Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: M. V. Alfimov & V. F. Razumov (1978): The Amorphism of the Polycrystal Phase Transition in the Course Of Cis-Trans Photoisomerization, Molecular Crystals and Liquid Crystals, 49:3, 95-97

To link to this article: http://dx.doi.org/10.1080/00268947808070334

Mol. Cryst. Liq. Cryst. Vol. 49 (Letters), pp. 95-97

Printed in the United States of America

THE AMORPHISM OF THE POLYCRYSTAL PHASE TRANSITION IN THE COURSE OF CIS-TRANS PHOTOISOMERIZATION

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(Submitted for Publication July 19, 1978)

This work is devoted to the study of cis-trans photoisomerization of 1,2-di(1-naphtyl)-ethylene (DNE) in the condensed phase. The reaction of photoisomerization of the diarylethylene is well known,[1] the reaction of cis-trans photoisomerization occurring even at 77°K. This reaction is believed to occur with a decrease of the molecular volume.[2] Therefore, we supposed that the reaction of cis-trans isomerization would occur in the condensed solid state.

All measurements were made at room temperature. The specimens were prepared by the evaporation of the benzene solution of cis-DNE (the concentration was equal to 10^{-4}M) on a glass supporter at room temperature. After this evaporation cis-DNE remained on the glass supporter in the form of amorphous droplets (Fig. 1a). Then these specimens were illuminated by the light of a high pressure Hg arc, the 366 nm line being resolved by the combination of glass filters. The intensity of this line was equal to $6.6\ 10^{-9}$ Einstein $cm^{-2}s^{-1}$. The square of the specimen was ca. 1 cm^2.

In the initial state the specimens of cis-DNE didn't fluoresce. This is in agreement with the observation that cis- isomers of diarylethylenes don't fluoresce in solution at room temperature. When irradiated for several minutes, the specimen began to fluoresce and the emission spectrum completely coincided with that of the specimen of trans-DNE obtained in the same way. Accordingly, the reaction of cis-trans isomerization occurs in the solid specimen of cis-DNE under irradiation.

The observation under a microscope shows that the embryos of the crystal phase begin to be created after several minutes of irradiation (Fig. 1b). These embryos have a strong emission. On further illumination the embryos grow until all

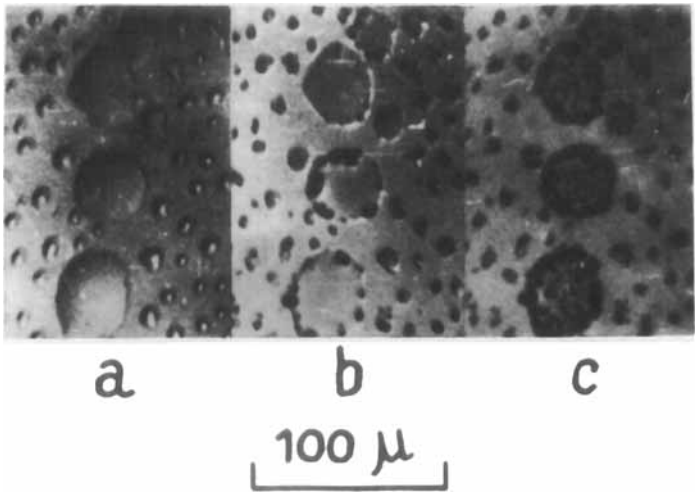

FIGURE 1. The specimen of cis-DNE:
a) in the initial state;
b) after 4 min of irradiation;
c) after 10 min of irradiation.

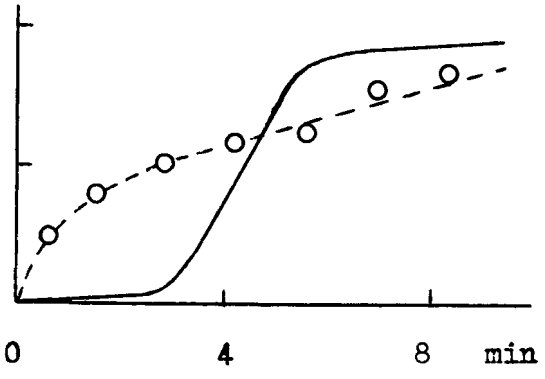

FIGURE 2. The intensity of fluorescence (solid line) and concentration (dotted line) of trans-DNE vs irradiation time.

this substance is transformed into the crystal state (Fig. 1c). If the irradiation is interrupted at some moment the growth of embryos will stop.

Figure 2 (the solid line) shows the change of the fluorescence intensity in the course of the irradiation. This observed dependence doesn't correspond to the monomolecular character of the reaction. We have found the fluorescence to appear together with the creation of the crystal phase. Figure 2 (the dotted line) shows the change of the concentration of trans-DNE during the irradiation. This dependence was obtained by using a series of the identical specimens irradiated during a different time. Then each of the irradiated specimens was dissolved in benzene and the relative concentration of trans-DNE was measured by the spectrofluorometric method. It is seen from Figure 2 the concentration of trans-DNE doesn't correspond to the intensity of the fluorescence. It is our belief that the observation may be explained in two different ways:

A) There is some conformation non-fluorescent state of trans-DNE in an amorphous phase. In transforming into the crystal phase this conformation changes and fluorescence appears.

B) In the amorphous phase the fluorescence of trans-DNE is quenched by the surrounding molecules of the cis-DNE form.

As stated above, the growth of the crystal phase occurs only under irradiation. It may be related to the acceleration of the photochemical reaction on the boundary surface of the two phases. Another explanation is the increase in the rate of crystallization which corresponds to what takes place in the case of the crystallization of anthracene.[3] It is beyond doubt that we deal with a photoinduced phase transition.

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