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: 28 Mar 2007.

To cite this article: Zeev B. Alfassi , Abraham P. Kushelevsky & Liviu Feldman (1977): The Effect of γ Irradiation of Solutions of Cholesteric Liquid Crystals on the Color Transition Temperature, Molecular Crystals and Liquid Crystals, 39:1-2, 33-37

To link to this article: http://dx.doi.org/10.1080/15421407708083907

Mol. Cryst. Liq. Cryst., 1977, Vol. 39, pp. 33–37

Printed in Holland

The Effect of γ Irradiation of Solutions of Cholesteric Liquid Crystals on the Color Transition Temperature

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(*Received July 6, 1976; in final form September 17, 1976*)

γ irradiation of solutions of cholesteric liquid crystals in organic solvents was found to lower the color transition temperatures of films made from these solutions. The lowering of the color transition temperature is proportional to the absorbed dose and inversely proportional to the concentration of the CLC, the proportionality coefficient being dependent on the solvent.

X-rays and γ irradiations of thin films and encapsulated cholesteric liquid crystals (CLC) have been found[1–3] to lower the color transition temperatures (the temperatures at which the films change color) of these films. UV irradiation was found to lower the color transition temperature of both thin films and solutions of CLC.[4,5] It is interesting to study the effect of γ irradiation of dilute solutions of CLC in organic solvents where most of the energy is absorbed by the solvent. An interesting feature of the irradiation of solutions is the possiblity of using a large variety of solvents and concentrations in the study of this effect.

Figure 1 shows the color transition temperatures (color change = green–red) of films evaporated from solutions of a mixture of cholesteryl oleyl carbonate and cholesteryl 2,4-dichloreobenzoate (80% COC and 20% CD, total concentration 25.1 mg/ml solvent) in carbon tetrachloride irradiated with ^{60}Co γ rays to various absorbed doses (dose rate = 0.9 Mrad/hr). These results indicate clearly that the color transition temperature is a linear function of the absorbed dose. Similar lines were obtained for other solvents

† Part of Ph.D Thesis.

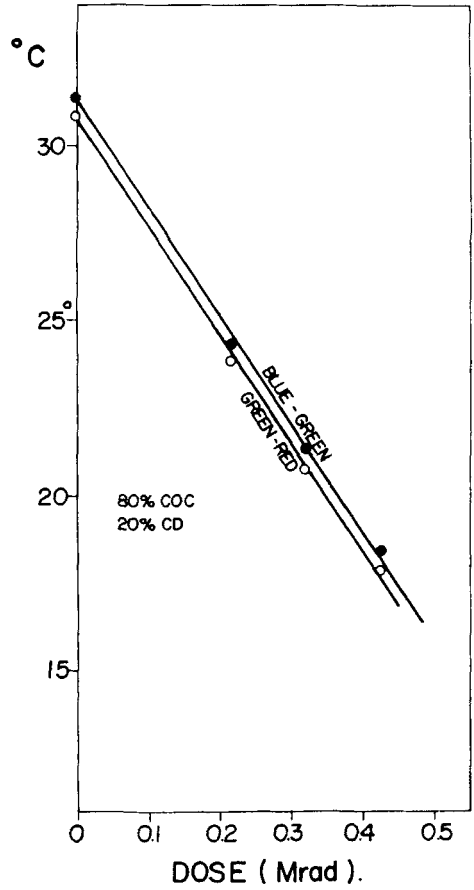

FIGURE 1 Green-red transition temperature of films produced from irradiated solution of CLC in CCl_4 as a function of the absorbed dose. (Total CLC concentration 25.1 mg/ml solvent. The CLC consists of COC and DC in proportion 1 : 4).

and other concentrations. Table I gives the rates of the color transition temperature lowering (in degrees Celsius per 1 Mrad) for various solvents. The temperature at the irradiation was found to have no effect on the lowering rate of the color transition temperature in the range of 0–35°C.

The effect of varying the concentration of CLC in CCl_4 is given in Table II. The decrease of the CLC concentration leads to higher rates of color transition temperature lowering. Figure 2 shows that the rate of color transition temperature lowering is proportional to the inverse of the concentration.

TABLE I

The lowering rate of the color transition temperature for various solvents (25.1 mg/lml solvent)

Solvent	C_6H_6	C_6H_5F	C_6H_5Cl	CH_2Cl_2	$CHCL_3$	CCl_4	*trans* $C_2H_2Cl_2$
Rate (°C/Mrad)	2.94	3.45	11.9	17.6	17.6	29.8	44

TABLE II

The lowering rate of the green-red transition temperature for various concentrations of CLC in CCl_4

Concentration (mg/ml)	58.8	36.6	33.5	27.4	25.1	21.9	20.2	16.8	14.5
Rate (°C/Mrad)	13.6	19.9	23.4	25.1	29.8	30.3	36.2	43.1	48.7

This inversely linear dependence on the concentration can be explained as follows: Irradiation of chemical compounds usually leads to the decomposition of the irradiated materials and the formation of new compounds.[6] In a dilute solution most of the energy is absorbed by the solvent[7] and therefore the number of modified molecules of CLC and the number of molecules of the newly formed compounds is independent of the concentration of the solute and is proportional to the absorbed dose—D. The proportionality constant is different for various solvents due to the difference in the number of radicals produced in the solvent and the chemical reactivity of these radicals. Novak *et al.*[8] found that the addition of methyl benzilate to cholesteryl nonanoate lowers the transition temperature linearly with the concentration of methyl benzilate. Assuming that the same relation holds also here, the color transition temperature lowering, Δt, is proportional to the ratio of the newly formed molecules to the number of molecules of CLC (since number is proportional to the concentration—C), hence

$$\Delta t \propto D/C$$

Therefore the rate of the lowering of the color transition temperature $\Delta t/D$ is inversely proportional to the concentration of CLC

$$\Delta t/D \propto 1/C$$

The possibility of obtaining wide variations of the lowering rate of the color transition temperature by changing the solvent and the concentration make CLC in solutions a good candidate for a γ ray dosimeter in the range of tens of Krads to tens of Mrads.[9]

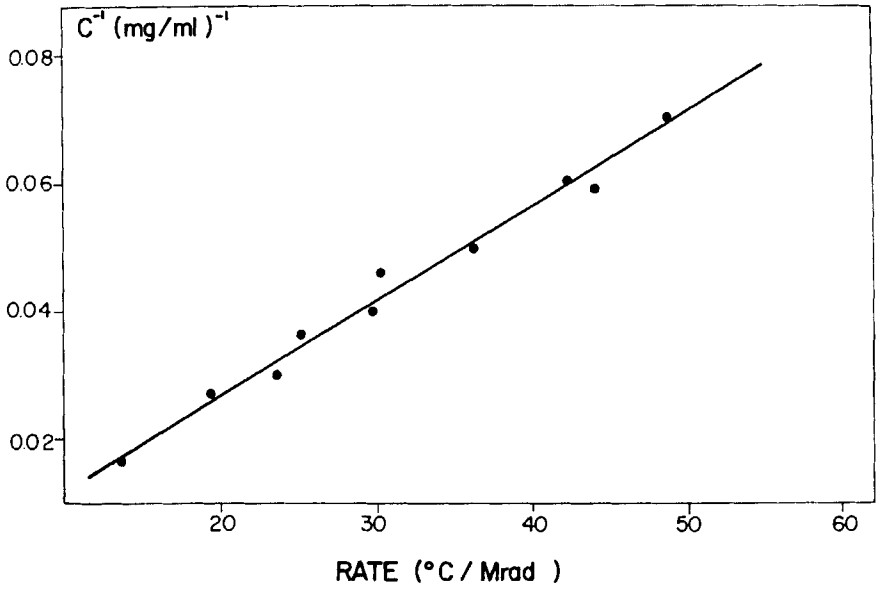

FIGURE 2 Rates of lowering of color transition temperature as a function of the inverse of the concentration.

It is probable that the color transition temperature lowering in the irradiated solutions are due to the formation of solvent free radicals and atoms initiated by the ionizing radiation. At this point we do not yet have any satisfactory correlation between the radiation chemistry of the solvents[6] and the lowering rate of the color transition temperature in their solutions and this is now studied further in our laboratory.

EXPERIMENTAL SECTION

Cholesteryl 2,4-dichlorobenzonate and cholesteryl oleyl carbonate were purchased from Eastman Kodak Company. All the organic solvents were analytical grade; they were distilled and only the middle fraction of the distillate was collected. After exposure to irradiation, a few drops of the irradiated solution were placed on a microscope slide 2 × 2 cm and allowed to evaporate forming a thin film of CLC. This was covered with a microscope cover 1 × 1 cm and the sandwich was cemented with nail lacquer. The sample was taped with a black tape to the internal wall of a beaker filled with water. The beaker was heated (cooled) to a few degrees Celsius above (below) the color transition temperatue and allowed to cool (warm) gradu-

ally. The various colors of the CLC sandwich were observed visually as a function of the temperature. The accuracy of the measurement of the green–red transition temperature is $\pm 0.2°C$.

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