

Radiation Effects on Polystyrene in Solution

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Synopsis

Four polystyrene samples, with molecular weight ranging from 43,300 to 1,112,000 have been irradiated in benzene solution by γ -rays, at four different intensities. Data obtained through intrinsic viscosity and light-scattering measurements on irradiated polymers indicate that, at each intensity, there exists a molecular weight below which any polymer chain is no further degraded. An equilibrium between absorbed and dissipated energy by the macromolecule is supposed, and the equation, $M_{\text{lim}}I = \text{const.}$ arrived at in a previous study, is verified also by the present experimental results.

It is well known^{1,2} that on γ -irradiation of styrene monomer in solution, a product is obtained whose molecular weight depends on radiation intensity, concentration, and solvent type.

If now we expose to γ -rays a solution of the polystyrene so obtained in the same solvent and at the same intensity, we believe that it will keep stable, without undergoing degradation or substantial structural changes.

We therefore suppose that such a molecular weight, which we shall term the limiting molecular weight, M_{lim} , is also the final product of degradation of some chain of higher molecular weight, irradiated in the same conditions.

Of course all this is valid apart from the decomposition due to γ -rays of substances present to hydrogen and other gaseous products as this destructive action takes place at a rate much lower than that of the process we are interested in.

The existence of a limiting molecular weight was shown in a preceding study³ carried out in our laboratories. On that occasion, an assumption based on absorption and dissipation of the energy received by a macromolecule was put forward and the two following relations established:

$$M_{\text{lim}} I = \text{const.} \quad (1)$$

$$(M - M_{\text{lim}})/(M_0 - M_{\text{lim}}) = e^{-at} \quad (2)$$

where M_{lim} is the limiting molecular weight, M_0 is the initial molecular weight, M is the molecular weight after an irradiation time t at intensity I and a is a constant ≥ 1 .

At that time, measurements were performed on polystyrene in chloroform in the presence of oxygen. Although eqs. (1) and (2) were veri-

fied, we decided to check their validity employing a different experimental technique because, as is well known,^{4,5} the presence of chloroform and oxygen affects the reaction mechanism and makes it much complicated. We have therefore performed the present series of irradiation experiments in benzene and in absolute absence of oxygen; under such conditions the mechanisms of ionic or radical type, certainly factors in the first set of experiments, may be neglected, and it is possible that an equilibrium between absorption and dissipation of energy by the macromolecule acts as a regulator of the main kinetic process. Furthermore, chlorination of the polymer, which is very probable in chloroform owing to the high doses given to solutions,⁵ may be avoided.

We have also improved the irradiation technique with respect to setting out samples and flux uniformity.

The course of degradation was followed by measurements of intrinsic viscosity and weight-average molecular weight. It was considered necessary to make direct measurements of molecular weight as radiation yields crosslinked products and therefore causes a change in the Mark-Houwink equation constants; for this reason viscosity measurements alone cannot give reliable molecular weight values and are meaningless in terms of any kinetic interpretation of the process.

EXPERIMENTAL

Materials

Polystyrene samples used in this work were prepared by high vacuum block polymerization at 80°C. (PS₈₀), 100°C. (PS₁₀₀), 140°C. (PS₁₄₀), and 200°C. (PS₂₀₀).

These products were not fractionated, but the lowest molecular weight material and unreacted monomer were removed by repeated precipitations with methanol from dilute benzene solutions.

Table I shows weight-average molecular weights obtained by light scattering measurements in toluene and intrinsic viscosity values in toluene at 25°C. From these data the $\log [\eta]$ - $\log \bar{M}$ relation of eq. (3) was obtained.

$$[\eta] = 1.78 \times 10^{-4} \bar{M}_w^{0.682} \quad (3)$$

TABLE I
 \bar{M}_w and $[\eta]$ for Initial Polystyrene Samples

Sample	\bar{M}_w	$[\eta]$ (toluene, 25°C.), dl./g.	(dn/dc) (toluene, 5640 Å.)
PS ₂₀₀	43,300	0.257	0.1174
PS ₁₄₀	240,000	0.847	0.1128
PS ₁₀₀	616,000	1.610	0.1065
PS ₈₀	1,112,000	2.280	0.103

TABLE II
Values of Radiation Intensities Used*

Sample	\bar{M}_w	Radiation intensity			
		I_1 (1240 r/min.)	I_2 (550 r/min.)	I_3 (280 r/min.)	I_4 (78 r/min.)
PS ₂₀₀	43,000	+			+
PS ₁₄₀	240,000	+	+	+	+
PS ₁₀₀	616,000		+	+	+
PS ₈₀	1,112,000			+	+

* Samples irradiated are indicated by a plus sign (+).

The benzene employed for solutions to be irradiated was dehydrated over Na and then distilled.

The toluene solvent for viscosity and light-scattering measurements was obtained by double distillation of a pure commercial product.

Sample Preparation

The 2% solutions in benzene were prepared by use of calibrated Pyrex vials (25 ml.) in which solvent was distilled after introducing a weighed amount of polymer.

This operation was performed by connecting the vial and the solvent container to a high vacuum line (10^{-5} mm. Hg) to assure the complete degassing of solutions.

Irradiation of Solutions

Table II shows the four intensities employed and, for each of them, the polystyrenes irradiated.

The intensity values were obtained by Fickte dosimetry⁶ ($G_{Fe^{+++}} = 15.5$ mole/100 e.v.).

Sample irradiation was performed by use of a circular table perfectly centered around the Co⁶⁰ source with four series of concentric holes, in which vials were introduced.

At regular 3 day intervals, for each polystyrene sample, a vial was drawn and replaced by an identical one containing pure benzene. In such a way we could be sure that the initial experimental conditions with respect to diffuse and reflected radiations, as well as intensity gradient, were kept constant throughout the whole time.

The temperature of the irradiation room was maintained constant at $25 \pm 1^\circ\text{C}$.

Testing of Irradiated Polystyrenes

After irradiation, solutions were evaporated at 60°C . under vacuum to constant weight and the polymer thus recovered was directly employed to make the solutions in toluene.

Light-scattering measurements were begun on a Series 1000 Brice-Phoenix apparatus and then continued on a standard type Sofica photogoniometer.

In the course of these measurements, we checked dn/dc of the irradiated samples in toluene for PS₁₀₀ and found that it is constant at different irradiation times and exactly the same as that of the starting polymer.

Viscosity measurements were made in a Bischoff suspended-level viscometer kept at $25 \pm 0.05^\circ\text{C}$.

TABLE III
 \bar{M}_w and $[\eta]$ at Different Doses for PS₈₀

Radiation intensity	Irradiation time, days	Dose, Mr	$\bar{M}_w \times 10^{-6}$	$[\eta]$ (toluene, 25°C .), dl./g.
I_4	0	0	1.112	2.280
	16	1.728	1.072	2.258
	24	2.592	1.049	2.242
	30	3.240	1.028	2.217
I_3	0	0	1.112	2.280
	12	4.838	—	2.157
	18	7.266	0.972	2.117
	24	9.677	0.932	2.022
	30	12.096	0.886	1.952

TABLE IV
 \bar{M}_w and $[\eta]$ at Different Doses for PS₁₀₀

Radiation intensity	Irradiation time, days	Dose, Mr	$\bar{M}_w \times 10^{-5}$	$[\eta]$ (toluene, 25°C .), dl./g.
I_4	0	0	6.16	1.610
	12	1.296	—	1.585
	24	2.592	6.15	1.565
	27.67	2.988	6.11	1.570
	30	3.240	6.21	1.560
I_3	0	0	6.16	1.610
	18	7.258	5.86	1.479
	22.67	9.139	—	1.438
	27.67	11.155	5.82	1.400
	30	12.096	5.71	1.380
I_2	0	0	6.16	1.610
	4.08	3.234	5.96	1.540
	9.08	7.194	5.82	1.475
	12	9.504	—	1.465
	16	12.672	5.59	1.413
	18	14.256	—	1.385
	22.67	17.952	5.38	1.305
	24	19.008	5.23	1.325
	30	23.760	5.30	1.232

TABLE V
 \bar{M}_w and $[\eta]$ at Different Doses for PS₁₄₀

Radiation intensity	Irradiation time, days	Dose, Mr	$\bar{M}_w \times 10^{-5}$	$[\eta]$ (toluene, 25°C.), dl./g.
I_4	0	0	2.40	0.847
	2.33	0.252	2.57	—
	9.16	0.990	2.45	—
	15.67	1.692	2.36	—
	18.21	1.967	—	0.8375
	27.67	2.988	2.30	—
	30	3.240	—	0.825
I_3	0	0	2.40	0.847
	16.21	6.535	2.34	0.822
	27.67	11.155	2.24	0.800
	30	12.096	2.17	0.790
I_2	0	0	2.40	0.847
	6	4.752	2.26	0.830
	9.16	7.260	2.18	—
	16.21	12.837	2.10	0.775
	18	14.256	2.21	0.785
	24	19.008	2.07	—
	30	23.760	2.04	0.725
I_1	0	0	2.40	0.847
	6	10.714	—	0.773
	12	21.428	2.12	—
	16.21	28.942	—	0.734
	18.21	32.513	1.75	0.725
	20.79	37.126	1.60	0.690
	27.67	49.394	—	0.642
	30	53.568	—	0.6125

RESULTS

Tables III–VI summarize the experimental values of \bar{M}_w and $[\eta]$ for each sample and intensity, at different irradiation times.

Figures 1 and 2 show the variation of \bar{M}_w and $[\eta]$ plotted against irradiation time for PS₁₀₀ at three different intensities.

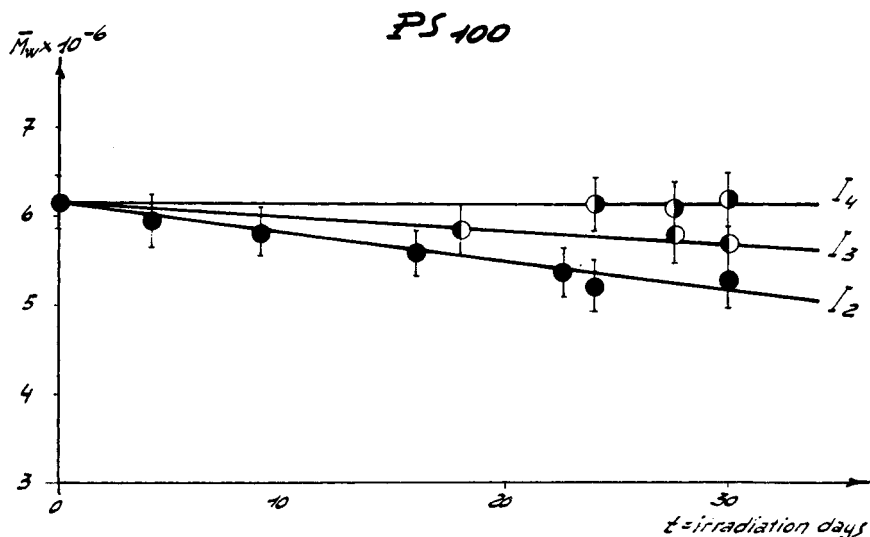
It is evident that the decrease in intrinsic viscosity is larger than that of molecular weight, as seen by a comparison of slopes of the lines corresponding to the lowest intensity; while \bar{M}_w does not change, $[\eta]$ decreases.

The same result was obtained for the other intensities on calculating from eq. [3] (valid for linear polystyrenes) the molecular weight values from measured intrinsic viscosities: \bar{M}_w values obtained are always lower than the experimental ones. This fact is attributable to the formation of crosslinked products.

Let us consider now the ratio $[\eta]_{\text{exp.}}/[\eta]_{\text{calc.}}$, between experimental intrinsic viscosity of an irradiated sample and that of the corresponding linear

TABLE VI
 \bar{M}_w and $[\eta]$ at Different Doses for PS₂₀₀

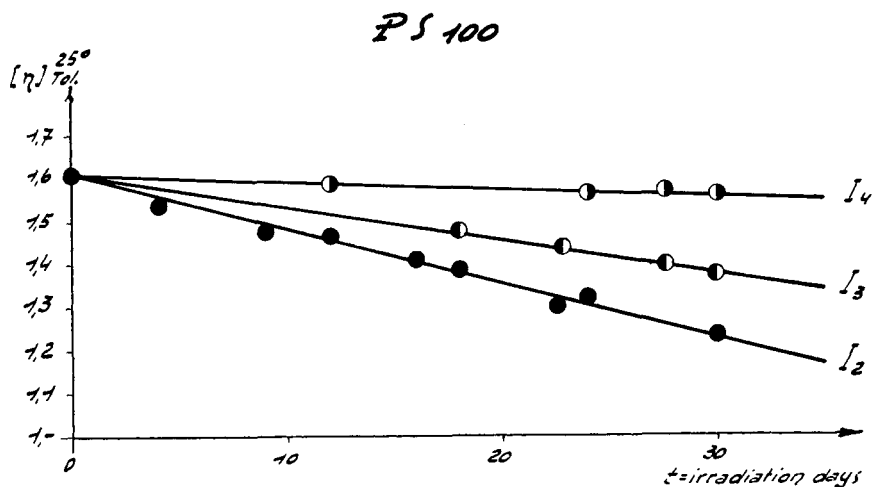
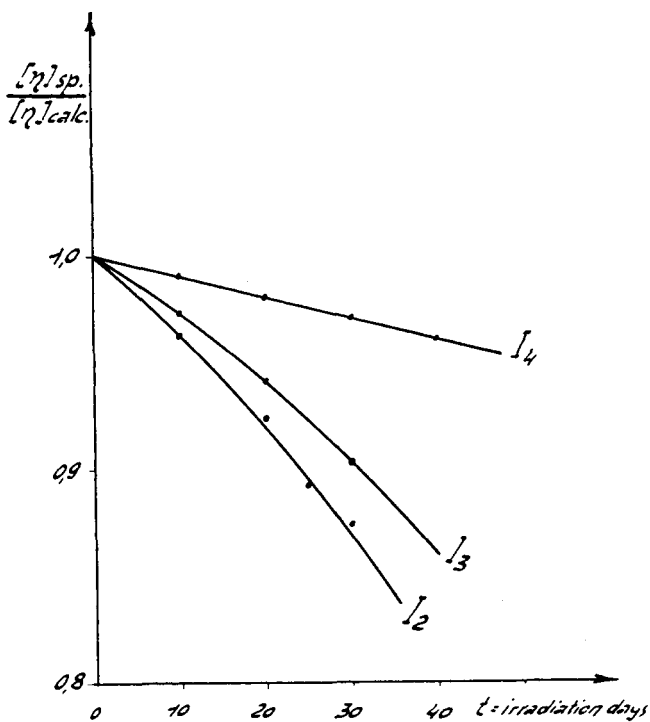
Radiation intensity	Irradiation time, days	Dose, Mr	$\bar{M}_w \times 10^{-5}$	$[\eta]$ (toluene, 25°C.), dl./g.	
I_4	0	0	0.43	0.257	
	2.33	0.252	0.52	0.265	
	6	0.648	0.52	0.260	
	9.16	0.990	0.37	0.260	
	12	1.298	0.48	0.270	
	16.21	1.750	0.43	0.265	
	18	1.944	0.41	0.270	
	20.92	2.259	0.47	0.262	
	23.12	2.497	0.38	0.250	
	26.12	2.821	0.42	0.260	
	30	3.240	0.39	0.252	
	I_1	0	0	0.43	0.257
		2.33	4.166	0.40	0.260
6		10.714	0.47	0.247	
9.16		16.363	0.47	0.248	
16.21		28.942	0.48	0.245	
23.12		41.292	0.48	0.243	
30		53.568	0.48	0.230	

Fig. 1. \bar{M}_w vs. irradiation time for PS₁₀₀.

chain with the same \bar{M}_w , calculated by eq. (3). This ratio is related to the degree of crosslinking of the polymer.⁷

Figure 3 shows this ratio plotted against irradiation time for PS₁₀₀.

The increasing slope of the curves indicates clearly that there is an in-

Fig. 2. $[\eta]$ vs. irradiation time for PS_{100} .Fig. 3. The $[\eta]_{sp.}/[\eta]_{calc.}$ ratio as a function of irradiation time for PS_{100} .

crease of the degree of crosslinking with time and with intensity. Therefore viscosity measurements have no meaning in calculating molecular weights, as $[\eta]$ may decrease while \bar{M}_w keeps constant. That is what happens for PS_{100} at I_4 .

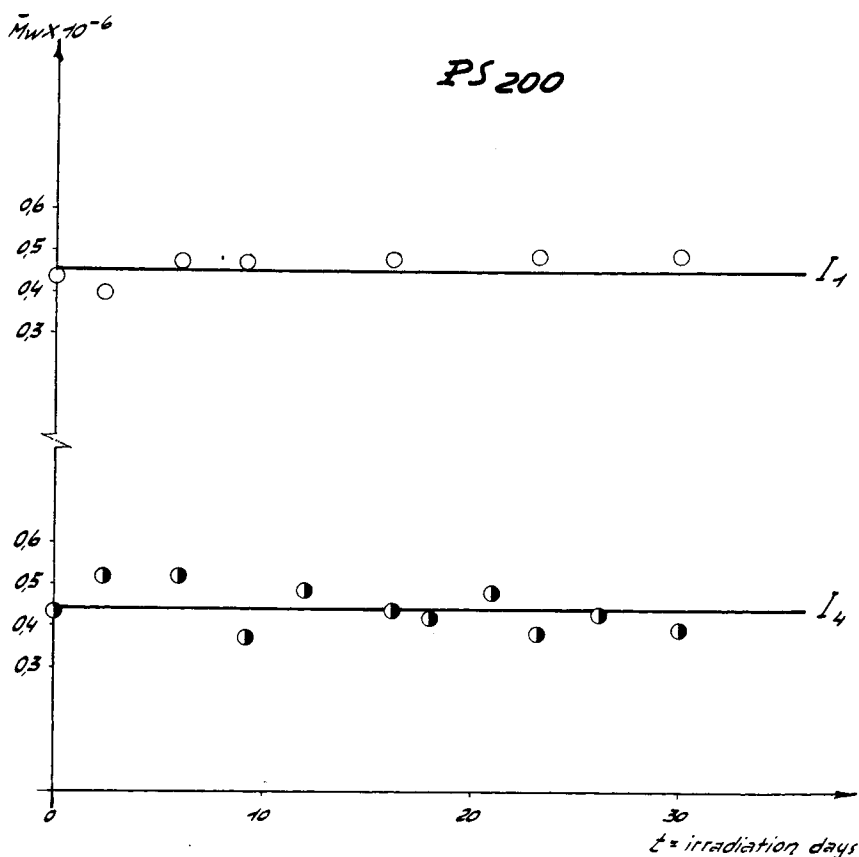


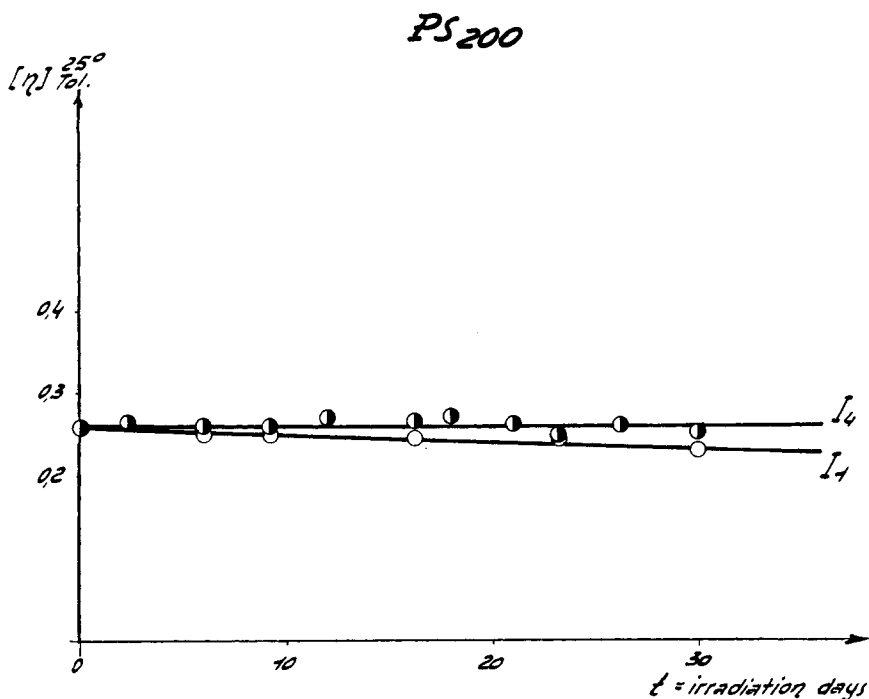
Fig. 4. \bar{M}_w vs. irradiation time for PS₂₀₀.

We arrive at a similar conclusion in the case of PS₈₀ and PS₁₄₀. For the lowest molecular weight sample, PS₂₀₀ (Figs. 4 and 5) it is noteworthy that at low intensity, both the molecular weight and the intrinsic viscosity remain constant; thus it appears that in this case, not even a molecular rearrangement takes place. This does not happen at the highest intensity I_1 , where again $[\eta]$ decreases while \bar{M}_w is constant, which means that the macromolecule undergoes a rearrangement.

We did not carry out irradiation experiments on PS₈₀ and PS₁₀₀ at the highest intensities as, in these cases, owing to their high initial molecular weights, we should have been too far away from the limiting molecular weight.

DISCUSSION

Tables III-VI and Figures 1-5 show clearly a general decrease of molecular weight as a consequence of irradiation. Within the limits studied, this decrease is apparently linear with time. While it is logical to expect slope

Fig. 5. $[\eta]$ vs. irradiation time for PS_{200} .

to decrease with intensity, it is interesting to note that, at the same irradiation intensity, it decreases also with decreasing molecular weight, approaching zero for sufficiently low molecular weights.

So, while PS_{100} shows a fair constancy in molecular weight only when irradiated at low intensity, \bar{M}_w for PS_{200} remains constant also at high intensity.

The slope of such lines, which gives the degradation rate $-d\bar{M}_w/dt$ (Table VII), tends therefore to zero for certain values of \bar{M}_w that are functions of radiation intensity.

The facts are best pointed out in Figures 6 and 7.

TABLE VII
Degradation Rates of the Four Polystyrene Samples at
Different Radiation Intensities

Sample	Degradation rate, $-d\bar{M}_w/dt^a$			
	I_4	I_3	I_2	I_1
PS_{200}	0	0	0	0
PS_{140}	0	0.21×10^2	0.52×10^2	1.25×10^2
PS_{100}	0	0.625×10^2	1.32×10^2	—
PS_{80}	1.1×10^2	3.2×10^2	—	—

^a Time expressed in hours.

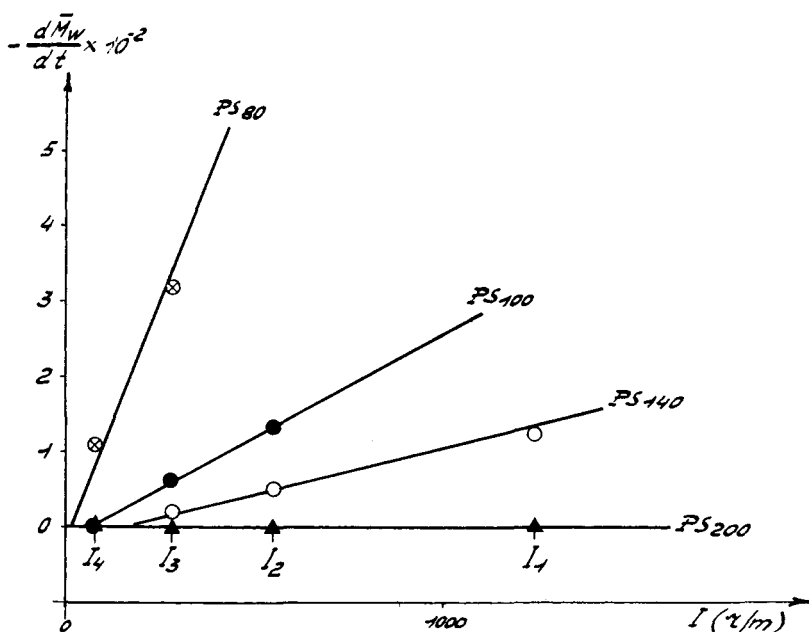


Fig. 6. Degradation rate vs. I for the irradiated polystyrenes.

In Figure 6 the degradation rate is plotted against radiation intensity. In the case of the polymer with lowest molecular weight ($M_0 = 43,300$) the rate value is zero whatever the intensity; this makes us think that the limiting molecular weight is higher than M_0 in any case.

PS₁₄₀ ($M_0 = 240,000$) is still degradable if intensity is at least equal to I_3 (280 r/min.). Interpolation on the corresponding line indicates that the degradation rate is zero for an intensity value between I_4 and I_3 (about 160–180 r/min.): we consider that this is the intensity to which a M_{lim} of about 240,000 corresponds.

Likewise a molecular weight of 616,000 would be the M_{lim} value for an intensity of about 70 r/min.

For the highest molecular weight ($M_0 = 1,112,000$) we had only two points, and the line shown in Figure 6 was drawn by analogy with the other ones.

For three of the polymers therefore, it appears that an intensity exists below which the chain is not degraded.

In Figure 7 the same degradation rates were plotted against M_0 values. The curves relative to each intensity intersect the abscissa at a point which is lower the higher the intensity.

The experimental data reported in these two plots seem to prove the existence of molecular weights stable to radiations.

We cannot say anything about the structural characteristics of such a molecule, but the curves of Figure 3 make us think that the chain is certainly more crosslinked than the starting polymer.

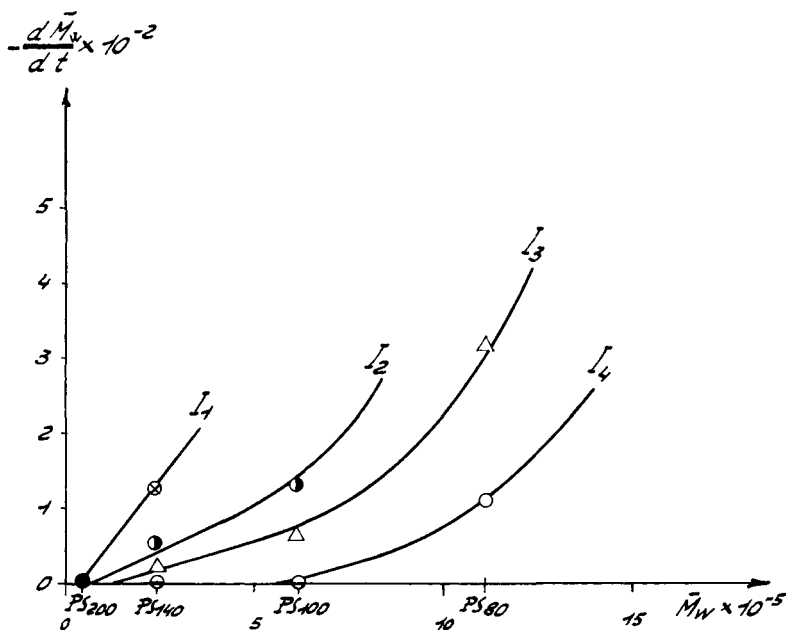


Fig. 7. Degradation rate vs M_0 for different I values

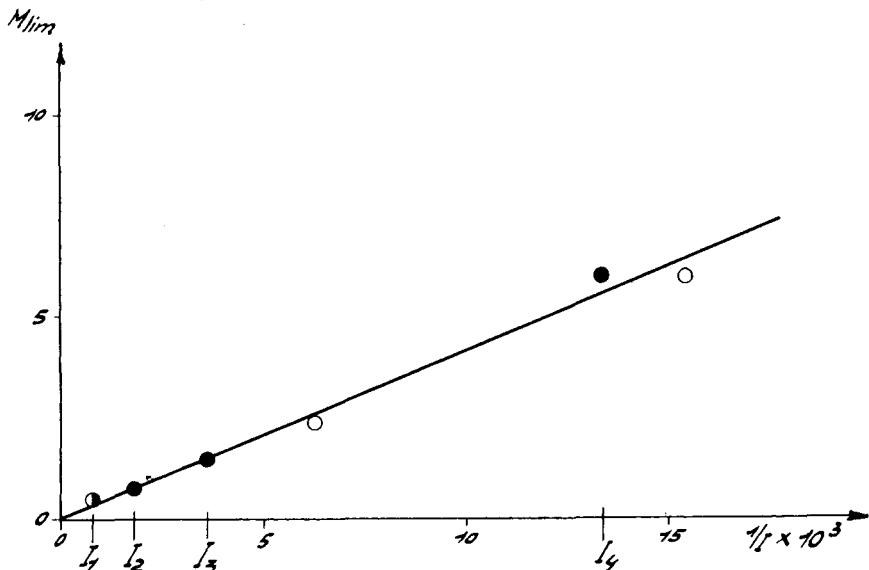


Fig. 8. Interpolated values of M_{lim} vs. $1/I$: (●) values of M_{lim} derived from Fig. 7, at which, for each intensity, $d\bar{M}_w/dt = 0$; (○) values of intensity derived from Fig. 6 at which, for each molecular weight, $d\bar{M}_w/dt = 0$.

However in the case of a polymer with sufficiently low molecular weight, like PS_{200} , not only is its \bar{M}_w constant, but its structure undergoes little or no change. In this case it would appear that an equilibrium between absorbed and dissipated energy is reached by the molecule.

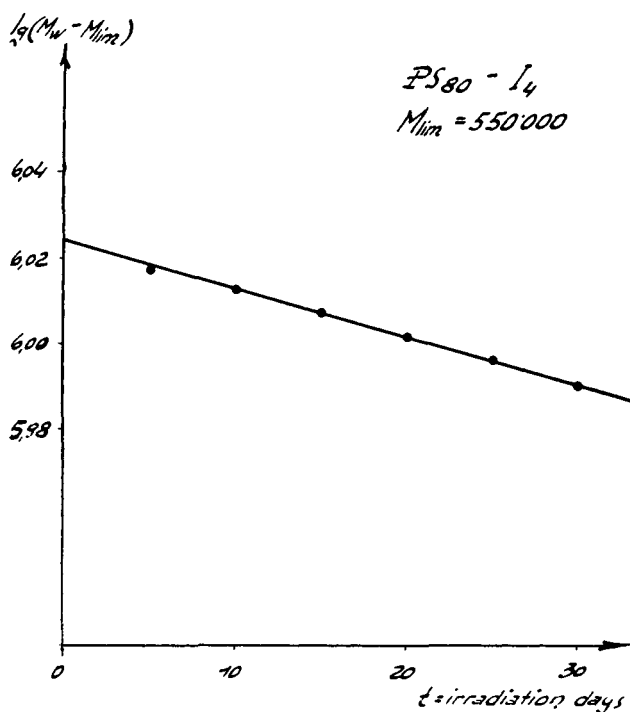


Fig. 9. Plot of $\log(M_w - M_{lim})$ as a function of irradiation time for PS_{80} at I_4 , assuming $M_{lim} = 550,000$.

It would have been interesting to irradiate the four samples at each intensity until M_{lim} were reached, but such a quantitative direct determination would take too long a time as, in our experimental condition, the degradation rates are very small. Only indicative values may be drawn from Figures 6 and 7.

Such interpolated values, plotted against $1/I$ (Fig. 8) lie on a straight line passing through the origin: eq. (1) is therefore verified also by the present experimental results.

It is possible also to check relation (2) put as:

$$\log(M - M_{lim}) = \log(M_0 - M_{lim}) - a'It \quad (4)$$

and we chose for this the data obtained for PS_{80} at I_4 , that is measurements which are far away from the M_{lim} value, so to avoid any errors due to the uncertainty of this interpolated value.

As it is shown in Figure 9, the points fall very well on a straight line.

CONCLUSIONS

More definite conclusions would require a larger number of data but, owing to the rigorous experimental technique necessary (purity of materials, complete exclusion of oxygen, accurate viscosity and light-scattering

measurements), each point requires laborious work and we were therefore obliged to limit the number of experiments.

Furthermore it must be pointed out that the phenomenon studied consists in small changes of viscosity and molecular weight and our results are affected by an experimental error of about $\pm 5\%$. Nevertheless, we believe that the following conclusions are valid.

(1) In complete absence of oxygen and in benzene solution polystyrene is degraded by γ -rays, the structure changing from a linear to a more or less crosslinked one.

(2) There is, at each intensity, a M_{lim} below which the polymer chain is not degraded; that is, a macromolecule, when irradiated, tends to break down to a limiting value characteristic of the employed intensity (temperature, concentration, and other factors being considered constant).

(3) A quantitative determination of such a M_{lim} is difficult; it is however possible to estimate its value by a rough interpolation of experimental curves. The M_{lim} values so obtained allow us to say that eqs. (1) and (2) appear to be valid.

(4) These experimental results are in accordance with our assumption of the existence of an equilibrium between absorbed and dissipated energy, connected with polymer molecular weight and radiation intensity. This conclusion would allow us to explain interaction mechanisms among radiations and macromolecules in a way different from usual.

We wish to thank Dr. G. Tealdo for helping during the preparation of samples under high vacuum.

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Résumé

Nous avons irradié avec les rayons γ quatre échantillons de polystyrène de poids moléculaires de 43.300 à 1.112.000, en solution benzénique à quatre intensités différentes. Les résultats expérimentaux obtenus par mesure de la viscosité intrinsèque et de la diffusion de la lumière sur les polymères irradiés nous ont conduit à confirmer que, à chaque intensité, il y a réellement un poids moléculaire au dessus duquel la chaîne polymérique n'est plus dégradée. Nous supposons l'existence d'un équilibre entre l'énergie que la macromolécule reçoit et l'énergie qu'elle peut dissiper. L'équation $M_{\text{lim}}I = \text{const}$, que nous avons supposée déjà dans un travail antérieur, est vérifiée par les résultats que nous avons obtenus.

Zusammenfassung

Vier Polystyrolproben mit Molekulargewichten von 43.000 bis 1.112.000 wurden in Benzollösung mit Gammastrahlen bei vier verschiedenen Intensitäten bestrahlt. Die Ergebnisse von Viscositäts- und Lichtstreuungsmessungen zeigen für jede Intensität die Existenz einer unteren Grenze des Molekulargewichts, unterhalb der die Polymerkette nicht mehr abgebaut wird. Es wird das Bestehen eines Gleichgewichtes zwischen der vom Makromolekül aufgenommenen und abgegebenen Energie angenommen. Die Versuchsergebnisse bestätigen die schon in einer früheren Arbeit abgeleitete Gleichung $M_{lim}I = const.$

Received February 11, 1964