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Progress in Studies on the Effect of Ionizing Radiation on the Physical Properties of Cholesteric Liquid Crystals

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Progress in Studies on the Effect of Ionizing Radiation on the Physical Properties of Cholesteric Liquid Crystals

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An overview of the present knowledge about the effect of ionizing radiation on properties of cholesteric liquid crystals is given. It includes the effects caused by either electromagnetic radiation or particles. Particular attention has been paid to the liquid-crystalline properties of cholesterol derivatives and their mixtures including non-mesogenic dopants. Some of the results are published for the first time.

Keywords: cholesteric liquid crystals, ionizing radiation, phase transitions

I. INTRODUCTION

The studies on the influence of ionizing radiation on the properties of cholesteric liquid crystals (CLC) have rather a long history. The very first work on this subject was done by Fergason[1] in 1969, but more extended studies have been started in 1976 by the Beer Sheva group.[2–7] Only a few research centers have been interested in this subject but now we have rather good knowledge of the effect of ionizing radiation on the cholesteric liquid crystals, especially cholesterol derivatives. In this contribution we present a brief summary of our knowledge of this subject.

The studies have been performed in a few essential systems:

—diluted solutions of cholesterogens in organic solvents,
—solid polycrystalline samples of individual cholesterogens and their mixtures,
—above mentioned substances in different liquid crystalline phases,
—mixtures of cholesterogens in bulk, thin layers and encapsulated dispersions.

Amongst different kinds of ionizing radiation, the special attention has been paid to gamma, neutron and proton radiations. The thermooptical, liquid crystalline

and electrical properties of cholesterogens have been studied. All known data have been obtained for cholesterol derivatives; it includes some data concerning the mechanism of radiolytic destruction of such compounds. As a useful parameter describing the influence of radiation on the liquid-crystalline properties of CLC the radiation (or dose) sensitivity η has been introduced[2]:

$$\eta = \frac{\Delta T_p}{D} \tag{1}$$

where: ΔT_p is the change of the given phase transition temperature (or colour transition temperature in case of colour response measurements) and D is exposure dose (D_e) or absorbed dose (D_a) of ionizing radiation. The diagrams presenting T_p vs. D dependence are called dose-temperature characteristics.

II. LIQUID-CRYSTALLINE PROPERTIES

Dilute Solutions of CLC in Organic Solvents

In this system the energy of ionizing radiation is absorbed mostly by the solvent due to the higher concentration of its molecules. The high-boiling products of solvent radiolysis, after evaporation of a solvent, are acting as admixtures changing the physical properties of CLC. This subject has been studied in details for gamma radiation only. As a rule the post-radiation dopants are decreasing the phase transitions temperatures[8] and so the temperatures of colour response transitions.[2-4] Examples are presented in Figures 1 and 2.

As one can see the dose-temperature dependencies are linear in a rather wide dose range but become non-linear for sufficiently high doses. This can be explained

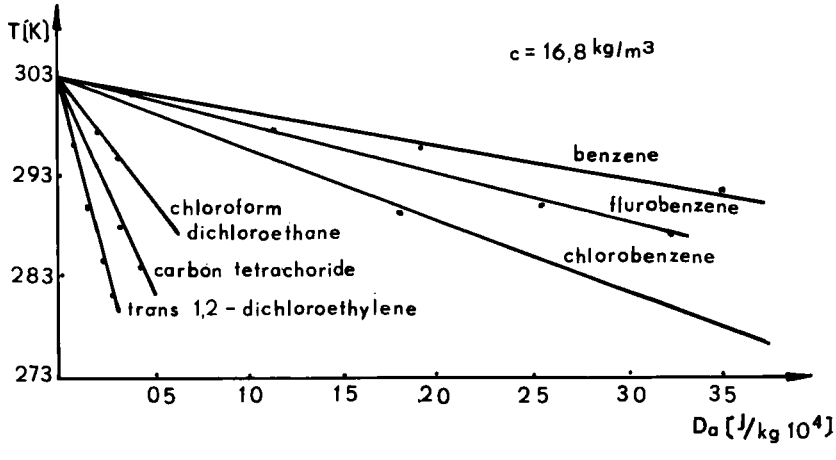

FIGURE 1 Temperature of the red-green colour transition vs. absorbed dose for different solutions of the mixture of cholesterol oleyl carbonate and cholesterol dichlorobenzoate (4:1 by weight), Co-60 source.[3]

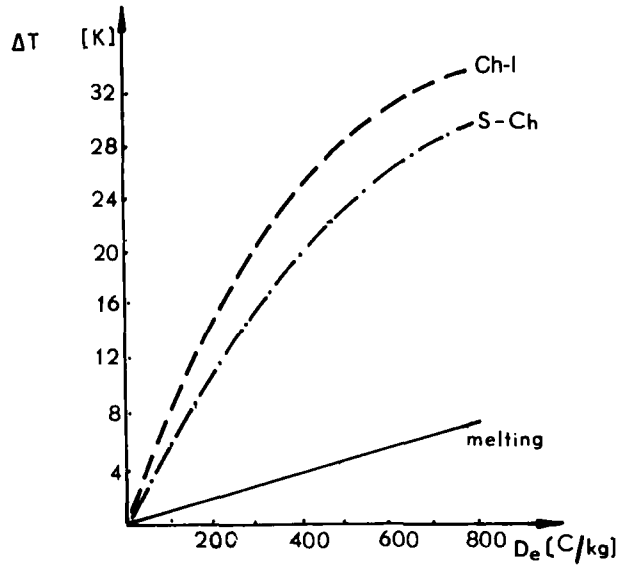

FIGURE 2 The change of phase transition temperatures for cholesterol nonanoate irradiated in tetrachloride solution (7×10^{-3} mole fraction) vs. exposure dose, $P_r = 4.5 \times 10^{-4}$ C/kgs, Co-60 source.[8]

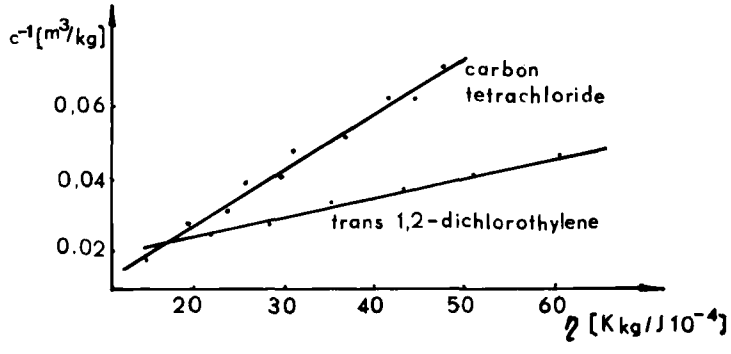

FIGURE 3 The reciprocal concentration vs. radiation sensitivity for the mixture of cholesterol oleyl carbonate and cholesterol 2,4 dichlorobenzoate irradiated in CCl_4.[2]

by disturbance of liquid-crystalline arrangement by post-radiation products as it will be described later.

Of course the concentration of a solution plays an important role.[9] For "low dilution" case (the concentration of a cholesterogen is higher than about 2×10^{-2} mole fraction) the concentration-temperature dependence is hyperbolic (see example in Figure 3). In the case of "high dilution" this dependence becomes more complex because the dopant concentration in a dry residue goes to non-linear range of concentration-T_p dependence (an example is given in Figure 4). Such a behaviour is caused by the fact that, for constant sample volume, the amount of post-radiation products (i.e. radiation derivatives of a solvent) is nearly the same for different concentrations of cholesterogen, but the amount of cholesterogen in dry residue

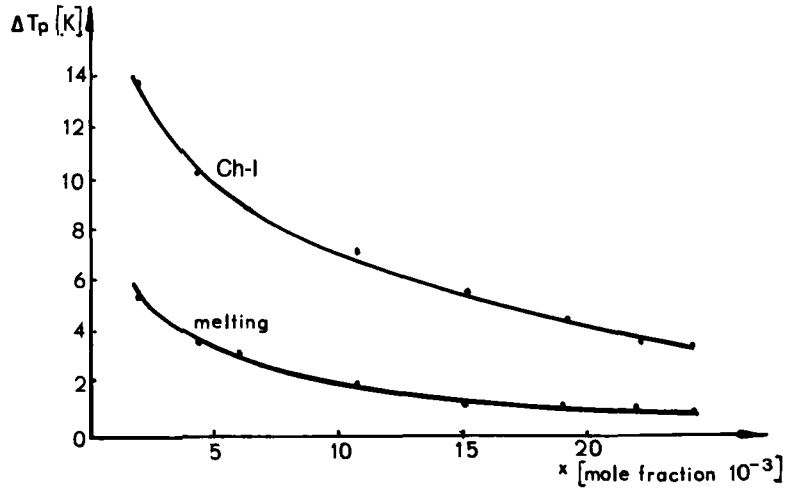

FIGURE 4 The change of the phase transition temperatures for cholesterol propionate vs. concentration of heptane solutions. D_e = 6.45 C/kg, P_e = 4 × 10^{-4} C/kgs, Co-60 source.[9]

is of course less for lower concentration of solution. In this way cholesterogen is doped to a more extent, its liquid-crystalline arrangement is more disturbed and eventually mesogenic properties are more changed.

In the case of "low dilute" solutions this picture can be complicated by the possibility of existence of radiolysis products of cholesterogen (due to its higher concentration in the solution and so higher probability of interaction with gamma radiation) and products of a reaction between cholesterogen and non-stable products of solvent radiolysis (as the effect of successive reactions).

The radiation sensitivities of some cholesterogens diluted in organic solvents are presented in Table I.

Individual Cholesterogens

In normal conditions most of individual cholesterol derivatives are solid; from synthesis techniques they are polycrystalline. Their radiation resistance is similar to other organic compounds. As a rule, gamma radiation causes decreasing of phase transition temperatures. The dose-temperature dependence is linear for relatively small doses and becomes non-linear for sufficiently high doses.[10] This effect is caused by doping of CLC material by products of its radiolysis. For sufficiently high doses post-radiation dopants decrease an order parameter of liquid-crystalline phases due to disturbing their molecular arrangement which leads to a change from enantiotropic to monotropic phases and in the end to total collapsing of liquid-crystalline arrangement. The examples are presented in Figure 5 and in Table II.

As one can see the η value decreases with elongation of the 3β-terminal substituent of a molecule of cholesterol derivative (and so the same molecule). It may be explained in terms of the theory derived by Martire and his co-workers.[11,12] This theory predicts that the effect of a dopant on the liquid-crystalline properties of a mesogen is more pronounced if molecules of the dopant are more spherical

TABLE I

Radiation sensitivities η for some cholesterogens diluted in organic solvents, concentration 10^{-2} mole fraction, Co-60 source, Ch-I phase transition, authors' results

η [K/Gy]	Solvent		
Cholesterol derivative	hexane	chloroform	benzene
cholesterol chloride	1.11	0.33	0.10
cholesterol iodide	1.10	0.36	0.11
cholesterol butyrate	0.93	0.30	0.09
cholesterol valerate	0.83	0.27	0.08
cholesterol caprinate	0.66	0.21	0.06
cholesterol nonanoate	0.39	0.13	0.05
cholesterol laurate	0.35	0.12	0.05
cholesterol mirystate	0.29	0.11	0.04
cholesterol palmitate	0.25	0.10	0.04
cholesterol stearate	0.24	0.08	0.03

in shape and the dopant/mesogen molecular dimensions ratio is larger. In our case the decomposition of cholesterol derivatives caused by radiation leads mainly to the cracking of 3β-bond (which will be described later). As a result we have two main groups of dopants: spherical-shaped derivatives of the steroid core and rod-like derivatives of the 3β-substituent. The former have the same dimensions for all presented compounds, the latter have increasing length for subsequent members of homologous series. In this way the influence of steroid dopants decreases for mesogens having longer molecules because dopant/mesogen molecular dimensions ratio decreases in this case and, on the other hand, the rod-like 3β-substituent derivatives with larger molecular length can more easily build in liquid-crystalline structure and, in this way, disturb it to less extent.

Of course the active cross-section of individual atoms plays an important role. It manifests, for instance, by comparison of the η values for CI and CC or for CB and CK having similar molecular dimensions. In the first case the active cross-section for gamma radiation is greater for iodine than for chloride atoms and in the second case the aromatic ring causes greater radiation resistivity of CB.

The effect of the energy of the photons of gamma radiation on the observed results is presented in Figure 6. A decrease of radiation effects with an increase of radiation energy is caused probably by the smaller value of LET (linear energy transfer) in this case which causes smaller concentration of post-radiation dopants.

Any dependence of the observed results on the dose ratio has been observed in the range from 5.5×10^{-4} to 6.6×10^{-3} C/kgs. However, this range is too narrow to draw any general conclusions.

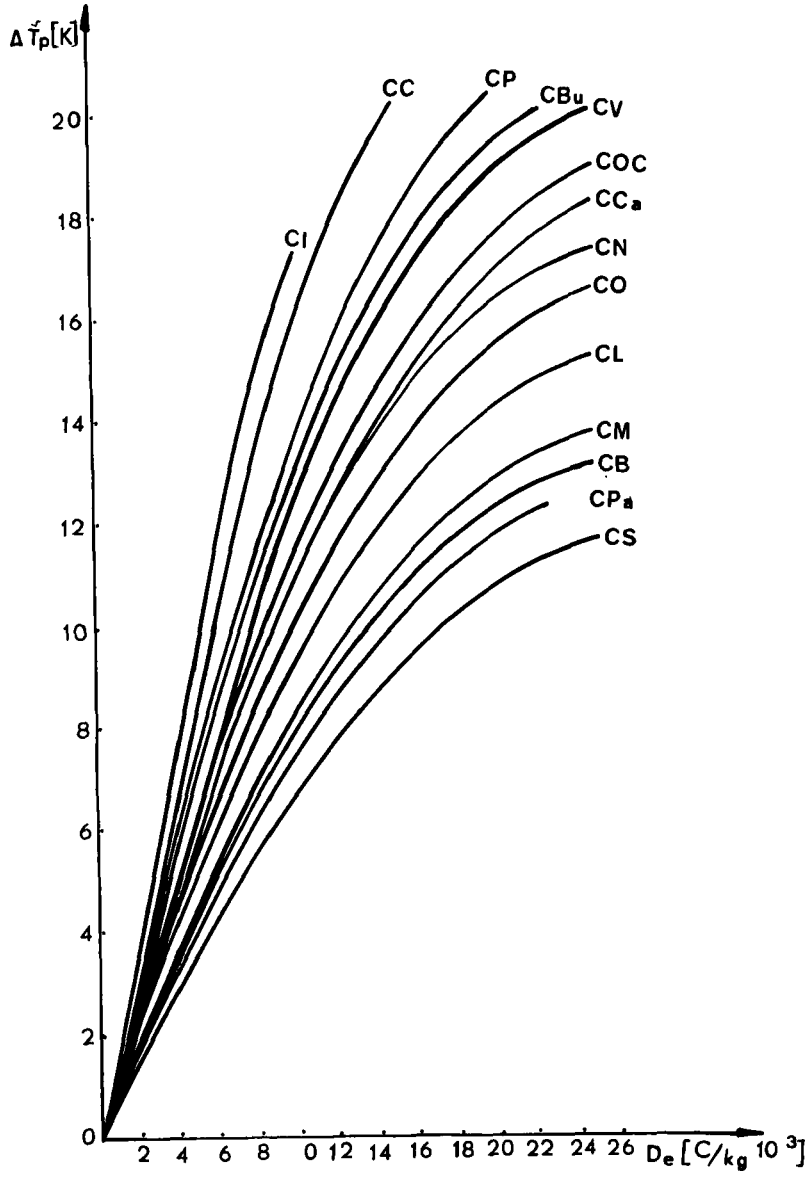

FIGURE 5 The change of cholesteric-isotropic phase transition temperature vs. exposure dose, Co-60 source, $P_e = 6 \times 10^{-3}$ C/kgs.[8]

It was observed that the η value is larger for less-ordered phases but no temperature dependence has been found within the temperature range of existence of a given phase (Table III). In other words this dependence manifests itself for the phase transitions only. This effect is probably caused by the higher possibility of successive reactions due to higher mobility of post-radiation products in less uniformed phases.

TABLE II

Radiation sensitivities of individual cholesterol derivatives irradiated in solid state[8,10]

Derivative	S-Ch		Ch-I	
	Cs-137	Co-60	Cs-137	Co-60
iodide	-	-	2.45	1.90
chloride	-	-	2.16	1.68
propionate	-	-	1.92	1.50
butyrate	-	-	1.74	1.36
valerate	-	-	1.70	1.34
caprylate	1.58	1.23	1.60	1.24
nonanoate	1.60	1.25	1.55	1.20
laurate	1.31	1.00	1.36	1.06
mirystate	1.15	0.90	1.12	0.88
palmitate	1.07	0.84	1.02	0.80
stearate	0.90	0.70	0.90	0.72
oleate	1.48	1.15	1.45	1.12
oleyl carbonate	1.75	1.35	1.65	1.28
benzoate	-	-	1.08	0.86

Mixtures of Cholesterol Derivatives

The radiation sensitivity for mixtures of cholesterol derivatives is, as a rule, greater than for individual compounds.[8] The larger is the concentration of the more sensitive compound, the larger the η value. However, the η is not an additive quantity, and moreover in multi-compound mixtures the effects are more complex because of the larger possibility of different reactions between mixture components. For these reasons in some mixtures non-linear dose-temperature characteristics have been observed. Figure 7 represents an example of dose-temperature characteristics for cholesterogenic mixtures.

By introducing especially sensitive non-mesogenic dopants one can increase the dose sensitivity up to 10^2 Gy.[13] However, in this case dramatically non-linear dose-temperature characteristics were observed for some mixtures.

The effect of gamma radiation on the CLC encapsulated in a polymer were studied by Alfassi *et al.*[2] and Kłosowicz *et al.*[13,14] for different encapsulation methods

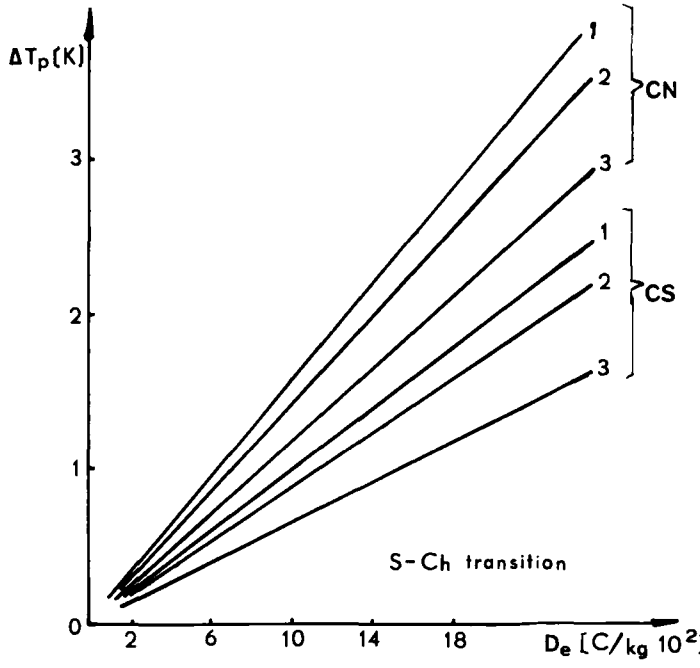

FIGURE 6 The dose-temperature characteristics for cholesterol nonanoate and cholesterol stearat irradiated by radiation with different energy[8]: 1—X-ray generator ($E_x \approx 3.2 \times 10^{-14}$ J), 2—Cs-13 source, 3—Co-60 source.

TABLE III

The radiation efficiency of selected cholesterol derivatives irradiated in different phases[10]

Cholesterol derivative	η_{Ch-I} [Kkg/C x 10^{-3}]			
	solid	smectic	cholesteric	isotropic
chloride	1.68	-	1.75	1.83
propionate	1.50	-	1.55	1.61
nonanoate	1.20	1.25	1.28	1.35
laurate	1.06	1.08	1.10	1.14
palmitate	0.80	0.83	0.85	0.88
oleyl carbonate	-	1.25	1.28	1.32

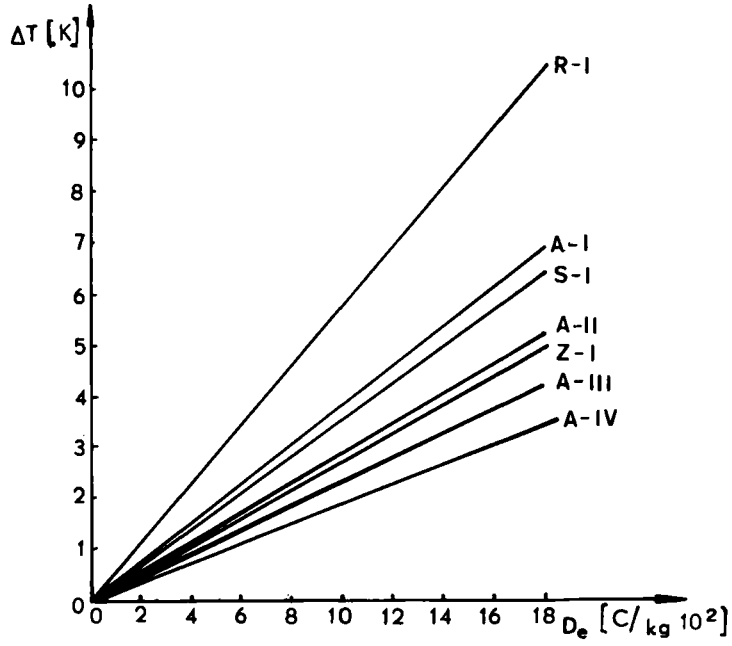

FIGURE 7 The dose-temperature characteristics for selected mixtures of cholesterol derivatives. Co-60 source, $P_e = 7 \times 10^{-4}$ C/kgs; A-I, A-II, A-III, A-IV: cholesterol nonanoate containing 1, 3, 5 and 10 percent b.w. of cholesterol iodide, respectively; Z-I, S-I and R-I: multicomponent mixture of cholesterol esters containing 1, 3 and 10 percent b.w. of cholesterol iodide, respectively; author's results.

and materials. All observed effects in this case are comparable to CLC irradiated in bulk but, as a rule, dose efficiencies are slightly lower, because of additional effects, e.g. anchoring effects in CLC droplets. It was found[14] that substrates of a film-forming polymer may introduce additional, non-predictable effects. The character of the polymer used for encapsulation is important, because especially for high doses, radiation curing or degradation of the polymer can overlap with the radiation processes in the CLC. This is the most interesting system for applications, however, because of simplicity and low cost of a detector.

III. OTHER PHYSICAL PROPERTIES

It is well-known that the electric properties of materials are very sensitive to ionizing radiation. This is true for CLC too. There are some works concerning this subject in the case of gamma radiation.[15,16] It has been found that temperature-conductivity and temperature-carrier mobility dependencies have activation character with different activation energies E_σ and E_μ, respectively (see Figure 8). The increase of conductivity σ is caused by ion effects due to radiolysis processes. In the case of cholesterol derivatives with long 3β-terminal chain new kinds of carriers are formed after irradiation (in comparison with non-irradiated sample) which is an effect of successive radiolytic reactions. The E_σ and E_μ values are larger for phases with greater molecular arrangement. Measurements of electric quantities are extremely

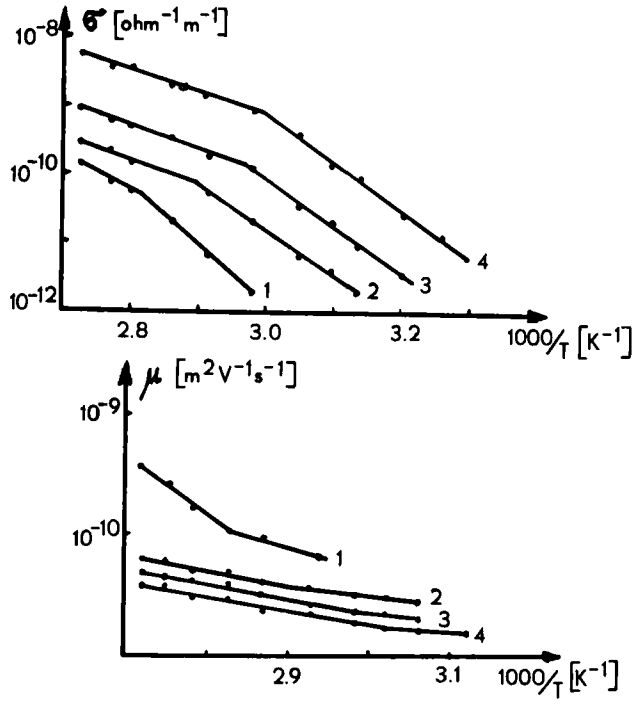

FIGURE 8 The temperature dependencies of conductivity σ (a) and carrier mobility μ (b) for cholesterol nonanoate; absorbed dose D_a: 1—0 Gy, 2—200 kGy, 3—400 kGy, 4—800 kGy.[15]

sensitive to the chemical purity of studied compounds which is due to recombination effects.

IV. EFFECT OF CORPUSCULAR RADIATION

The effect of neutron and proton radiation on the properties of CLC have been studied by some authors.[17–19] The obtained results were similar for both particles, since recoil protons are the main ionizing agent in the case of neutron radiation. For fast neutrons ($E_n > 1$ MeV) non-linear dose-temperature characteristics were observed.[18,19] This behaviour is different from that with gamma radiolysis. The phase transition temperatures increased for relatively small doses, reached a maximum for a certain dose and then decreased for higher doses. The total temperature changes were very small (about 1 K) and the value of D_{am}—the dose corresponding to a maximum of T_p depends slightly on molecular dimensions of CLC (see Figure 9). It suggests the existence of two competing effects. The first is probably the destruction of CLC molecules by radiolysis and the second, as it was proved by liquid chromatography,[16] is destruction of trace dopants which exist in cholesterol esters after preparation. The latter effect caused an increase of T_p because these substances are decreasing the phase transition temperatures and their removal (this term means creation of gas products and low-molecular derivatives which are less

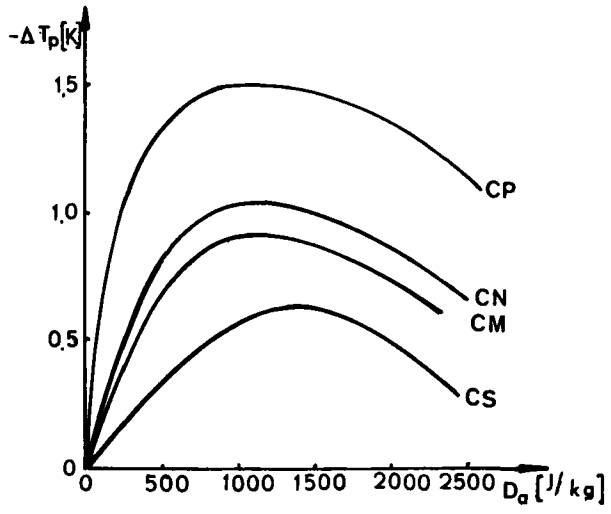

FIGURE 9 The dose-temperature characteristics for cholesterol esters irradiated by fast neutrons ($\bar{E}$ = 8.8 × 10^{-13} J, E_{max} = 2.8 × 10^{-12} J) Ch-I transition, authors' results.

affecting on the liquid-crystalline properties of a mesogen) may draw this effect back.

Thermal and epithermal neutron radiation did not cause any reproducible effects up to 200 J/kg.

It is worth mentioning that some studies have been done on the thermal (the particle energy is absorbed as a heat) or concentration (the particle energy is absorbed in molecule destruction processes) traces in CLC caused by heavy ions,[20] elementary particles[21] or electrons.[22] In the case of corpuscular radiation with large LET value, the concentration traces play a serious role because of radiolytic effects. These effects may be used in detection of such particles.

V. DIRECTIONS OF RADIOLYTIC DESTRUCTION

Recently studies have been started on the mechanism of radiolysis of cholesterol esters.[16] From NMR, UV, and IR spectroscopy as well as chromatographic studies it was found that the main mechanism of cholesterol esters radiolysis is the rupture of the ester bond on the 3β carbon atom. For cholesterol iodide this was confirmed also by colorimetric measurements indicating the formation of free iodine. Other processes of destruction of the steroid ring were also observed, but they have not been explained satisfactorily yet.

Gas chromatography studies showed that the main gaseous products of cholesterol esters radiolysis are CO_2, CO and H_2O. This confirmed spectroscopy conclusions concerning bond rupture in molecular skeletons. The example of these results is shown in Figure 10.

As it was mentioned above, the electric measurements showed that ions, and not electrons are formed by gamma radiation. This observation confirms the nature of radiolysis of cholesterol derivatives.

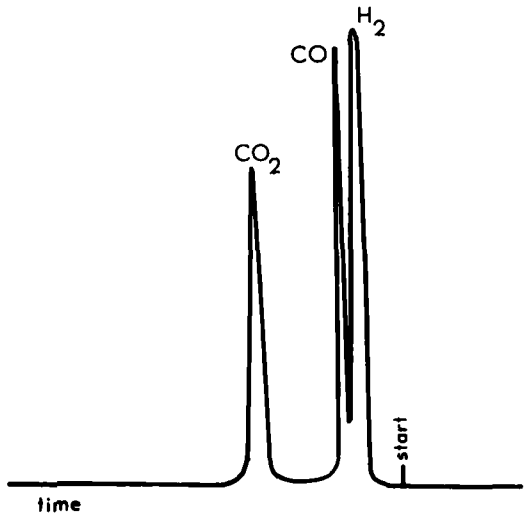

FIGURE 10 The GLC chromatogram of gas products of cholesterol propionate irradiated in solid state by gamma radiation of Co-60 source, $D_e = 2.0 \times 10^3$ C/kg.[16]

SUMMARY

Gamma radiation leads to the destruction of cholesterol derivatives probably mainly by ester bond cracking. This effect decreases the phase transition temperatures of cholesterogens and eventually destroys the liquid-crystalline arrangement. This effect is clearly pronounced in colour response of cholesterics. The change of CLC composition, caused by gamma radiation, leads to the change of other physical properties of cholesterogens, especially electric properties.

Neutron radiation has very low effect on liquid-crystalline arrangement, but fast neutrons can destroy impurities present in the cholesterogen.

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