

Studies in Radiation-Induced Polymerization of Vinyl Monomers at High Dose Rates.

I. Styrene

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Synopsis

The kinetics and degree of polymerization of the radiation-induced polymerization of styrene were investigated at dose rates up to 3 Mrads per sec. It was found that both the polymerization rates and the molecular weights at high dose rates lie well above the values predicted by extrapolation from low dose rate studies where the mechanism is primarily free radical in nature. The evidence obtained indicates that with increasing dose rate there is an increase in the ionic contribution to the polymerization mechanism. At the highest dose rates investigated, 3 Mrads per sec, the ionic mechanism dominates while the free-radical mechanism contributes insignificantly. There was no inhibition of the polymerization of styrene by dissolved air at the higher dose rates. Investigation of the polymerization of styrene saturated with water tends to support the ionic mechanism via free cations. Investigation of equimolar solutions of styrene and methyl methacrylate further support the ionic mechanism, yielding predominately polystyrene and a small amount of 50-50 copolymer. In the intermediate dose rate range, 1000 rads per sec, there is evidence that the high dose rate free-radical kinetic mechanism is the principal mechanism.

INTRODUCTION

Numerous reports on the polymerization of various vinyl monomers and in particular styrene initiated by x-rays, radiation from nuclear reactors, gamma rays, and high-energy electrons have appeared in the literature during the past two decades. In the main, these investigations of radiation-induced polymerization have been limited to low dose rates such as obtainable with ^{60}Co sources since electron accelerators have not been favored, as the high dose rates obtained were known to lead to experimental difficulties due to excessive and almost unsurmountable heat effects. In addition, the penetration pattern leads to difficulties with uniform fields and accurate dosimetry. On the other hand, in recent years, interest in high-speed industrial radiation processing has led to the development of high-power accelerators and has created considerable interest in understanding the nature of polymerization processes at the high dose rates achieved with these electron accelerators.

The mechanism for the polymerization of liquid styrene at low radiation dose rates appears to be well understood as a result of efforts conducted during the past decade. During this period, several discoveries about the mechanism of polymerization of styrene under a variety of conditions have been published. It is clear that under normal conditions of purity and dryness, styrene alone and in solution polymerizes with radiation by a predominately free-radical mechanism; a full account of this topic may be found in Chapiro.¹ It is now also well established that styrene alone²⁻⁴ or in certain solvents⁵ when extremely dry polymerizes with radiation by an ionic mechanism,²⁻⁴ and at intermediate levels of dryness free-radical and ionic polymerization may take place simultaneously.⁶⁻⁸

The investigations reported in this paper are concerned with the radiation-induced polymerization of nonanhydrous styrene at dose rates up to 3 Mrads per sec. Rate and degree of polymerization data obtained indicate that the ionic mechanism is dominant at high dose rates, as the enhanced rate of polymerization and nondiminishing molecular weights observed with increased dose rates is due to an increasing ionic contribution with increasing dose rate. Both the rate of polymerization and the degree of polymerization at high dose rates are found to lie well above the values predicted by extrapolation from lower dose rate studies.

EXPERIMENTAL

Preparation of Styrene Samples

Styrene monomer obtained from Eastman Organic Chemicals and of the highest purity was washed with sodium hydroxide and then with distilled water four times to remove the inhibitor. The washed styrene was distilled in a Fisher Unitized Fractional Distillation apparatus under vacuum. The distilled styrene was then dried overnight with CaH_2 . The dried styrene was degassed by successive freeze-thaw cycles for three times under continuous pumping. Ampoules and sample tubes of varying shapes and sizes were filled with vacuum-distilled styrene and flame sealed at a pressure of 10^{-5} mm Hg. Brass sample cells used with the Van de Graaff accelerator were filled with the degassed styrene in a glove box in nitrogen atmosphere. In all cases, samples were kept at -78°C before and after irradiation until analyzed.

Sample irradiation was carried out using a cobalt 60 facility at North Carolina State University, a 1-MeV 250- μA Van de Graaff accelerator located on the Duke University campus and a 2.5-MeV 10-mA Dynamitron accelerator which is operated by the Columbia Research Corporation at its Gaithersburg, Maryland facility.

Sample analysis was done by the gravimetric method. The molecular weights and their distribution were determined by gel permeation chromatography using a Waters Model 200 unit and by standard viscosity measurements.

Cobalt 60 Radiation Facility

In the experiments being reported, as in many radiation-induced polymerization studies, the precise control of the temperature of the irradiated sample is indeed difficult. In the cobalt 60 irradiations, with a dose rate of 250 rads/sec the sample tubes were kept in a Dewar filled with water at 35°C during the period of irradiation. Only small temperature changes were observed. Dosimetry was confirmed by use of styrene as a standard. The use of this facility presented no difficulties.

Van de Graaff Accelerator Radiation Facility

The 1-MeV Van de Graaff electrostatic generator used as a radiation source provided a continuous source of 1 MeV electrons in the form of a steady horizontal, circular beam with a diameter of $\frac{7}{8}$ in. at the sample site. Variation of the current density at the sample site allowed absorbed doses up to the order of 10^5 rads/sec to be obtained. To facilitate accurate control of irradiation times, a remotely operated shutter was installed in the electron beam. During irradiations the sample chamber was evacuated. Specially designed brass cells were required for the irradiation of liquid samples using the available horizontal beam. A discussion of the dosimetry determinations and experimental techniques utilized with the Van de Graaff accelerator are reported in the Appendix.

Columbia Research Dynamitron Radiation Facility

Columbia Research Corporation operates a Dynamitron at its Gaithersburg, Maryland facility which produces a 2.5-MeV, 10-milliampere electron beam. Its high-voltage power supply is essentially a cascade generator, operating on a frequency of 140 kHz. The accelerator itself and the associated power supplies are located in a tower so that the beam is accelerated in a vertical direction and is spread on the ground floor by means of a horn that sweeps an area varying in width between 24 and 48 in.

The material to be irradiated is placed on carts which are moved at an adjustable speed under the beam. Thus, the speed at which the material is being moved under the horn, as well as the current of the beam, can be varied during operation. This arrangement allows a great degree of flexibility in both total dose and dose rate. Dose rates up to 3×10^6 rads/sec are obtainable.

The beam width, the beam current, and the speed of the carts are constantly monitored to control the irradiation dose and dose rate. Dosimetry is determined in practice by the use of the blue cellophane as described in the Appendix. As dose rates up to 3×10^6 rads/sec are obtainable, beam heating can be a major problem. Some degree of cooling was achieved by immersing the glass ampoule sample tubes in water. Even so, at the higher dose rates and slower cart speeds, the sample temperature went beyond our planned 35°C. Fortunately, as this investigation indicates, this control of temperature is not a major factor as

the mechanism of polymerization is found to be primarily ionic in nature, with a correspondingly low overall activation energy.

RESULTS

The experimentally measured rates of radiation-induced polymerization of styrene monomer at 35°C are reported in Table I at dose rates ranging from 250 rads/sec to 3 Mrads/sec. The calculated values of $G(-m)$ are also listed in this table. In Table II, the corresponding molecular weights

TABLE I
Rate of Polymerization of Styrene as a Function of Dose Rate at 35°C

Radiation source	Dose rate, rads/sec	R_p , mole/l. sec	$G(-m)$
⁶⁰ Co	2.50×10^2	4.87×10^{-6}	208
Van de Graaff	8.50×10^2	1.03×10^{-4}	130
Van de Graaff	8.50×10^3	3.32×10^{-4}	42
Van de Graaff	6.70×10^4	2.59×10^{-3}	41
Van de Graaff	1.26×10^5	5.24×10^{-3}	44
Dynamitron	3.33×10^5	8.22×10^{-3}	26
Dynamitron	1.00×10^6	2.11×10^{-2}	23
Dynamitron	3.00×10^6	3.42×10^{-2}	12

TABLE II
Molecular Weight Data by Gel Permeation Chromatography for the Radiation-Induced Polymerization of Styrene at 35°C

Radiation source	Dose rate, rads/sec	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$\frac{M_w}{M_n}$	$M_n \times 10^{-4}^a$	G_i
⁶⁰ Co	2.50×10^2	5.94	2.73	2.1	2.22	.79
Van de Graaff	8.50×10^2	6.01	2.47	2.4		.55
Van de Graaff	8.50×10^3	5.07	2.17	2.3	2.80	.20
Van de Graaff	6.70×10^4	3.78	2.46	1.5	2.12	.11
Van de Graaff	1.26×10^5	2.21	1.16	1.9	1.13	.12
Dynamitron	3.33×10^5				1.04	
Dynamitron	1.00×10^6				1.04	
Dynamitron	3.00×10^6				1.13	

^a $M_n = 167000 (\eta)^{1.37 \cdot 13}$

TABLE III
Effect of Temperature on the Rate of Polymerization of Styrene and Methyl Methacrylate at High Dose Rates^a

	Conversion per second, %		
	0°C	25°C	50°C
Styrene	0.44	0.46	0.56
Methyl Methacrylate	0.7	3.1	4.5

^a 1.9 Mrads/sec.

determined by gel permeation chromatography and by viscosity measurements are tabulated along with G_t values. The $G(-m)$ values were calculated directly from the per cent conversion data, while the G_t values were obtained from the relationship $G_t = G(-m)/DP_n$, where DP_n was determined by using the number-average molecular weights determined by gel permeation chromatography. In Figure 1, all of the rate and molecular weight data are plotted together with typical values from the literature obtained at low dose rates. All of the literature values are normalized to 20°C with the assumption that the process is free radical in nature and that the activation energy has the usually accepted value of energy 6.0 kcal/mol. The data points at the higher dose rates are plotted with no normalization, as the experimental evidence indicates that the rate of

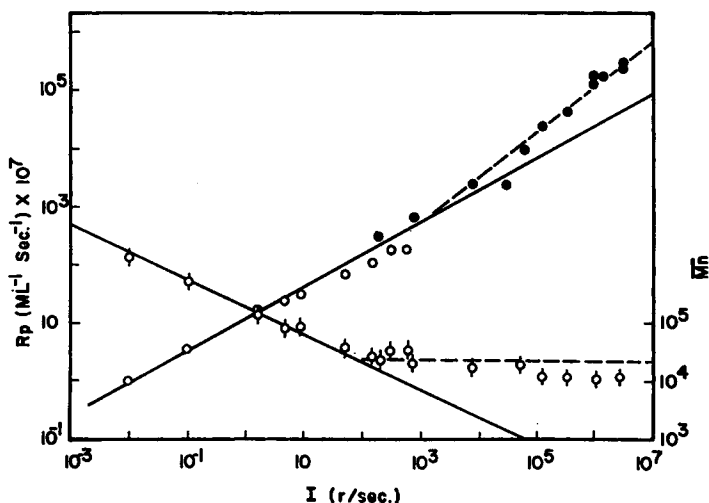


Fig. 1. Effect of dose rate upon the rate of polymerization and molecular weight of styrene. Results are normalized to 20°C except for the high dose rate values.

polymerization is nearly independent of the temperature range. It was observed that there was considerable heating of the water bath at the very high dose rates and at slow cart speeds in using the Dynamitron as a radiation source. However, this effect of increased temperature did not manifest itself in the observed rates of polymerization. Further, in our investigation of posteffects, it was observed that the variation of temperature had little effect up on the rate of polymerization.

This study was performed by varying the speed of the cart under the electron beam fourfold. In this way there were four periods of about 3 min duration between irradiations, compared with only 1 min in the case of the slowest cart speed. The same total dose was used at the highest dose rate of 3 Mrads per sec. No significant difference was found with one pass versus four passes with the same total dose, indicating no noticeable posteffects. That no posteffect was found is not surprising, as the per cent

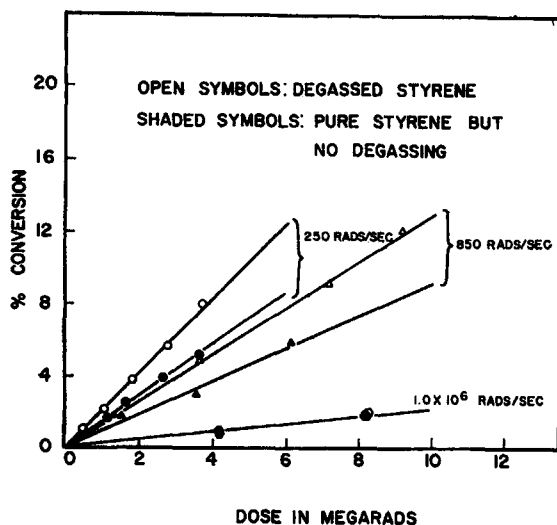


Fig. 2. Effect of oxygen on the radiation polymerization of styrene.

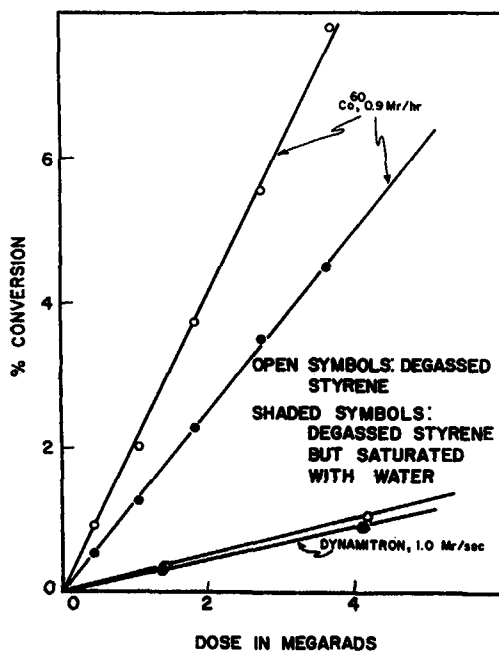


Fig. 3. Effect of water on the radiation polymerization of styrene.

conversion was only about 1%. The possibility of posteffects will undoubtedly be higher at higher conversion.

The effect of oxygen upon the rate of polymerization at dose rates varying from 250 to 10^6 rads per sec is illustrated in Figure 2. At the lowest dose rate, the presence of dissolved air resulted in approximately a

30% reduction in rate from that of the degassed monomer. However, at the higher dose rates, greater than about 4×10^4 rads/sec, no difference was observed between the two sets of experiments.

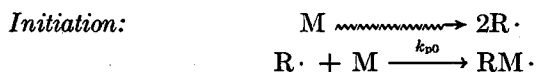
In order to obtain further insight into the nature of the ionic mechanism, experiments were performed at two extreme dose rates, of 250 and 10^6 rads per sec, with monomer saturated with water, a well-known ionic polymerization retarder. These results are shown in Figure 3. It can be seen that the addition of water retards the rate considerable at the lower dose rates but has no effect at the high dose rates.

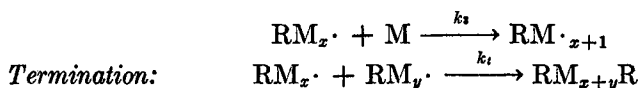
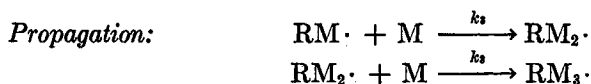
In addition, experiments were performed on sample tubes of differing diameters and also with flattened ampoules in order to check the sensitivity of the results on ampoule size and shape. It was found that there were no effects on rates of polymerization or on the molecular weights within experimental error.

DISCUSSION

It was recognized during this past decade that styrene under certain conditions would polymerize by an ionic mechanism using high energy radiation. With ultradry monomer, the polymerization takes place ionically at low dose rates. It was found that at low temperatures, e.g., 0°C and below, and at higher dose rates, the polymerization of even normally dried styrene occurred to a considerable extent by an ionic mechanism. At higher temperatures, it was also shown that the polymerization of styrene can proceed via an ionic mechanism to some extent. Osborn et al.⁸ have found that carefully dried styrene polymerized at 30°C in methylene chloride solution with cobalt 60 gamma radiation results in a marked increase in average molecular weight due to the increased ionic contribution. Some experiments have been reported with a dose rate of about 10^3 rads/sec with the experimental data, indicating that for the styrene system studied the polymerization is by a free-radical mechanism with a slight ionic contribution. Thus, there is considerable evidence that styrene under suitable conditions can polymerize ionically with high-energy radiation.

Our experimental data indicates that with increasing dose rates there is an increasing ionic contribution to the polymerization of styrene which has not even been dried extensively, and it has been found that the number-average molecular weights tend to level off as the dose rate increases, rather than to continue to decrease with dose rate according to the free-radical mechanism as shown in Figure 1. It is well known that the free-radical mechanism valid at low dose rates, if extrapolated to the high dose rate region, would predict that if the dose rate is high enough little or no polymer would be produced. The reactions for the free-radical mechanism at low dose rates are:





These lead, under steady-state conditions, to the well-known relationships for the rate (R_p) and degree of polymerization (\overline{DP}_n) of

$$R_p = \frac{k_p R_i^{1/2} (M)}{k_t^{1/2}} \quad \text{and} \quad \overline{DP}_n = \frac{k_p (M)}{k_t^{1/2} R_i^{1/2}}$$

At high dose rates, two additional termination steps become important, viz.,



and



The additional steps led to expressions for the rates and degree of polymerization which do not have a simple form. Chapiro¹ has discussed in detail the various expressions which can be developed in a number of limiting cases. The simplest and most interesting case is where all the growing chains are terminated by primary radicals. This leads to the following expressions for the rate and degree of polymerization:

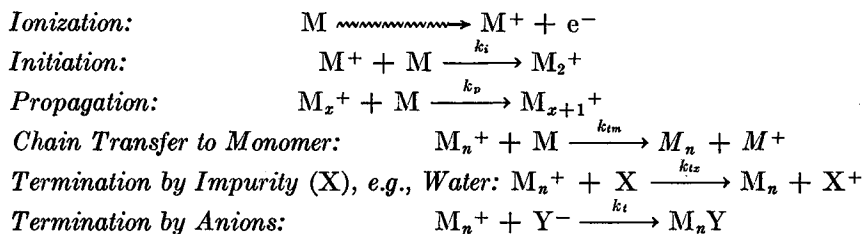
$$R_p = \frac{k_p k_{p0} (M)^2}{k_{t0}} \quad \text{and} \quad \overline{DP}_n = \frac{k_p k_{00} (M)}{k_{t0} R_i^{1/2}}$$

Since the rate of initiation is directly proportional to the dose rate, it is clear that as the dose rate increases the rate of polymerization first increases with the square root of the dose rate and then reaches a rate which is independent of the dose rate. The degree of polymerization, on the other hand, decreases with the square root of the dose rate and then continues to decrease linearly with the dose rate. This assumes of course that no significant chain-transfer reactions are taking place. Eventually, it is clear that at extremely high dose rates the rate of polymerization will drop to zero and only dimers will be produced.

The experimental data presented in Figure 1 are not in agreement with the free-radical kinetics developed by Chapiro and summarized above. Instead of following the square root dependent line and then dropping off, as indicated by the entirely valid free-radical kinetics of Chapiro, the rate increases at high dose rates and in fact increases roughly proportional to the first power of the dose rate. The molecular weights presented in Figure 1 and Table II also do not decrease according to the

extrapolated square root line but tend to almost level off to a value of about 50,000 for the viscosity average.

These results, obtained at extremely high dose rates, are strongly indicative of an ionic mechanism which is possibly the dominant mechanism in the extremely high dose rate range. In fact, our data do indeed indicate that this is the case. The kinetics of radiation polymerization by free cations has been developed in an elegant manner by Williams et al.⁹ and is based on the following set of kinetic equations:



These lead under steady-state conditions to the following expressions for the rate and degree of polymerization:

$$R_p = \frac{k_p R_i (M)}{(R_i k_i)^{1/2} + k_{tx} (X)}$$

$$\overline{DP}_n = \frac{k_p (M)}{(R_i k_i)^{1/2} + k_{tm} (M) + k_{tx} (X)}.$$

A full discussion of this process, and of the case of styrene in particular, has been presented by Williams et al.⁹ and need not be pursued in detail here. It is clear, however, that at reasonably high water contents the rate will become proportional to the first power of the dose rate. The molecular weights, on the other hand, are known to be mainly governed by chain transfer to monomer (see, for example, the work of Potter and Metz.¹⁰ The small decrease in molecular weight with increasing dose rate is probably due to the increasing participation of free anions in the chain-termination process.

On a kinetic basis, it is reasonable to propose therefore that with high dose rates the ionic mechanism for polymerization of styrene is dominant. Naturally, the question of the level of dryness is always present, and one would like to have additional evidence to confirm the conclusion reached kinetically. In order to obtain confirmatory evidence of ionic polymerization, the following systems were investigated: styrene saturated with water, styrene in air, equimolar mixture of styrene and methyl methacrylate, α -methyl styrene, and methyl methacrylate. The results and discussion of the methyl methacrylate system are to be published as a separate paper. Studies of the effect of temperature on the polymerization of styrene and the other systems were also conducted.

The effect of oxygen (air) and water at various dose rates is shown in Figures 2 and 3. It is clear that both additions retard the reaction at low

dose rates but have little or no effect at very high dose rates. Since both ionic and free-radical processes are retarded by oxygen, no conclusion regarding the mechanism can be drawn regarding the retardation by small quantities of oxygen. However, the retardation by water at the lower dose rates clearly indicates some contribution by the ionic mechanism. At high dose rates, it is puzzling that little or no retardation by water or oxygen was found. It is gratifying, however, from a practical viewpoint that at the high dose rates to be used for the commercial polymerization of coatings, for example, little inhibition can be anticipated. Presumably this is due to the high rates of reaction compared with the diffusion rates of the impurities to the growing chain ends. The small effect of saturating with water at the very high dose rates is still surprising, however, and not consistent with the comments made earlier regarding the mechanism of the reaction. It could be that the water is clustered in the styrene and loses its effectiveness since it would diffuse slowly in the hydrocarbon matrix.

A study of effects of high dose rates on the polymerization of an equimolar mixture of styrene and methyl methacrylate in the dry state revealed that the polymer products obtained were largely composed of styrene components. Spectroscopic analysis indicated that the polymer product obtained using high dose rates was nearly all polystyrene. An investigation of the products, however, using thin-layer chromatographic methods revealed that most of the product polymer was polystyrene and also showed that there was a small quantity of the 50:50 copolymer present. The 50:50 copolymer was also found to be the product which resulted at low dose rates with the cobalt 60 source, again showing the essentially free-radical nature of the low dose rate polymerization. It is concluded that the polystyrene is formed via free cations while the copolymer forms via free radicals. There has been no indication of the polymerization by radiation of methyl methacrylate via an ionic mechanism. In addition, from an extensive investigation of the polymerization of methyl methacrylate at high dose rates to be reported in a separate article, it was concluded that this monomer polymerizes almost exclusively via a free-radical mechanism even at a dose rate of 3 Mrads/sec. Of course, the considerable influence of the gel effect is quite evident at this dose rate.

The temperature dependence of the rate of polymerization of styrene and methyl methacrylate monomers are indicated in Table II. While there is some spread in the data points, the indication is clear that at the high dose rates investigated, there is little temperature dependence of the rate of polymerization of styrene compared with methyl methacrylate which would also indicate an ionic mechanism.

A cursory study of the polymerization of α -methyl styrene was also conducted at these high dose rates, as this monomer only polymerizes ionically. Substantial yields were obtained indicating ionic polymerization. With the Dynamitron, rates of polymerization of 3.7×10^{-2} M/sec and 3.2×10^{-2} M/sec were observed at dose rates of 1.7 and 1.0 Mrads/sec, respectively.

In summary, it is concluded that the vinyl monomer styrene can polymerize with radiation via both the ionic mechanism and the free-radical mechanism and simultaneously via both mechanisms. The extent of the contribution of the free-radical mechanism and the ionic mechanism to the overall polymerization processes depends strongly on the conditions. The conditions or controlling factors are principally the temperature, the degree of dryness, and the dose rate. At sufficiently high dose rates, of the order of 1 Mrad per second, the dominant mechanism is the ionic mechanism. Under extremely dry conditions and at low temperatures, the ionic mechanism again dominates even at low dose rates such as 250 rads per second. Under intermediate conditions of dryness and temperature, it has been found that both mechanisms are of nearly equal importance as can be noted from the work of Huang and Westlake⁷ and Osborne et al.⁸ Thus, the utilization of high dose rate sources gives an entree into the problem field of ionic polymerization under difficult conditions which has, however, the possibility for numerous technological applications.

We thank Dr. Ray Knorr for conducting the thin-layer chromatographic experiments and for his helpful advice on that topic. The generous financial support of the Continental Can Company and the U.S. Army Research Office, Durham, is appreciated.

Appendix

Experimental Procedures and Dosimetry Used With the Van de Graaff Accelerator

The sealed brass sample cells compatible with the available sample holder in the irradiation chamber were constructed from $1/4$ -in.-thick brass stock. The cylindrical cavity in the brass cell is $3/4$ in. in diameter with a depth of 4 mm. The diameter was thus slightly smaller than the diameter of the focused beam. The depth of the sample cell cavity was limited by the depth of penetration of the 1-MeV electron beam. The window covering the sample cavity was secured to the cell with $1/8$ -in. brass stock through which a matching $3/4$ -in. hole was drilled. A series of ridges and grooves in the brass components aided in assuring a tight fit of the window on the sample cell.

A number of window materials were evaluated for use with these brass cells, including aluminum, tin, and titanium foils, and Mylar film. The tin foil was found to be sufficiently soft to provide a good seal with the brass cell and was therefore used in much of the present study as a window material. The main disadvantages of the tin foil are: considerable attenuation of beam intensity, bulging out of the window when placed under vacuum, and unknown possible chemical effect with sample materials.

The titanium foil was acquired later and has proved to be quite superior to all previous window materials tested. First of all, the 1-mil titanium was found to provide an excellent seal with the ridge and groove design of the brass cell. Secondly, the titanium is rather stiff compared to the tin and remains flat when the vacuum is drawn in the sample chamber. An additional advantage of the titanium over the tin is the lessened beam attenuation due both to the thinner window and the lower atomic number of much more consistent dosimetry data.

The compilation of accurate dosimetry data is an absolute necessity for a meaningful interpretation of any study involving radiation effects. This is particularly important in the case of high-energy electrons, where the penetration of radiation is rather low. For electrons, the dose-depth relationship must be determined for each particular sample cell geometry. This relationship should also be determined separately for the

materials being irradiated if such samples vary widely in electron density, for example, the dose rate-versus-depth relationship was found quite different for cellulose films spaced with tin disks than for the same cellulose films spaced with Mylar spacers.

There are two main types for dosimetry which may be used with high-energy electrons in our brass sample cells. First, one could use a liquid dosimeter such as the Fricke dosimeter system. In principle, liquid dosimetry would provide the most meaningful information for interpreting chemical effects of the radiation where the irradiated sample is in the liquid phase. However, the experimental problems with all known liquid dosimeter systems would seem to preclude this type of dosimeter for accelerated electron dosimetry, especially for our particular system where the sample size is small, approximately 1 ml in volume, and the precise cleaning techniques necessary and available with glass vessels are denied us.

The second major type of dosimetry available for use with accelerated electrons is polymer film dosimetry. In this method, some property of a thin polymer film is measured before and after exposure to the electron beam. Film dosimetry offers several advantages over liquid dosimetry. First of all, where the sample to be treated is itself a solid film, the physical state and geometry of the film dosimeter may be made to very closely approximate the material of interest. A second major advantage is that by assembling a stack of dosimeter films perpendicular to the electron beam axis, the variation of adsorbed dose may be studied as function of depth into the sample. Thus, we see that the use of film dosimetry does not preclude the use of this dosimetry data for the interpretation of effects in a liquid sample since the dose rate-versus-depth plots may be integrated over the known depth of the liquid sample.

A number of polymeric films have been used as dosimeters for high-energy electrons. One of the earliest polymers used was poly(methyl methacrylate). In this method, the yellowing of Lucite was calibrated as a function of dose rate. Another widely used polymer film dosimeter involves measuring the increase in the ultraviolet absorption peak at $325\text{ m}\mu$ of Mylar film on exposure to an electron beam. There are two major disadvantages to this technique. First, the development of the $325\text{ m}\mu$ chromophore is dose rate dependent, thus necessitating the preparation of separate calibration curves for many different dose rates. A second major disadvantage of Mylar film dosimetry is the postirradiation effect upon the absorption intensity of the $325\text{ m}\mu$ chromophore. The intensity of the chromophore was observed by Ritz to fade to 35% of its initial value in 14 hr for certain Mylar films.

Probably the most widely used film dosimeter at the present time is the blue cellophane dosimeter. This dosimeter is the one we chose for this study since it is dose rate independent in the dose rate range used and also has no postirradiation effects. The dosimeter is a cellophane film impregnated with a dimethoxy-diphenyl-diazobis-8-aminoacid dye (du Pont MSC-300). This dosimeter was first reported by Henley and Richman.¹¹ Our work utilizes calibration curves prepared by Thomas et al.¹² The dye in the film undergoes irreversible destruction when placed in the high-energy electron beam.

The blue cellophane dosimeter is used in the following manner. Disks of the 1-mil-thick film are cut with a diameter slightly smaller than the diameter of the brass sample cell. These disks are then assembled in the sample cell and are spaced within the cell with the desired spacer material. The window is then secured to the cell and the sample cell placed in the Van de Graaff sample chamber for irradiation. The sample is then irradiated for a period of time such that the total dose received by the sample will not be greater than the range of calibration for the blue cellophane (0-25 Mrads). Following irradiation, each blue cellophane disk in the sample cell is mounted on a paper frame, noting the position of each disk in the stack with respect to the sample cell window. The per cent transmission of the $655\text{ m}\mu$ absorption peak is measured on a Perkin Elmer Model 202 spectrophotometer. The original per cent transmission (before exposure to electron beam) is then subtracted from the per cent transmission for each disk. This Δ transmission value is then used to read the total dose received from the calibration curve

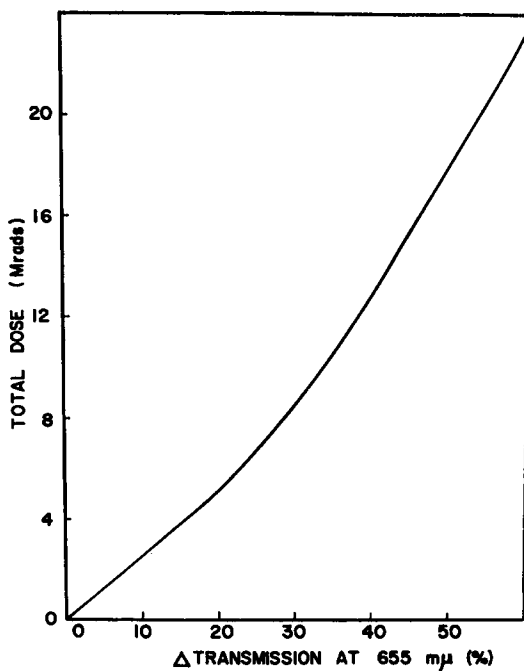


Fig. 4. Calibration curve for blue cellophane dosimeter.

(Fig. 4). The dose rate-versus-depth curves are then plotted from these values. A correction for the mass density of the absorbing material (i.e., window material, dosimeter film, and spacer material) is used in calculating the abscissa value, thus the unit of "depth" is g/cm^2 . This correction allows the use of that particular dose rate-versus-depth curve for materials of different mass densities.

A typical dose rate-versus-depth curve is shown in Figure 5. This curve shows the dose-depth relationship found at the highest dose rate employed using a 1-mil titanium window. The average dose rate received by a styrene-filled cell is proportional to the area under the curve, which extends from the inside of the window to the back inside face of the cavity in the brass cell. (The abscissa distance is calculated as the product of the depth of the brass cell and the mass density of the styrene.)

Data points in Figure 6 are the average dose rates received by a styrene-filled brass cell with a 1-mil titanium window. Each datum point is determined from individual dose-depth curves similar to Figure 6. Figure 6, therefore, enables selection of any desired average absorbed dose rate within the range available on the Van de Graaff by setting the target current at the correct value.

The problem of temperature control at the sample site becomes particularly important for the relatively high dose rates attained with the Van de Graaff electron accelerator. For example, a dose rate of 10^6 rad/sec corresponds to an energy deposition of over 1 calorie per gram per second. The temperature rise within the sample will depend upon several factors, the proportion of absorbed energy converted to heat energy, the specific heat of sample material, cell material and interfaces, and the physical state of the sample material, to mention a few. In addition, the heat of polymerization can become highly important at the dose rates used.

In order to gain some insight into the magnitude of this temperature problem, one of the brass cells was equipped with a Chromel-Alumel thermocouple. The thermocouple bead was positioned in the center of the circular cavity with the bead being located

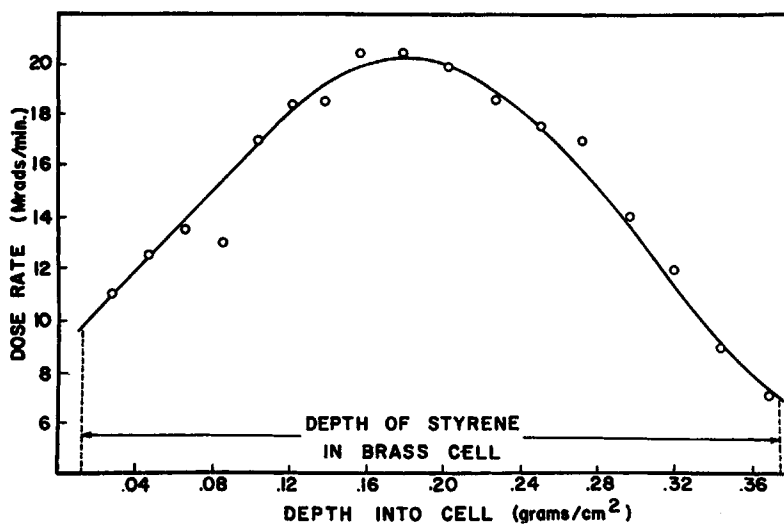


Fig. 5. Dose rate as a function of depth into brass sample cells for a target current of $15 \mu\text{A}$.

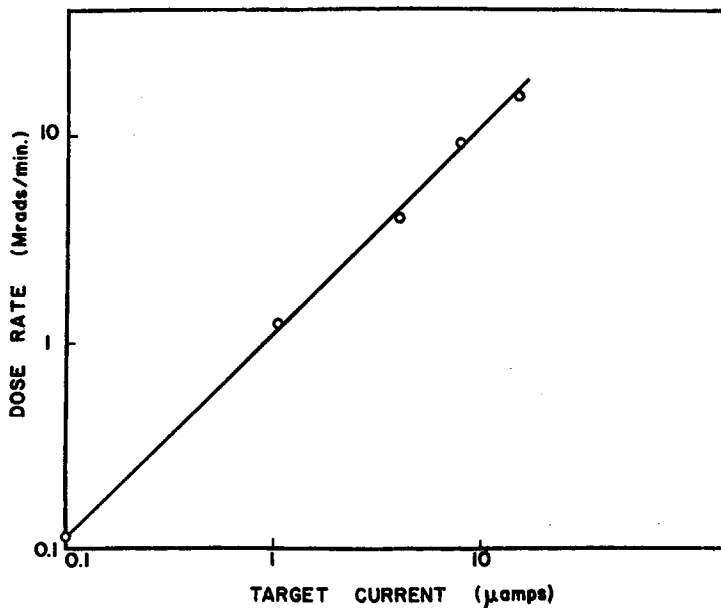


Fig. 6. Average dose rate for a styrene-filled brass sample cell as a function of target current setting.

about 2 mm from the back face of the brass cell (or half-way between the inside of the window and the back face of the cell). The thermocouple lead wires were drawn through two small holes in the top surface of the cylindrical cavity in the brass cell. The thermocouple wires were subsequently sealed in these two holes so that the sample cell cavity remained sealed once the window material was in place.

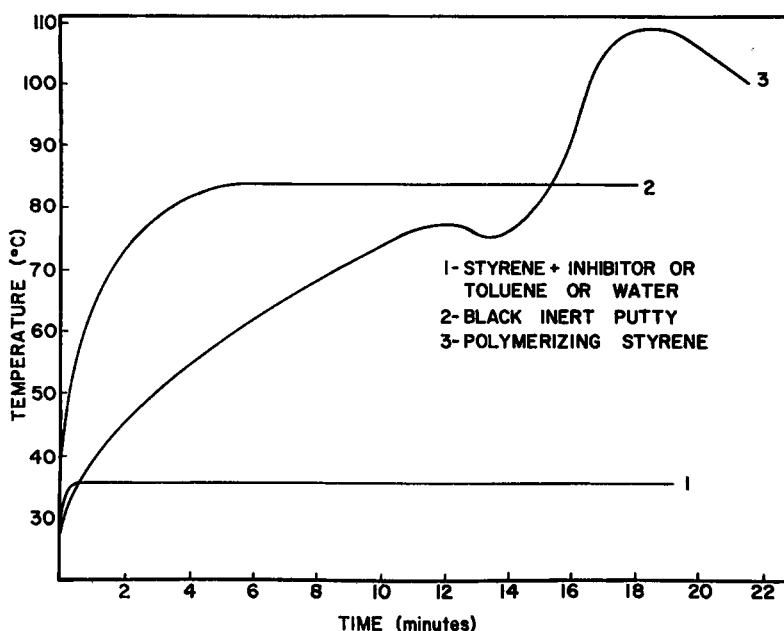


Fig. 7. Temperature within brass cell filled with different materials as a function of irradiation time with a target current of $15 \mu\text{A}$.

The brass cell thus fitted with the thermocouple was then used to measure the temperature rise when filled with various materials. The temperature was recorded on a millivolt recorder since the initial rate of temperature increase was so great. In Figure 7, the thermocouple temperature is shown as a function of irradiation time for the cell when filled with a number of materials. In each case the exit window current was stabilized at $15 \mu\text{A}$ before the beam shutter was deactivated. Figure 7 shows that when the brass cell is filled with an inert liquid, the temperature rapidly rises to about 35°C and levels off. When the liquid in the cell is replaced with an inert semisolid, the temperature plateau attained is much higher, about 85°C . These data seem to suggest that the heat transfer above 35°C is largely controlled by the conversion of the liquid. Note in Figure 7 that the plot for polymerizing styrene lies between that for the inert liquid and the inert solid. Parallel studies indicate that the styrene conversion-versus-time curve occurs within the same time scale, with a maximum conversion of 80% in 23 min. Therefore, it seems quite likely that a portion of the temperature rise of curve 3 in Figure 7 is due to the increased viscosity of the polymerizing styrene which hinders heat transfer by liquid convection. The rapid increase in the temperature of the polymerizing styrene at 14 min accompanies the rapid increase in styrene polymerization (gel point), which was likewise observed to occur at about 14 min. This rapid increase in polymerization rate at the gel point is accompanied by the liberation of considerable heat which increases the temperature of the sample temporarily above the previously observed ceiling temperature (85°C) in the inert solid (curve 2). Thus, the downward trend of curve 3 after 18 min may reflect the dissipation of this additional heat of polymerization.

A measure of the true average temperature of the material contained within the brass cell is rather difficult. The presence of the measuring device itself will undoubtedly affect the measured temperature, especially in this case where the thermocouple bead and lead wires absorb more energy than the surrounding material (since they have a relatively high mass density). The question thus occurs as to whether the temperature

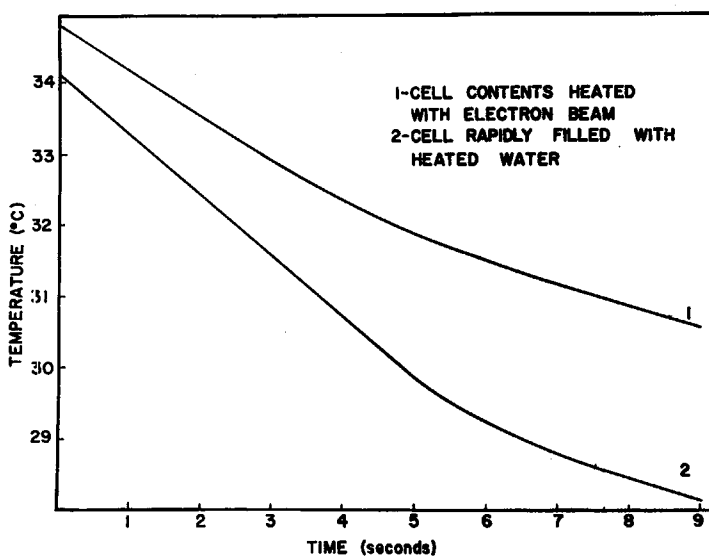


Fig. 8. Cooling rates of water-filled brass sample cells.

plots in Figure 8 represent the average temperature of the material within the cell or if these data are overestimates of the temperature, wherein one pictures the measurement of the temperature only in the near vicinity of the thermocouple bead, say, in a spherical volume element of about 2 mm in diameter. The problem here involves investigation of the thermocouple reading when the cavity contains a material of known temperature, and the heat transfer properties are similar to those which exist when the sample cell is positioned in the sample chamber. Another factor which may be affecting the thermocouple reading when the electron beam is striking the sample is possible stray electric currents flowing through the thermocouple circuit. In order to eliminate this possible effect, the rate of cooling of the thermocouple tip was studied. This was accomplished by filling the sample cell with water and heating the water with the electron beam until a steady temperature was attained. At this point the beam shutter was activated in order to shut the beam off from the cell. The rate of cooling of this sample is shown as curve a in Figure 8. Curve b in Figure 8 represents the cooling rate when warm water was rapidly poured into the open cell. The slopes of the two lines in Figure 8 therefore show that the rate of cooling of the thermocouple tip is nearly equal in both cases. If the heating with the electron beam really did heat only a small volume in the vicinity of the bead, one would expect a more rapid cooling rate than that observed in curve b, where the entire volume of the cell was known to be at the initial temperature. The similarity of the cooling rate plots of Figure 8, therefore, suggest the validity of interpreting the curves of Figure 7 as average temperatures of the material in the brass cells.

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