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Electrical and optical studies on γ-irradiated pure and chromium-chloride-doped polyvinyl alcohol

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Measurements of optical absorption, electrical conductivity and of the dielectric constant were used to study the changes that occur due to γ-radiolysis of pure and $CrCl_3$-doped polyvinyl alcohol (PVA) thin films. Identification of the structure and assignments of energy bands were derived in terms of ligand field theory. Induced changes in the absorbance at 282 and 222 nm bands in pure and doped PVA samples, respectively, appeared to be dose dependent. The direct-current (d.c.) electrical conductivity of the samples was measured in the temperature range 296–433 K, and the results obtained revealed that γ-irradiation enhances the conductivity. The calculated activation energy in the lower temperature region also proved to be dose dependent. Plots of the dielectric constant, ε', against temperature show an interesting behaviour which depends on the dopant concentrations and exposure to γ-irradiation. The results obtained suggest that these materials may have an application in dosimetry.

1. Introduction

The general sequence which takes place in high polymers on irradiation [1–4] is the formation of excited, ionized molecules, and the creation of free radicals, electrons and ions. The addition of transition-metal compounds to the polymer network will cause a remarkable change in their properties. They may also change their valency under the action of radiation [5–7]. At the same time, irradiation can affect the electronic state of the ligand molecules in the doped polymer.

Optical and electrical measurements of polyvinyl alcohol (PVA) doped with some selected transition-metal chlorides were investigated [8–10]. The effect of γ-irradiation on the optical absorption of PVA doped with $CoCl_2$ has also been investigated [11]. In addition, the effects of neutron irradiation on some physical properties of PVA and PVA–$CrCl_3$ composites have been reported [12].

The aim of this present work is to investigate the effect of γ-irradiation on the optical absorption and electric properties of PVA film doped with different amounts of a $CrCl_3$ compound.

All measurements were carried out after 1 week of radiation exposure.

2. Experimental procedure

The PVA and $CrCl_3 \cdot 6H_2O$ used in this work were prepared from BDH chemicals. The components (nominally free from impurities) were dissolved in distilled water, and PVA–$CrCl_3$ composites were made in percentages of 2.5, 5, 10 and 30 by weight of $CrCl_3 \cdot 6H_2O$. Thin films approximately 0.3 mm thick were cast on glass plates from distilled-water solutions and dried in an air oven at 40 °C for 48 h in order to minimize gelation effects. Samples were irradiated by different doses of γ-rays in the range $1–10 \times 10^4$ Gy using a ^{60}Co source at room temperature. It must be mentioned that relatively low doses were considered in order to follow the initial changes in the samples under investigation.

Optical absorption measurements were carried out on the above samples before and after γ-irradiation in the wavelength range 200–900 nm using a Berkin Elmer 4B spectrophotometer. The d.c. electrical conductivity was measured by applying a constant voltage of 1 V and measuring the conduction current using a Keithley electrometer, model 616. For ohmic contacts, the surfaces of the sample were coated with silver paste. The dielectric constant, ε', was measured at room temperature using a capacitance bridge (type PLCR8B) working at 800 Hz with a least count of 1 pF. Measurements were made at a moderate heating rate of 1 K min^{-1} from 293 up to 433 K.

3. Results and discussion

3.1. Optical absorption

The absorption spectra of pure PVA samples before and after γ-irradiation in the range $1–10 \times 10^4$ Gy are shown in Fig. 1. The spectra observed showed two broad absorption bands at about 408 and 280 nm. The band at 408 nm was weak while the band at

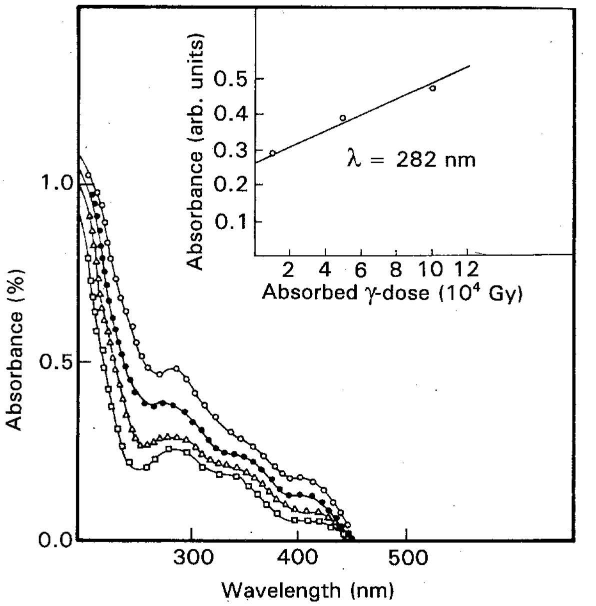

Figure 1 The optical absorption of unirradiated and irradiated pure PVA samples with γ-doses of: (□) unirradiated, (△) 1×10^4 Gy, (●) 5×10^4 Gy, and (○) 1×10^5 Gy. The inset shows the variation of absorbance at the 282 nm band as a function of the γ-dose.

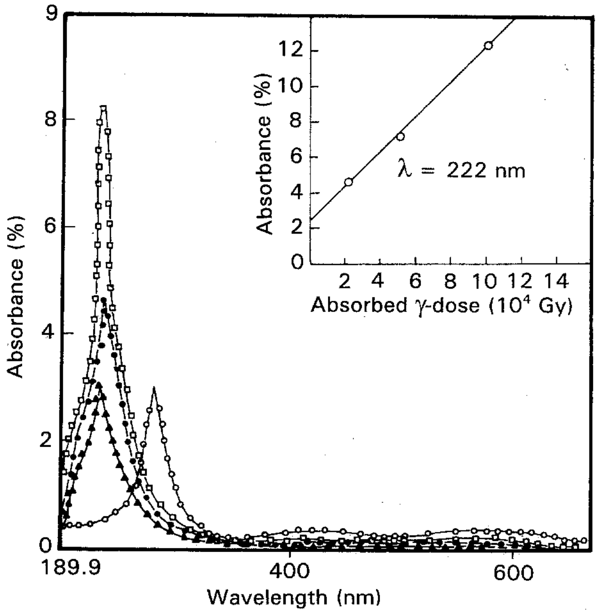

Figure 2 The optical absorption of unirradiated and irradiated doped PVA (with 30 wt % $CrCl_3$) with different γ-doses: (○) unirradiated, (▲) 1×10^4 Gy, (●) 5×10^4 Gy, and (□) 1×10^5 Gy. The inset shows the variation of absorbance at the 222 nm band as a function of the γ-dose.

280 nm was moderately intense. There was no observable change in the band positions with the γ-dose. On the other hand, the absorption intensity of the bands increased with increasing radiation dose. The inset of Fig. 1 shows that the absorbance at the 282 nm band increased linearly with the γ-dose.

The absorption spectra of doped PVA samples containing 30 wt % $CrCl_3$ before and after γ-irradiation in the range of 10^4–10^5 Gy are shown in Fig. 2. Spectra for other composites containing 2.5, 5 and 10 wt % $CrCl_3$ were found to show approximately the same behaviour, and they are, therefore, not presented here. The spectra of the unirradiated samples are characteristic of Cr^{3+} ions in octahedral symmetry and consist of three bands centred at 590, 421 and 276 nm. Among these observed bands, the band at 276 nm is quite intense, while the bands at 590 and 421 nm are broad and weak. The energy bands v_1, v_2 and v_3 around 590, 421 and 276 nm have been attributed to the electronic transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$, ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F), and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (P), respectively [13]. The predicted position of the v_2 transition 23503 cm^{-1} is in good agreement with that observed at 421 nm (23752 cm^{-1}).

In the case of the irradiated samples, a new band developed around 222 nm due to the absorption of carbonyl groups formed from radiolytic oxidation of hydroxyl groups in the PVA matrix by γ-rays. In addition, two absorption bands were observed at 590 and 421 nm. The disappearance of the absorption band at 276 nm may indicate that the ligand PVA matrix becomes opaque in the ultraviolet region [14]. These observations are similar to those reported for PVA doped with $CrCl_3$ and irradiated with fast neutrons [12].

It is clear from Fig. 2 that the position of the absorption bands does not change with increasing radiation dose. On the other hand, the absorption intensity of the bands increases with increasing radiation dose and with the concentration of $CrCl_3$ in the PVA matrix [12]. The inset of Fig. 2 shows that the absorption intensity at the intense band at 222 nm increases linearly with the absorbed γ-dose.

It is clear from the insets of Figs 1 and 2 that percentage changes in the absorbance of about 81 and 412 per cent are obtained after exposure to 10^5 Gy for pure PVA and PVA doped with 10 wt % $CrCl_3$ respectively.

The good linearity of the dose-absorbance relation shown in Figs 1 and 2 suggests the need for further studies of the use of such materials in dosimetry.

3.2. D.c. electrical conductivity

The effect of γ-irradiation on the d.c. electrical conductivity, σ, of pure PVA and PVA films doped with different concentrations of $CrCl_3$ (2.5, 5, 10 and 30 wt %) were studied. The dependence of log σ on $1/T$ for the unirradiated and irradiated pure and doped PVA samples containing 2.5, 5 and 10% $CrCl_3$ shows the same behaviour. Accordingly, Fig. 3 is given here as a representative of the whole series. In the range of temperature investigated, the plots in Fig. 3 can be divided into three straight sections obeying the normal Arrhenius equation. This shows a good resemblance to the previously reported data [9, 15]. It can be seen that the general trend of conductivity–temperature curves is similar; the curves themselves sometimes overlap and intersect. Furthermore, Fig. 3 shows that the d.c. electrical conductivity increases with the γ-dose, particularly in the temperature range above 310 K. This is probably because the effect of ionizing γ-radiation on polymers is to rupture chemical bonds and to create energetic free electrons, ions and radicals. Therefore, the change in the mobility of

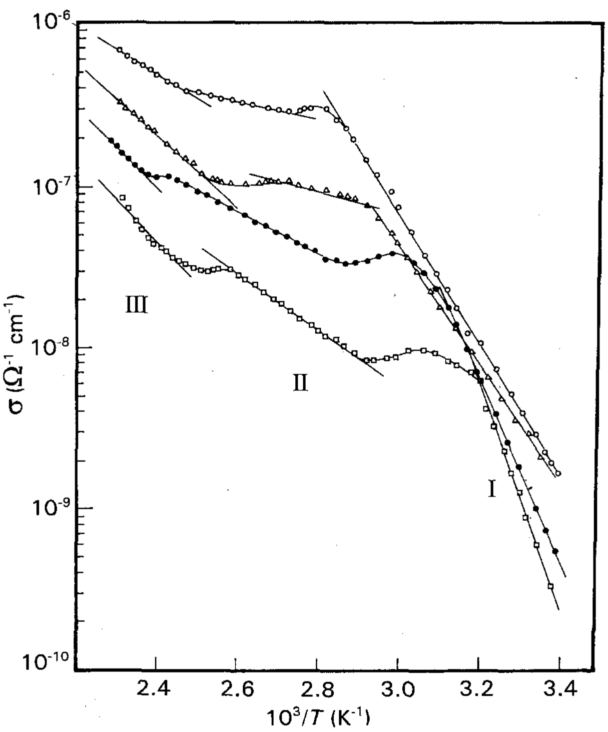

Figure 3 Variation of the electrical conductivity of unirradiated and irradiated PVA samples containing 10 wt % $CrCl_3$ with the reciprocal of temperature at 1 V: (□) unirradiated, (●) 1×10^4 Gy, (▲) 5×10^4 Gy, and (●) 1×10^5 Gy.

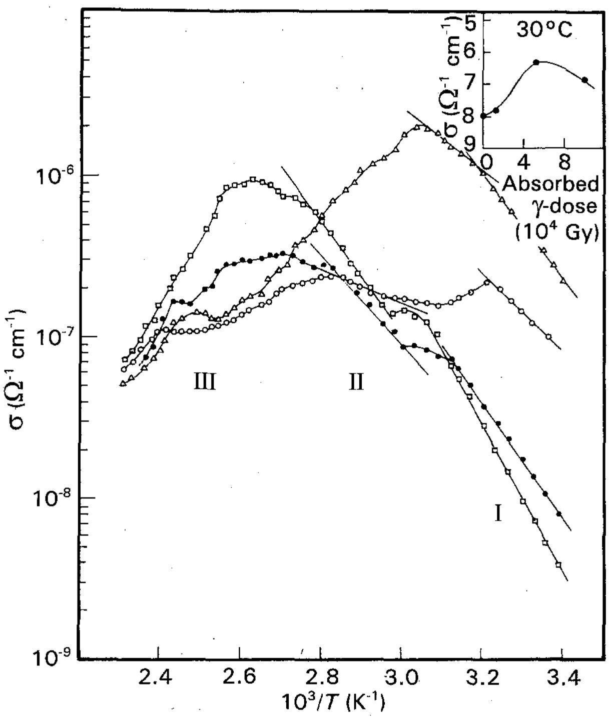

Figure 4 Variation of the electrical conductivity of the unirradiated and irradiated PVA samples containing 30 wt % $CrCl_3$ with the reciprocal of temperature at 1 V: (□) unirradiated, (●) 1×10^4 Gy, (△) 5×10^4 Gy, and (○) 1×10^5 Gy. The inset shows the variation of the d.c. electrical conductivity with the absorbed γ-dose at 303 K.

these carriers due to the energy absorbed in the irradiated polymer will affect the d.c. conductivity measurements.

In the case of the sample containing 30 wt % $CrCl_3$, the plots of log σ against $1/T$ show that at room temperature (296 K) the electrical conductivity for the unirradiated sample is less than for the irradiated sample (see Fig. 4). A relatively irregular trend is observed for the induced changes in σ with the γ-dose. This may find an interpretation in the fact that the number of mobile carriers generated by γ-rays or due to a break of recombination is enhanced by a temperature rise. Meanwhile, region I shows a resemblance in systematic variation of σ with dose. This is manifested by the σ–dose relation showing a competition between opposing conduction processes of an unspecified nature (inset of Fig. 4). Unfortunately, this behaviour is difficult to follow at higher temperatures (regions II and III) because of the existence of more complicated conduction mechanisms [9]. Instead, region III shows a decrease in conductivity with increasing temperature reflecting drastic changes in the polymer structure.

The activation energy of conduction can be estimated from the slope of the log σ versus $1/T$ plot using the equation

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \qquad (1)$$

where σ_0 is a constant. ΔE is the thermal activation energy, and k is Boltzmann's constant. The activation energies evaluated for the unirradiated and irradiated samples are listed in Table I. It is obvious that the values of the activation energy vary as a function of the absorbed dose; they decrease with increasing γ-dose for each particular sample. It has been found [16, 17] that values of the activation energy greater than 0.6 or 0.8 eV would normally be associated with ionic transport, and values less than 0.2 eV should be undoubtedly considered as an electronic mechanism. Therefore, the data of Table I may allow the predominance of ionic-conduction mechanisms to be attributed to the samples under investigation, within the whole temperature range.

In all samples studied, the activation energy is dose dependent. In the temperature range corresponding to region I, the variation of the activation energy with γ-dose shows good linearity (see Fig. 5). Such a linear behaviour may encourage further studies with the purpose of developing reliable dosimeters.

3.3. Dielectric constant

The dielectric properties of pure and $CrCl_3$-doped PVA samples, before and after irradiation, as a function of temperature were studied. The temperature dependence of the dielectric constant, ε′, for pure and doped PVA samples with concentrations of 2.5 and 5 wt % $CrCl_3$ generally describe a nearly similar behaviour. Fig. 6 illustrates, as a representation, the variation of ε′ versus T for PVA containing 2.5 wt % $CrCl_3$. It can be seen that there are two peaks characterizing the glass transition and α-relaxation at about 353 and 393 K, respectively, for unirradiated samples [18]. A slight peak shift towards higher temperatures has been observed with increasing exposure dose.

Starting from room temperature, the value of ε′ slightly increases up to the glass-transition temperature, T_g, while after α-relaxation the rise becomes

TABLE I Values of the activation energy calculated from d.c. conductivity measurements

Sample	Activation energy (eV)											
	Unirradiated			1×10^4 Gy			5×10^4 Gy			1×10^5 Gy		
	I	II	III	I	II	III	I	II	III	I	II	III
PVA	1.53	0.28	1.00	1.44	0.26	0.75	1.12	0.25	0.49	0.80	0.24	0.42
PVA + 2.5% $CrCl_3$	1.80	0.44	0.87	1.44	0.25	0.77	1.18	0.23	0.58	0.96	0.23	0.48
PVA + 5% $CrCl_3$	1.74	0.67	0.69	1.52	0.58	0.64	1.35	0.56	0.56	1.26	0.51	0.30
PVA + 10% $CrCl_3$	1.42	0.35	0.52	1.13	0.26	0.47	0.96	0.22	0.42	0.79	0.20	0.30
PVA + 30% $CrCl_3$	0.88	0.66	–	0.70	0.53	–	0.65	0.36	–	0.49	0.21	–

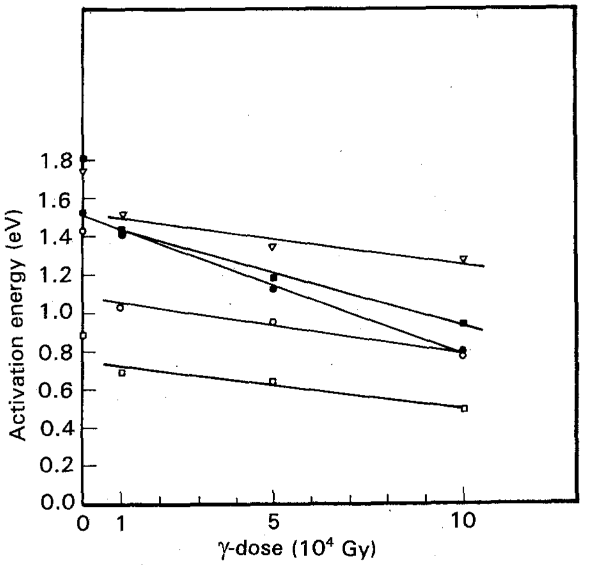

Figure 5 The variation of the activation energy in the low-temperature region, region, I, with the absorbed γ-dose for pure and doped PVA samples: (●) PVA, (■) 2.5% $CrCl_3$, (▽) 5.0% $CrCl_3$, (○) 10.0% $CrCl_3$, and (□) 30.0% $CrCl_3$.

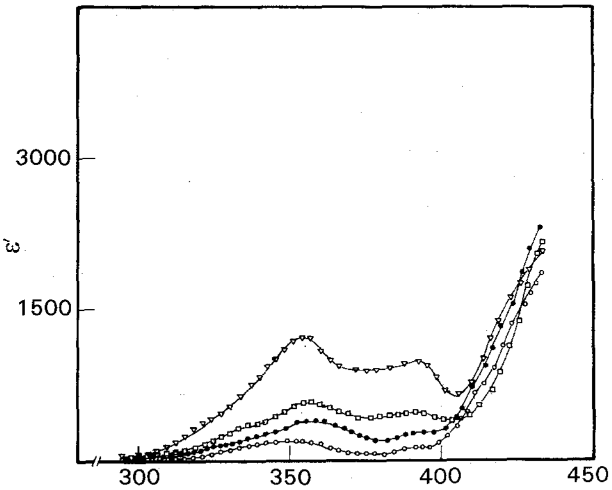

Figure 6 The temperature dependence of ε' for doped PVA with 2.5 wt % $CrCl_3$ at different γ-doses: (○) unirradiated, (●) 1×10^4 Gy, (□) 5×10^4 Gy, and (▽) 1×10^5 Gy.

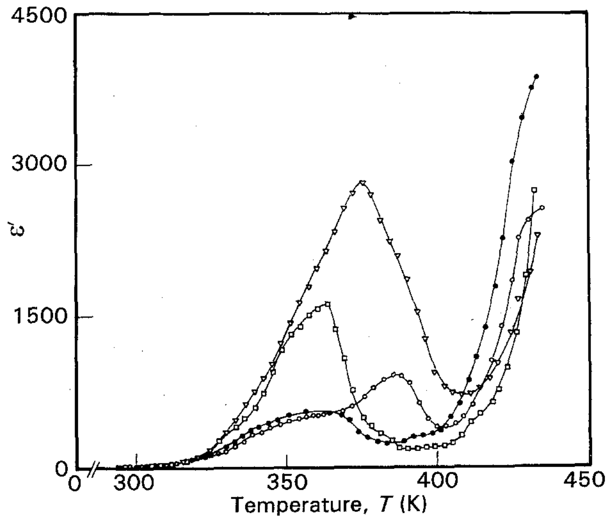

Figure 7 The temperature dependence of ε' for doped PVA with 10 wt % $CrCl_3$ at different γ-doses: (○) unirradiated, (●) 1×10^4 Gy, (□) 5×10^4 Gy, and (▽) 1×10^5 Gy.

rapid. The remarkable increase of ε' with temperature after α-relaxation is probably due to an increase of polarization arising from the facilitation of the molecular motion of polymer-chain segments which allows orientation of dipolar units in the applied electric field. Trapped charge carriers are also expected to contribute to the total polarization since the polymer systems normally contain large numbers of trapping sites [19]. Polarization of trapped charge carriers is more significant at high temperatures. Also, in the range 300–430 K, the value of ε' increases with an increase in the exposure dose. Creation of the carbonyl groups, which are highly polar, causes an increase in the dielectric constant.

Fig. 7 for the 10 wt % $CrCl_3$ composite shows that the two peaks corresponding to the glass transition and α-relaxation are replaced by one pronounced glass-transition peak with irradiation. The peak position is shifted towards higher temperatures than the glass transition peak for the unirradiated sample. The disappearance of the α-relaxation peak with irradiation may be attributed to structural changes in the polymer matrix.

At higher concentrations of dopants, namely 30% $CrCl_3$, completely different $\varepsilon'(T)$ curves are obtained, indicating the important role of metal additions which tend to increase ε'. All curves exhibit only highly pronounced glass-transition peaks. The position of the glass-transition peak is shifted towards the lower temperature values while the ε'-value at the peak position increases with increasing γ-dose. Above T_g, the decrease in ε' with temperature is attributed to the increase in chaotic thermal oscillations of the molecules and the diminishing degree of order of the

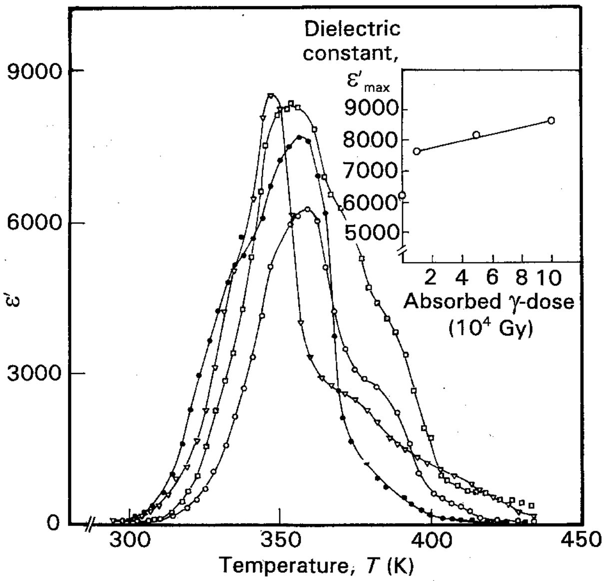

Figure 8 The temperature dependence of ε' for doped PVA (with 30 wt % $CrCl_3$) at different γ-doses: (○) unirradiated, (●) 1×10^4 Gy, (□) 5×10^4 Gy, and (▽) 1×10^5 Gy. The inset shows the variation of ε'_{max} as a function of the γ-dose.

TABLE II Values of the electric-dipole moment for PVA + $CrCl_3$ composites at 1 kHz

Sample	$\mu \times 10^{-18}$ (e.s.u.)			
	Unirradiated	1×10^4 Gy	5×10^4 Gy	1×10^5 Gy
PVA + 10% $CrCl_3$	22.90	19.00	14.90	7.96
PVA + 30% $CrCl_3$	6.86	4.33	3.62	2.70

orientation of the dipoles. Furthermore, it is worthwhile reporting that the maximum dielectric values, ε'_{max}, show a linear dependence on the γ-exposure dose up to 1×10^5 Gy (see the inset of Fig. 8).

The classical theory of dielectric properties relates the dielectric constant, ε' to the permanent dipoles, μ by the Debye equation [20]

$$\frac{\varepsilon' - 1}{\varepsilon' + 2} = \frac{4}{3}\pi N\left[(\alpha_e + \alpha_a) + \frac{\mu^2}{3kT}\right] \qquad (2)$$

where N is the number of molecules per unit volume, k is Boltzmann's constant, and α_e and α_a are the electronic and atomic polarizabilities, respectively. For the samples containing 10 and 30 wt % $CrCl_3$, the slope of straight lines (not shown) of the relation between $(\varepsilon' - 1)/(\varepsilon' + 2)$ and $1/T$ above the glass temperature and the use of Equation 2 yields the values of the dipole moment. They are calculated and presented in Table II. It is clear that the value of μ decreases with increasing γ-dose as well as with increasing dopant concentration. This behaviour can be attributed to the decrease in the free volume between dipoles in the polymer network due to radiation and increasing concentration of the dopant.

Finally, we can conclude that the optical absorption, electrical conductivity and dielectric constant reflect a good response of pure and doped PVA samples to γ-radiation. This suggests further studies of the use of these materials in dosimetry.

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