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Kinetics of photochemical processes in photochromic azobenzene derivatives. Effect of matrix and of the phase stability

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The contribution discusses the effect of environmental constraints on the kinetics of photochromic processes occurring in two groups of azobenzene derivatives: azobenzene-containing crown ethers dissolved in various polymer matrices, and *para*-disubstituted azobenzenes dissolved in liquid-crystalline matrices. In the azobenzene-containing crown ethers, the presence of the crown is expected to affect the isomerisation kinetics. The experiments demonstrated that the crown create constraints which modify the molecular structure, thus influencing the isomerisation kinetics as was indeed found in our experiments. In the shortest crown, the room-temperature rate constant of the thermal isomerisation is c.a. two orders of magnitude lower than the respective rate in the parent azobenzene. Measurements of the kinetics of isomerisation of photochromic 4-fluoro-4′-methoxyazobenzene dissolved in the liquid-crystalline pentylocyanobiphenyl (5CB) were carried out. Deviations from the expected Arrhenius behaviour were observed for the thermal *cis–trans* reaction near the phase transition temperature of 5CB (308 K). It was also found that the isomerisation reaction may trigger the nematic-to-isotropic phase transition at the temperature substantially lower than the thermodynamic transition temperature.

Key words: *photochromism; azobenzene derivative; kinetics*

1. Introduction

Recent years have brought a revival of interest in photochromic molecular systems due to their potential use as components of information-processing media [1]. For practical purposes, photoactive species are often used as solid solutions (e.g., in polymer matrices). There has also been a growing interest in properties of photoactive dye-doped liquid crystals owing to their emerging applications in information processing [2, 3]. As most photochromic reactions are space-demanding processes, a possible existence of a distribution of microenvironments of reactive species (due to defects,

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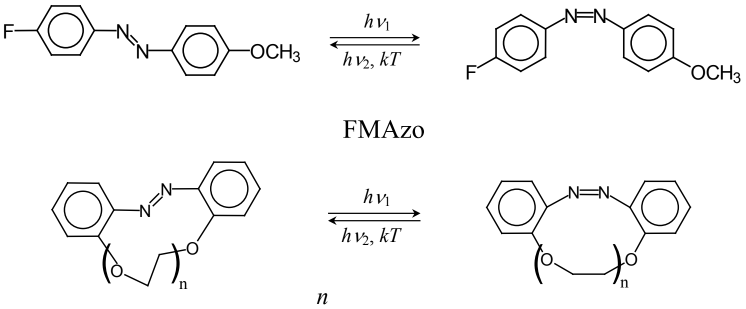
mesoscopic-scale inhomogeneities, etc.) is likely to influence the reaction kinetics in a solid state. On the other hand, the stability of phases can be modulated by photochemical reactions following excitations of photoactive dye molecules.

The aim of the contribution, supplementing results presented at the previous ICEPOM Conference [4], is to discuss the effect of environmental constraints on the kinetics of photochromic processes occurring in azobenzene-containing crown ethers – a family of photoactive molecules in which the phenyl froups of the azobenzene moiety have been additionally linked with an $-(-O-CH_2-CH_2)_n-O-$ crown [5, 6] dissolved in various polymer matrices. The presence of the crown creates constraints which should modify the molecular structure, thus influencing the isomerisation kinetics.



FMAzo

n	
1	O2N2
2	O3N2
3	O4N2
4	O5N2

Fig. 1. Chemical formulae of the azobenzene derivatives studied in this work

The contribution will also present the results of kinetic studies of the isomerisation of photochromic 4-fluoro-4′-methoxyazobenzene (FMAzo) dissolved in a liquid-crystalline pentylocyanobiphenyl (5CB) matrix. Although reports on light-driven phase transitions in dye-doped liquid crystals can be found in the literature [7–11], little is known about relations between the photochromic process and the phase transition. The formulae of the molecules under study are shown in Fig. 1.

2. Experimental

The azobenzene-containing crown ethers have been obtained from Professor J.F. Biernat and Dr. E. Luboch (Technical University of Gdańsk). FMAzo was offered by Dr. Z. Galewski (University of Wrocław). The methods of syntheses of the molecules under study have been described elsewhere [12–15]. The crown-ether containing polymer samples were obtained by casting solutions of polymers (polystyrene or PMMA) and the ethers in appropriate solvents. Additionally, some samples were prepared by the thermal polymerisation of mixtures containing pre-polymerized PMMA, monomer MMA (1:1), an initiator (benzoyl peroxide) and a suitable amount of the crown ether. As will be shown later, some features of the kinetics of the thermal isomerisation in samples prepared in such a way (hereafter referred to as ‘polymerized PMMA’) differ from those in cast samples. Typically, the thicknesses of the samples were of the order of 10–100 μm, the concentrations of the photoactive molecules being of the order of 10^{-2} M.

Solutions of FMAzo in 5CB were prepared in two concentration ranges: the mole fraction of FMAzo (x_{Azo}) in those used in spectroscopic and kinetic measurements was of the order of 10^{-3}, whereas x_{Azo} in samples used in optical experiments ranged between 0 and 0.02. The samples were placed in cells 5 μm or 10 μm thick.

The measurements of UV-VIS absorption spectra and of the isomerisation kinetics were performed with Perkin Elmer Lambda 20 spectrophotometer. The samples were irradiated using a high-pressure mercury lamp equipped with an appropriate combination of colour glass filters. The isomerisation was measured by monitoring changes of the spectra.

To investigate optical properties of the system, a polarising microscope Olympus BX60 was used, equipped with a Linkam 350 thermostated stage. UV or VIS irradiation was performed *in situ* with a mercury lamp or a halogen lamp via appropriate combinations of colour filters.

3. Results

The spectra of all molecules used in the present study are shown in Fig. 2. In their main features, all spectra resemble that of parent azobenzene displayed in the uppermost section of the figure. Under irradiation with UV light (λ = 365 nm), the stable *trans* form of an azobenzene derivative converts into the metastable *cis* form (cf. Fig. 1), the reverse reaction may occur either thermally or upon illumination with visible light (λ = 440 nm). It has been well documented that the thermal isomerisation in all systems under study follows the first-order kinetics [4, 16–19] although a dispersion of rate constants has been observed in some matrices. Thus the momentary concentration of the reactant ($n_R(t)$) should follow the equation

$$n_R(t) = n_R(0)\exp(-kt) \tag{1}$$

where $n_R(0)$ is the initial concentration and k stands for the rate constant.

The isomerisation kinetics was investigated by monitoring the absorbance of the *trans* forms of the substituted azobenzenes at ca. 350 nm (see infra). Making use of the Lambert–Beer law, it is straightforward to demonstrate that the concentration ratio $n_R(t)/n_R(0)$ is given by the equation

$$\frac{n_R(t)}{n_R(0)} = \frac{A(\infty) - A(t)}{A(\infty) - A(0)} \tag{2}$$

where $A(0)$, $A(t)$ and $A(\infty)$ are initial, momentary and final values of the absorbance at a given wavelength (350 nm in our case), and the subscript R refers here to the *cis* form.

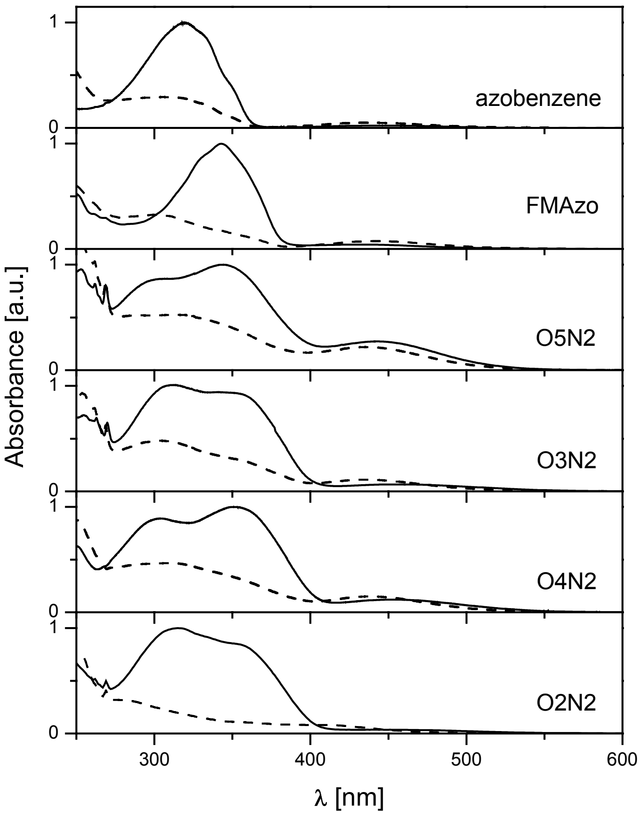


Fig. 2. Absorption spectra of the azobenzenes under study. Full lines – spectra of thermodynamically stable (*trans*) isomers; dashed lines – spectra of the same samples after UV irradiation (the samples contain mostly *cis* isomers

Semilogarithmic decays, indicative of the first order kinetics, were observed in solutions of the crown ethers in ‘common’ solvents (alkanes, DMSO, etc.), as well as in some matrices (cf. Fig. 3a). In some polymer matrices (such as polymerized PMMA), deviations from the expected behaviour were found (Fig. 3b) though the reactions have obviously been the same. This feature can be attributed to distributions of rate constants associated with distributions of micorenvironments of reacting species [20, 21]. We assumed that the former distribution could be described by a single pre-exponential factor and a Gaussian distribution of activation energies in the Arrhenius equation. Under such an assumption, we employed the method described in the preceding section: parameters controlling the kinetics were determined from the widths, positions and temperature shifts of the maxima on $t\times n(t)$ vs. $\ln t$ curves [22].

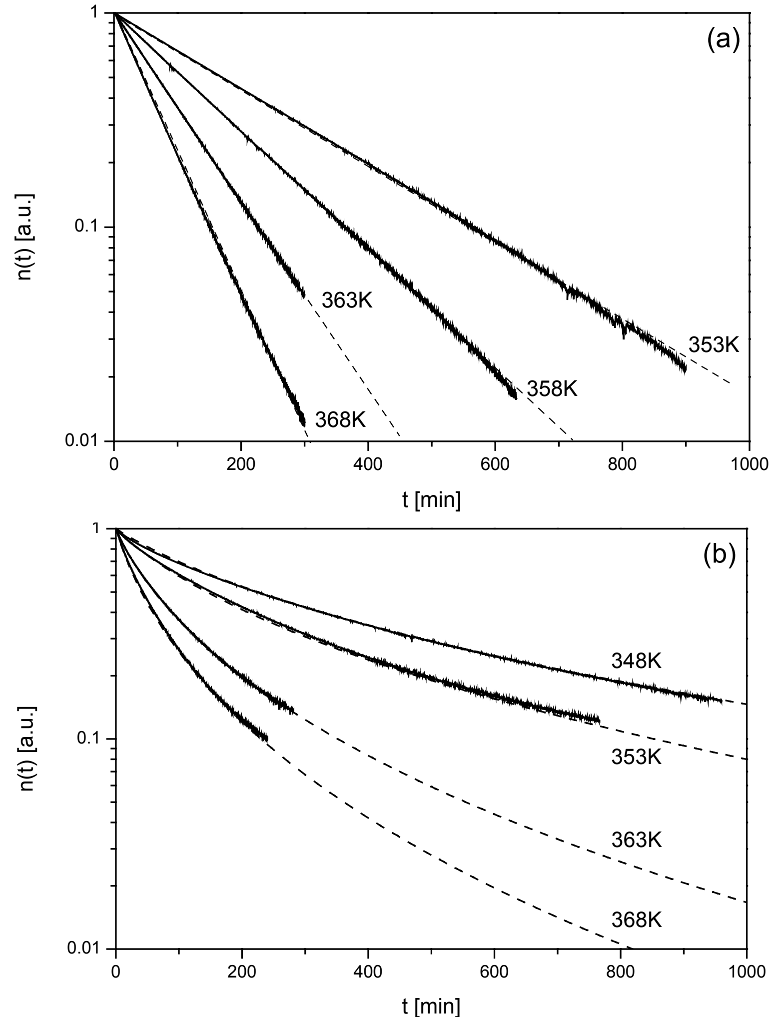


Fig. 3. Kinetics of the thermal isomerisation of O3N2 in various polymer matrices: a) cast PMMA; b) polymerized PMMA. Solid lines correspond to experimental results, dashed lines have been calculated taking the activation energies, pre-exponential factors and distribution parameters given in Table 1. See text for further discussion

Experiments on the same samples were also performed in the non-isothermal regime. To interpret the results, we employed an approximate method described in detail in [17, 18].

The temperature dependences of the rate constants determined for the crown ethers under study are shown in Fig. 4. The results are given in Table 1.

Interesting results were obtained for solutions of FMAzo in the liquid-crystalline matrix (5CB). The liquid crystal is known to undergo a phase transition between the nematic and isotropic phases at 308 K [23, 24]. The measurements of the kinetics of the isomerisation were performed in the temperature range of the stability of both the nematic and isotropic phases of 5CB. In the vicinity of the phase transition, we observed deviations from the expected Arrhenius behaviour for the thermal *cis–trans* reaction as is shown in Fig. 5. It should also be noted that the rate constants of the thermal isomerisation of FMAzo in 5CB were systematically higher than those in any common solvent, irrespective of its polarity. A comparison of the results obtained for FMAzo in a non-polar solvent (*n*-heptane), a polar solvent (DMSO), and in 5CB is given in Table 2.

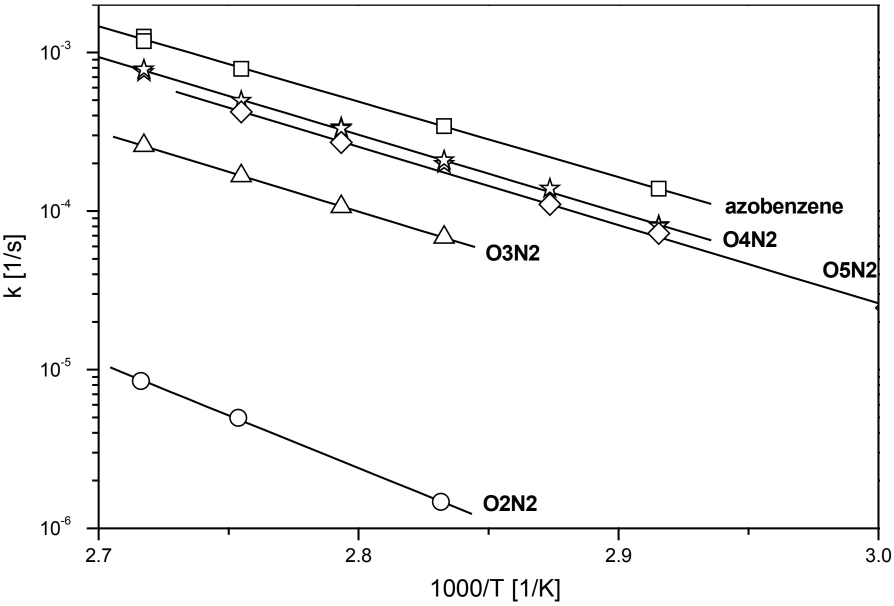


Fig. 4. Temperature dependences of the rate constants of the thermal *cis–trans* isomerisation of azobenzene-containing crown ethers in cast PMMA. The parameters determined from the Arrhenius fits to the experimental data are given in Table 1

Table 1. Parameters determined from the Arrhenius fits to the temperature dependences of the thermal isomerisation rates of azobenzene-containing crown ethers*

Molecule	E_a (kJ/mol)		ν (min^{-1})		σ (kJ/mol)	
	Cast PMMA	Polym. PMMA	Cast PMMA	Polym. PMMA	Cast PMMA	Polym. PMMA
O2N2	118	–	$6\cdot10^{11}$	–	~0	–
O3N2	97	92	$1.4\cdot10^{10}$	310^{10}	~0	2.8
O4N2	92	89	$8.7\cdot10^{9}$	$4\cdot10^{9}$	~0	2
O5N2	94	93	$1.3\cdot10^{10}$	$1.2\cdot10^{10}$	~0	2.2

*The values given in the table refer to the results obtained for the ethers dissolved in the PMMA matrices; the results obtained for other polymer matrices vary little.

We also carried out microscopic observations of the phase transition in the solutions of FMAzo in 5CB. It was found that the isomerisation reaction may trigger the nematic-to-isotropic phase transition of solutions at temperatures substantially lower than the thermodynamic transition temperature of pure 5CB, even at concentrations below 1%.

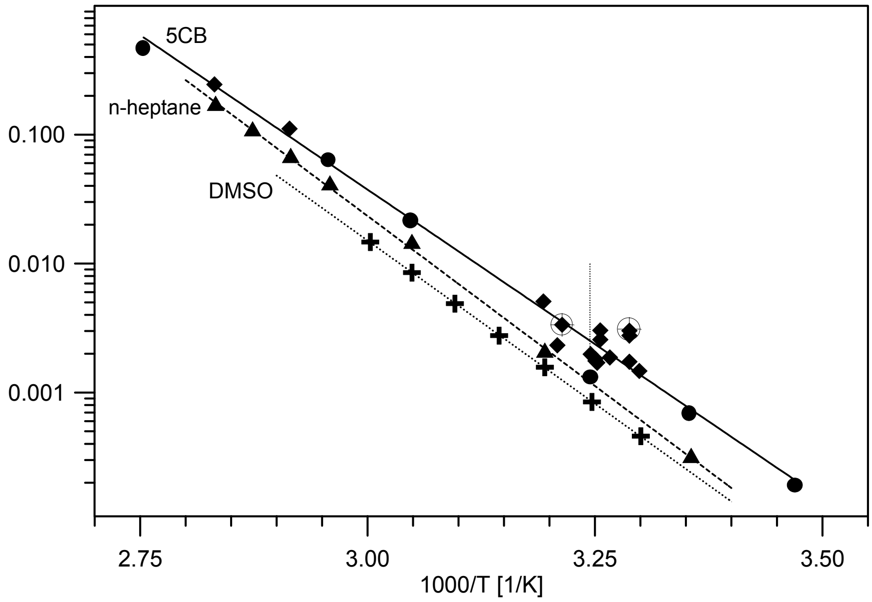


Fig. 5. Temperature dependence of the rate constant of the thermal *cis–trans* isomerisation of FMAzo in common solvents and in 5CB. Note the deviations from the Arrhenius dependence in the vicinity of the phase transition temperature of 5CB (indicated by the vertical dotted line). Runs performed on different samples are represented by different symbols. The parameters determined from the Arrhenius fits to the experimental data are given in Table 2

Table 2. Parameters determined from the Arrhenius fits to the temperature dependences of the thermal isomerisation rates of FMAzo in various solvents

Solvent	E_a (kJ/mol)	ν (10^{13} s^{-1})
n-Heptane (non-polar)	101	15.3
DMSO (polar)	97	2.2
5CB (liquid crystal)	92	0.9

Samples containing the stable (*trans*) form of the dye dissolved in 5CB were illuminated with the 365 nm radiation absorbed by the dye molecules and giving rise to the photochemically driven *trans–cis* transition. Upon illumination at temperatures below the thermodynamic phase transition temperature of pure 5CB, one could notice appearance of the isotropic phase at the temperature as low as 290 K. It was found that the incubation time of the isotropic phase (the time necessary to detect first droplets, hereafter denoted t_1) depends on the temperature, light intensity and concentration of the dye.

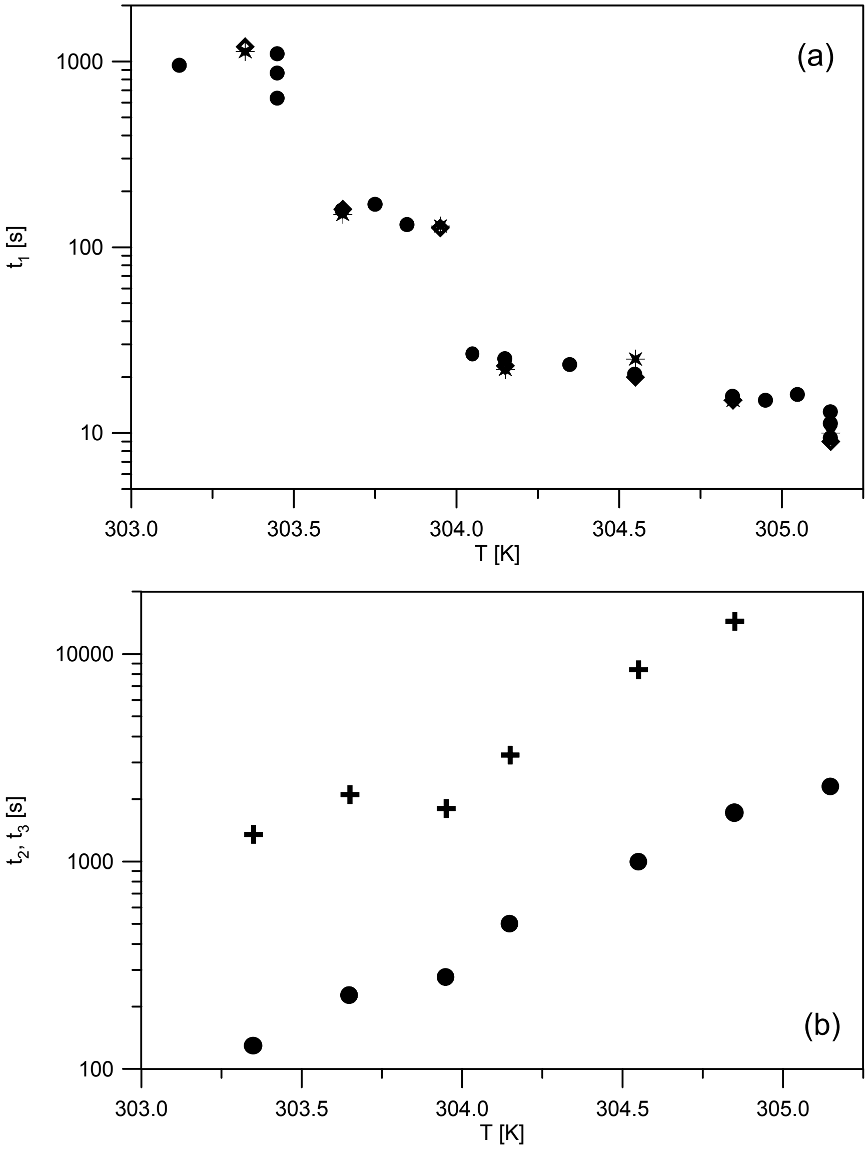


Fig. 6. Temperature dependences of the characteristic times of the phase transition solutions containing FMAzo dissolved in 5CB. Incubation time (t_1) of the N–I phase transition triggered by the photo-induced *trans–cis* isomerisation (a). Runs performed on different samples are represented by different symbols. I–N phase transition triggered by the thermal *cis–trans* isomerisation of FMAzo (b). Circles – time of reappearance of the nematic phase (t_2); crosses – time of disappearance of the isotropic phase (t_3)

Experiments reported in this paper were performed on a diluted system ($x_{\mathrm{Azo}} = 0.011$), in order to avoid any possible effects associated with aggregation of the dye. The dependences of the incubation time on the temperature and light intensity are shown in Fig. 6a. A further illumination was found to result in disappearance of the nematic phase inside the illuminated region of the sample. Pre-irradiated samples, when kept in the dark, were found to undergo a reverse process: after a certain time, depending on the temperature of the experiment, the nematic phase reappears. Both, the time of reappearance of first droplets of the nematic phase (t_2) and time of disappearance of last portions of the isotropic phase (t_3) were temperature-dependent, as is shown in Fig. 6b.

4. Discussion

It is interesting to note that the rate constants determined for O2N2 are systematically lower than the rate constants in the other crown ethers under study. The analysis of the results obtained on the series of azobenene-containing crown ethers in various matrices, given in Table 1, shows that the activation energy of the thermal *cis–trans* isomerisation in O2N2 is much higher than in other systems, being also practically independent of the matrix used (though in some matrices we observed a dispersion of the rate constants). Thus, for sufficiently large crowns, the height of the energy barrier for the thermal isomerisation appears weakly dependent on the size of the crown (and hence on the conformation of the crown). A relation between the experimental values determined in our experiments and microscopic parameters characterizing the isomerisation of the azobenzene-containing crown ethers remains, however, to be determined.

The dependence of the temperature of the nematic-to-isotropic phase transition on the isomerisation reaction can be rationalized based on a simple model taking into account differences in the solubility of FMAzo in 5CB, due to the differences in molecular shapes of the *trans* and *cis* forms of the dye. The photochemical *trans–cis* reaction results in production of *cis* molecules, incompatible with 5CB, and hence poorly soluble in the matrix. Thus the increase of the concentration of the former molecules should result in saturation of the solution, followed by a phase separation and, finally, by a disappearance of the nematic phase.

The validity of the model can be assessed as the concentration of *cis* molecules can be calculated from the equation describing the first-order kinetics provided the initial concentration and the rate constants are known. Assuming that the forward (*trans–cis*) reaction is only photochemically driven and the sample is uniformly illuminated, Eq. (1) can be transformed to the form

$$x_{\mathrm{cis}} = x_{\mathrm{trans}}(0)\bigl(1 - \exp(-k_{ph}t)\bigr) \tag{3}$$

where x is the mole fraction of either the *cis* or *trans* form of FMAzo, and k_{ph} stands for effective rate constant of the photochemical *trans–cis* reaction, depending on the light intensity and quantum yield of the reaction. Thus the incubation time t_1 is directly related to the concentration of *cis*-FMAzo in its saturated solution in the nematic phase of 5CB. Similarly, changes of the concentration of *cis*-FMAzo during the thermally driven *cis–trans* reaction are described by the equation

$$x_{\text{cis}} = x_{\text{cis}}(0)\exp\left(-k(T)t\right) \tag{4}$$

Consequently, the time of reappearance of first droplets of the nematic phase (t_2) should be related to the concentration of *cis*-FMA in its saturated solution in the isotropic phase of 5CB, whereas the time of disappearance of last portions of the isotropic phase (t_3) should be related to the concentration of *cis*-FMA in its saturated solution in the nematic phase of 5CB.

The results obtained explain on a semi-quantitative basis photochemically driven phase transition appearing below the thermodynamic temperature. One should realize, however, that the model contains several simplifications. First, the model neglects all but chemical processes occurring in the system. Secondly, it takes into considerations only the binary system 5CB–*cis*-FMAzo, neglecting the presence of the *trans* form of FMAzo in the system. We believe, however, that all neglected factors may qualitatively modify the dependence but its general form will remain unchanged.

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