

## The Effect of Radiation on Poly- $\alpha$ -Methylstyrene\*

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### INTRODUCTION

When high molecular weight polymers are exposed to ionizing radiation, the changes in physical and chemical properties which take place are determined primarily by whether the polymers undergo chain scission, crosslinking, or a combination of both. These processes may be accompanied by such phenomena as gas evolution, free radical reactions, and formation of double bonds. Bibliographies are available covering the work in this field.<sup>1,2</sup>

In the present investigation, poly- $\alpha$ -methylstyrene was used for study because it undergoes predominantly chain scission upon exposure to radiation, has incorporated in its structure a phenyl group which offers resonant stabilization, and has a comparatively low ceiling temperature (about 60°C.).<sup>3</sup> It is hoped that a comparison of the changes observed with this and other polymers will give helpful information as to the mechanisms involved and offer some clues to the determining factors.

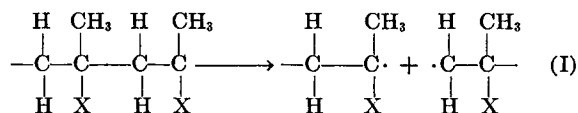
### THEORY

The sequence of steps assumed to take place during irradiation is as follows. (1) A primary break occurs in a polymer chain due to rupture of a C—C bond. (2) The resulting chain radicals undergo partial depolymerization, producing monomer molecules at a rate rapid compared to the initiation rate and the time necessary for a significant portion of the monomer molecules to diffuse away. The chain radical is thus pictured as being surrounded by a monomer cloud which is a good radical scavenger. (3) The chain radical terminates by transfer to a monomer molecule; with a momentary excess of monomer surrounding the radical, this corresponds to a pseudo-unimolecular termination process. (4) The monomer radical thus formed may add additional

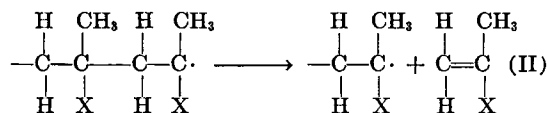
monomer units before termination with another growing monomer radical or transfer to a monomer molecule. The lifetime of a growing monomer radical is assumed to be sufficient to permit the relatively more mobile monomer cloud to diffuse to an average distribution prior to any significant polymerization. This is indeed possible, considering the sluggish reactivity of the  $\alpha$ -methylstyrene radical.

These four steps may be depicted schematically as follows.

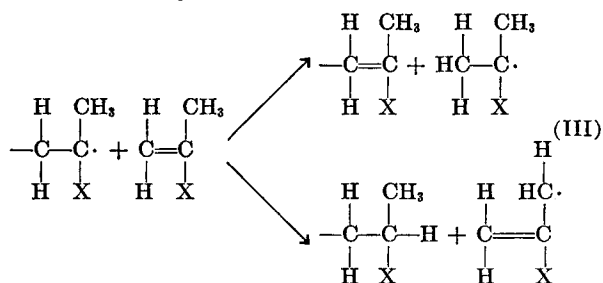
Initiation:



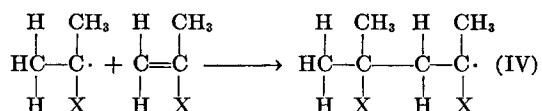
Depolymerization:



Termination by chain transfer:



Polymerization:



In the above steps, X represents a phenyl group.

An additional step, describing the termination of the growing monomer, is necessary to give a complete cycle. It is represented below as termination by disproportionation. The exact mechanism of the termination, however, is immaterial to the following analysis.

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$2R\cdot \rightarrow 2$  polymer molecules

In deriving the rate equations, the following assumptions are made.

(a) Initially only chains of one length  $P_0$  are present and are homogeneous in constitution.

(b) The initiation step is random in nature, all primary bonds between monomer units having an equal probability of being broken.

(c) The number of bonds severed per unit of absorbed energy is proportional to the number of bonds in the system and independent of dose rate. For low degrees of degradation, this number remains essentially constant.

(d) The kinetic chain length, defined as the number of monomer units split off per primary chain scission, is generally much less than the chain length of the fragment produced and is independent of the amount of any excess monomer present, provided the concentration of the latter is small with respect to the local concentration produced by the monomer cloud.

(e) Inter- and intramolecular transfers between initial chains are negligible. Transfer between monomer and growing radical chains is permitted.

(f) The polymerization of monomer has a negligible effect on the average molecular weight of the polymer.

(g) Radiation-induced polymerization of the monomer, other than the amount due to the transfer process and degradation, is negligible.

On the basis of these assumptions, the rate equations describing the four steps pictured above are as follows.

Initiation:

$$dn_r/dt = k_1'm_0r = 1/2(dn/dt)$$

Depropagation:

$$dm_1/dt = k_2n_r = 1/2(k_2n\cdot) \quad (1)$$

Termination by chain transfer:

$$-dn\cdot/dt = k_3n\cdot$$

Polymerization:

$$-dm_1/dt = k_4m_1R\cdot = fk_4m_1n\cdot$$

where  $k_1'$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are the specific rate constants of the steps shown,  $n_r$  is the number of chain scissions produced,  $n\cdot$  the number of chain radicals,  $m_0$  the total number of skeletal chain bonds originally present (i.e., essentially the number of bound monomer units),  $m_1$  the number of free monomer molecules present,  $r$  the absorbed dose rate,  $t$  the

time, and  $R\cdot$  the number of growing monomer radicals in step (IV).  $R\cdot$  is proportional to  $n\cdot$ , the constant of proportionality being the factor  $f$ . It is convenient to express  $t$  in hours,  $r$  in electron volts absorbed per gram per hour, and  $n_r$ ,  $n\cdot$ ,  $m_0$ , and  $m_1$  in number per gram. The net rates at any time  $t$  are then

$$dn\cdot/dt = 2k_1'm_0r - k_3n\cdot \quad (2)$$

$$dm_1/dt = 1/2k_2n\cdot - fk_4m_1n\cdot$$

If it is assumed that the depolymerization and transfer rates are rapid compared to the initiation rate, the steady state method (i.e.,  $dn\cdot/dt = 0$ ) gives:

$$dm_1/dt = \epsilon k_1r - k_1k_5m_1r \quad (3)$$

where

$$\begin{aligned} k_1 &= k_1'm_0 \\ \epsilon &= k_2/k_3 \\ k_5 &= 2fk_4/k_3 \end{aligned}$$

Integration of eq. (3) gives

$$m_1 = (\epsilon/k_5)(1 - e^{-k_1k_5D}) \quad (4)$$

where total dose  $D = rt$  ( $k_1$  is expressed in scissions per electron volt,  $k_5$  in grams per scission, and  $D$  in electron volts per gram). The symbol  $\epsilon$  represents the kinetic chain length.

When free monomer  $m_{10}$  is initially present in the sample before irradiation, eq. (4) becomes

$$(\epsilon - k_5m_1)/(\epsilon - k_5m_{10}) = e^{-k_1k_5D} \quad (5)$$

The limiting value of eq. (4) gives  $\epsilon/k_5$  from the experimentally determined  $m_1$ . Values of  $m_1$  at various absorbed doses  $D$  then allow a calculation of  $k_1k_5$ . Hence the product  $k_1\epsilon$  can be evaluated. Individual values of  $k_1$  and  $\epsilon$  can then be determined from number-average molecular weight measurements in the following manner.

The number of moles originally present in one gram is  $m_0/P_0$ , where  $m_0$  is the number of monomer units in the original polymer sample and  $P_0$  is the initial chain length. The number of additional molecules formed during irradiation is

$$n_r + m' = k_1D + k_1\epsilon D = k_1D(1 + \epsilon) \quad (6)$$

where  $m'$  is the number of monomer molecules formed prior to any repolymerization. The number-average degree of polymerization  $\bar{P}_n$  is then

$$\bar{P}_n = \frac{\sum_{P=1}^{P_0} n_P P}{\sum_{P=1}^{P_0} n_P} = m_0/[k_1D(1 + \epsilon) + m_0/P_0] \quad (7)$$

where  $n_P$  is the number of moles of length  $P$ . The number-average degree of polymerization without monomer is then

$$\bar{P}_n' = \frac{\sum_{P=2}^{P_0} n_P P}{\sum_{P=2}^{P_0} n_P} = (m_0 - k_1 \epsilon D) / (k_1 D + m_0 / P_0) \quad (8)$$

The experimental determination of  $\bar{P}_n'$  (from osmotic pressure measurements on solutions of irradiated polymer) at various values of  $k_1 \epsilon D$  and  $P_0$  permits the evaluation of  $k_1$  from eq. (8). When  $\epsilon = 0$  (i.e., there is no depolymerization subsequent to the primary bond break), eq. (8) is reduced to

$$(1/\bar{P}_n) - (1/P_0) = kD \quad (9)$$

which is the relationship for random splitting of bonds when  $P_n$  and  $P_0 \gg 1$ .<sup>4</sup>

The  $k_1$  values for primary chain scission calculated from eqs. (4) and (8) are based on number-average molecular weights obtained from osmotic pressure measurements. The  $G$ -value from primary chain scission (i.e., bonds broken per 100 e.v. absorbed) can also be determined from weight-average molecular weights obtained from viscosity measurements on solutions of irradiated polymer. The necessary relationship is developed as follows:

The probability  $\alpha$  that any one link in the polymer chain will be broken is defined by

$$\alpha = S / (P_0 - 1) \approx S / P_0 \quad P_0 \gg 1 \quad (10)$$

where  $S$  is the average number of links broken per chain and  $P_0$  is the original chain length. The number of moles of chains of length  $P$  per base mole that are formed as a result of the degradation is then calculated to be

$$N_P = (1/P_0) [(P_0 - 1) - (P + \epsilon)] \alpha^2 (1 - \alpha)^{P + \epsilon - 1} + 2\alpha (1 - \alpha)^{(P + \epsilon/2) - 1} \quad (11)$$

The moles of polymer chains remaining undegraded is given by

$$N_{P_0} = 1/P_0 (1 - \alpha)^{P_0 - 1} \quad (12)$$

The first term within the brackets in eq. (11) is the probability of forming a chain of length  $P$  from a fragment of a chain which undergoes a depropagation of  $\epsilon/2$  monomer units from each fractured end; the second term is the probability of forming a chain of length  $P$  by starting from one end of the molecule and splitting off  $\epsilon/2$  monomer units from the other end of the produced fragment. The proper weight distribution function is then obtained by multiplying eq. (11) and (12) by  $P$  and  $P_0$  respectively:

$$m_P = N_P P \quad (13)$$

$$m_{P_0} = N_{P_0} P_0$$

where  $m_P$  represents the amount in grams of chains of length  $P$  in one gram of starting material. By definition, the weight-average chain length  $\bar{P}_w$  is:

$$\bar{P}_w = \frac{\sum_{P=1}^{P_0} m_P P}{\sum_{P=1}^{P_0} m_P} \approx \int_0^{P_0} m_P P dP / \int_0^{P_0} m_P dP \quad (14)$$

Substituting eq. (13) in eq. (14), and using the approximation  $(1 - \alpha)^P = e^{-\alpha P}$ , we obtain

$$\begin{aligned} \bar{P}_w / P_0 = e^{-S} + e^{\alpha(1-\epsilon)} [1 + (1/P_0) - (\epsilon/P_0)] \times \\ \{ (2/S) - e^{-S} [S + 2 + (2/S)] \} \\ - [(6/S^2) - e^{-S}] [S + 3 + (6/S) + (6/S^2)] \\ + 2e^{\alpha(1-\epsilon)/2} \{ [(2/S^2) - e^{-S}] [1 + (2/S) + (2/S)] \} \end{aligned} \quad (15)$$

When  $\epsilon = 0$  this expression reduces to

$$\bar{P}_w / P_0 = (2/S^2)(e^{-S} + S - 1) \quad (16)$$

previously derived by earlier workers.<sup>5</sup>

Equation (15) gives the desired relation between the average number of breaks  $S$  and the weight-average chain length  $\bar{P}_w$ . It should be noted that one of the parameters in this equation is the kinetic chain length. Although an accurate determination of the  $G$ -value for primary chain scission requires a knowledge of the kinetic chain length as a function of the length of the broken fragment, this function is generally not known, and only the average kinetic chain length  $\epsilon$  can be derived from eqs. (4) and (8). Use of this average value unavoidably introduces an error, but for the low degrees of degradation and large  $P_0$  considered here this error is small.

## EXPERIMENTAL

### Materials

The poly- $\alpha$ -methylstyrene used in this work was experimental plastic Q-817.1, obtained from the Dow Chemical Company. The material was carefully fractionated twice from benzene solution by the slow addition of methanol. The selected fractions were again dissolved in benzene, filtered, freeze-dried, and vacuum-dried at 50°C. to remove residual solvent. The  $\bar{M}_w/\bar{M}_n$  ratios for fractions used were 1.1 or better.

All solvents used were reagent grade. Benzene

for osmotic pressure measurements was distilled over sodium through a 40-plate column, the middle fraction being used. The solvent was again dried over sodium prior to use.

The membranes for osmometry were wet regenerated cellulose film, type 300, supplied by the American Viscose Corporation, Fredericksburg, Virginia. The membranes were conditioned<sup>6</sup> by washing with water at 50°C. for several minutes to destroy inhibitor, followed by gradual exchange through the series of solvents: water, alcohol, and benzene. The membranes were aged at least a week before the use in the osmometers. The conditioned membranes showed negligible disymmetries.

### Molecular Weights

The number-average molecular weights,  $\bar{M}_n$ , were determined from osmotic pressure measurements on solutions of the material in benzene, the Stabin-type osmometer<sup>7</sup> being used. Four osmometers were used to minimize any errors due to disymmetries arising during the determination. All measurements were carried out at  $30 \pm 0.002^\circ\text{C}$ . Equilibrium was reached within 6 hr., and extrapolation to zero time was usually not necessary. The osmometers were rinsed three times with solution prior to filling. The first rinse was allowed to remain in the osmometer for 1 hr. to minimize errors due to adsorption.

The weight-average molecular weights,  $\bar{M}_w$ , were calculated from viscosities measured with an Ubbelohde-type dilution viscometer. The intrinsic viscosity  $[\eta]$  was determined analytically from the relationship

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c$$

The experimental value of  $k'$  at 30°C. remained constant at 0.28 in the concentration range of 0.2 to 0.9 g./100 ml. and for different fractions, giving values of  $[\eta]$  ranging from 0.42 to 1.11. The weight-average molecular weight  $\bar{M}_w$  was then calculated from the empirical relationship for fractionated poly- $\alpha$ -methylstyrene in benzene at 30°C.:<sup>8</sup>

$$[\eta] = 0.17 \times 10^{-4} \bar{M}_w^{0.87}$$

The number- and weight-average molecular weights determined are reliable to within  $\pm 5\%$ .

### Irradiation

Irradiations were carried out in glass vessels at room temperature, the NRL Co<sup>60</sup> gamma source

previously described being used.<sup>9</sup> Calibration of the radiation field by means of a ferrous sulfate dosimeter at the two positions used during the irradiations showed exposure dose rates of  $6.1 \times 10^5$  and  $3.8 \times 10^5$  roentgens/hr. based on a  $G$ -value for the dosimeter of 15.5 (number of ferrous ions oxidized per 100 e.v. absorbed). The energy absorbed per gram of material per roentgen is approximately the same as that for water, taken as 97.5 ergs/g.-roentgen; this is equivalent to  $6.1 \times 10^{13}$  e.v./g.-roentgen. The absorbed dose thus calculated for the irradiated polymer is reliable to within  $\pm 3\%$ .

### Infrared Spectra

The transmission spectra of irradiated and un-irradiated polymer samples were determined on films cast from dilute benzene solutions. All measurements were made with a Perkin-Elmer Model 21 infrared spectrophotometer.

### Volatile Products

A single 14-g. sample of unfractionated material in a closed evacuated vessel was given a total absorbed dose of  $73 \times 10^{20}$  e.v./g. During the irradiation, any volatile products evolved were allowed to collect in the upper portion of the sample container. Following the irradiation, analysis of the components present in the gaseous phase (with the sample at room temperature) was made with a Consolidated Electrodynamics Model 21-103B mass spectrometer.

### Monomer Formation

The amount of free monomer present in the polymer sample after irradiation is assumed to be equal to the measured total unsaturation less any residual unsaturation left in the polymer after precipitation in methanol; molecular weights of the polymer less than 1,000 being soluble in methanol.<sup>10</sup> The unsaturation present was determined by dissolving the irradiated polymer in dichloromethane and treating with a measured amount of 0.1*N* bromine solution in carbon tetrachloride. After standing for 30 min. in the dark, the solution was treated with an excess of aqueous sodium iodide, and the liberated iodine titrated with thiosulfate. Addition of potassium iodate solution at the end of this titration indicated that no measurable substitution reaction had occurred between the bromine and the material present. The identification of the measured unsaturation with free monomer is based on the comparison of the ultraviolet spectrum of

TABLE I  
Spectral Correlation between radiation-produced Unsaturation and Free Monomer

Sample no.	Absorbed dose, $\times 10^{-20}$ , e.v./g.	Initial no. free monomer molecules/g. ( $m_{10}$ ) $\times 10^{-19}$	Total no. free monomer molecules/g. ( $m_1$ ) $\times 10^{-19}$	Calculated monomer extinction coefficient at 244 $m\mu$ l., $\times 10^{19}$ , dl., molecule-cm.
1	0	pure monomer	51.0	$1.85 \pm 0.03$
2	21.7	$18.2 \pm 0.3$	$21.8 \pm 0.3$	$1.83 \pm 0.04$
3	0	$18.2 \pm 0.3$	$18.2 \pm 0.3$	$1.91 \pm 0.04$
4	13.3	0	$14.2 \pm 0.3$	$1.85 \pm 0.05$
5	3.1	0	$6.4 \pm 0.3$	$1.95 \pm 0.12$
6	29.7 <sup>a</sup>	0	$2.0 \pm 0.3$	$1.35 \pm 0.40$

<sup>a</sup> Irradiated in oxygen.

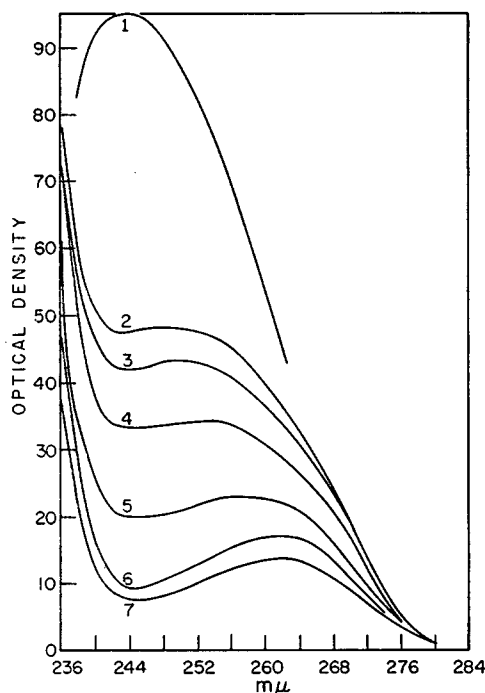


Fig. 1. Absorption spectra of polymer-monomer mixtures. Curve numbers correspond to sample numbers of Table I.

monomer with that of polymer plus monomer mixtures, including irradiated samples. The measurements were made with a Beckman DU spectrometer at 25°C. The representative determined extinction coefficients for monomer at 244  $m\mu$  and monomer plus polymer are compared with that of the produced unsaturation in Table I. In Figure 1 are plotted the absorption curves of these representative mixtures containing varying amounts of monomer; in addition, there is plotted the curve (No. 7) for unirradiated polymer. The curves show clearly the increased absorption at 244  $m\mu$  with increase in amount of free monomer, the latter being determined from unsaturation measurements. Infrared measurements on irradiated polymer show

an increase in the optical density at 845  $\text{cm.}^{-1}$  corresponding to the formation a  $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$  type of group, which supports the above identification. An additional rather weak increase at 888  $\text{cm.}^{-1}$ , corresponding to  $\text{R}_1\text{R}_2\text{C}=\text{CHR}$  was also found.

## RESULTS AND DISCUSSION

### Irradiation In Vacuo

The number of monomer units formed as a function of absorbed dose is plotted in Figure 2. Curve no. 1 of Figure 2 shows that the amount of monomer formed is independent of the initial molecular weight of the polymer. Within the range of dose rates used ( $2.2 \times 10^{19}$  to  $3.5 \times 10^{19}$  e.v./g.-hr.), the formation of monomer is also independent of dose rate, depending only on total absorbed dose. The initial slope of the curve gives an average value for  $k_1\epsilon$  of 0.25, corresponding to a  $G$ -value for monomer production of 25 monomer molecules formed per 100 e.v. absorbed. The limiting value of eq. (4), corresponding to the leveling off of the curve, gives for

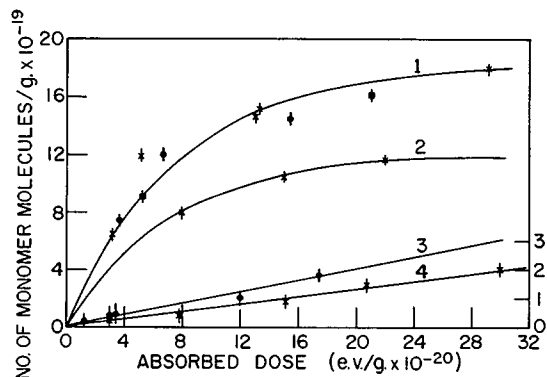


Fig. 2. Formation of monomer vs. dose (1); in vacuum: ( $\times$ )  $\bar{M}_{n_0} = 112,000$ , ( $\blacksquare$ )  $\bar{M}_{n_0} = 218,000$ , ( $\bullet$ )  $\bar{M}_{n_0} = 512,000$ ; (2) in a  $\text{H}_2$  atmosphere: ( $\times$ )  $\bar{M}_{n_0} = 286,000$ ; (3) in air: ( $\bullet$ )  $\bar{M}_{n_0} = 286,000$ ; (4) in an  $\text{O}_2$  atmosphere: ( $\times$ )  $\bar{M}_{n_0} = 286,000$ .

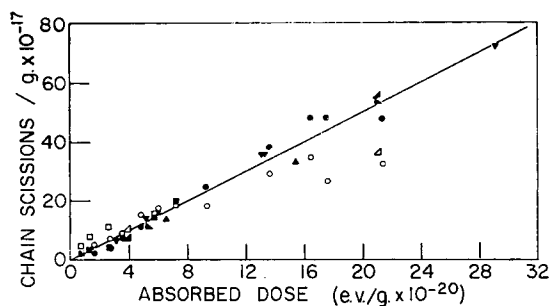


Fig. 3. Degradation *in vacuo*. Open and filled points calculated from  $\bar{M}_n$  and  $\bar{M}_w$  data, respectively, for  $\bar{M}_n$ : (▼) = 112,000; (■) = 190,000; (▲) = 218,000; (●) = 260,000; (▲) = 286,000; (◆) = 512,000.

$\epsilon/k_5$  a value of  $1.8 \times 10^{18}$  monomer molecules/g. The average value of the product  $k_1k_5$  is then calculated to be  $1.4 \times 10^{-21}$  g./e.v. This represents the amount of repolymerized material per electron volt absorbed. Lowry<sup>11</sup> has reported a value for the direct radiation-induced formation of polymer of  $1.7 \times 10^{-24}$  g./e.v. The magnitude of the difference between these two values for polymerization is strong support for the proposed repolymerization by chain transfer initiation mechanism.

In Figure 3, the number of chain scissions per gram versus absorbed dose is plotted for various samples having different initial molecular weights.

An average value for  $k_1$  of  $2.5 \times 10^{-3}$  bonds broken/e.v., determined from osmotic pressure and unsaturation measurements [eqs. (4) and (8)], was used to construct the solid line; the uncertainties associated with the individual  $k_1$  values are indicated by their distribution about this mean. The high  $k_1$  values at low absorbed dose are due to the inherent inaccuracy associated with taking a small difference between two large numbers; the determination of  $k_1$  from eq. (8) involves the difference between  $(m_0 - k\epsilon_1 D)/\bar{P}_n$  and  $m_0/P_0$ , which have very nearly the same value for low doses, and whose accuracy is limited by the accuracy of determining  $\bar{P}_n$  and  $P_0$  from osmotic pressure measurements. The decrease in  $k_1$  values at higher doses is due mainly to the permeability of the membrane to some of the resulting polymer chains, since the values based on viscosity measurements do not show this effect. On the basis of the theory presented, it appears that the  $\bar{M}_n$  values in question are about 25% too high. This would correspond to a cut-off value of about 30,000 for the membranes, which is quite reasonable. The contribution to the molecular weight of the repolymerized monomer, a few per cent at the most, is of minor consequence. For the purpose of comparison, the points obtained from viscosity measurements [calculated from eq. (15)] are also plotted in Figure 3. They are in good

TABLE II  
Effect of Added Monomer on Repolymerization

Absorbed dose $\times 10^{-20}$ , e.v./g.	Intrinsic viscosity [ $\eta$ ]	$\bar{M}_w \times 10^{-5}$	Initial no. free monomer molecules/g. ( $m_{10}$ ) $\times 10^{-19}$	Total no. free monomer molecules/g. ( $m_1$ ) $\times 10^{-19}$	$k_5 \times 10^{10}$
0	0.82	2.42	0	0	
5.2 <sup>a</sup>	0.72	2.08	0	9.2	5.4 <sup>e</sup>
5.2 <sup>a</sup>	0.71 <sup>c</sup>	2.05 <sup>c</sup>	0		
5.2 <sup>a</sup>	0.71	2.05	18.2	19.1	4.9 <sup>d</sup>
5.2 <sup>a</sup>	0.71 <sup>c</sup>	2.05 <sup>c</sup>	18.2		
21.0 <sup>b</sup>	0.47	1.27	0	16.3	5.4 <sup>e</sup>
21.0 <sup>b</sup>	0.49 <sup>c</sup>	1.34 <sup>c</sup>	0		
21.7 <sup>b</sup>	0.51	1.83	18.2	21.8	4.5 <sup>d</sup>
21.7 <sup>b</sup>	0.52 <sup>c</sup>	1.87 <sup>c</sup>	18.2		
0	1.59	5.17	0	0	5.4 <sup>e</sup>
6.5 <sup>a</sup>	1.15	3.56	0	11.9	5.4 <sup>e</sup>
6.5 <sup>a</sup>	1.13 <sup>c</sup>	3.49 <sup>c</sup>	0		
6.5 <sup>a</sup>	1.12	3.46	29.5	28.0	3.6 <sup>d</sup>
15.4 <sup>b</sup>	0.80	3.06	0	14.3	
21.0 <sup>b</sup>	0.66	1.88	29.5	26.5	3.7 <sup>d</sup>

<sup>a</sup>  $2.2 \times 10^{19}$  e.v./g.-hr.

<sup>b</sup>  $3.5 \times 10^{19}$  e.v./g.-hr.

<sup>c</sup> Precipitated in methanol.

<sup>d</sup> Calculated from eq. (5).

<sup>e</sup> Average value from eq. (4).

agreement with the values determined from osmotic pressure measurements. The values derived from the number-average and the weight-average data show no dependency on either initial molecular weight or dose rate in the ranges studied.

The preferential breaking of weak bonds, if they are present in the order of about one per molecule, is not indicated. The leveling-off effect described above could be ascribed in part to weak bonds, were it also present in values calculated from viscosity data. This, however, is not the case.

In Table II are tabulated the results obtained on addition of excess monomer to the polymer before irradiation. The  $k_5$  values listed were calculated from eq. (5), on the basis of average values for  $\epsilon$  and  $k_1$  of 98 and  $2.5 \times 10^{-3}$ , respectively; they are in every case significantly less than the average value of  $5.4 \times 10^{-19}$  for  $k_5$  calculated from eq. (4) when no excess monomer is present initially. A possible reason for this difference is that some repolymerization occurs before the monomer cloud resulting from the depolymerization has become diffuse enough to be considered as an average macroscopic concentration surrounding the growing monomer radical. Comparison of the resulting intrinsic viscosities at high doses when monomer is and is not present initially supports the contention that repolymerization does take place.

### Irradiation in the Presence of Hydrogen

The results of irradiation under hydrogen are plotted in Figure 4. As compared to the results in irradiation *in vacuo*, the relative degradation (i.e., decrease in molecular weight) is only slightly reduced, the values of  $k_1$  and  $k_5$  obtained being  $2.4 \times 10^{-3}$  and  $5.9 \times 10^{-19}$ , respectively. However, the kinetic chain length  $\epsilon$  is decreased by about half to a value of  $\epsilon = 49$ . This suggests that the presence

of hydrogen has an influence on the termination of the depropagating chain, possibly a reaction between hydrogen and the chain radical. However, the difference between the measured molecular weight averages for irradiation *in vacuo* and in hydrogen are small, and the data rather limited; it is therefore equally possible that the only real effect taking place is hydrogenation of the radiation-produced monomer, which would account for the observed decrease in  $\epsilon$ .

### Irradiation in the Presence of Oxygen

The effect of oxygen present during irradiation is shown in Figure 4. The amount of monomer formation and the decrease in molecular weight observed *in vacuo* are both reduced with increasing oxygen pressure up to a pressure of one atmosphere; further increases in  $O_2$  pressure to two atmospheres appear to have no further effect. Since monomer formation is inhibited in the presence of oxygen, eq. (9) was used to calculate the  $G$ -values for bond scission (bonds broken per 100 e.v. absorbed); these were found to be 0.16 and 0.08 in air and oxygen, respectively, both at one atmosphere pressure.

The inhibition of monomer formation in the presence of oxygen is very likely due to interference with the depropagation reaction by the formation of oxygenated terminal groups after chain scission. The effect of oxygen in reducing the  $G$ -value for primary bond scission is more difficult to explain. It is possibly due to formation of peroxide linkages, which, by inhibiting the depolymerization step, may promote recombination of fractured chains. The addition of *tert*-butyl catechol, which has been found to decompose benzoyl peroxide,<sup>12</sup> produced small but consistent decreases of the order of 0.5%, in the intrinsic viscosity of polymer irradiated in the presence of oxygen. Wall and Brown<sup>12</sup> have found that the viscosity of the solutions of irradiated polymethyl methacrylate is reduced upon the addition of *tert*-butyl catechol, about the same extent as found above at corresponding degrees of degradation, and attribute this to the destruction of some peroxide structure formed during irradiation. Bovey<sup>13</sup> has suggested that the oxygen reacts with only one of the resulting polymer radicals and that recombination takes place with a formation of a peroxy link which may then be severed upon reduction by the *tert*-butyl catechol. However, the reduction in the viscosity is insufficient to account for the reduction in the  $G$ -value for bond scission. This link is rather weak and should be broken completely by the reagent. An alternative explanation

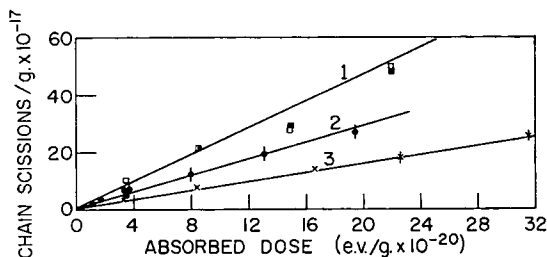


Fig. 4. Degradation in hydrogen and oxygen: (1) degradation in  $H_2$  atmosphere ( $\square$ ) calculated from  $\bar{M}_n$  for  $\bar{M}_n = 286,000$ , ( $\blacksquare$ ) calculated from  $\bar{M}_w$  for  $\bar{M}_w = 296,000$ ; (2) degradation in an air atmosphere: ( $\bullet$ )  $\bar{M}_n = 286,000$ ; (3) degradation in an  $O_2$  atmosphere: ( $\times$ )  $\bar{M}_n = 286,000$ .

is deactivation of the excited molecule prior to chain scission by energy transfer to an oxygen species by some unknown mechanism.

### Volatile Products

The gases evolved during irradiation, determined by mass spectrometry with the sample at room temperature, are listed in Table III. An estimate of the  $G$ -value for hydrogen production gives  $G(\text{H}_2) = 0.035$ . A similar value of 0.023 has been reported

TABLE III  
Gases Evolved During Irradiation of Poly- $\alpha$ -methylstyrene<sup>a,b</sup>

Product	% by volume	$G$ -Value $\times 10^3$
Hydrogen	58	35
Methane	5.2	3.1
Water	0.8	0.5
Carbon monoxide	1.9	1.1
Oxygen	trace	—
Carbon dioxide	2.1	1.3
Isobutane	0.4	0.2
Isobutene	0.5	0.3
1-Butene	0.5	0.3
2-Butene	4.2	2.5
Benzene	26	—
Toluene	trace	—
Isopropylbenzene	trace	—
$\alpha$ -Methylstyrene	0.3	0.2

<sup>a</sup> Gas sampling at room temperature; 14 g. sample, absorbed dose  $73 \times 10^{20}$  e.v./g.

<sup>b</sup> Estimated reliability  $\pm 10\%$ .

for gamma irradiation of polystyrene.<sup>12</sup> Both gamma- and electron-irradiated benzene give a  $G(\text{H}_2)$  yield of 0.035.<sup>14</sup> These rather low values are as yet unexplained. Similarly, the  $G(\text{CH}_4)$  value of 0.003 is also quite small, indicating a preferential breaking of the carbon bond linking monomer units. This is in agreement with the rather low heat of polymerization, low ceiling temperature, and stability of the  $\alpha$ -methylstyrene radical. The rather large amount of benzene is most probably due to residual solvent. The small amount of  $\alpha$ -methylstyrene present is what one would expect, since most of it is retained by the polymer at room temperature.

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### Synopsis

Degradation studies on poly- $\alpha$ -methylstyrene at 25°C. under vacuum and in hydrogen and oxygen were carried out with the use of a  $\text{Co}^{60}$  gamma source. The degradation results are explained as a random breaking of skeletal chain bonds accompanied by a depropagation of the resulting fragments. The termination step for depropagation is considered as a chain transfer of the degrading radical to the produced monomer cloud, the monomer radical thus formed repolymerizing to some extent prior to termination. The necessary relationships are derived which permit the evaluation of the  $G$ -value for bond scission, the kinetic chain length for depropagation from the resulting  $\bar{M}_n$  and  $\bar{M}_w$  values, and the unsaturation produced. The determined  $G$ -values for chain scission are 0.25 in vacuum and hydrogen, 0.16 in air, and 0.08 in oxygen, the gases being at a pressure of one atmosphere. The number of monomer units split off per break was found to be 100 in vacuum, 50 in hydrogen, and essentially zero in the presence of oxygen. It is believed that hydrogen and oxygen terminate the depropagating radical, reducing the kinetic chain length. The reduction in the  $G$ -value for chain scission in the presence of oxygen may be due to either recombination of the terminal peroxide groups formed or deactivation of the chain prior to cleavage. The  $G$ -values for volatile products at room temperature are listed, the important ones being  $G(\text{H}_2) = 0.035$  and  $G(\text{CH}_4) = 0.003$ .

### Résumé

On a étudié la dégradation du poly- $\alpha$ -méthylstyrène à 25°C sous vide et dans une atmosphère d'hydrogène et



d'oxygène au moyen d'une source gamma au cobalt-60. Les résultats de la dégradation sont expliqués comme une rupture statistique de liaisons du squelette carboné, suivie d'une dépropagation des fragments en résultant. La terminaison de la dépropagation est due à un transfert de chaîne du radical dégradant avec le monomère produit, et le radical monomérique ainsi formé repolymérise à un certain degré avant de se terminer. Les relations nécessaires sont dérivées et permettent une évaluation de la valeur de  $G$  pour la rupture de chaîne et de la longueur de chaîne cinétique de la dépropagation aux dépens des valeurs  $\bar{M}_n$  et  $\bar{M}_w$  et de la non-saturation produite. Les valeurs déterminées de  $G$  pour la rupture de chaîne s'élèvent à 0,25 sous vide et sous atmosphère d'hydrogène, 0,16 à l'air et 0,08 à l'oxygène, ces gaz étant sous la pression d'une atmosphère. Le nombre de monomères produits par scission de chaîne s'élevait à 100 sous vide, à 50 sous hydrogène, et essentiellement à zéro en présence d'oxygène. On croit que l'hydrogène et l'oxygène terminent le radical dépolymérisant réduisant ainsi la longueur de chaîne cinétique. La diminution de  $G$  pour la rupture de chaîne en présence d'oxygène peut être due soit à la recombinaison des groupes peroxydiques terminaux formés, soit, à la désactivation de la chaîne avant la rupture. Les valeurs de  $G$  pour les produits volatils à température de chambre sont rapportées, les plus importants étant  $G(\text{H}_2) = 0,035$  et  $G(\text{CH}_4) = 0,003$ .

### Zusammenfassung

Untersuchungen über den Abbau von Poly- $\alpha$ -methylstyrol bei 25°C in Vakuum und in Wasserstoff- und Sauerstoffatmosphäre wurden unter Verwendung einer  $\text{Co}^{60}$ - $\gamma$ -Quelle

ausgeführt. Die Ergebnisse der Abbauprobe können als statistische Spaltung der Bindungen in der Polymarkette verstanden werden, die von einer Abspaltungsreaktion an den gebildeten Bruchstücken begleitet ist. Der Abbruchschritt der Abspaltungsreaktion wird als eine Kettenübertragung zwischen dem im Abbauprozess befindlichen Radikal und der von ihm erzeugten Monomerwolke betrachtet; die so gebildeten Monomerradikale gehen vor ihrem Abbruch in gewissem Umfang eine neuerliche Polymerisation ein. Es werden die für die Ermittlung der  $G$ -Werte für die Kettenspaltung und der kinetischen Kettenlänge der Abspaltungsreaktion aus den erhaltenen  $\bar{M}_n$ - und  $\bar{M}_w$ -Werten sowie der Zahl der gebildeten Doppelbindungen notwendigen Beziehungen abgeleitet. Die Bestimmung der  $G$ -Werte für die Kettenspaltung ergibt 0,25 für Vakuum und Wasserstoff, 0,16 für Luft und 0,08 für Sauerstoff, wobei die Gase unter dem Druck von einer Atmosphäre stehen. Die Zahl der Monomereinheiten, die pro Kettenspaltung abgespalten werden wurde im Vakuum zu 100, unter Wasserstoff auf 50 und in Gegenwart von Sauerstoff praktisch zu Null bestimmt. Es wird angenommen, dass Wasserstoff und Sauerstoff eine Abbruchreaktion mit dem Radikal der Abspaltungsreaktion eingehen und daher die kinetische Kettenlänge herabsetzen. Die Herabsetzung des  $G$ -Wertes für die Kettenspaltung in Gegenwart von Sauerstoff kann entweder auf Rekombination der gebildeten peroxydischen Endgruppen oder Deaktivierung der Kette von der Spaltung zurückgeführt werden. Die  $G$ -Werte für die Bildung bei Raumtemperatur flüchtiger Produkt werden tabelliert; wichtig sind die Werte  $G(\text{H}_2) = 0,035$  und  $G(\text{CH}_4) = 0,003$ .

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