Electrical conductivity of γ-irradiated cholesteric liquid crystals

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We have studied for the first time basic electrical properties, such as the electrical conductivity σ and the charge-carrier mobility μ, for liquid crystals which have been subjected to ionizing radiation. The results show that the conductivity mechanisms are different from those of liquid crystals which have and have not been irradiated.

The test samples were cholesterin derivatives [cholesteryl pelargonate (CP) and cholesteryl fromate (CF)], which are used widely, both in practical applications and in biological systems. We have previously shown that this class of liquid crystals ranks among the most sensitive to ionizing radiation.[1]

The liquid crystals were irradiated in a standard K-100000 apparatus (^{60}Co), at doses of 200, 400, and 800 KGy. Before irradiation, the samples were purified by the recrystallization method described in Ref. 2, but the control and irradiated samples were not given any special purification immediately before the measurements of σ and μ. The σ measurements were carried out in a static electric field by a method like that described in Ref. 3. The carrier mobility μ was determined from the carrier flight time upon a reversal of the voltage polarity.[4] The error in the temperature measurements was 0.1°, and that in the dose measurements was 25%.

Figure 1 shows the temperature dependence of σ for CP and CF for various γ doses. It can be seen from the data that the value of σ increases with irradiation dose D. It follows from an analysis of the experimental curves that the electrical conductivity is activated:

$$\sigma = \sigma_0 \exp(-U_\sigma/KT),$$

where U_σ is the activation energy for the electrical conductivity, T is the temperature, and K is the Boltzmann constant. Values of U_σ are listed in Table I. It can be seen from this table that in the CP samples which have and have not been irradiated the values of U_σ are different, while for the CF samples the value of U_σ is not altered by the irradiation. Furthermore, the values of U_σ in CP are different in different phase states.

Figure 2 shows the temperature dependence of μ for various does for CP and CF. If follows from these curves that, as in the case of the conductivity, the $\mu(T)$ dependence has an activated behavior. The activation energies U_μ for CP and CF in various phase states are listed in Table I. The value of μ at T = const in CF increases, while that in CP decreases, with increasing γ dose. For these two substances, the mobility tends toward values which are equal in order of magnitude.

Charge transport in a liquid crystal is provided mostly by the motion of ions.[5] In especially pure liquid crystals, the electrical conductivity is known[3,6] to be described by the Frenkel' model, i.e., $U_\sigma \approx U_\mu$. If follows from our data that this condition holds only for CP which has not been irradiated. In all other cases, the activation energy for the electrical

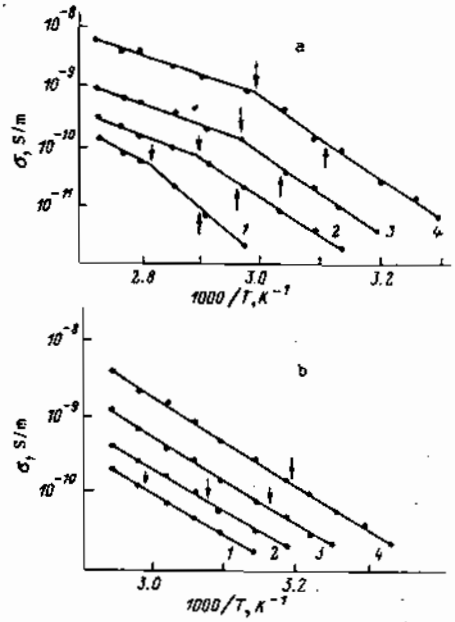

FIG. 1. The electrical conductivity σ versus the reciprocal temperature T^{-1} for (a) CP and (b) CF. Dose in kGy: 1) 0; 2) 200; 3) 400; 4) 800 The arrow ↑ means (isotropic liquid)–(cholesteric liquid crystal) phase transition; the arrow ↑ means (cholesteric liquid crystal)–(smectic liquid crystal) phase transition.

conductivity and that for the mobility of the charge carriers are unequal, with $U_\sigma > U_\mu$ (Table I). Consequently, in the irradiated CP and CF the nature of the electrical conductivity is determined by the temperature dependence of not only the mobility but also of the concentration of the charges (ions). In this case, we can assume $U_\sigma = U_\mu + U_n$, where U_n determines the temperature dependence of the carrier concentration,[7]

$$n = n_0 \exp(-U_n/KT) \qquad (1)$$

(n_0 is the total number of ions which are capable of participating in the electrical conductivity).

It can be seen from (1) that the quantity n_0 is an important measure of how effective ionizing radiation is in altering the properties of a liquid crystal. This quantity can be estimated by extrapolating the temperature dependence of n in the isotropic phase to the limit $T \to \infty$. The results of such estimates, shown in Table I, indicate that $n_0 \sim D^m$, where $m \approx 2$ for CP and $m \approx 1$ for CF. The quantity n_0 may be thought of as the number of radiation-induced impurities from which charge carriers are generated. Irradiation in a dose of 800 kGy has the consequence that n_0 becomes equal to 20% of the number of initial liquid-crystal molecules in the CP and 16% in the CF.

A comparison of the data obtained for CF in samples which have and have not been irradiated

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TABLE I

Substance	Dose, kGy	IC				CLC		
		N, m^{-3}	U_σ	U_μ	U_n	U_σ	U_μ	U_n
CP	0	10^{20}	1.31	1.24	0.07	1.73	0.65	1.08
	200	10^{25}	0.66	0.26	0.4	1.47	0.15	1.32
	400	$4\cdot10^{25}$						
	800	$2\cdot10^{26}$						
CF	0	$1.5\cdot10^{25}$	0.83	0.49	0.34	0.83	0.49	0.34
	200	$3\cdot10^{25}$						
	400	10^{26}						
	800	$1.6\cdot10^{26}$						

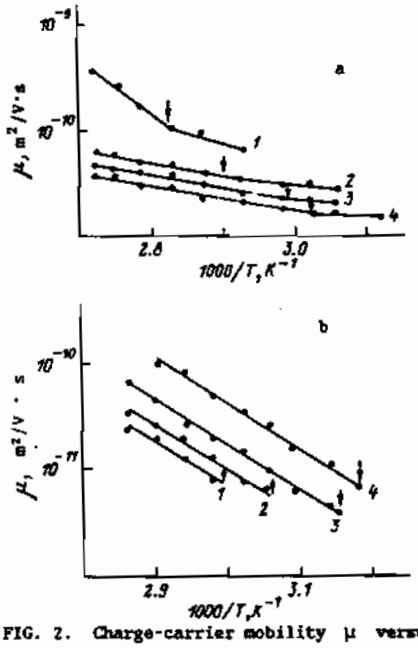

FIG. 2. Charge-carrier mobility μ versus the reciprocal temperature for (a) CP and (b) CF. The notation is the same as in Fig. 1.

shows that the γ irradiation changes only the value of σ_0, not changing the activation energy U_σ. When we note that the control sample (not irradiated) was held in air for the same time as the irradiated sample (up to 3 months), i.e., was subjected to natural aging, we can draw a conclusion about the nature of the effect of γ radiation on a liquid crystal: The γ irradiation causes an accelerated aging of the liquid crystal, most probably due to processes which are associated with the effect of atmospheric oxygen. In CP, the values of U_σ in the samples which have and have not been irradiated are different, most probably because this substance is less subject to aging processes than the CF is. Further evidence for this interpretation comes from the equality of U_σ and U_μ for the CP samples which have not been irradiated; this equality is characteristic of well-purified liquid crystals, as has been mentioned previously.

The difference between the characteristics of the γ-irradiated CP and CF is most important in terms of the value of μ. While μ decreases in the irradiated CP, as would be typical of most irradiated solids (i.e., solid containing large numbers of defects as a result of the irradiation), in CF, in contrast, μ increases. The behavior of $\mu(D)$ can be examined from two points of view. As we mentioned earlier, the values of μ at T = const for CP and CF tend toward the same value during irradiation. It follows from this result that if the electrical conductivity of CP and CF before the irradiation are determined by carriers which differ in characteristics, after γ irradiation some radiation-induced charge carriers having approximately identical characteristics from in these substances. Furthermore, the different behavior of $\mu(D)$ in CP and CF can be discussed from the standpoint of the Frenkel' model.[6] According to that model, μ is determined by the vibration frequency ν in the field of the molecule and by the mean free path δ, which is approximately equal to the average size of a molecule: $\mu \sim \delta^2\nu$. During irradiation of a substance, ν should decrease because of the decrease in the elastic constants of the interaction, with the result that μ will decrease, in accordance with the experimental data for CP. For CF, the situation is different, since μ increases with D. The increase in μ can be explained by assuming that there is an increase in δ with increasing D. This assumption is justified, since data which we obtained earlier by IR spectroscopy provide evidence that hydrogen-bonded dimers consisting of two "defect" molecules from in CF.

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