[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY, ST. LOUIS]

Electrical and Chemical Effects of β-Radiation in Polystyrene[1]

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Electric conductivity of polystyrene, polyethylene and Teflon under β-irradiation has been studied by investigation of the potentials produced by the passage of β-rays through the dielectrics. A potential of 60 kv. has been produced in a single stage and 88 kv. in two stages. The potentials agree reasonably well with values calculated from the assumptions that the dielectric conductivity is proportional to the concentration of radiation-produced ions and that these ions disappear by bimolecular reaction. Irradiation of polystyrene by β-particles is found to cause degradation if air is present but to cause further polymerization if air is excluded. Bombardment of polystyrene in a helium atmosphere by deuterons caused extensive cross linkage. The data obtained in studies of the radiation chemical effects in polystyrene show that the rate of polymerization depends on the square root of the radiation intensity. In the presence of air the rate of degradation varies with something between the square root and the first power of the radiation intensity.

The electric conductivity of insulators under radiation and the resistance of dielectrics to radiation damage have been the subject of investigation by many researches.[3] Direct measurement of the conductivity of solid dielectrics under β-radiation by current or resistance measurements has the difficulty that the current produced by moderate potentials may be less than the β-current. We have studied the electric conductivity induced by β-radiation by measurement of the limiting potential generated by the passage of β-particles through a solid dielectric. The limiting voltage obtained is directly related to the conductivity of the system. Investigations of this type are of interest in the preparation of high potential sources.[4] In addition, to gain information on the effect of β-radiation on a dielectric for a prolonged period of time in potential-generating devices, we investigated also some of the chemical effects of β-radiation on polystyrene.

Experimental

Radioactive Sources.—The equilibrium mixture of Sr^{90} and Y^{90} was obtained from Isotopes Division, U. S. Atomic Energy Commission, Oak Ridge, Tennessee. The Sr^{90}–Y^{90} was deposited on silver or stainless steel electrodes either by a procedure similar to that used for radium and barium by Haissinsky[5] or by direct evaporation of the radioactive solution. Sources with activities from 2.3 to 77.5 mc. cm.$^{-2}$ were prepared. The complete sources were canned in a vacuum tight layer of nickel, thickness about 30 mg. cm.$^{-2}$, by the thermal decomposition of nickel carbonyl vapor.[6] A few Po^{210} α-particle sources, about 0.3 mc. and about 1 mm.^{2}, were prepared on Pd by hydrogen deposition.[7] These were used in the vacuum potential measurements.

Potential Generation and Measurement.—The electrode assembly for potential generation "in air" consisted of two electrodes on opposite sides of a polystyrene insulator. One of the electrodes contained the Sr^{90}–Y^{90} β-source and is called the anode; the other was a grounded metal collector for the β-particles which had penetrated the polystyrene dielectric and is called the cathode. Both electrodes were silver disks one-half inch in diameter. The anode was connected through a coaxial cable to an electrostatic voltmeter. Air ionization near the source was minimized by a construction which filled the surrounding space with polystyrene. Ionization in the neighborhood of the voltmeter due to the proximity of radioactivity was made negligible by the use of lead brick walls surrounding both the radioactive source and the voltmeter. All the high voltage leads were protected with grounded metal shields.

Gas ionization currents were completely eliminated in the vacuum apparatus shown in Fig. 1. The dielectrics were usually in the form of disks about 3.7 cm. in diameter and from 0.02 to 1 cm. in thickness. The glass apparatus was connected through a Dry Ice–acetone trap to a mercury diffusion pump. Voltage measurement was accomplished by determination of the difference in the range of the α-particles from the polonium source on the anode and from a reference polonium source which was always grounded. The α-range measurements were made in a conventional way with a gas-flow proportional counter as detector and with an absorption chamber containing dry air at variable pressure. The uncertainty of the potential measurements by this method is within ±5 kv.

In some of the experiments a two-stage potential generator was used. This assembly had a grounded cathode, a first dielectric disk, an intermediate anode with Sr^{90}–Y^{90} source, a second dielectric disk, and a final anode with Sr^{90}–Y^{90} and Po^{210} sources as before.

Radiation Chemical Effects in Polystyrene.—Most of these studies used disks 1 cm. in diameter cut from $^1/_{32}$ inch thick commercial unfractionated polystyrene sheets supplied by Acadia Synthetics, Chicago, Illinois. Stacks of five of these disks, in an aluminum holder, were irradiated from one face with a Sr^{90}–Y^{90} source of effective strength 17.1 mc. cm.$^{-2}$, either in air or *in vacuo*. Average relative radiation intensities in the five disks are known from direct absorption measurements; we estimated the absolute intensities to be 11.7, 5.9, 3.05, 1.57 and 0.81 $\times$ 10^{18} ev. g.$^{-1}$ hr.$^{-1}$. At the end of the irradiation, the disks were studied for chemical changes by (1) measurement of the optical density of the resulting colored substance (both in the solid disks and in solutions in toluene) with a model DU Beckman spectrophotometer, and (2) determination of the intrinsic viscosity of toluene solutions of the irradiated polystyrene. The viscosity measurements were performed in specially made Ostwald pipets requiring only 0.5 to 2 ml. of solution for each measurement. The standard procedure of double extrapolation of η_{sp}/C and $1/C \ln (\eta/\eta_0)$ was followed, where η_{sp} is the specific viscosity of the solutions and η and η_0 refer to the relative viscosities of the solution and of the solvent, respectively, and C is in grams of polymer per 100 ml. of the solution.[8]

In some cases the molecular weight distribution of the irradiated polystyrene was determined by fractionation.

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(2) Manu-Mine Research and Development Co., Reading, Pennsylvania.

(3) S. Mayburg and W. L. Lawrence, *J. Appl. Phys.*, **23**, 1006 (1952); J. H. Coleman and D. Bohm, *ibid.*, **24**, 497 (1953); J. Warner, F. A. Muller and H. G. Nordlin, *ibid.*, **25**, 131 (1954); P. Rappaport and E. G. Linder, *Phys. Rev.*, **91**, 202 (1953), and *J. Appl. Phys.*, **24**, 1110 (1953); J. W. Ryan, *Modern Plastics*, **31**, No. 2, 152 (1953); E. J. Lawton, S. J. Balwit and A. M. Bueche, Abstract of Papers, 125th National Meeting, Amer. Chem. Soc., March, 1954, page 7R; and *Nature*, **172**, 76 (1953); L. A. Wall and M. Magat, *Modern Plastics*, **30**, No. 11, 111 (1953) and *J. chim. phys.*, **50**, 308 (1953); A. Charlesby, *J. Polymer Sci.*, **11**, 513 (1953), *ibid.*, **11**, 521 (1953); *Nature*, **171**, 167 (1953); A. Charlesby and M. Rose, *Nature*, **171**, 1153 (1953).

(4) P. Rappaport and E. G. Linder, *Phys. Rev.*, **91**, 202 (1953), and *J. Appl. Phys.*, **24**, 1110 (1953); J. H. Coleman, *Nucleonics*, **11**, No. 12, 42 (1953).

(5) M. Haissinsky, *J. chim. phys.*, **34**, 321 (1937).

(6) Mr. Ernest Bryant gave assistance to this work by the preparation of some of the radioactive sources.

(7) W. R. Kanne, *Phys. Rev.*, **52**, 380 (1937).

(8) F. Daniels, *et al.*, "Experimental Physical Chemistry," 4th ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 242–246.

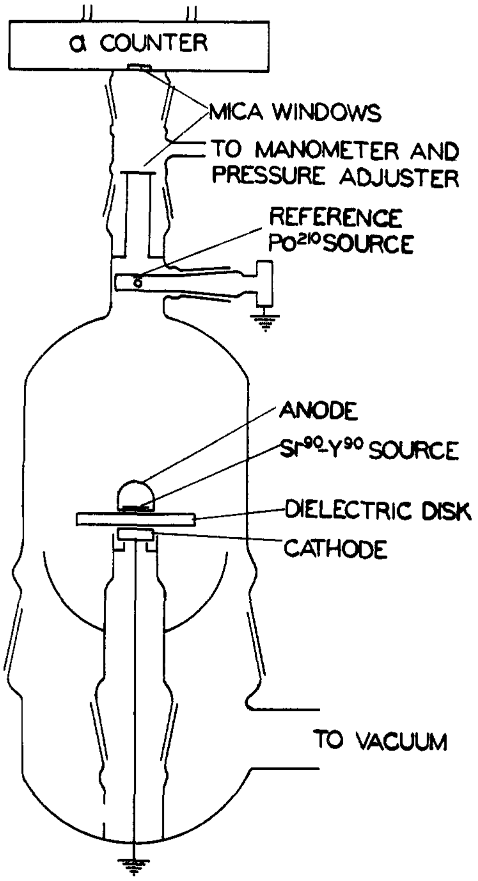

Fig. 1.—Apparatus for potential generation *in vacuo*.

The separation into fractions having narrower ranges of molecular weight distribution through fractional precipitation by methanol of the polymer either from a methyl ethyl ketone solution or from a toluene solution followed the procedure described by Fox and Flory.[9] In the same way the composition of the original polystyrene also was determined. In one series of experiments the disks for irradiation were pressure molded from separated fractions prepared by this procedure from the commercial polystyrene.

In one experiment polystyrene sheets, 0.003 inch thick, were bombarded by 10 Mev. deuterons in the Washington University cyclotron, with helium cooling. In this way radiation dose rates as high as 10^{24} ev.g.$^{-1}$ hr.$^{-1}$ and total dose as large as 3×10^{23} ev. g.$^{-1}$ were obtained. The sheets showed a high activity of N^{13} after bombardment and were treated with toluene after the N^{13} activity had decayed.

Theoretical

Electric Conductivity of Dielectrics under β-Irradiation.—The electric conductivity of dielectrics under β-irradiation is considered to be due principally to the radiation-produced ion pairs. By assuming the ion pairs are formed at a rate proportional to the rate of energy dissipation in the dielectric and that they recombine according to second order kinetics, we derive a relation between source intensity, dielectric thickness, and limiting voltage, as follows.

The transmission of β-particles through absorbers is given by the empirical relationship $N_x = N_0e^{-\mu x}$, where N_x is the flux of β-particles transmitted per square centimeter per second, N_0 is the initial flux of β-particles, μ is the mass absorption coefficient, and x is the thickness of the dielectric in g. cm.$^{-2}$ We evaluate μ by direct measurement in a geometrical arrangement similar to that used for potential generation.

The maximum energy of a β-spectrum is related to its range by the relation[10] $E = 1.84R + 0.295$, where E is the energy (in Mev.) and R is the range of the particles (in g. cm.$^{-2}$). This relation, intended for aluminum absorbers, is a good approximation for most dielectrics. Furthermore, $R = R_0 - x$, where R_0 is the initial range and x is the thickness of the absorber already traversed. The average energy $\bar{E}$ of the β-spectrum, at least in the first few half-thickness of absorber, can be shown to be about 0.4 of the maximum energy E. The loss of energy in each infinitesimal layer of a dielectric between x and $x + \mathrm{d}x$ is then calculated from the change in energy flux.

$$N_x\bar{E}_x - N_{x + dx}\,\bar{E}_{x + dx} = N_0e^{-\mu x}\,[0.74 + (0.118 + 0.74R_0)\mu - 0.74\mu x]$$

From the two assumptions already stated, the concentration of ion pairs per unit volume at the steady state is

$$n_x = (\alpha z)^{-1/2}N_0^{1/2}e^{-1/2\mu x}\,[0.74 + (0.118 + 0.74R_0)\mu - 0.74\mu x]^{1/2}$$

where z is the average energy (in Mev.) used to form an ion pair and α is the rate constant for the second-order recombination reaction. The conductivity of the irradiated layer is $\sigma_x = Gn_x$, where G is a proportionality constant related to the mobility of the charge carriers. The volume resistivity of such a dielectric layer is then $R_x = \sigma_x^{-1}$, and for a piece of dielectric whose thickness is w g. cm.$^{-2}$, the resistance per square centimeter is

$$R_w = \int_0^w R_x\mathrm{d}x = kN_0^{-1/2}\int_0^w e^{1/2\mu x}\,[0.74 + (0.118 + 0.74R_0)\mu - 0.74\mu x]^{-1/2}\,\mathrm{d}x$$

where $k = (\alpha z)^{1/2}G^{-1}$.

At steady state, the number of electrons returning to the source electrode from any layer of the dielectric is equal to the number of beta particles stopped in that layer. Hence $I_x = I_0e^{-\mu x}$, where I_x is the returning current density, related to the β-activity by the relation $I = 6(10)^{-12}N$, where I is in amperes cm.$^{-2}$ and N is in millicuries cm.$^{-2}$. The steady state potential is then given by

$$V_w = \int_0^w I_xR_x\,\mathrm{d}x = \int_0^w 6(10)^{-12}kN_0^{1/2}e^{-1/2\mu x}[0.74 + (0.118 + 0.74R_0)\mu - 0.74\mu x]^{-1/2}\,\mathrm{d}x$$

If attention is confined to values of x small enough so that higher powers of the 0.74 μx term may be neglected, the integral is

$$V_w = 6(10)^{-12}KN_0^{1/2}\,\{(1 - e^{-1/2\mu w})\,[2\mu^{-1}(0.74 + (0.118 + 0.74R_0)\mu)^{1/2} + 2(0.74\mu)(0.74 + (0.118 + 0.74R_0)\mu)^{-1/2}\mu^{-2}] - (0.74\mu)(0.74 + (0.118 + 0.74R_0)\mu)^{-1/2}\mu^{-1}we^{-1/2\mu w}\}$$

where K is an empirical constant for each dielectric, to be evaluated experimentally. From our derivation, $K = (\alpha z)^{1/2}/G[0.74 + (0.118 + 0.74R_0)\mu]$.

Inserting numerical values, particularly $\mu = 6.93$ cm.^{2} g.$^{-1}$ and $R_0 = 1.116$ g. cm.$^{-2}$ for the yttrium-90 radiation, we obtain finally

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[9] T. G. Fox, Jr., and P. J. Flory, THIS JOURNAL, **70**, 2384 (1948).

[10] N. Feather, *Proc. Camb. Phil. Soc.*, **34**, 599 (1938).

$$V_w = 6(10)^{-12}KN_0{}^{1/2}[0.85(1 - e^{-3.47w}) - 0.274we^{-3.47w}] \tag{1}$$

applicable for $w < 0.35$ g. cm.$^{-2}$. (We obtain also $k = 7.28\ K$.) With the same approximation the integral for R is evaluated

$$R_w = KN_0{}^{-1/2}[0.70(e^{3.47w} - 1) + 0.274we^{3.47w}]$$

In a subsequent section values computed from equation 1 are compared with experimental results.

Radiation Chemical Effects in Polystyrene.—We picture the reaction of radiation with polystyrene as follows. The impact of β-particles on polystyrene may impart sufficient energy to a molecule to cause cleavage of a bond with the formation of activated fragments. These fragments may recombine with or without interaction of other neutral molecules, which gives in some cases the possibility of increased polymerization, or the fragments may react with oxygen to produce degradation. In our analysis we assume that the average energy required to produce primary cleavage of a bond is independent of the molecular size and of the radiation intensity and that the position of cleavage is entirely random.

It can be shown that after exactly n bonds are cleaved (in random positions) in each molecule, the final intrinsic viscosity is[11]

$$[\eta]_n \cong \frac{B\int_0^{\mathbf{x}} (x - i)^{n-1} i^{1.62} \mathrm{d}i}{\int_0^{\mathbf{x}} (\mathbf{x} - i)^{n-1} i \, \mathrm{d}i}$$

where $\mathbf{x}$ is the number of styrene units in the polymer molecule and $n << \mathbf{x}$. Evaluation of this integral gives

$$[\eta]_n = n(n + 1)[(0!)^{-1}(2.62)^{-1} - (1!)^{-1}(3.62)^{-1}(n - 1) + (2!)^{-1}(4.62)^{-1}(n - 1)(n - 2) - \ldots\ldots][\eta]_0$$

where $[\eta]_0$ is the intrinsic viscosity of the original polymer given[12] by $[\eta]_0 = B\mathbf{x}^{0.62}$. For the case of a small amount of degradation in a system originally containing polystyrene molecules of a single size only, if the average number of bonds cleaved per molecule is p, the probability that n bonds is cleaved per molecule is given by the Poisson approximation, $W(n) = (n!)^{-1}p^n e^{-p}$. Since

$$[\eta] = \Sigma_i f_i [\eta]_i = \Sigma_i w_i [\eta]_i$$

we have

$$[\eta]_p = \Sigma_n (n!)^{-1} p^n e^{-p} [\eta]_n$$

By numerical computation for values of p less than 2, we find that the result is given very closely by

$$[\eta]_p = (1 + 0.2375p)^{-1}[\eta]_0$$

Finally, account must be taken of the distribution of molecular sizes in polystyrene. If $\mathbf{x}_j$ is the number of styrene units in a molecule of the jth species, and if the average number of bonds cleaved per molecule is proportional to the molecular size, the average number of bonds cleaved per molecule of size $\mathbf{x}_j$ is $p_j = p(\mathbf{x}_j/\mathbf{x})$. The intrinsic viscosity after irradiation of a polystyrene originally containing f_j weight fraction of the jth species is then given by

$$[\eta]_p = \Sigma_j f_j [\eta]_j (1 + 0.2375\ p\mathbf{x}_j/\mathbf{x})^{-1}$$

The polystyrene in these experiments was found by fractionation to have the composition shown in Table I. We have substituted these values of f_j and $[\eta]_j$ with various values of p, and find a relation correct to a few per cent. for $p < 1$

$$[\eta]_p = (1 + 2.0p)^{-1}[\eta]_0 \tag{2}$$

TABLE I

FRACTIONATION OF THE POLYSTYRENE USED

Wt. %	Intrinsic viscosity	Wt. %	Intrinsic viscosity
12.43	1.61	4.22	0.288
18.40	1.32	3.54	.178
17.76	1.06	2.43	.13
8.80	0.883	3.80	.052
8.81	.715	2.31	Not precipitated by methanol
17.50	.480		

For the case of polymerization by irradiation, there are many possible combinations of fragments with neutral molecules that produce an increase in intrinsic viscosity. If we define a polymerization as a reaction which has the same effect on $[\eta]$ as a combination of two molecules into one in an originally homogeneous polymer, then the fraction of the molecules polymerized, f, is related to the intrinsic viscosity change by

$$[\eta]_f = 2^{0.62} f[\eta]_0 + (1 - f)[\eta]_0 = (1 + 0.55f)[\eta]_0 \tag{3}$$

Results and Discussion

Potential Generation.—The range of the electrostatic voltmeter, 7500 volts, was usually exceeded in the experiments performed in air, although in some cases the system sparked down to a lower potential suddenly before reaching the end of the voltmeter scale. The potentials thus generated are comparable to those obtained by Rappaport and Linder[4] and by Coleman,[4] but are far below 2.18 million volts, corresponding to the maximum energy of the spectrum, which would be obtained in an idealized case with a perfect insulator. The practical limitation is due not only to conduction in the dielectric, but also to leakages across the insulation of the cable and the voltmeter and to ionization of the air. In the experiments performed *in vacuo* and without the voltmeter, these incidental leakages are removed, and higher potentials result. Vacuum experiments were performed with sources from 2.3 to 77.5 mc.cm.$^{-2}$ and with dielectrics from 0.02 to 1 g. cm.$^{-2}$ in thickness. As dielectrics polystyrene, polyethylene, Teflon, Lucite, glass and fused silica have been tried, all with positive results. The data for polystyrene, polyethylene and Teflon dielectrics are in Table II. Also given in the table for comparison are the potentials calculated from the theoretical equation 1 with these K values chosen to give the best fit with the experimental potentials: 4.17×10^{15} for polystyrene, 1.52×10^{15} for polyethylene and 8.8×10^{14} for Teflon.

The agreement between the calculated and observed values is good enough to indicate that many of our assumptions are valid. (The largest discrepancies occur in the cases of the highest potentials, and in these cases some leakage across the vacuum space is not improbable.) Briefly, the conductivity of the dielectrics under β-irradiation is proportional to the square root of the radiation intensity. From

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(11) P. Y. Feng, Ph.D. Thesis, Washington University, 1954, p. 73.

(12) A. I. Goldberg, *et al.*, *J. Polymer Sci.*, **2**, 502 (1947).

Table II

Comparison of Calculated and Observed Potentials with Polystyrene, Polyethylene, Teflon Dielectrics

Source strength mc. cm. $^{-2}$	Dielectric	Dielectric thickness, g. cm. $^{-2}$	Potential, kv. Calcd. from eq. 1	Potential, kv. Obsd.
18.7	Polystyrene	0.085	21.6	23
18.7	Polystyrene	.061	16.1	22
18.7	Polystyrene	.17	38.2	42
2.3	Polystyrene	.17	13.4	12
7.3	Polystyrene	.17	23.8	21
2.3	Polystyrene	.34	21.3	18
7.3	Polystyrene	.34	37.9	40
23.5	Polystyrene	.34	67.9	60
17.1	Polystyrene	.025	6.7	8
17.1	Polystyrene	.062	15.4	18
18.7	Polystyrene[a]	.085	21.6	25
7.3, 7.5	Polystyrene[b]	.085, 0.085	13.5+13.7=27.2	30
7.3, 7.5	Polystyrene[b]	.17, .17	23.8+24.2=48.0	46
18.7, 77.5	Polystyrene[b]	.085, .085	21.6+44.0=65.6	60
7.5, 18.7	Polystyrene[b]	.085, .085	13.7+21.6=35.3	34
7.5, 18.7	Polystyrene[b]	.34, .34	38.4+60.6=99.0	88
18.7	Polyethylene	.265	19.0	19
17.1	Polyethylene	.265	18.2	15
7.3	Polyethylene	.265	11.9	14
18.7	Teflon	.33	12.6	12
18.7	Teflon	.17	8.0	5
17.1	Teflon	.365	12.7	10
17.1	Teflon	.27	10.7	17

[a] Irradiated by 10^{23} ev. g. $^{-1}$. [b] Double-stage experiments.

the K values we can make comparisons of the volume resistivity of the respective dielectrics in an imaginary case where the thickness of the dielectric is 1 mm. and the source strength is 1 mc. cm. $^{-2}$. This comparison is shown in Table III.

Table III

Comparison of the Volume Resistivities of Irradiated and Unirradiated Dielectrics

Dielectric	Reported vol. resistivity of unirradiated sample, ohm-cm.	Calcd. vol. resistivity of 1 mm. samples irradiated by 1 mc. cm. $^{-2}$ (ohm.-cm.)
Polystyrene	3×10^{20}	1.5×10^{16}
Polyethylene	$\cong 10^{18}$	0.43×10^{16}
Teflon	$>10^{16}$	0.62×10^{16}

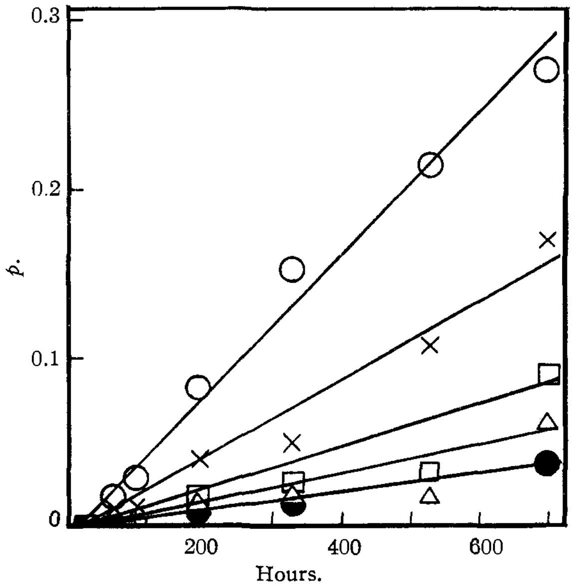

Fig. 2.—Average number of bonds cleaved per molecule of number average molecular weight (4.5×10^4). Radiation intensities (in 10^{18} ev./g./hr.): ○, 11.7; ×, 5.9; □, 3.05; △, 1.57; ●, 0.81.

Radiation Induced Degradation and Polymerization in Polystyrene.—The results of the β-irradiation of polystyrene *in air* are summarized in Fig. 2. A comparison of the rates of degradation, as found from the slopes, with the square root and with the first power of the average radiation intensity is shown in Table IV. The results of the β-irradiation of polystyrene *in vacuo* are summarized in Fig. 3. The rates of polymerization, as found from the slopes, are compared with the square root of the average radiation intensity in Table V.

Table IV

Rate of Bond Cleavage and Radiation Intensity

Rate in 10^{-4} bonds/hr.	4.0	2.17	1.2	0.8	0.45
Intensity in 10^{18} ev./g./hr.	11.7	5.9	3.05	1.57	.81
Rate/intensity	0.34	0.37	0.39	0.51	.56
Rate/(intensity)$^{1/2}$	1.2	0.9	0.7	0.64	.5

Table V

Rate of Polymerization and Radiation Intensity

Rate in 10^{-4} hr. $^{-1}$	29.5	18.5	14	10	7.5
Intensity in 10^{18} ev./g./hr.	11.7	5.9	3.05	1.57	0.81
Rate/(intensity)$^{1/2}$	8.6	7.4	8.0	8.0	8.3

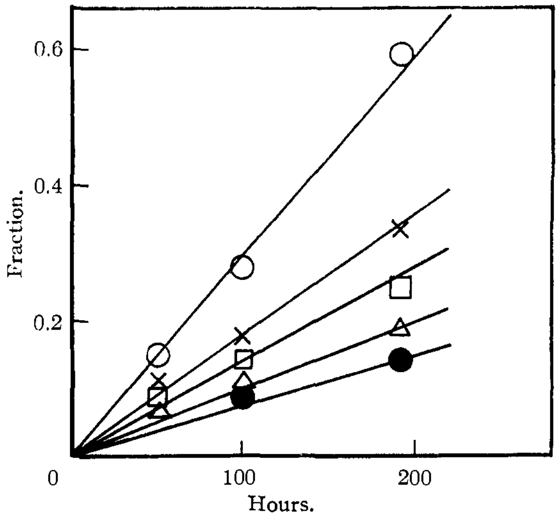

Fig. 3.—Fraction of molecules polymerized *versus* time. Radiation intensities (in 10^{18} ev./g./hr.): ○, 11.7; ×, 5.9; □, 3.05; △, 1.57; ●, 0.81.

Two extreme cases may be mentioned here. One is the solubility in methanol of the surface area of a piece of polystyrene after irradiation by a 77.5 mc.cm. $^{-2}$ source in air for a month. The other is the insolubility of polystyrene in toluene after bombardment by 10 Mev. deuterons at approximately 0.5×10^{-6} amp. cm. $^{-2}$ for 15 minutes in helium.

In the comparison of the rate of degradation with radiation intensity, it is seen that the rate is neither proportional to the square root nor to the first power of the radiation intensity. We therefore assume that oxidative reactions leading to degradation and recombination reactions occur at comparable rates. In the absence of air, apparently the main reactions occurring are recombination reactions leading in part to polymerization, and the rate of polymerization is seen to be proportional to the square root of the radiation intensity. The coloration produced in polystyrene by β-irradiation in air is approximately proportional to the radiation dosage. The maxima of absorption occur at approximately 340 mμ. Very little color change is observed in the case of irradiation in vacuum.

We have assumed that the amount of energy required to cleave a bond in a molecule is independent of the molecular size. If this assumption is true, the number of bonds cleaved per unit time per unit weight of the polymers should be the same for a given radiation intensity regardless of the molecular size or distribution. On the other hand, the fraction of the molecules polymerized under such conditions should be inversely proportional to the number of molecules per unit weight of the molecules. This is indeed borne out in the radiation-induced polymerization of fractionated styrene polymers as shown in Table VI.

TABLE VI

COMPARISON OF FRACTION OF MOLECULES POLYMERIZED WITH INITIAL MOLECULAR WEIGHT

Initial mol. wt. (M)	$[\eta]_0$	$[\eta]_f$	f	Time, hr. (t)	f/t	$f/tM \times 10^{18}$
7.97×10^4	0.41	0.43	0.09	113	8×10^{-4}	1
2.445×10^5	0.82	0.92	0.22	117.5	19×10^{-4}	0.76
6.97×10^6	1.575	2.04	0.54	121.17	44×10^{-4}	0.64

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

Densities, Molal Volumes and Electrical Conductivities of the Molten System Molybdenum Trioxide–Sodium Molybdate[1]

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A report is contained herein of densities, molal volumes and electrical conductivities of molten mixtures of molybdenum trioxide and sodium molybdate. Values for these properties at 825° for the mixtures have been obtained by extrapolation and interpolation of the data plotted. New data for the single components are compared with those of other investigators. Activation energies were found to be 5.39 kcal. mole^{-1} for the oxide and 4.88 kcal. mole^{-1} for the salt.

Introduction

In recent years, increasingly larger numbers of investigators have reported data for various transport processes for molten materials. This increased interest in studying fundamental properties of such systems has been motivated largely, in many instances, by the desire to find out if there exist correlations among properties of molten systems just as have been found with reasonably good success, at lower temperatures, for electrolytes and their solutions in various media.

When one recognizes the fact that a molten salt, for example, is essentially a highly concentrated and strong electrolyte, it is understandable why one would hope that, in the future, it will be possible to extend existing theories, for concentrated aqueous solutions of strong electrolytes, to molten salts. Moreover, the finding of a molten solvent, of high dielectric constant and extremely low conductivity, for salts would permit perhaps more meaningful comparisons between dilute molten mixtures involving that solvent and aqueous solutions.

The work of this paper includes measurements of the densities and electrical conductivities of molten mixtures of molybdenum trioxide and sodium molybdate. No literature reports have been found, up to the present time, for the mixtures with which this paper is concerned. However, a few reports appear in the literature on the single components. van Arkel and others[2] include molybdenum trioxide in their study of the electrical conductivity of molten oxides. However, their work for this substance may be open to some question because of certain inconsistencies, *viz.*, (1) their data indicate a higher specific conductivity for molybdenum trioxide (4.65 ohm^{-1} cm.$^{-1}$ at 950°) than that reported by Edwards and co-workers[3] for an ionic salt like sodium chloride (4.05 ohm^{-1} cm.$^{-1}$ at 950°) and (2) their melting point value of 847° for the oxide is considerably different from the 795 ± 4° reported by others[4,5] for molybdenum trioxide. The data of the present paper are considerably different from those of van Arkel[2] for molybdenum trioxide. No density data for this oxide are found in the literature.

For sodium molybdate, electrical conductivity data[6] (range 843–1408°) and density data[7] (range 699–1212°) have been reported by Jaeger and his associates. Both sets of measurements appear to have been carried out with considerable care. In fact, their data above 1200° are surprisingly consistent in view of the fact that Spitsyn and Kuleshov[8] report that the heating of sodium molybdate for 6 hours at 1200° results in a loss of weight and

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[2] A. E. van Arkel, E. A. Flood and N. H. F. Bright, *Can. J. Chem.*, **31**, 1009 (1953).

[3] J. D. Edwards, C. S. Taylor, A. S. Russell and L. F. Maranville, *J. Electrochem. Soc.*, **99**, 527 (1952).

[4] D. H. Killefer and A. Linz, "Molybdenum Compounds: Their Chemistry and Technology," Interscience Publishers, New York, N. Y., 1952, p. 32; F. M. Jaeger and H. C. Germs, *Z. anorg. Chem.*, **119**, 145 (1921).

[5] F. Hoermann, *ibid.*, **177**, 145 (1928); E. Groschuff, *ibid.*, **58**, 117 (1908); G. D. Rieck, *Rec. trav. chim.*, **62**, 429 (1943); L. A. Cosgrove and P. E. Snyder, THIS JOURNAL, **75**, 1227 (1953).

[6] F. M. Jaeger and B. Kapma, *Z. anorg. allgem. Chem.*, **113**, 27 (1920); *I. C. T.*, **6**, 149 (1928).

[7] F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1 (1917); *I. C. T.*, **4**, 444 (1928).

[8] V. I. Spitsyn and I. M. Kuleshov, *J. Gen. Chem.*, (*U.S.S.R.*), **21**, 445 (1951) (English translation); *C. A.*, **46**, 1907b (1952); *ibid.*, **45**, 5553i (1951).