

Molecular Weights of Polymethyl Methacrylate in Rubber-Methyl Methacrylate Graft Copolymers

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INTRODUCTION

In an earlier communication¹ ultraviolet and gamma radiation were shown to be effective initiators for the preparation in latex form of graft polymers from natural rubber. The methyl methacrylate system afforded reproducible data, and an attempt was made² to estimate the speeds of the fundamental reactions involved from kinetic considerations. The experimental findings for γ -radiation-induced graft copolymerization of methyl methacrylate (MMA) and rubber were consistent with a slow propagation reaction from the stem polymer radicals and a rapid cross-termination reaction between these radicals and the growing methacrylate chains. In arriving at these conclusions it was assumed that methacrylate chains terminated by disproportionation, whereas the cross-termination reaction was combination. It is the purpose of this paper to examine how far the molecular weights and molecular weight distributions of the polymerized methyl methacrylate agree with this hypothesis.

EXPERIMENTAL

The graft polymers were prepared as described previously,¹ and samples of homopolymer were isolated by extraction with acetone. Rubber was removed from the graft polymer by treatment with ozone and the liberated polymethyl methacrylate (PMMA) isolated and purified. Fractionations were carried out by the method described by Baker and Williams.³ Certain modifications in the solvent feed and fraction collection assemblies were made which gave more satisfactory operation over long periods of time than did the original apparatus described by Baker and Williams. The column had the dimensions 35×2.4 cm. and the Ballotine glass beads (0.1 mm. diameter) were supported on a No. 2 sinter. A temperature gradient of 50° C. along its length was used. Jets

were not satisfactory in maintaining steady flow rates through the apparatus and the best results were obtained with the use of a direct solvent feed and with control of the flow by means of a long taper needle valve. This valve required some adjustment at intervals during a run as the viscosity increased, but a constant flow was generally maintained over long periods without altering the setting. The mixing vessel was connected to the solvent reservoir, a mercury seal being used to prevent ingress of air. A magnetic stirrer (Nilo K) was used to mix the solvents. A simple make-break electrical circuit in the collecting vessel proved unreliable due to contact chatter. Siphoning of the sample near the time at which the turntable operated frequently resulted in an empty tube and transfer of two fractions to one tube; on occasions the solution siphoned over as the turntable was moving and the fraction was lost. This trouble was overcome completely by using a change in the inductance in a coil wound on the collection chamber, brought about by the rise of a metal float, to actuate the turntable mechanism. This system has the advantage that there are no internal electrical contacts. The circuit used is shown in Figure 1. It was desirable to collect about 5% of the sample in each tube and, as there was a tendency for somewhat larger fractions to be obtained in the later stages of the fractionation, solvent was added manually from a vessel at the base of the column. In practice about forty 10-ml. fractions were collected, but 97% of the polymer would be collected in twenty-five tubes. The time for fractionation depended on the molecular weight of the sample, but in the molecular weight region 10^5 – 5×10^5 , samples were collected at intervals of 2 hours. If shorter periods were used, fractionation would proceed normally until 50–75% of the polymer had left the column; then the molecular weights of the later fractions would fall steadily as fractionation proceeded. This regres-

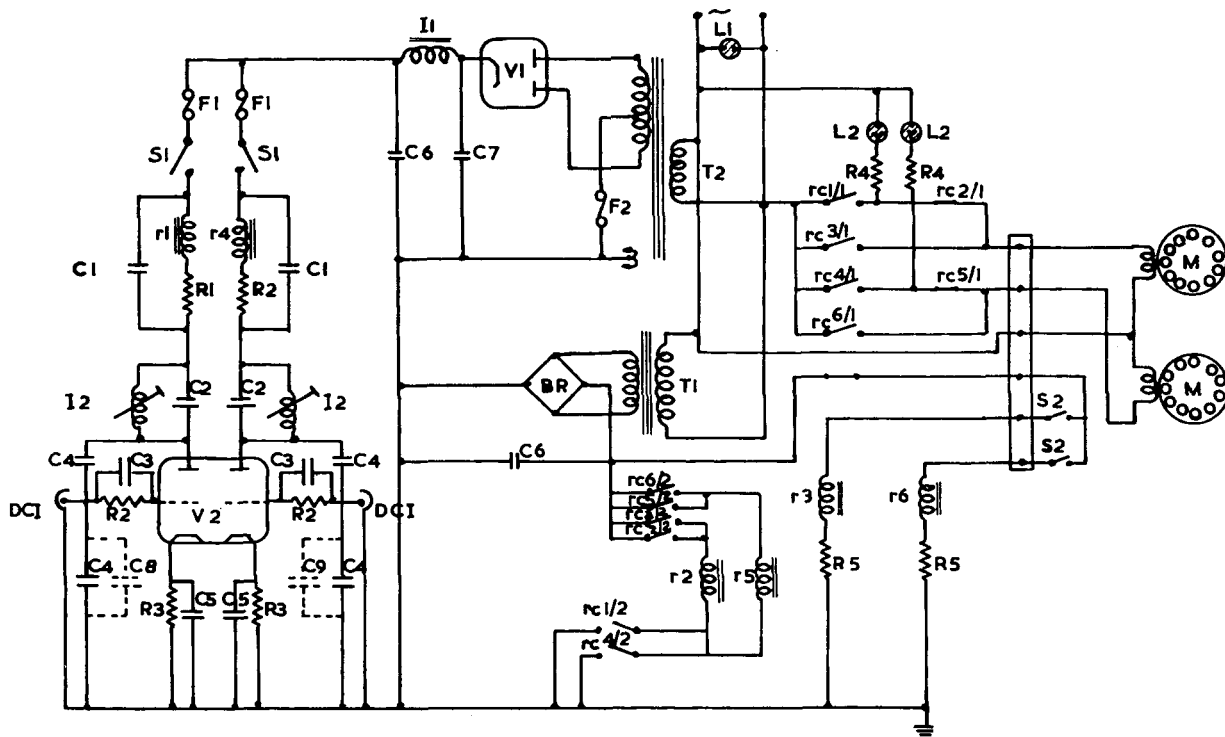


Fig. 1. Circuit diagram of fraction collecting apparatus designed to allow the simultaneous operation of two columns. *Resistors*: (R1) $10^4 \omega$, 1 w.; (R2) $3.3 \times 10^6 \omega$; (R3) $1.5 \times 10^5 \omega$; (R4) $1.2 \times 10^5 \omega$; (R5) $10^3 \omega$. *Capacitors*: (C1) 0.01 $\mu\text{f.}$; (C2) 147 pf.; (C3) 10^3 pf.; (C4) 5 pf.; (C5) 5 $\mu\text{f.}$; (C6) 16 $\mu\text{f.}$; (C7) 8 $\mu\text{f.}$; (C8) and (C9) effective capacitance of coaxial down lead. *Lamps*: (L1) 230 v., 0.5 w.; (L2) 120 v., 0.1 w. *Inductances*: (I1) 20 H, 40 $\mu\text{a.}$; (I2) 40 μH , dust core variable. *Relays*: (r1), (r3), (r4), and (r6) $2 \times 10^3 \omega$; (r2) and (r5) $6 \times 10^3 \omega$. *Valves*: (V1) EZ80 rectifier; (V2) ECC 82 double triode. *Switches*: (S1) main switches; (S2) cam operated microswitches to limit motor movement to $1/24$ rev. (M) Turntable motors (1 r.p.m.). (BR) Bridge rectifier S.T.C. type B25-2-lw. (DCI) Detector coil input. *Transformers*: (T1) 230-24 v., 2a.; (T2) 350-0-350, 35 ma.; 3.15-0-3.15, ma. *Fuses*: (F1) 10 ma.; (F2) 100 ma.

sion of molecular weights was a general phenomenon and often occurred to some extent with other polymers, particularly when molecular weights were over 5×10^5 . It could, however, be greatly reduced by slowing down the flow rate through the column. The equipment used is shown in Figures 2, 3, and 4.

The capacity of this column was about 250 mg., and the choice of solvents to give satisfactory elution of polymethyl methacrylate was 80/20 petroleum naphtha/benzene in the mixing vessel at the head of the column and 25/75 petroleum naphtha/benzene in the reservoir.

The fractions obtained were transferred to small tared flasks and solvent removed by freeze drying. After being weighed, the polymers were dissolved in benzene (3 to 8 ml., depending on the size of the sample) and the viscosities determined in small Ostwald viscometers.

RESULTS AND DISCUSSION

The systems examined are outlined in Table I. It can be seen that the average molecular weights of the two homopolymers differ only

TABLE I

Composition of system	Rubber, 100 MMA, 50	Rubber, 100 MMA, 60
Initiation	Photo (9.6×10^{17} q/kg./sec.) (1% CAQ on monomer) ^a	⁶⁰ Co gamma radiation (3.6×10^{11} e.v./kg./sec.)
Temperature, °C.	30	30
Conversion, %	~100	91
Graft, %	66	87
[η] Extracted PMMA	0.83	1.18
[η] Grafted PMMA	0.90	1.10

^a 1-Chloroanthraquinone.

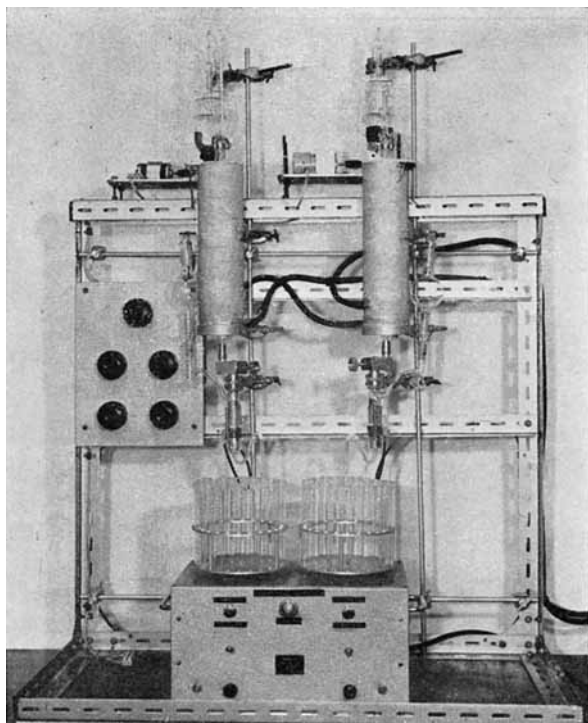


Fig. 2. Column fractionating apparatus.

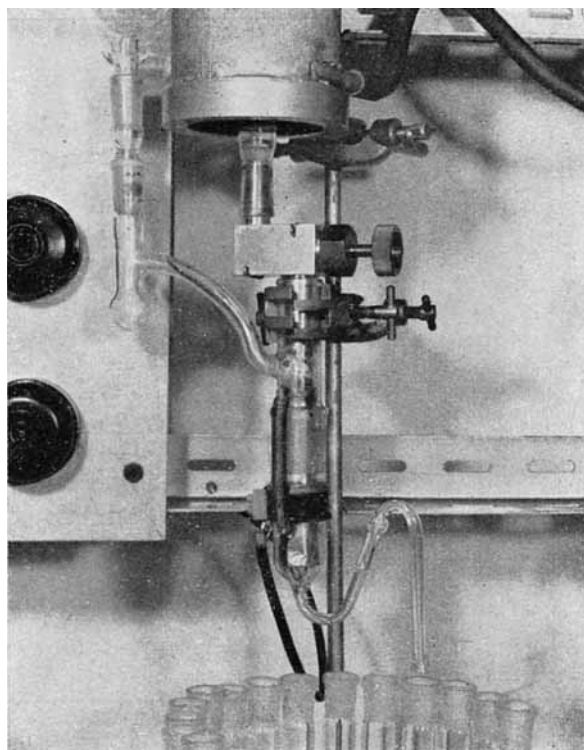


Fig. 3. Details of tap, siphon, detector coil, and float of fractionation apparatus.

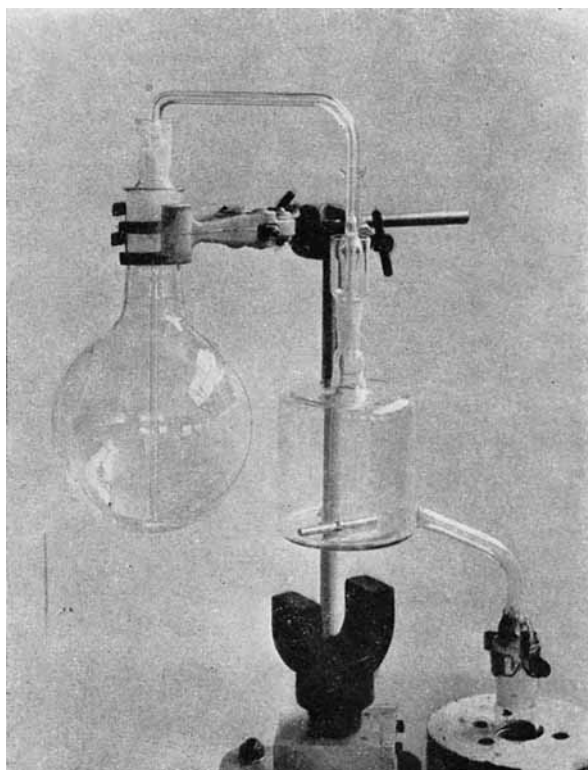


Fig. 4. The apparatus used for obtaining the necessary solvent gradient and mixing. The composition of solvents in the two vessels and the capacity of the mixing vessel determine the actual gradient used.

slightly from those of the corresponding grafted polymers. This is as would be expected, since the growing methacrylate radicals, whether grafted or not, are subject to the same terminating mechanisms.

The integral distribution curves afforded by fractionation are shown in Figures 5 and 6. Several features are apparent. The distributions of the two homopolymers are broad, with no single well defined peak. Changes in slope of the curve show peaks rising from the broad distribution of species at molecular weights of 100,000 and 450,000 in the case of the γ -initiated reaction, and at molecular weights of 100,000 and 400,000 for the photo-initiated polymerization. With the grafted polymers there is a similar breadth of distribution, but the peaks of low molecular and high molecular weight polymer are more clearly defined. For the gamma-initiated system they are at molecular weights of 100,000 and 550,000, and for the photo-initiated system at molecular weights of 40,000 and 510,000.

The mechanism proposed for this process is one in which there is a constant input of free radicals throughout the reaction, these free radicals result-

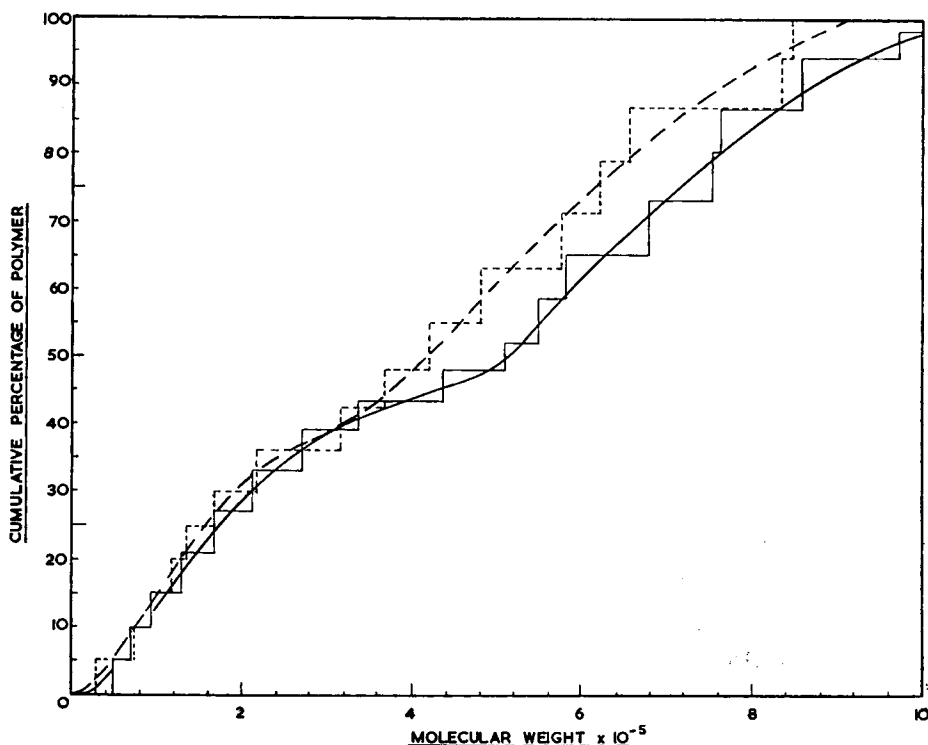


Fig. 5. Integral weight distribution curves for γ -initiated graft copolymers of natural rubber and methyl methacrylate. (—) grafted polymethyl methacrylate; (---) free polymethyl methacrylate.

ing from the solvent (natural rubber), the monomer, and the polymer produced. As a first approximation it was assumed that the G value for these components was the same. In the kinetic scheme which was suggested, the degree of polymerization \overline{DP} is given by the relationship:

$$\overline{DP} = \frac{k_p[M][\Sigma Mr\cdot] + k_p'[M][R\cdot] + k_p''[M][Pu_1\cdot]}{k_t[\Sigma Mr\cdot]^2 + k_{t_1}[R\cdot][\Sigma Mr\cdot] + k_{tr}[M][\Sigma Mr\cdot]} \quad (1)$$

where the concentration of rubber radicals $[R\cdot]$ is given by:

$$[R\cdot] = \frac{k_{t_2}[\Sigma Mr\cdot]^2 - [M]DG/N}{k_p'[M] - k_{t_1}[\Sigma Mr\cdot]} \quad (2)$$

and where

- $[\Sigma Pu\cdot]$ = Concentration of ungrafted radicals
- $[\Sigma Pg\cdot]$ = Concentration of grafted radicals
- $[\Sigma Mr\cdot] = [\Sigma Pg\cdot] + [\Sigma Pu\cdot]$
- D = dose rate, e.v./g./sec.
- G = radical yield/100 e.v.
- N = Avogadro's number

and k_p, k_p', k_p'' are the propagation constants from methacrylate, rubber, and monomer radicals,

respectively; k_{t_2} and k_{t_1} are the rate constants for mutual and cross termination between methacrylate and rubber radicals, respectively; and k_{tr} is the monomer transfer constant.

The observed rates of polymerization were in the region of 10^{-4} to 10^{-3} moles/kg./sec., and, since the particle sizes of the lattices were *ca.* 1μ , the number of free radicals per particle must have been in the region of 20–200. The application of bulk kinetics to the system is therefore justified.⁴ It follows that the molecular weight will be approximately proportional to the monomer concentration at any time, and, therefore, that it will fall during the polymerization.

On the basis of the values taken in the previous investigation, the dependence of the instantaneous molecular weights calculated as a function of monomer concentration is given in Table II.

Values of $k_{t_1}, k_{t_2}, k_{tr}, k_p,$ and k_p' were taken as $10^7, 2 \times 10^8, 2 \times 10^8, 3 \times 10^2,$ and 3 kg./mole/sec. , respectively (see reference 2).

The intrinsic viscosities found for the total polymers are given in the seventh column of Table II. Degrees of polymerization are given in the last column of Table II. The relationship $\overline{DP} = 1.49 \times 10^3[\eta]^{1.32}$ used for this conversion was

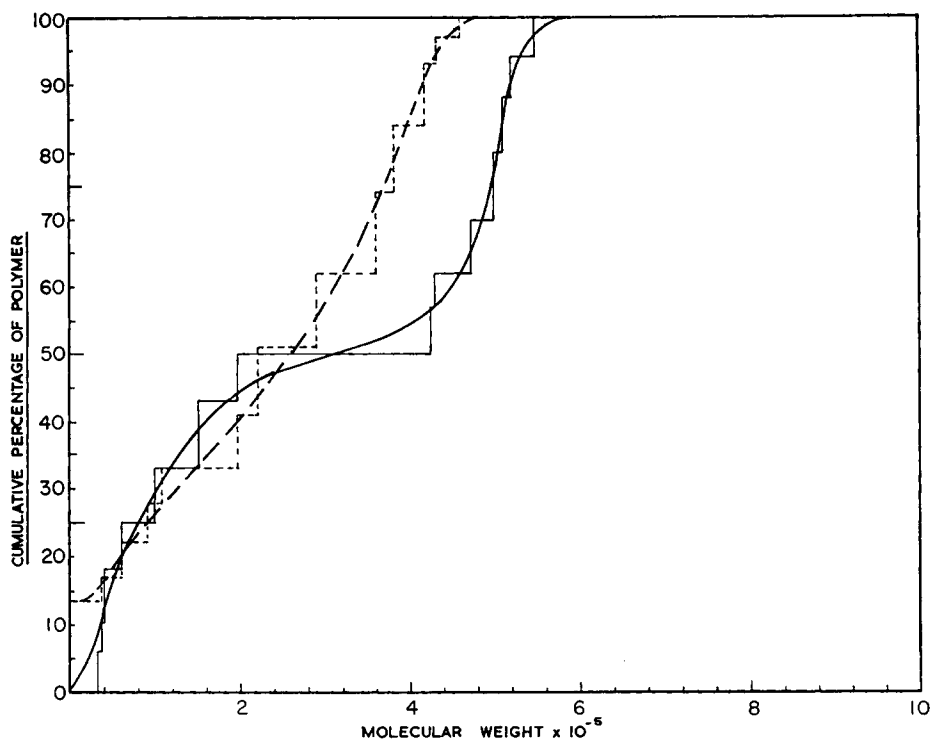


Fig. 6. Integral weight distribution curves for photoinitiated graft copolymers of natural rubber and methyl methacrylate: (—) grafted polymethyl methacrylate; (---) free polymethyl methacrylate.

derived from the equation of Evans et al.⁵ for $\bar{M}_w = 1.89 \bar{M}_n$. This equation is not of great accuracy when applied to such broad distributions as are obtained in these systems, and the calculated degrees of polymerization for summation of the polymer fractions are rather higher than those obtained from the viscosity relationship.

The positions of the peaks in the distribution curves are not easy to explain. Low molecular weight polymer could result either from degradation of previously formed polymer during polymerization, degradation during ozonolysis of the rubber, or from the presence of chain transfer agents in the rubber latex, particularly unsaturated fatty

acids and carotinoids. The observed effects are probably the result of all three mechanisms, although the fact that the position of the low molecular weight fraction is the same in homo and grafted polymer when only the latter has been subjected to ozone and, even then, in the presence of a protective agent,⁶ suggests that ozone degradation is not important.

Although provision was made in the kinetic scheme for combination termination, it has not been taken into account in the molecular weight calculations. Most of the evidence suggests that disproportionation is the dominant method of termination,⁷ and, in fact, no evidence was found

TABLE II
Dependence of Experimental and Calculated Degree of Polymerization on Monomer Concentration

M_0	$[\Sigma Mr] \times 10^7$	$[R \cdot] \times 10^9$	Initial $\bar{DP} \times 10^{-3}$ calc.	Conver- sion, %	Final $\bar{DP} \times 10^{-3}$ calc.	$[\eta]$	$\bar{DP} \times 10^{-3}$ exptl.
10	4.53	0.0	33.1	—	—	3.69	8.3
7.5	4.44	0.47	24.1	80	10.8	2.80	5.8
5.0	4.17	1.30	15.6	95	3.5	2.30	4.46
3.76	3.86	1.92	11.7	91	3.1	1.17	1.84
2.31	3.54	4.57	5.9	94	1.5	0.74	1.0
0.91	2.12	13.18	1.58	60	0.86	0.36	0.40

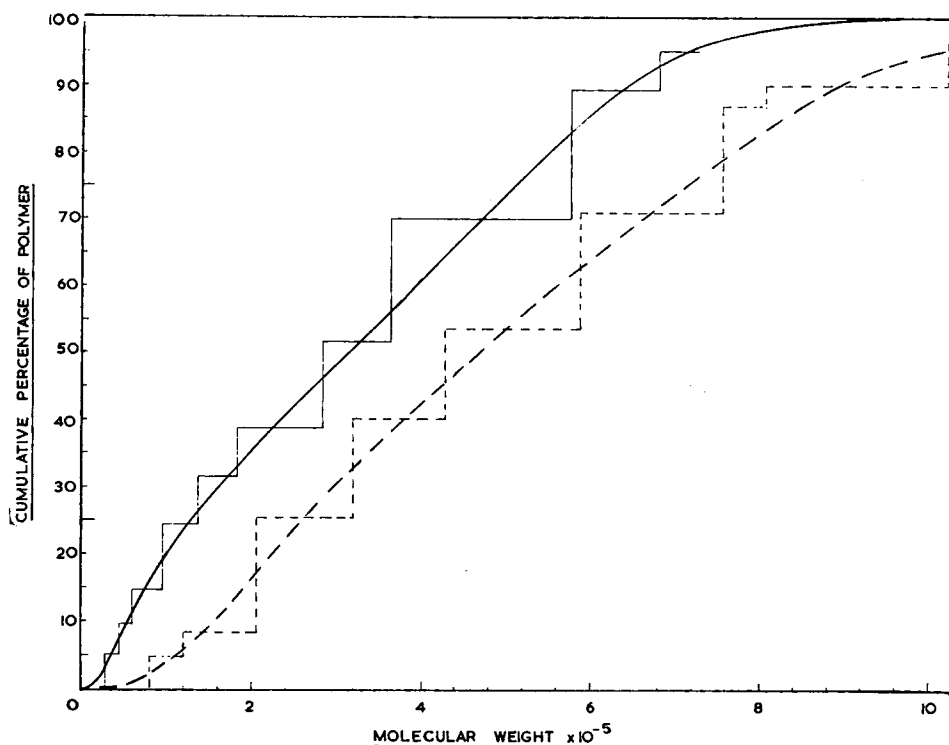


Fig. 7. Integral weight distribution curves for peroxamine-initiated graft copolymers of natural rubber and methyl methacrylate from the data of Kobryner and Bandaret: (—) grafted polymethyl methacrylate; (---) free polymethyl methacrylate.

for high molecular weight species which would be formed by combination. In order to obtain experimental data to compare with the calculated values given in Table II it would be necessary to examine low conversion polymers. This, however, would involve serious experimental problems. It would be difficult to ensure that no degradation occurred during the destruction of large proportions of rubber by ozone and moreover, the presence in the latex of chain transfer agents and inhibitors (which give rise to a short induction period) would vitiate the results. It would clearly be necessary to use highly purified rubber, and the latex system employed would be unsuitable for this purpose. The system is, however, analogous to the conventional photoinitiated polymerization terminated by mutual disproportionation for which the average degree of polymerization can be calculated for any conversion.⁸ Although the relationships for the grafting system do not lend themselves to explicit solution, it is possible, from the instantaneous values, to calculate the degree of polymerization at the appropriate conversion by graphical integration. The values obtained by this method, given in the sixth column of Table I, are not in good agreement

with the observed values. However, in view of the low molecular weight polymer from transfer reactions and the possibility of degradation, better agreement than this is unlikely, since the participation of even a small monomer transfer reaction, would considerably lower the calculated values for the degree of polymerization. The results cannot be used to calculate velocity constants for the reactions, but they are not inconsistent with the mechanism previously advanced and are in agreement with the general order of magnitude of the velocity constants suggested by the rate data.

Kobryner and Bandaret⁹ have also fractionated polymethyl methacrylate from peroxamine-initiated graft systems. They obtained similarly broad, two-peaked distributions (see Fig. 7), which they interpreted as being the result of combination and disproportionation termination, respectively. The fact that both chemical and radiation systems show the broad distribution of molecular weights and the two peaks indicates this to be a general feature of the reaction. The dependence of molecular weight on monomer concentration and conversion would also follow in the chemically

initiated system, since the continuous passage of free radicals, initially formed in the aqueous phase, into the latex particles would give rise to a situation not very different from the case of radiation initiation (except for the localization of free radicals near the surface of the particle¹⁰). We do not agree, however, with the assignment of the two peaks to different termination mechanisms. In the case of the free homopolymer, neither the position of the peaks nor the proportions of polymer are in agreement with the accepted mechanism for the polymerization of methyl methacrylate (the pure monomer gives essentially a single-peaked distribution). Further, the general similarity between the distribution curves of both grafted and free polymers suggests that common propagation and termination mechanisms operate in the formation of both molecules. We prefer to assign the high molecular weight peaks to disproportionation termination in the homopolymer or cross termination in the grafted polymer and the low molecular weight peaks to chain transfer reactions in the early stages of polymerization.

The authors wish to thank A. J. Stubbs and P. Hollins in connection with the design of the fractionation apparatus, and the Dunlop Rubber Co., Ltd., for permission to publish the paper.

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Synopsis

Molecular weight distributions of homopolymer and graft polymer obtained from the gamma and photoinitiated polymerization of methyl methacrylate with natural rubber latex have been determined. Broad distributions were found with peaks of low and high molecular weight polymer. The distributions were insufficiently defined to make definite assignments to the speeds of the reactions involved but were not inconsistent with the mechanism proposed in an earlier paper from kinetic considerations. Details are given of the column fractionation apparatus employed.

Résumé

Les distributions de poids moléculaires ont été déterminées pour le homopolymère et pour le polymère greffé, obtenus par polymérisation radiochimique (rayons gamma) et photochimique du méthacrylate de méthyle en présence de latex de caoutchouc naturel. On a trouvé des distributions larges avec des pics situés dans les domaines des bas et des hauts poids moléculaires. Les distributions ne sont pas suffisamment définies pour permettre de les relier de façon précise aux vitesses de réaction considérées mais ne sont pas en désaccord avec le mécanisme proposé dans un travail antérieur concernant des considérations cinétiques. Des détails sont fournis quant à la colonne de fractionnement utilisée.

Zusammenfassung

Molekulargewichtsverteilungen von Homopolymeren und Graftpolymeren, wie sie bei der durch γ -Strahlen und photochemisch angeregten Polymerisation von Methylmethacrylat in Naturkautschuklatex entstehen, wurden bestimmt. Es wurden breite Verteilungen mit Maxima bei niedrigen und hohen Polymerisationsgraden erhalten. Die Verteilungen waren nicht scharf genug definiert, um sichere Angaben über die Geschwindigkeiten der beteiligten Reaktionen zu erlauben, die waren aber mit dem in einer früheren Arbeit an Hand kinetischer Überlegungen aufgestellten Mechanismus nicht unvereinbar. Einzelheiten über die verwendete Fraktionierungssäule werden mitgeteilt.

Received January 16, 1959