with metastable and stable crystalline phases of the same systems. That is because the structures of the former phases have much in common with glassy states, and are characterised by reduced molecular mobility, which in turn is the essential condition of their existence.

The high efficiency of di-tert-butylnitroxide formation in crystalline phases of cyanobiphenyls may be due to localization of 2-methyl-2-nitrosopropane molecules in regions of flexible alkyl groups of CB's during co-crystallization, this localization does not interfere with the packing of central rigid aromatic fragments of CB's molecules. In contrast to the statistically uniform distribution of molecules in matrices of plastic crystals (dimensions of plastic crystals molecules and nitrosocompound molecule are similar),the LC systems containing several nitroso compound molecules showed a non-random distribution of nitroso molecules. In these cases, the nitroso molecules were found in adjacent sites in the crystal lattice.

This tendency grows with a decrease in temperature, and the reaction of the tert-butyl radical with 2-methyl-2-nitrosopropane becomes more feasible. Along with other reasons this can lead to extrema on φ and ν_r temperature dependences, which in fact were observed experimentally (see Figs.1-6).

Analogous self-ordering mechanisms of formation of solid 2-methyl-2-nitrosopropane solutions in the crystalline host matrix can take place in PC's. This is supported by experimental φ and ν_r temperature dependences in 1,1,1- trichlorethane (Fig. 3).

One can foresee the structures of stable and metastable crystalline CB phases with the help of the corresponding states for polymorphic modifications in homologous series of LC's[5].

The available structural data and above-mentioned principle allow us to suppose that the crystalline K_1 phase of 5CB (for them the lower φ and ν_r values are characteristic) are formed from dimeric units in which molecules interact only through CN groups (see Figs.5-6).

Crystalline K_2 phases of alkyloxycyanobiphenyls and crystalline K_1 phases of 5CB are formed from dimers of other structures when two molecules interact, again through their aromatic rings. Such considerations are helpful for understanding the differences in φ and ν_r values and their temperature dependences in various crystalline phases of CB's.

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