Polymerization Mechanisms and Molecular Weight Distributions. III. Gamma-Radiation-Initiated Polymerization of Methyl Methacrylate

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Synopsis

The termination mechanism in gamma-radiation-initiated polymerization of methyl methacrylate was investigated. The termination mechanism and the associated rate constants were determined by comparing the theoretical molecular weight distribution (MWD) and the experimental MWD, which was determined by gel permeation chromatography. Disproportionation occurs 1.2 times as frequently as combination at 30°C and 0.5 times as frequently at 0°C. The activation energy for disproportionation is 5.5 kcal/mole greater than that for combination. The rates of initiation were determined by a new method and were found to compare well with those reported in the literature. It is also suggested that it is necessary for the theoretical MWD to have the same shape as the experimental MWD before a mechanism can be authenticated.

INTRODUCTION

In many radical chain polymerizations it is found that the rate of polymerization is proportional to the square root of the initiator concentration. Kinetic analysis shows that the deactivation can occur in two distinct mechanisms, namely, combination and disproportionation.

Since a polymer chain is initiated by a fragment of an initiator molecule, termination by combination will lead to two such fragments per molecule, and disproportionation, on the other hand, will lead to one fragment per molecule.

Initiator molecules containing radioactive atoms have been employed in investigation of the termination mechanism of several monomers.[1,2] Termination by combination has been shown[1,3] to be the predominant mechanism for polystyrene. However, poly(methyl methacrylate) has been reported to terminate by both mechanisms,[1,2] the ratio of the two steps being a function of temperature.

In a previous paper[4] a new method for determining the kinetic rate constants from the molecular weight distributions (MWD) was proposed. The method utilizes the molecular weight distributions as the main criterion for evaluating the mechanism and the associated kinetic rate constants. The particular criterion function applied is

$$\underset{\theta}{\text{Minimize}} \int_0^\infty [y(r,\theta) - y_E(r)]^2 \, dr$$

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where $y(r,\theta)$ is the theoretical MWD and is a function of r, the molecular chain length, and θ, the vector of kinetic rate constants, and $y_E(r)$ is the experimental MWD.

The work described in this paper pertains to the termination mechanism and the G values of poly(methyl methacrylate) as calculated from the molecular weight distribution.

EXPERIMENTAL

The experimental details and results have been published elsewhere.[5] However, for continuity of thought, the experimental details pertaining to the molecular weight distribution, which is the central theme of this paper, will be described in detail.

The molecular weight distributions of the poly(methyl methacrylate) PMMA were determined by gel permeation chromatography using a Waters model 200 GPC unit. Four elution columns packed with crosslinked polystyrene gel of pore sizes 10^6, 10^5, 10^4, and 10^3 Å, respectively, were used.

Calibration was performed using 11 monodisperse polystyrene standard samples (Pressure Chemical Company) having average molecular weights of 900, 2,100, 4,800, 10,300, 19,800, 51,000, 97,000, 160,000, 411,000, 860,000, and 1,800,000. Calibration followed the universal calibration concept proposed by Boni.[6] Resolution factors were determined by following the method proposed by Tung.[7]

Tetrahydrofuran (THF) was used as the eluting solvent. Samples for analysis were made up as 0.25 wt % solutions and filtered to remove foreign material. A 2-ml portion of each of these samples was maintained. The oven temperature was kept at $(25 \pm 0.5)°C$.

Since monodisperse poly(methyl methacrylate) standards were not available, the polystyrene calibration curve was transformed to a PMMA calibration curve. The relation

$$\log M_{\text{MMA}} - \log M_{\text{STY}} = \frac{1}{1 + a} \log \frac{K_{\text{MMA}}}{K_{\text{STY}}} \tag{1}$$

proposed by Williams and Ward[8] was used to transform the polystyrene calibration curve to PMMA calibration curve. Equation(1) correlates the molecular weight of two different molecular species by assuming that the hydrodynamic volume is the important parameter causing separation. The constants K and a are the constants in the Mark–Houwink equation. The values of these constants measured under identical conditions[9] are, for poly(methyl methacrylate), $K = 0.76 \times 10^4$, $a = 0.76$; for polystyrene, $K = 1.03 \times 10^4$, $a = 0.745$.

Taking a mean value of a the relation between the calibration curves is

$$M_{\text{MMA}}/M_{\text{STY}} = 1.018$$

This means that both curves are nearly identical. The calibration curve for polystyrene is shown as Figure 2 in reference 10.

The number-average $(\overline{M}_n)$ and weight-average $(\overline{M}_w)$ molecular weights and the corrected molecular weight distributions were calculated according to the method of Tung.[11]

DISCUSSION

The MWD of poly(methyl methacrylate), PMMA, will prove to be most interesting since the termination mechanism is a function of temperature. Thus, one would expect the broadness of the MWD to change with temperature because the polydispersity ratio is related to the termination mechanism.

Bevington et al.[1] have shown termination by disproportionation to be favored by higher temperatures. The ratios of combination to disproportionation (k_{tc}/k_{td}) was reported at 60°C as 0.174, at 25°C as 0.47, and at 0°C as 0.67; and an activation energy for termination ($E_{td} - E_{tc}$) was reported as 4.0 kcal/mole.[1] Schulz et al.[2] reported an activation energy between 6 and 7 kcal/mole.

The method proposed for mechanistic and kinetic analyses in the previous paper[4] was applied to the molecular weight distribution of PMMA. Results obtained are shown in Table I; included for comparison are the results of Bevington et al.[1] The activation energy calculated from these data is 5.5 kcal/mole.

The quantitative analysis carried out above yielded values for the ratio of the two types of bimolecular termination made possible by polymeric free radicals. However, an inherent assumption, concerning the shape of the MWD, was made in the above analysis; that is, one expects the experimental distribution to follow the "normal" distribution which is typical of the free-radical polymerization of vinyl monomers. Thus, a qualitative treatment of the MWD should also be conducted.

The polydispersity ratio, $\overline{M}_w/\overline{M}_n$, is generally used as a measure of the broadness of MWD; for example, at −40°C the polydispersity ratio is 1.50, which indicates termination by combination and negligible chain transfer. However, in order to make the above conclusion the distribution must be normal, and only then will there be some relationship between the mechanism of polymerization and polydispersity ratio.

The normal distribution can be conveniently defined by Schulz's distribution[12]:

$$W_M = \frac{(-\ln \alpha)^{b+2}}{\Gamma(b + 2)} M^{b+1}\alpha^M \qquad (2)$$

TABLE I

Polydispersity and Proportion of Termination by Disproportionation for Methyl Methacrylate at Various Temperatures[a]

Temp., °C	$\overline{M}_w/\overline{M}_n$	Standard deviation	Variance	k_{tc}/k_{td}[b]	k_{tc}/k_{td}[c]
60	—	—	—	—	0.17
45	2.4231	0.1017	0.0078	0.0	—
30	1.9643	0.1865	0.0261	0.85	—
25	—	—	—	—	0.47
15	2.0332	0.1804	0.0260	1.32	—
0	1.7525	0.1431	0.0154	2.01	0.67
−25	1.6269	0.1354	0.0122	7.32	—
−40	1.5151	0.0649	0.0280	—	—
−45	1.5693	0.0921	0.0057	—	—

[a] Values based on at least three separate experiments.
[b] Values calculated from MWD.
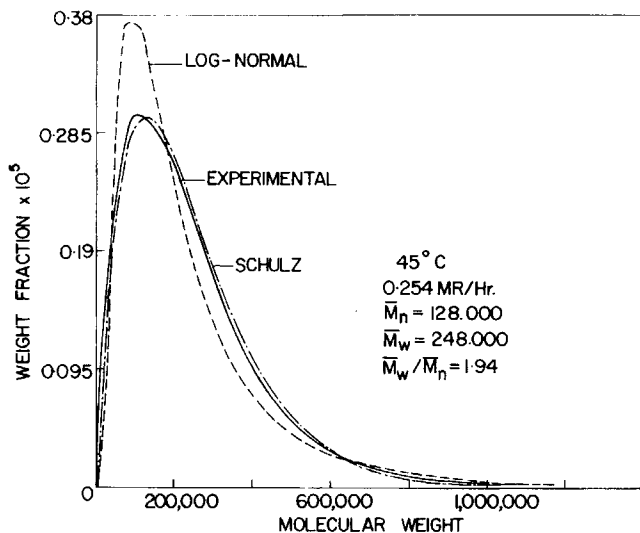[c] Data of Bevington et al.[1]

Fig. 1. Plot of weight fraction versus molecular weight for γ-ray-induced polymerization of MMA: 45°C; 0.254 Mrad/hr, $\overline{M}_n = 128.000$, $\overline{M}_w = 248.000$, $\overline{M}_w/\overline{M}_n = 1.94$.

where α and b are constants and M is molecular weight.

The log-normal distribution as given by Lansing and Kraemer[13] is

$$W_M = \frac{1}{\beta\sqrt{\pi}} \frac{1}{M} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{M}{M_0}\right) \qquad (3)$$

where β and M_0 are constants.

It turns out, however, that the distributions at -25, -40, and $-45°C$ are closer to the log-normal distribution than to the normal distribution. The MWDs of samples at 45, 15, -25, -40, and $-45°C$ are shown in Figures 1 to 5, respectively.
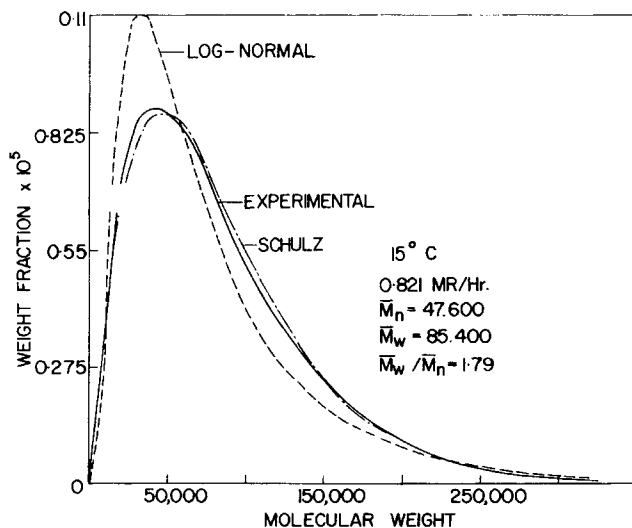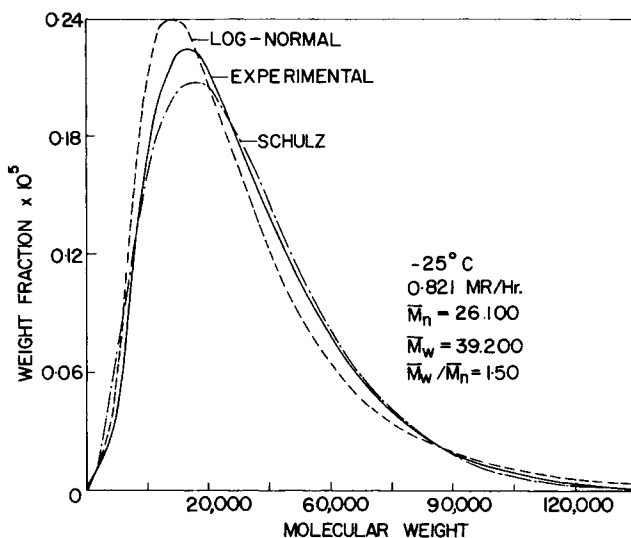

Fig. 2. Plot of weight fraction versus molecular weight for γ-ray-induced polymerization of MMA: 15°C, 0.821 Mrad/hr, $\overline{M}_n = 47.600$, $\overline{M}_w = 85.400$, $\overline{M}_w/\overline{M}_n = 1.79$.

Fig. 3. Plot of weight fraction versus molecular weight for γ-ray induced polymerization of MMA: $-25°C$, 0.821 Mrad/hr, $\overline{M}_n = 26.100$, $\overline{M}_w = 39.200$, $\overline{M}_w/\overline{M}_n = 1.50$.

We see that the MWD at 15°C still has the typical shape of normal distribution; however, at $-25°C$ the MWD is noted to be closer to log-normal than to normal distribution; at -40 and $-45°C$ the distributions show definite conformity to the log-normal distributions. The change in the shape of the MWD seems to indicate some abnormalities in the reaction mechanism at these low temperatures. Casey and Jenkins[14] have recently reported unexplainable reactivity ratios for the copolymerization of methyl methacrylate and styrene between -30 and $-55°C$, which tends to strengthen the above findings.

The log-normal distribution may be a result of low molecular weight polymer "cutoff" during precipitation of polymer from solution, where K is a characteristic
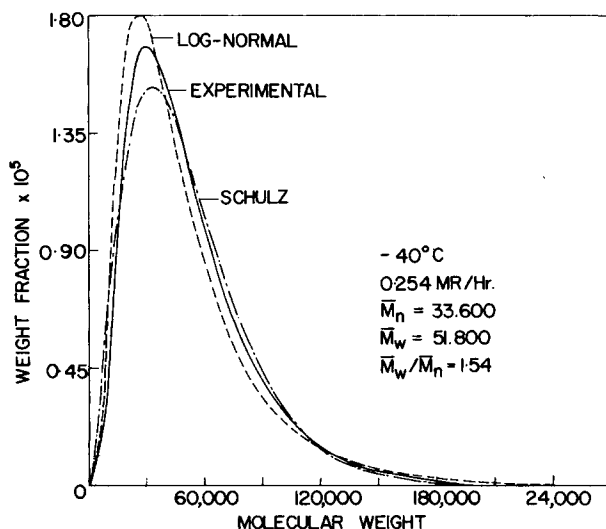

Fig. 4. Plot of weight fraction versus molecular weight for γ-ray-induced polymerization of MMA: $-40°C$, 0.254 Mrad/hr, $\overline{M}_n = 33.600$, $\overline{M}_w = 51.800$, $\overline{M}_w/\overline{M}_n = 1.54$.
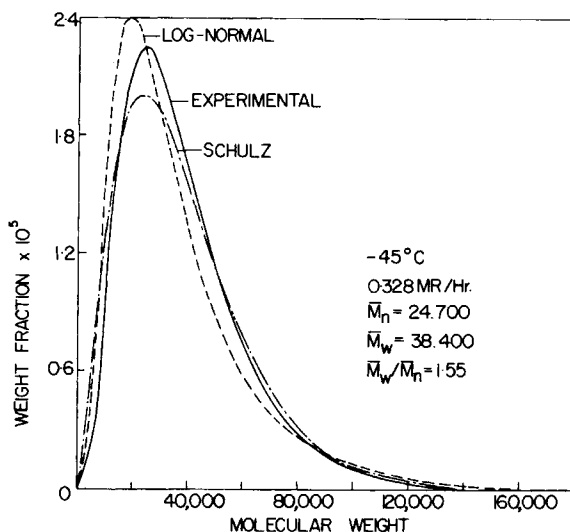
Fig. 5. Plot of weight fraction versus molecular weight for γ-ray-induced polymerization of MMA: $-45°$C, 0.328 Mrad/hr, $\overline{M}_n = 24.700$, $\overline{M}_w = 38.400$, $\overline{M}_w/\overline{M}_n = 1.55$.

constant for a particular system and is 0.955×10^{-9} for methyl methacrylate[18] and I is the dose rate in rad/sec. The method developed for determining the rate of initiation from the MWD can also be modified so as to be useful for radiation initiated polymerizations:

$$G = \frac{R_p}{IK}\left(\frac{1-p}{p} - C_M\right) \qquad (5)$$

The data of Mayer,[5] including the C_M values, were utilized in calculating the G values for methyl methacrylate. Table II shows the G values calculated from eq. (5).

Values obtained using eq. (5) are in good agreement with those reported in the literature.[18] It is worthwhile to point out that these values were calculated without the $(k_{tc} + k_{td})/k_p{}^2$ values, which is the standard way of calculating G.[18]

In conclusion, then, the molecular weight distribution has been shown to yield the bimolecular termination mechanism and G values for methyl methacrylate. In a more general sense, the molecular weight distribution of polymers contains considerable information regarding the mechanism and kinetics of its formation.

TABLE II
G Values for Gamma Radiation-Initiated Polymerization of Methyl Methacrylate

Temp., °C	Dose rate, rad/sec	G^a	G^b
45	228	3.56	3.76
	22	7.90	6.98
15	91	4.30	3.18
	71	3.60	2.96
	22	3.44	2.88

[a] Values obtained from eq. (4).
[b] Data reported by Mayer.[5]

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