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Radiation-Induced Changes in the Index of Refraction, Density, and Dielectric Constant of Poly(methyl Methacrylate)*

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Synopsis

Samples of commercially prepared poly(methyl methacrylate) (Lucite) were irradiated with 13-M.e.v. electrons in the dose range 0–11 Mrad, and the induced changes in the index of refraction, density, and dielectric constant were observed. An attempt is made to interrelate the observed changes theoretically.

INTRODUCTION

The effects of ionizing radiation on the physical and electrical properties of organic plastics have been investigated for a number of years.[1–6] Other studies have mentioned the coloration induced in these irradiated plastics.[6–12] However, many of these studies were done to evaluate the performance of the plastic as a dielectric associated with some electrical apparatus operating in a radiation field, or as a dosimeter. In spite of the large amount of information currently available, the details of the processes that result in coloration and in changes in the electrical properties are still uncertain. Very few accurate data have been published on the changes in the refractive index of irradiated plastics, although such changes have been observed in the past.[13] It was thought that such a study might provide additional information concerning changes in the chemical bonds and in the production of separated charges in the irradiated plastic. Poly(methyl methacrylate) (PMMA) was chosen for study primarily because of its clarity and because it has been the material used in other radiation studies in this laboratory for several years. Density changes were measured because the refractive index should vary in a known way with density. A few measurements of relative changes in the dielectric constant were also made, merely to see if they were consistent with the changes in the high-frequency dielectric constant that could be computed from the refractive-index data.

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EXPERIMENTAL DETAILS

Irradiation Procedure

The samples were cut from 0.32-cm. thick sheets of commercial Lucite into 1 × 2-cm. pieces. The LINAC electron accelerator at the Argonne National Laboratory was used to provide electrons about 13 M.e.v. in energy. Samples were sandwiched between 1.27-cm. thick pieces of Lucite in an attempt to approach electronic equilibrium and to minimize variations in dose with depth within the sample. Blue cellophane dosimetry was employed.[14] This dosimeter had been satisfactorily employed with PMMA samples in the past.[10] The estimated error in the dose measurements is 7%. Pieces of the cellophane were enclosed with every sample irradiated.

Some samples were irradiated without temperature control by attaching them to the rim of a 1-rpm rotating wheel that passed through the electron beam at a distance of about 1.5 m. from the exit window of the LINAC. As the electron beam passed through the air it diverged enough to ensure a uniform irradiation of the sample. The LINAC pulse rate was varied from 30 to 150 pps and the current so adjusted that each sample received a few tenths of a megarad per rotation. In some runs compressed air was directed at the samples during irradiation to effect some cooling.

Other samples were irradiated in an insulated irradiation cell. The samples were placed in a central container filled with water. This container was surrounded by a second container, which was filled with an ice–water mixture or with liquid nitrogen (thereby freezing the water in the central container). Thus nominal sample temperatures close to 0°C. and −196°C. were maintained. The actual sample temperatures were not measured and were certainly somewhat higher than the nominal temperatures. However, the cell did allow a reasonably constant temperature to be maintained during the irradiation.

Index of Refraction Measurements

A Bausch and Lomb Model 3787-A dipping refractometer was employed. The samples were attached to the surface of the dipping prism with monobromonaphthalene, and the prism was enclosed with a watertight metal cup which was maintained at 25°C. by a constant-temperature water bath. Repeated measurements on the same sample indicated that the standard deviation in the measurements was about 2×10^{-5}, and that a typical refractive index of a PMMA sample prior to irradiation was 1.49137. PMMA does not have a unique refractive index since it depends on the orientation of the polymer chains and on other factors. In the commercial samples used here the measurements on a given sample varied considerably depending upon the orientation of the sample on the prism. Care was taken to insure that the samples were oriented in the same way when the measurements before and after irradiation were made.

Density Measurements

A pycnometer of the type shown in Figure 1 was used. The distilled water used as the immersion fluid was boiled shortly before the pycnometer was filled. A similar pycnometer was used as a tare during the weighing; a buoyancy correction was made according to Weissberger[15] and the density of water was computed using the equation given by Tilton and Taylor.[16]

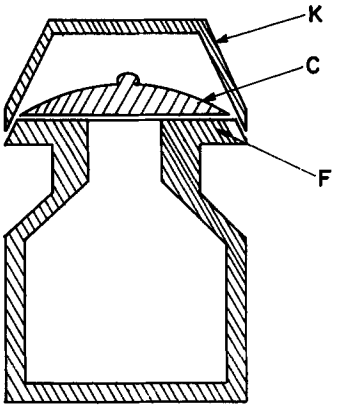

Fig. 1. Pycnometer used in the density measurements. A flat cap C rests on the flat surface of flange F and is enclosed by cap K.

The temperature of the constant temperature bath was 25°C. A typical value for the density of unirradiated PMMA is 1.1792 g./ml., and the typical standard deviation in the density measurements is estimated to be 5×10^{-4} g./ml.

Dielectric Constant Measurements

Changes in the dielectric constant were measured with a heterodyne beat instrument[17] operating at a frequency of 955 kc./sec. The distance between the parallel copper plates in the sample holder was controlled by a micrometer. No absolute measurements were made in this case; only a value proportional to the change in the dielectric constant of a sample after exposure to the electron beam was determined. No particular effort was made to control the sample temperature, although the ambient temperature was always reasonably close to 25°C. The absolute uncertainty in these measurements, estimated from repeated measurements on the same sample, was independent of the dose delivered to the sample in the range 0–11 Mrad. Beyond a dose of 11 Mrad. the gas production within the sample caused a nonuniform expansion of the sample, which made positioning of the sample between the holder plates difficult. The percentage error in the measurements ranged from ±70% at a dose of 1.5 Mrad to ±8% at a dose of 4.5 Mrad.

RESULTS

Refractive Index Measurements

The first irradiations were made with no attempt to control the temperature of the sample during irradiation. Figure 2 illustrates the kind of results that were obtained. While the variation of Δn with dose was reasonably linear within each run, the magnitudes of the variations were

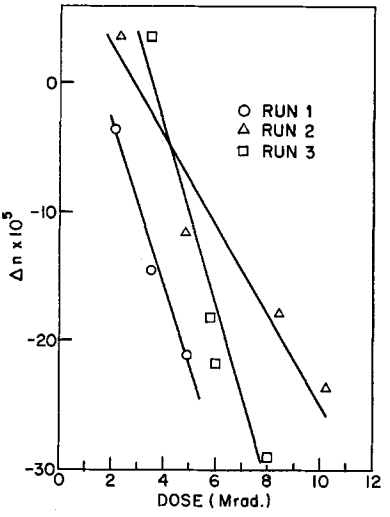

Fig. 2. Changes in the refractive index with dose. No temperature control. Runs were made on different days and under different conditions of dose rate and cooling.

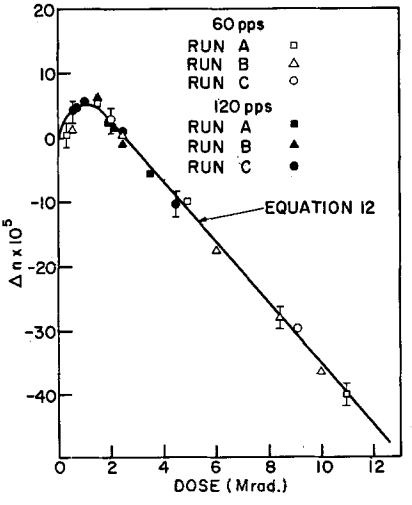

Fig. 3. Change in refractive index with dose. Nominal sample temperature of −196°C. LINAC pulse rates of 60 and 120 pps were employed. Solid line is that computed from eq. (12). Typical error bars are included on a few points.

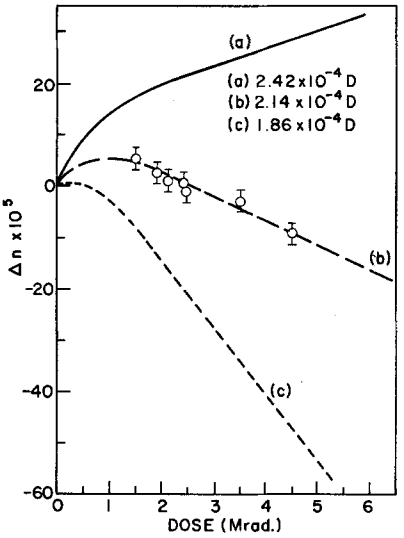

Fig. 4. Change in refractive index with dose. Nominal sample temperature of 0°C. Typical error bars are shown. See text for the meaning of the three curves marked (*a*), (*b*), and (*c*).

not reproducible from run to run if changes occurred in dose rate, ambient temperature, or air cooling between runs.

When the samples were irradiated in the constant-temperature irradiation cell the results were reproducible. Figure 3 shows the experimental results obtained at −196°C., and in Figure 4 are the results obtained at

TABLE I
Change in Refractive Index with Dose at a Nominal Sample Temperature of −196°C.

LINAC pulse rate 60 pps			LINAC pulse rate 120 pps		
Dose, Mrad	Run number[a]	$\Delta n \times 10^5$	Dose, Mrad	Run number[a]	$\Delta n \times 10^5$
0.3	A	0.4 ± 1.7	0.6	C	4.2 ± 1.7
0.5	B	1.1 ± 1.7	0.7	C	4.7 ± 1.7
1.5	A	5.1 ± 1.7	1.0	C	5.5 ± 1.7
2.0	C	2.9 ± 1.7	1.5	B	6.2 ± 1.7
2.4	B	0.4 ± 1.7	1.9	A	2.6 ± 1.7
4.9	A	−9.8 ± 1.7	2.1	B	1.8 ± 1.7
6.0	B	−17.5 ± 1.7	2.4	C	0.7 ± 1.7
8.4	B	−27.7 ± 1.7	2.45	B	−1.0 ± 1.7
9.1	C	−29.5 ± 1.7	3.5	A	−5.5 ± 1.7
10.0	B	−36.4 ± 1.7	4.5	C	−10.2 ± 1.7
11.0	A	−40.0 ± 1.7			

[a] The letters indicate different days.

0°C. Figure 3 shows that doubling the dose rate did not affect the results. Tables I and II contain the data plotted in Figures 3 and 4.

TABLE II
Change in Refractive Index with Dose at a Nominal Sample Temperature of 0°C.

Dose, Mrad	$\Delta n \times 10^5$
1.50	5.5 ± 1.7
1.90	2.5 ± 1.7
2.10	1.6 ± 1.7
2.40	0.4 ± 1.7
2.45	−1.0 ± 1.7
3.50	−2.4 ± 1.7
4.50	−9.1 ± 1.7

Density Measurements

As was found in the refractive-index measurements, reproducible results could not be obtained when the sample temperature was uncontrolled during irradiation. Table III presents typical results that were obtained

TABLE III
Change in Density with Dose

Dose, Mrad	LINAC pulse rate, pps	$\Delta d \times 10^4$, g./ml.	
		−196°C.	0°C.
0.5	60	5.7 ± 5	
1.50	120	23 ± 5	
1.50	60	17 ± 5	
1.70	120		22 ± 5
1.80	120		31 ± 5
1.90	120	31 ± 5	
1.90	60	26 ± 5	
2.10	120	41 ± 5	
2.10	60	37 ± 5	
2.40	60	40 ± 5	
2.45	120	50 ± 5	
2.90	120		64 ± 5
3.50	120	72 ± 5	
4.00	120		109 ± 5

at −196°C. and at 0°C. The results obtained at −196°C. are displayed in Figure 5. It appears that there is a slight dose-rate effect, but the data are not accurate enough to definitely confirm it.

Dielectric Constant Measurements

Table IV presents the relative changes in the dielectric constant. The scale chosen is convenient when these changes are related to the changes in the index of refraction.

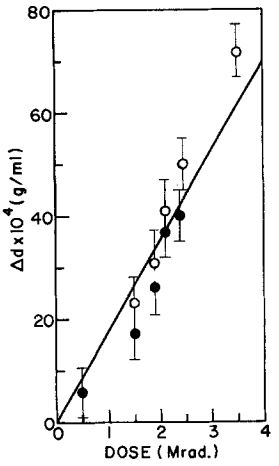

Fig. 5. Change in density with dose. Nominal sample temperature of −196°C. at LINAC pulse rates of (●) 60 and (○) 120 pps; (——) corresponds to 4.92×10^{-4} ml./Mrad. The positive change in Δd corresponds to a volume expansion.

TABLE IV
Relative Changes in the Dielectric Constant with Dose at Frequency = 955 kc.

Dose, Mrad	$\Delta\epsilon \times 10^3$ (arbitrary units)	
	Irradiation temp. −196°C.	Irradiation temp. 0°C.
1.50	−13.4 ± 5	−6.7 ± 5
1.90	−19.7 ± 5	−12.7 ± 5
2.10	−25.0 ± 5	−19.3 ± 5
2.40	−36.8 ± 5	−26.2 ± 5
2.45	—	−30.4 ± 5
3.50	−52.5 ± 5	−46.2 ± 5
4.50	−67.0 ± 5	−63.0 ± 5

DISCUSSION

PMMA is a linear polymer that contains permanent dipoles, exhibits dielectric dispersion, and is not crystalline at room temperature in its usual (predominantly syndiotactic) form. Studies of the dielectric loss factor as a function of temperature indicate that there are two major transitions: α around 120°C. and β around 50°C. The first transition probably involves movement of large chain segments, whereas the second may involve ester group movement. PMMA undergoes essentially only chain scission during irradiation. The decrease in the molecular weight due to scission could free the molecular motion and thus affect the dielectric constant and the refractive index, but at the doses used here this effect is expected to be small. The observed changes in these quantities more likely arise from other causes.

Although the structural interpretation of the dielectric constant of almost every pure polymer is incomplete, considerable work has been done in this area.[18-20] The dielectric constant is related to molecular properties through the polarizability. For the purpose of this discussion it is assumed that the Debye modification of the Clausius-Mosotti equation is an adequate formulation of this relation for the PMMA system. This is not strictly correct, since the units in the polymer chain do interact and are not randomly oriented, and some improvement could be made through the introduction of Kirkwood's g factor. We shall only be concerned with relative changes in the dielectric constant and hence eq. (1) is appropriate.

$$[(\epsilon - 1)/(\epsilon + 2)]\, M/\rho = (4\pi N/3)\, [\alpha_E + (\mu^2/3kT)] \qquad (1)$$

Here ϵ is the dielectric constant, M is the molecular weight, N is Avogadro's number, α_E is the electronic polarization, μ is dipole moment, k is Boltzmann's constant, and T is the temperature. It can be assumed that M, α_E, and μ refer to a unit in the polymer chain, and thus α_E and μ are average, effective quantities. Furthermore, we can write

$$[(n^2 - 1)/(n^2 + 2)]\, M/\rho = 4\pi N\alpha_E/3 = [(\epsilon_\infty - 1)/(\epsilon_\infty + 2)]\, M/\rho \qquad (2)$$

where n is the refractive index, which is related to the high-frequency dielectric constant ϵ_∞ by $n^2 = \epsilon_\infty$. In this way the changes in the refractive index induced by the irradiations can be related to a part of the change in the dielectric constant measured around 10^6 cps. The difference between ϵ and ϵ_∞ is due to the motion of the permanent dipoles.

In eq. (2) the quotient involving n or ϵ_∞ depends upon the number of permanent and induced dipoles per unit volume. If either the number of dipoles or the volume (or both) change, the quotient will also change. During the irradiation of PMMA a number of chemical changes occur.[9,21] Chain scission takes place, double bonds are introduced into the chain, and gases such as H_2, CH_4, CO, and CO_2 are produced from the destruction of the ester groups attached to the carbon backbone of the polymer molecule. The irradiation also generates electron-hole pairs and free radicals, as evidenced by the observed increase in conductivity during and after irradiation,[6] by the color produced in the material,[11] and by electron-spin resonance data.[22] The evidence indicates that the production of separated charges during irradiation soon reaches an equilibrium concentration that depends upon the intensity of the radiation. After irradiation the electron-hole pairs tend to recombine, and the color fades. Much of the color disappears in a matter of minutes, but some remains for years in samples kept at room temperature and not exposed to intense light sources. The coloration tends to saturate in PMMA at doses between 1 and 2 Mrad.[10,11]

The refractive index and dielectric constant measurements should reflect the three changes discussed above: electron-hole or space-charge production, which saturates at a dose around 1 or 2 Mrad.; the replacement of the ester groups by double bonds and radiolytic gases; and the expansion of the sample due to gas production. The volume expansion changes the

concentration of the polarizable groups, which appears to be approximately linear according to the data presented above. Thus we can represent the volume by

$$V(D) = V_0 + k_1 D \tag{3}$$

Here V_0 is the sample volume prior to irradiation and D is the dose in megarads. The constant k_1 can be evaluated by the data in Table III, and it appears to depend in a reasonable way on temperature. The production of electron-hole pairs saturates when additional electrons must come to rest within the critical distance from a hole at which the Coulomb force of attraction will bring about their annihilation. Thus the concentration of electron-hole pairs as a function of dose should exhibit a typical growth shape, represented by an equation of the form

$$C_{eh}(D) = C_{eh}^{\infty} (1 - e^{-k_2 D}) \tag{4}$$

The k_2 is a constant and C_{eh}^{∞} is the concentration at saturation. Finally, the replacement of the ester group during scission by double bonds and the radiolytic gases is a linear function of dose

$$C_{est}(D) = C_{est}^{0} - k_3 D \tag{5}$$

It is reasonable to expect that the volume expansion will decrease the refractive index[23] and that the pair production will increase it.[24] In view of the structural contributions to the refractive index,[19] the replacement of the ester groups should also increase its value.

Consider a small change Δn in the initial refractive index n_0 of a PMMA sample due to receiving a dose D which caused changes ΔV and $\Delta(N\alpha_E)$. Thus, if n_0 is the refractive index prior to irradiation

$$n = n_0 + \Delta n$$

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_0^2 + 2n_0\Delta n - 1}{n_0^2 + 2n_0\Delta n + 2} \approx \frac{[(n_0^2 - 1)/2n_0] + \Delta n}{[(n_0^2 - 1)/2n_0] + (3/2n_0)} \tag{6}$$

Now

$$(n^2 - 1)/(n^2 + 2) = k_4 \{ [N\alpha_E + \Delta(N\alpha_E)]/(V_0 + \Delta V) \} \tag{7}$$

When $D = 0$, $n = n_0$, and

$$(n_0^2 - 1)/(n_0^2 + 2) = k_4 N\alpha_E / V_0$$

and thus

$$k_4 = \frac{V_0}{N\alpha_E} \left(\frac{n_0^2 - 1}{n_0^2 + 2} \right) \tag{8}$$

Combining eqs. (6), (7), and (8) leads to

$$\Delta n = \left(\frac{n_0^2 - 1}{2n_0} + \frac{3}{2n_0} \right) \frac{V_0}{N\alpha_E} \left(\frac{n_0^2 - 1}{n_0^2 + 2} \right) \left[\frac{N\alpha_E + \Delta(N\alpha_E)}{V_0 + \Delta V} \right] - \left(\frac{n_0^2 - 1}{2n_0} \right) \tag{9}$$

From the previous discussion we may say

$$\Delta V = k_1 D$$
$$\Delta(N\alpha_E) = K_I(1 - e^{-k_2 D}) + K_{II} D$$

Equation (9) now has the form

$$\Delta n = \left(\frac{n_0^2 - 1}{2n_0} + \frac{3}{2n_0}\right)\left(\frac{n_0^2 - 1}{n_0^2 + 2}\right)\frac{V_0}{N\alpha_E} \times \left[\frac{N\alpha_E + K_I\,(1 - e^{-k_2 D}) + K_{II} D}{V_0 + k_1 D}\right] - \left(\frac{n_0^2 - 1}{2n_0}\right) \quad (10)$$

Consider first the changes in refractive index produced when the samples were irradiated at −196°C. The density data yield a value for k_1 of 4.92×10^{-4} ml./Mrad. A typical value for n_0 was 1.49137, and for V_0 we have used 0.33 ml. Inserting these values into eq. (10) yields

$$\Delta n = \frac{0.1354395}{N\alpha_E}\left[\frac{(N\alpha_E + K_I) - K_I e^{-k_2 D} + K_{II} D}{0.33 + 4.92 \times 10^{-4} D}\right] - 0.410423 \quad (11)$$

When eq. (11) was fitted to the data in Table I the following was obtained:

$$\Delta n + 0.410423 = \frac{0.135481 + 1.86 \times 10^{-4} D - 4.2 \times 10^{-5} \exp\{-1.54 D\}}{0.33 + 4.92 \times 10^{-4} D} \quad (12)$$

One term that is expected to be sensitive to the temperature of the sample during irradiation is the volume expansion term in the denominator. The experimental data in Table III are consistent with the expression

$$V(D) = 0.33 + 5.60 \times 10^{-4} D \quad (13)$$

at 0°C.

It has also been shown by Charlesby and Black[4] and others[6] that the G value for chain scission of PMMA is temperature-dependent. Unfortunately there is some disagreement as to the magnitude of this effect.

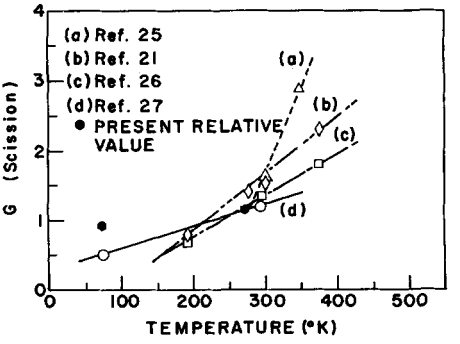

Fig. 6. G(scission) as a function of temperature: (●) relative values found here at −196°C. and 0°C., normalized to the value at 0°C.

Figure 6 shows the results currently available pertaining to this temperature effect.[25–27] It is obvious that the curves marked (*a*) and (*b*) do not extrapolate to the correct low-temperature G value, and that the function G versus T must exhibit a much smaller slope at low temperatures. Nonetheless, there seems to be no question that the rate of scission at −196°C. should be lower than at 0°C.

In Figure 4 we have shown the observed changes at 0°C. in the refractive index versus dose. The three additional curves were obtained from eq. (12) by replacing the volume term in the denominator by that given in eq. (13). Then the term $1.86 \times 10^{-4}D$ in eq. (12), which represented the destruction of the ester group, was changed to $2.14 \times 10^{-4}D$ and then to $2.42 \times 10^{-4}D$. The middle curve represents the data very well. It

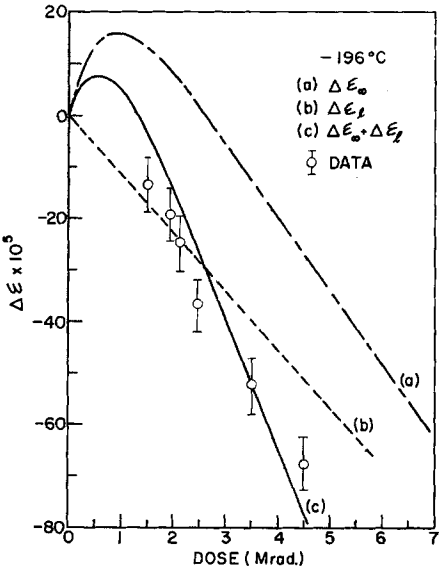

Fig. 7. Predicted change in the dielectric constant with dose. Nominal sample temperature of −196°C. The relative experimental values were normalized at a dose of 3.5 Mrad.

appears, therefore, that there is only about a 15% decrease in the G value for scission, going from 0°C. to −196°C. With a value assumed for G scission at 0°C. the two points in Figure 6 indicated by stars were determined. The fact that this work predicts such a large G value at −196°C. may be partly due to the fact that our actual sample temperatures could have been higher than the stated nominal temperatures.

There are only two significant aspects of the dielectric constant data reported in Table IV: ϵ decreases with increasing dose, and the data do not extrapolate to $\Delta\epsilon = 0$ at zero dose. Taking n_0 as 1.49137, we find that $\epsilon_\infty = 2.22418$. Hence at a sample temperature of −194°C.,

$$\Delta\epsilon_\infty + 1.22418 = 2.98274 \times \left[\frac{0.135481 + 1.86 \times 10^{-4}D - 4.2 \times 10^{-5} \exp\{-1.54D\}}{0.33 + 4.92 \times 10^{-4}D}\right] \quad (14)$$

Experimental measurements[28] at frequencies approaching 10^6 cps indicate that the ϵ of the PMMA samples prior to irradiation should be about 2.7 around room temperature.

The difference between ϵ and ϵ_∞ is termed here ϵ_l and is largely related to the movement of the ester group on the polymer chain. When the ester group is destroyed during irradiation ϵ_l will change linearly with dose.

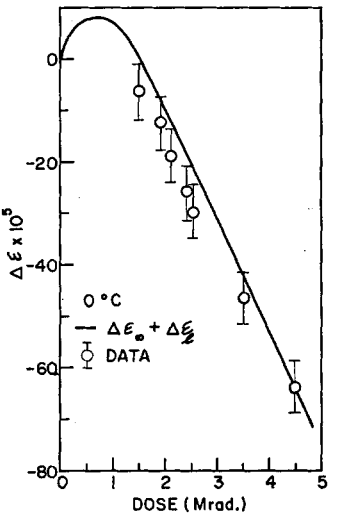

Fig. 8. Predicted change in the dielectric constant with dose. Nominal sample temperature of 0°C.

If ϵ_l becomes smaller with increasing dose, the general form of the dielectric-constant measurement is consistent with what would be expected from the refractive-index results. Figure 7 shows the $\Delta\epsilon_\infty$ computed from the refractive-index data for samples irradiated at −196°C. If $\Delta\epsilon_l$ is taken as $7.25 \times 10^{-5}D$, the curve representing $\Delta\epsilon_\infty + \Delta\epsilon_l$ in Figure 7 is obtained. This last is compared with the experimental data, which have been normalized at a dose of 3.5 Mrad. With the refractive-index equation for 0°C., and with $\Delta\epsilon_l$ increased by 15% to compensate for the increased G value for scission at 0°C. over that at −196°C., a curve for $\Delta\epsilon_\infty + \Delta\epsilon_l$ was computed which is compared with experiment in Figure 8. The experimental points have been multiplied by the same normalization factor used with the points at −196°C.

CONCLUSIONS

The observed changes in the refractive index of PMMA with dose can be satisfactorily accounted for by considering the production of separated

charges, the destruction of the ester side chain, and the volume expansion arising from the radiolytic gas production in the samples. The expansion is dependent upon the temperature of the sample during irradiation, and experimental values for the dependence of the expansion on dose at sample temperatures of −196°C. and 0°C. were obtained from density measurements.

The changes in refractive index with dose at −196°C. could be used to predict similar changes at 0°C. if the G value for scission increases by 15% over this temperature range. This is less of an increase than has been previously found. The refractive-index changes were also used to predict changes in the high-frequency dielectric constant. These changes were consistent with the general trend of the data, which was decreasing with increasing dose and which did not extrapolate through zero change at zero dose.

One of the original motivations for this work was to see whether the changes in refractive index in irradiated PMMA could be used as a convenient dosimeter. Because these changes are sensitive to sample temperature and because the volume change at doses above 15 Mrad makes measurements difficult, this approach will probably not compete with more convenient dosimeters.

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Résumé

Les échantillons de polyméthacrylate de méthyle préparés commercialement (Lucite) sont irradiés avec des électrons à 13 Mev dans un domaine de dose de 0 à 11 Mrad. et les changements induits dans l'indice de réfraction, la densité, et la constante diélectrique sont observée. On essaie de relier entre-elles théoriquement les variations observées.

Zusammenfassung

Proben von handelsüblichem Polymethylmethacrylat (Lucite) wurden mit 13-Mev-Elektronen im Dosisbereich von 0 bis 11 Mrad bestrahlt und die dadurch hervorgerufene Änderung von Brechungsindex, Dichte und Dielektrizitätskonstante bestimmt. Es wird versucht, theoretischen Beziehungen zwischen den beobachteten Änderungen aufzustellen.

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