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Received 10th October 1984

Translated from *Zhurnal Fizicheskoi Khimii*, 61, 1634–1639 (1987)

U.D.C. 532.783;548-14

Effect of Ionising Radiation on the Phase Diagrams of Liquid Crystals

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We have studied the effect of ionising radiation (proton and γ radiation) on the phase diagrams of various liquid crystals, including derivatives of cholesterol. A shift in the phase transition temperature and a change in the region of existence of the mesophase have been observed. The changes in the phase diagram of cholesterol derivatives, which contain the steroid nucleus, are much more marked than the corresponding changes in irradiated liquid-crystalline substances with non-steroid nuclei (cyanobiphenyls, alkyloxybenzoic acids, etc.). Possible mechanisms for the effect of the molecular structure on the properties of the phase diagram of the irradiated substances are discussed.

Liquid-crystalline (LC) derivatives of cholesterol with a helix structure form a class of liquid crystals (cholesteric) which has found practical applications and is of interest in studies of various biological systems. In practice the most important property of cholesterics is their ability to vary the pitch of the helical structure under the influence of various external agencies: pressure, temperature, impurities, etc.[1] The changes in pitch of the helix produce a change in colour of the cholesteric if the Bragg reflection lies in the visible region of the spectrum. It is reasonable to assume that changes in the pitch of the helix will be caused also by various types of ionising radiation as a result of the formation of radiation-induced impurities in the system. These impurities can shift, or widen, or narrow the temperature region of existence of the cholesteric mesophase, and hence they can influence the region of selective reflection. Indeed, effects of this type have been reported in derivatives of cholesterol[2] and in their solutions,[3] but the observations were confined to γ radiation.

The aim of this work was to study the changes in the phase diagrams for a homologous series of n-alkanoates and other derivatives of cholesterol exposed to ionising radiations of two types: proton and γ radiation. The effects have been compared with the corresponding changes in other liquid crystals.

EXPERIMENTAL

The experimental substances were exposed to ionising radiations of two types: proton and γ radiation.

Proton irradiation was carried out in a synchrocyclotron (U-240) with an applied dose of 10^{14} R cm^{-2}, corresponding to an absorption of 14–15 Mrad in substances of the given molecular weight. In some of the compounds we studied the dependence of the phase transitions on the dose of radiation (for doses of 5×10^{11}, 10^{12}, 5×10^{12}, 10^{13}, and 10^{14} R cm^{-2}). The proton energy was 70 MeV. The applied dose of radiation was measured with a Faraday cage.

Irradiation with γ quanta was carried out in a K-100 000 apparatus (^{60}Co), using various doses of γ radiation (2, 13, 66 Mrad) to study the dose dependence of the phase transition temperatures.

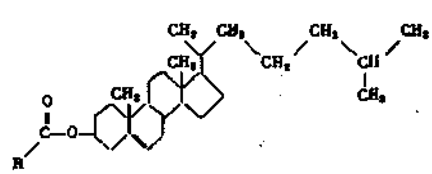
During the irradiation the samples were contained in polyethylene capsules in which the thickness of the LC layer was not more than 0.5 cm; the design of the apparatus ensured uniform irradiation of the entire LC volume. The samples were heated by the irradiation, but their temperature did not rise above 50 °C. In other words, the irradiation was carried out under solid crystal conditions, since all the melting points are higher than 50 °C.

The phase transition temperatures were measured by polythermal polarisation microscopy, using a modified "Peraval Interphaco" microscope (Carl Zeiss, Jena, GDR). Temperatures were measured to within 1 K, rates of change of temperature to within 1 K min^{-1}. The wall thickness of the cells was 30–50 μm, which eliminated the influence of surface effects on the phase transformations.

DISCUSSION

The measured phase transition temperatures are shown in Tables 1–5. Because of differences in absorption capacity the doses adsorbed by particular samples may differ from those stated in the Tables, but by not more than 5%. The following symbols are used in the Tables. For the phases, C is the solid phase, S is the smectic, Ch is the cholesteric (including the blue phases), N is the nematic, and I is the isotropic phase. For the substances, I is n-azoxyanisole, II is cholesteryl chloride, III is cholesteryl cinnamate, IV is cholesteryl nonanoyloxybenzoate, V is cholesteryl oleate, VI is cholesteryl pelargonate, VII is propyloxycyanobiphenyl, and n-VIII is the series of n-alkyloxybenzoic acids of general formula $C_nH_{2n+1}OC_6H_4COOH$.

As Table 1 shows, for all types of phase transition in substances having the structural formula



$R = C_nH_{2n+1}$, $n = 0, 1, 2 \ldots$

the transition temperatures of the irradiated samples are

5–15 K lower than those of the non-irradiated. In most cases the temperature range of the mesophases (both cholesteric and smectic) was also narrowed. Repeated measurements on a given sample (i.e. annealing of the sample) did not alter the phase transition temperatures.

Table 1. Phase transition temperatures (t, °C) of a series of cholesteryl n-alkanoates before and after (in brackets) proton irradiation with an absorbed dose of 14.5 Mrad.

Cholesteryl ester	Heating			Cooling		
	C–I	C–Ch	Ch–I	I–Ch	Ch–S	S–C
Formate	95(89)	–	–	60	55 [2]	(49)
Acetate	111(105)	–	–	103(98)	97(86) [2]	
Propionate	–	92(88)	106(100)	106(98)	70(72) [2]	–
Butyrate	–	97(91)	110(98)	107(95)	89(78) [2]	
Valerate	–	90(88)	99(87)	98(82)	71(62) [2]	
Caproate	–	98(89)	96(95)	92(77)	69(62) [2]	
Oenanthate	110(106)	–	–	–		103(87) [4]
Pelargonate	–	77(72)	90(78)	83(73)	75(61)	40(36)
Undecylate	89(86)	–	–	84(71)	78(66)	40(37)
Laurate	91(88)	–	–	85(74)	77(71)	42(38)
Myristate	70(68) [1]	76(73) [3]	82(78)	78(73)	76(71)	51(52)
Pentadecylate	67(61) [1]	74(68) [3]	78(72)	75(68)	71(64)	44(39)
Palmitate	–	74(66)	78(70)	75(68)	72(64)	47(38)
Stearate	80(78)	–	–	74(68)	70(64)	60(43)

[1]C–S, [2]S–Ch, [3]Ch–C, [4]I–C.

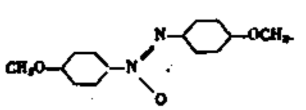
Table 2. Phase transition temperatures (t, °C) of substances with non-steroid molecules before and after (in brackets) irradiation with protons (absorbed dose 14.5 Mrad).

Substance	Heating			Cooling		
	C–S	S–N	N–I	I–N	N–S	S–C
I	–	116(116) [2]	132(130)	131(130)	81(83) [3]	–
VII	71(70) [1]	–	–	68(67)	53(53) [3]	–
5-VIII	–	121(120) [2]	147(145)	147(145)	115(114) [3]	–
7-VIII	97(96)	105(103)	144(142)	144(142)	122(120)	93(91)
8-VIII	101(99)	108(107)	146(145)	145(145)	107(105)	100(99)
9-VIII	94(92)	118(112)	142(139)	142(139)	118(112)	95(89)
10-VIII	94(92)	120(117)	136(135)	136(135)	121(117)	93(90)
12-VIII	86(86)	126(125)	131(131)	131(131)	125(125)	84(84)

[1]C–I, [2]C–N, [3]N–C.

This behaviour of the irradiated n-alkanoates of cholesterol is not found in non-steroid molecules. As Table 2 shows, the phase transition temperatures of these substances were very little affected by the irradiation: not more than 1–2 K. The following explanation can be suggested.

The molecules of nematic LC substances (Table 2), unlike those of cholesterol derivatives, have a non-steroid nucleus and a rod-like shape, exemplified by the structure of the (I) molecule



We may assume that the final product of the irradiation of these molecules, after the initial dissociation stage, will include a proportion of defect molecules, still rod-shaped but shorter than the initial molecules, as well as some abnormally long (hybrid) rods produced by recombination. Theoretical calculations show[5] that these mixed structures do not significantly affect the state of order of the initial phase if the concentration of defect molecules is less than 10%.

Let us calculate the number of radiation-induced impurity molecules formed in the LC by proton irradiation with an applied dose of 10^{14} R cm^{-2}. We know that the dissociation of organic molecules similar in mass and structure to the LC molecules requires an energy of ~34 eV.[5] A proton with an initial energy of 70 MeV loses ~2 MeV for a range of 1 mm.[6] Energy calculations show that under these conditions ~6×10^{19} defect molecules are formed in 1 cm^3 of LC, amounting to ~6% of the total number of molecules in 1 cm^3. In other words, for a dose of 10^{14} R cm^{-2} the proportion of defect (impurity) molecules is not more than 10%. This explains the very small shift in the phase transition temperatures for these substances (Table 2).

Table 3. Phase transition temperature (t, °C) of some cholesterol derivatives not belonging to the n-alkanoate series before and after proton irradiation (absorbed dose 14.5 Mrad).

Substance	Heating			Cooling		
	C–S	S–Ch	Ch–I	I–Ch	Ch–S	Ch–C
II	95(85) [1]	–	–	65(50)	–	48(27)
III	160(153) [2]	–	206(190)	205(187)	–	127(116)
IV	128(123)	171(161)	210(202)	208(196)	172(158)	88(72) [3]
V	–	–	46(41)	–	–	–

[1]C–I, [2]C–Ch, [3]S–C.

Table 4. Dependence of the phase transition temperatures (t, °C) of various liquid-crystalline substances on the absorbed dose of proton radiation (D, Mrad).

D	Heating					Cooling					
	C–I	C–Ch	Ch–I	C–N	N–I	I–Ch	Ch–S	Ch–C	S–C	I–N	N–C
					Cholesteryl pelargonate						
–	–	77	90	–	–	83	75	–	40	–	–
0.7	–	78	89	–	–	85	74	–	36	–	–
1.5	–	77	90	–	–	85	73	–	47	–	–
5.8	–	73	83	–	–	81	68	–	42	–	–
14.5	–	72	81	–	–	79	64	–	33	–	–
					Cholesteryl chloride						
–	95	–	–	–	–	66	–	48	–	–	–
0.7	94	–	–	–	–	64	–	44	–	–	–
1.5	94	–	–	–	–	63	–	48	–	–	–
5.8	87	–	–	–	–	52	–	30	–	–	–
14.5	85	–	–	–	–	50	–	27	–	–	–
					n-Azoxyanisole						
–	–	–	–	116	132	–	–	–	–	131	81
5.8	–	–	–	117	133	–	–	–	–	133	83
14.5	–	–	–	116	130	–	–	–	–	129	81

A different situation exists for the n-alkanoates of cholesterol, whose molecules have a rigid, disk-shaped steroid nucleus. The molecule as a whole acquires an effectively elongated, rod-like shape because of the presence of two long alkyl chains. However, irradiation with partial loss of the chains produces defect molecules having an effectively disk-like shape. The presence of disk-like molecules may be directly responsible for the large changes in the phase diagrams of the cholesteryl n-alkanoates. An indirect confirmation of this hypothesis was obtained by a model experiment, measuring the phase transition temperatures in non-irradiated cholesteryl pelargonate (VI) as a function of the concentration of added impurity (cholesterol). The cholesterol molecules differ from those of (VI) in not having an alkyl chain. Our experiments show that impurity concentrations of ~5–10% are needed to shift the phase transition temperatures by 5–10 K. This conclusion is consistent with experimental data on irradiated cholesteryl n-alkanoates, and also with the above calculation of the concentration of radiation-induced impurities. For other cholesterol derivatives (Table 3) the shift in the phase transition temperatures is similar to the shift for the n-alkanoates, and it probably has a similar origin.

As was stated above, we also studied the dose dependence of the phase diagrams (Table 4). The presence of a correlation between the dose of proton radiation and the shift in the phase transition temperatures is clear from Table 4. This observation also confirms that the change in the phase transition temperatures is due to the formation of stable radiation-induced impurities whose concentration increases with the dose of radiation and results in an increasing shift of the phase transition temperatures.

Table 5. Dependence of the phase transition temperatures (t, °C) of various liquid-crystalline substances on the absorbed dose of γ radiation (D, Mrad).

D	Heating					Cooling					
	C–I	C–Ch	C–N	Ch–I	N–I	I–Ch	Ch–S	S–C	I–N	N–C	Ch–C
					Cholesteryl chloride						
–	95	–	–	–	–	65	–	–	–	–	48
2	92	–	–	–	–	64	–	–	–	–	43
13	91	–	–	–	–	61	–	–	–	–	39
66	90	–	–	–	–	54	–	–	–	–	39
					Cholesteryl pelargonate						
–	–	77	–	90	–	83	75	40	–	–	–
66	–	76	–	85	–	81	64	26	–	–	–
					p-Azoxyanisole						
–	–	–	116	–	132	–	–	–	131	81	–
66	–	–	114	–	130	–	–	–	130	82	–

Table 5 shows the phase transition temperatures for substances subjected to γ irradiation. Comparing these data with those of Tables 1–3 shows that equal doses of different types of radiation produce shifts in the phase diagrams differing in kind as well as in magnitude. In other words, the shift depends not only on the dose but also on the type of ionising radiation. This can be explained as follows. As we know, the primary process during irradiation is the ionisation of the molecules of the substance.[7] The main difference between the effects of proton and γ radiation is the formation of ionic regions having different distributions in space. Protons, being heavy charged particles, create ionised regions in the form of tracks, whereas the γ quanta produce an approximately uniform ionisation.[7] During the formation of impurity molecules the denser ionic regions must play the major role, since the ion-radicals formed in these regions are most likely to take part in chemical reactions. In a substance containing a uniform distribution of ionic density recombination of the ion-radicals is possible. This may explain the difference in character between the changes in the phase diagrams of LC irradiated with equal doses of protons and of γ quanta.

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Received
24th December 1985