

Molecular Weight Distribution of γ -Irradiated Poly(methyl methacrylate)

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ABSTRACT: The molecular weight distribution (MWD) of poly(methyl methacrylate) (PMMA) was measured as a function of the dose absorbed during γ -irradiation. MWD's were obtained from gel-permeation chromatograms with the aid of an analog computer, applying essentially a method proposed by Tung. If the initial MWD was rather broad, γ -irradiation caused it to become more narrow and, *vice versa*, if the initial MWD was rather narrow it became broader upon irradiation. In all cases a limiting value of $(\bar{M}_w/\bar{M}_n)=2$ was approached. This behavior meets with the expectations from the theory of random degradation and is, therefore, taken as evidence for radiation-induced random main-chain scissioning of PMMA.

KEY WORDS Molecular Weight Distribution / GPC / γ -Rays / Poly(methyl methacrylate) / Random Main-Chain Degradation /

The concept of random degradation of linear polymers has usually been applied for the evaluation of the radiation chemical yield $G(S)$ of main-chain scissions and for the development of theories concerning changes of the molecular weight distribution (MWD) of such polymers induced by ionizing radiation.¹⁻⁸ The term random degradation simply implies that the probability of bond rupture is equal for all base units of the system considered. The essential criterion for the occurrence of random main-chain scissions consists in the fact that the MWD changes with the absorbed dose in a well defined mode,⁹ as shall be explained below.

Only scarce experimental evidence for random degradation induced by ionizing radiation based on changes of MWD as a function of absorbed dose is available. Danon¹⁰ reported the narrowing of the MWD of a polyisobutylene sample possessing a rather broad initial MWD under the influence of γ -radiation. That result was obtained from combined measurements of the viscosity-average molecular weight \bar{M}_v and the number-average molecular weight \bar{M}_n (from osmotic pressure measurements). Furthermore, MWD changes measured by gel-permeation chromatography (GPC) by Herrick¹¹ with poly-

styrene irradiated in dilute solution with γ -rays indicated random degradation.

In the following we report on the changes of MWD derived from GPC measurements carried out with poly(methyl methacrylate) (PMMA) which was irradiated with ⁶⁰Co- γ -rays at room temperature. The radiation induced changes of PMMA have been investigated previously by several authors.¹²⁻²⁰ From these works it is inferred that PMMA is not simultaneously crosslinked upon main-chain degradation. The reported radiation chemical yields $G(S)$ vary considerably in the range of 1.2 to 2.6.

Changes of MWD Due to Random Degradation

Theoretical derivations of the dose dependence of MWD changes have to start with the assumption that the polymer sample possesses an initial molecular weight distribution of a defined type. In many cases the distribution is of the so-called Schulz—Zimm type.^{21,22} Based on Saito's integrodifferential equation¹ for random main chain scission, Inokuti and Dole⁷ have investigated theoretically the radiation induced MWD changes by assuming an initial Schulz—Zimm type distribution and no simultaneous crosslinking. They derived the following relationship for the dependence of the ratio $b=(\bar{M}_w/\bar{M}_n)$ on

the absorbed dose:

$$b = \frac{2(1+y_n)}{y_n} \left\{ 1 - \frac{1}{y_n} \left[1 - \frac{1}{(1+y_n/\sigma_0)^{\sigma_0}} \right] \right\} \quad (1)$$

with

$$y_n = \frac{G(S)D\bar{M}_{n,0}}{100N_A} \quad (2)$$

y_n , number of scissions per initial number average molecule;

σ_0 , $\bar{M}_{w,0}/(\bar{M}_{w,0}-\bar{M}_{n,0})$;

$\bar{M}_{n,0}$, initial number average molecular weight;

$\bar{M}_{w,0}$, initial weight average molecular weight;

$G(S)$, number of main chain scissions per 100 eV of absorbed energy;

N_A , Avogadro's number;

D , absorbed dose in eV/g.

For a so-called random distribution with $\sigma_0=1$, the initial value of b is two, and according to eq 1 it remains at this value upon random degradation. It is, furthermore, inferred from eq 1 that for a broad initial MWD, with $b>2$, b will decrease and approach 2 with increasing absorbed dose. On the other hand, b will increase and approach two if the initial MWD

is narrow ($b<2$).

Figure 1 shows curves calculated according to eq 1 for three samples of PMMA which were investigated during this work. The curves were calculated for values of $G(S)$ varying between 1.2 and 2.6. Since the variation of $G(S)$ in this range influences the relative position of the curves only slightly, it turns out that $G(S)$ can be estimated only roughly from the dependence of b on the absorbed dose, provided the initial value of b differs from two. However, if $b\neq 1$, it should be possible to find evidence of random degradation by measuring b as a function of the absorbed dose.

Characterization of Polymer Samples

The polymers used for the irradiations are compiled in Table I. Sample Z was provided by Röhm and Haas, Darmstadt. They were reprecipitated 4 times from acetone solution with methanol. Samples Z-II-4 and Z-I-4 were obtained by fractionation of sample Z from acetone solution with methanol.

The values of \bar{M}_w given in Table I were obtained by light-scattering measurements using a Sofica instrument (solvent: acetone). \bar{M}_n was determined by membrane osmometry in toluene using a Mechrolab Osmometer. In the cases of samples Z-II-4 and Z-I-4 values of both \bar{M}_w and \bar{M}_n agreed within the error limit of $\pm 10\%$ with the corresponding values derived by GPC (see below). For the unirradiated sample Z, the \bar{M}_w value is rather close to the exclusion limit of the GPC column set used. Thus in this case only the b_0 value obtained by light scattering and osmotic measurements was considered.

Irradiation of Samples

Polymer samples were degassed in glass ampoules by pumping on a vacuum line. The sealed glass ampoules containing polymer were irradiated with γ -rays of a cobalt-60 source.

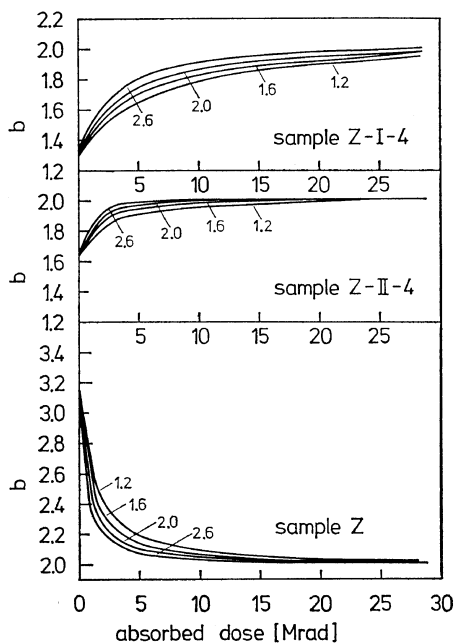


Figure 1. b vs. the absorbed dose. Values calculated according to eq 1 for $G(S)$ values given at the curves.

Table I. Characterization of PMMA samples used for irradiation experiments

Sample	\bar{M}_w	\bar{M}_n	$b_0 = \frac{\bar{M}_{w,0}}{\bar{M}_{n,0}}$	σ_0
Z	9.8×10^5	3.1×10^5	3.16	0.463
Z-II-4	5.3×10^5	3.3×10^5	1.6	1.65
Z-I-4	3.8×10^5	2.9×10^5	1.31	3.22

The absorbed dose rate as determined by the Fricke dosimeter ($G(\text{Fe}^{3+})=15.5$) was 0.63 or 1.8 Mrad hr⁻¹. A dose rate effect was not observed.

Determination of Molecular Weight Distributions

Gel-permeation chromatograms of irradiated and unirradiated samples were recorded with an apparatus of Waters in tetrahydrofuran solutions at 40°C using a set of 4 styragel columns. The flow rate was 1 ml/min. The evaluation of the MWD from the chromatograms was based on the calibration curve shown in Figure 2. It was obtained with a series of PMMA fractions of narrow MWD covering the range $M=3 \times 10^4$ to $M=2 \times 10^6$. For our computation scheme we applied a method proposed by Tung.²³ According to this method it is assumed that a chromatogram of a monodispersed sample can be represented in terms of the elution volume v by the Gaussian function:

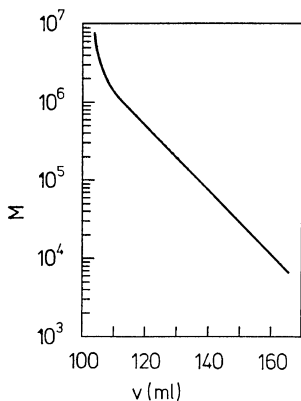


Figure 2. Calibration curve used for the determination of molecular weight distributions. Molecular weight vs. elution volume: four 1-m styragel columns, 3×10^3 , 3×10^4 , 10^5 , and 1.5×10^6 A.

Table II. Resolution factors of the GPC column system^a

\bar{M}_w	\bar{M}_n	Elution vol. v_0 , ml	Resolution factor, ml^{-2}		
			h_f	h_r	h
1.23×10^4	1.21×10^4	165.2	0.0519	0.0107	0.0177
9.81×10^4	9.76×10^4	142.2	0.0431	0.0153	0.0226
5.07×10^5	4.98×10^5	119.6	0.0373	0.0157	0.0220

^a Determined with polystyrene standard samples, obtained from Mann Research Laboratories, Inc.

$$F(v) = A \exp(-h(v-v_0)^2) \quad (3)$$

v_0 denotes the elution volume at the peak of the chromatogram. A is a constant related to the concentration of the sample. h is a factor referring to the width of the Gaussian curve and depends on the resolution of each column system. We determined h by the reversed flow method of Tung²³ for three polystyrene samples of different molecular weights. The results are shown in Table II. The overall resolution factor h was calculated according to the formula

$$h = \frac{2}{(1/h_f) + (1/h_r)} \quad (4)$$

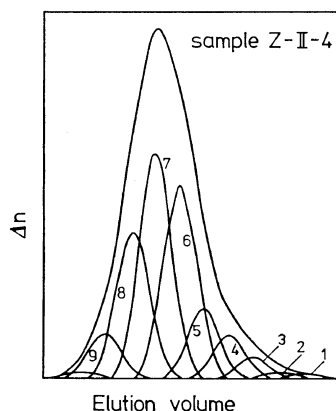


Figure 3. Typical example for the resolution of a chromatogram with the aid of the curve resolver, unirradiated sample Z-II-4.

Table III. Resolution of a chromatogram of Z-II-4

Fraction number	v_0 , ml	$\bar{M} \times 10^{-5}$	Area, ^a arbitrary units	Weight fraction w , %	$I(M)$ ^b
1	150	0.33	4	0.53	0.265
2	145	0.52	4	0.53	0.794
3	140	0.83	19	2.5	2.32
4	135	1.31	41	5.4	6.28
5	130	2.09	65	8.6	13.3
6	125	3.33	199	26.3	30.8
7	120	5.30	225	29.8	58.8
8	115	8.44	150	19.8	83.6
9	110	13.4	44	5.8	96.4
10	105	21.4	5	0.66	99.7

^a Area under the Gaussian curve.

^b Total weight fraction up to M_i .

where h_f and h_r designate the resolution factors for the front half and the rear half of the column system. From Table II it can be inferred that the variation of h as a function of v is negligibly small. Thus, the constant value $h=0.022$ was used throughout the calculations. It was assumed that the chromatogram of a polydispersed sample is a composite of the Gaussian curves of all its components. Thus, an analog computer (310 Curve Resolver of DuPont) was used to resolve the chromatograms. Figure 3 and Table III show as a typical example the resolution of the chromatogram of the unirradiated sample Z-II-4 into 10 Gaussian curves. Molecular weight values M_i were obtained from the $v_{0,i}$ values of the Gaussian curves. Weight fractions w were calculated from the areas under the Gaussian curves. Based on these w values the function $I(M)$ of the integral MWD was derived. Average molecular weight values were obtained according to the following expressions:

$$\bar{M}_n = \frac{\sum w_i}{\sum (w_i/M_i)}, \quad \bar{M}_w = \frac{\sum w_i M_i}{\sum w_i}$$

Molecular Weight Distributions of Irradiated Polymer Samples

Figure 4 shows typical examples of the gel-permeation chromatograms obtained with PMMA samples of initially broad (Figure 4a) and narrow (Figure 4b) distribution. The chromatograms demonstrate that the molecular weight decreases with increasing absorbed dose and that the MWD

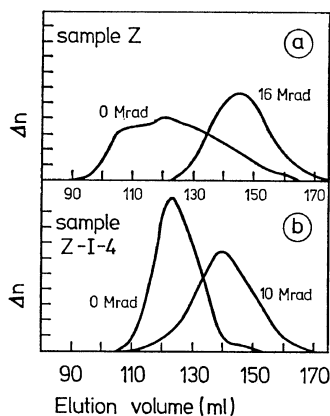


Figure 4. Gel-permeation chromatograms of unirradiated and irradiated PMMA samples: (a) initially broad MWD; (b) initially narrow MWD.

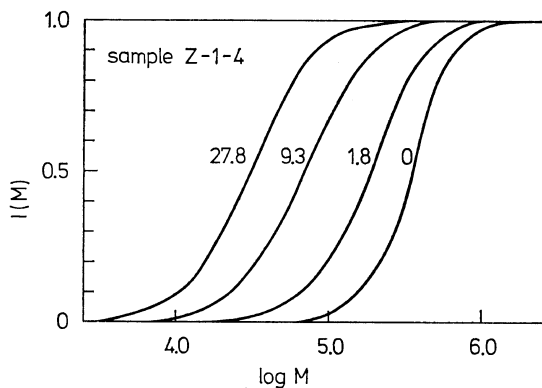


Figure 5. Integral distribution curves obtained from gel-permeation chromatograms obtained with sample Z-I-4. Absorbed doses are given at the curves in Mrad.

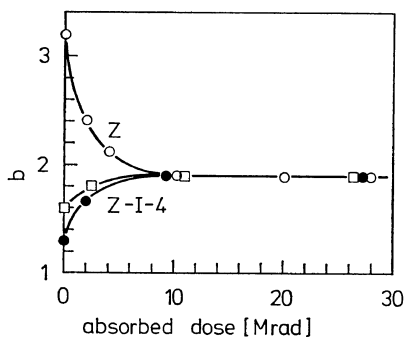


Figure 6. b as a function of absorbed dose. Values obtained from gel-permeation chromatograms of irradiated and unirradiated samples as described in the text: \circ , sample Z; \bullet , sample Z-I-4; \square , sample Z-II-4.

becomes more narrow for the initially broad distribution. In the cases of initially narrow MWD, the distributions become broader with increasing absorbed dose. Figure 5 shows typical examples for the integral distribution curves obtained from the chromatograms as described above. b values obtained from the MWD curves were plotted versus the absorbed dose in Figure 6. As expected for random degradation, b decreases and approaches a value close to two with increasing dose. Conversely, b is augmented with increasing dose in the two cases with initially narrow MWD. The fact that b does not become exactly equal to two is probably due to inaccuracies concerning the cali-

bration curve. However, the general behavior observed for the radiation induced changes of the MWD corresponds widely to the expectations based on the theory of random degradation. Thus, the reported results may be taken as evidence for radiation-induced main-chain ruptures occurring at random.

Reciprocal values of \bar{M}_w obtained in the dose range between 10 and 30 Mrad, where the MWD does not change any more, were plotted *versus* the absorbed dose. The slopes of the straight lines thus obtained yielded $G(S)=1.75 \pm 5\%$.

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