

AN ABSOLUTE EXPERIMENTAL TEST OF THE MOLECULAR WEIGHT DISTRIBUTION EQUATIONS OF HIGH POLYMERS

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INTRODUCTION

A large amount of experimental work (Schulz and Dinglinger, 1939; Baxendale, Bywater and Evans, 1946; Dostal and Mark, 1936; Morey and Tamblyn, 1945; Harris and Miller, 1951; Boyer, 1952) on the distribution of molecular weight in high polymers has been reported in the literature but a very few of them are concerned with the really quantitative study of the same, especially the effect of transfer on distribution. Perhaps this might be ascribed firstly to the long and tedious experimental procedure and, secondly, to the lack of knowledge of the absolute values of the different rate constants. Of late, the accurate values of the rate constants have been obtained by different authors (Matheson, Auer, Bevilacqua and Hart, 1951; Bamford and Dewar, 1948) which have opened up the possibility of comparing the experimental distribution of molecular weights with the theoretical distribution.

The present paper is an attempt to find out experimentally the distribution curves of polystyrene as affected by the chain transfer occurring in different solvent media and to compare them with the theoretical curves as deduced lately by Palit and Majumdar (1954). In addition, we have tested with our experimental data some theoretical relations deduced by Palit and Majumdar involving statistical quantities of the distribution, namely the number average D.P., the interquartile range, maximum weight fraction corresponding to the most probable D.P., etc. The results of the above absolute comparisons are weighed to decide between alternative mechanism of polymerization process particularly termination process as due to combination or disproportionation.

EXPERIMENTAL

Materials.—Monomeric styrene was washed three times with 10 per cent caustic soda solution to remove the inhibitor and then three times with water. The monomer was dried with calcium chloride and twice distilled at a reduced pressure of about 15 mm. of mercury.

The solvents used were mostly A.R. quality samples. They were all scrupulously purified by the usual methods, dried and fractionally distilled twice before use.

Polymerization Experiments.—Polymerizations were carried out in Pyrex glass ampules of 40 c.c. capacity. These were thoroughly cleansed with chromic acid, washed with water, then with sulphurous acid, again with water and dried. Different mixtures of solvent and monomer were taken in the ampules, frozen in liquid oxygen, evacuated, and sealed. Reaction was carried out in an oil bath thermostat at 60°C. (accurate within $\pm 0.01^\circ$). After a specified time, tubes were removed and cooled, ampules were broken open and the polymer freed from monomer by double precipitation from benzene solution with methyl alcohol. The polymer was then dried *in vacuo* at 60°C. for six hours. The yields were in most cases about 10 per cent and in a few cases within 18 per cent.

Fractionation of Polymers.—Separation of polystyrene into samples of different molecular weight was carried out by the process of fractional precipitation. This method is based on the fact that if a precipitant is added to a solution of high polymer, the molecules of the highest molecular weight are thrown out of the solution first. It is necessary to choose the solvent precipitant carefully, so that the precipitant is neither too powerful, in which case control of the fractionation is difficult to achieve, nor too weak, in which case excessively large volumes are necessary. It was found that the most convenient system for polystyrene was M.E.K. as solvent and methyl alcohol as precipitant.

To a nearly 1.5 per cent solution of the polymer, methanol was added carefully just to give a permanent turbidity and then a measured excess of methanol was added, the system was warmed until the liquid cleared, and it was then allowed to cool, to 35°C., slowly with stirring. The liquid was allowed to stand at 35°C. overnight, without disturbances for the gel to settle. The supernatant liquid was quickly and carefully decanted off. The gel was then dissolved in benzene and precipitated with methanol. The precipitate was then dried at 60°C. in vacuum. Further fractions were obtained from the liquid decanted off gel by the repetition of the process.

Determination of Molecular Weight.—Molecular weight was determined viscometrically by using the following equations due to Bevington, Guzman and Melville (1954) for each fractionated and unfractionated samples of polymer

$$[\eta] = 2.62 \times 10^{-4} [M]^{0.68} \text{ for unfractionated polymers} \quad \dots \quad (1)$$

$$[\eta] = 1.72 \times 10^{-4} [M]^{0.70} \text{ for fractionated polymers} \quad \dots \quad (2)$$

Intrinsic viscosity $[\eta]$ was obtained by extrapolating the graph η_{sp}/C against C to zero concentration. The viscosity measurements were carried out with benzene solutions at 35°C. ($\pm 0.01^\circ\text{C}.$) using Ostwald capillary viscometers.

Analysis of the Experimental Data.—The differential molecular weight distribution curve in which we are more interested cannot be directly obtained from the experimental data, owing to the fact that the D.P. range of polymer fractions are unknown while the mean chain length of each fraction is only measured. For sharp fractions, however, it is quite possible to construct with fairly good accuracy the integral weight distribution curve from which the differential weight distribution curve can be obtained by graphical differentiation. The integral distribution curve is generally obtained after plotting the cumulative weight proportions of the polymer fractions against the corresponding mean chain lengths and then drawing a smooth line through such plot of points. The use of mean chain length of polymer fraction as abscissa is however not fully justified (Baxendale, Bywater and Evans, 1946). As a matter of fact if W is the weight of the total polymer, W_{r_1} the weight of the first polymer fraction whose D.P. ranges from infinity to some unknown value, say r_1 , the mean D.P. of the range being \bar{r}_1 , then to construct the integral weight

distribution curve we should plot $F_{r_1} = \left(1 - \frac{W_{r_1}}{W}\right)$ against r_1 and not against \bar{r}_1 .

Similarly, if W_{r_2} is the weight of the second polymer fraction whose D.P. ranges from r_1 to r_2 with the measured mean D.P. \bar{r}_2 , then $F_{r_2} = 1 - \frac{(W_{r_1} + W_{r_2})}{W}$ should be plotted

against r_2 and not against \bar{r}_2 and so on. But since r_1 and \bar{r}_2 , etc., are not known experimentally Baxendale *et al.* (1946), assuming that the distribution of chain lengths in each fraction is symmetrical about the measured mean chain length, added one-half of the weight of the corresponding polymer fraction, i.e. $\frac{1}{2} W_{r_1}/W$ to F_{r_1} , $\frac{1}{2} W_{r_2}/W$ to F_{r_2} , etc., and then obtained the integral weight distribution curve by plotting

$F'_{r_1} = \left(1 - \frac{1}{2} \frac{W_{r_1}}{W}\right)$ against \bar{r}_1 , $F'_{r_2} = \left(1 - \frac{1}{2} \frac{W_{r_2}}{W} - \frac{W_{r_1}}{W}\right)$ against \bar{r}_2 and so on. The assumption made above is also, however, not justified as this introduces negative error for the portion to the left of the mode of distribution curve and positive error for the remaining portion. We, therefore, smoothen the mean chain length and the weight of the successive polymer fractions by the method of overlapping means, that is, by taking moving averages of the type $\frac{1}{4}(a_1 + 2a_2 + a_3)$. Such a moving average also greatly eliminated the overlapping effect of the polymers of the contiguous fractions which might occur due to the fact that all polymers of D.P. from ∞ to r_1 , r_1 to r_2 , etc., might not have been precipitated during first, second, etc., fractionations respectively. After so smoothening F_j values are plotted against the corresponding \bar{r}_j and the plot of the points are connected with the help of an elastic celluloid scale. Practically all the points are found to lie on the integral weight distribution curves thus obtained (Fig. 1). These curves will generally read higher values than those of the plots of F_1 against r_1 , etc., but owing to the smoothening the two curves are expected to be uniformly wide apart, so that differential weight distribution curve and the interquartile range obtainable from the two will be identical.

The differential molecular weight distribution curves are obtained to a close approximation by applying differencing process (Kendall, 1951) on the integral weight distribution curves. The usual procedure is, however, to draw tangents by trial method. In differencing method we read off from the integral distribution curves the values $F_1, F_2 \dots F_k$ at close intervals of the D.P.s $r_1, r_2 \dots r_k$ respectively. Then $\frac{F_2 - F_1}{r_2 - r_1}$ gives the weight fraction W_1 whose D.P. is the middle value of r_2 and r_1 , i.e. $\frac{r_2 + r_1}{2}$. In such case the nearer the two values r_2 and r_1 are, the closer will be the approximation and the lesser the error. It may be noticed that $W_1 = \lim_{r_2 \rightarrow r_1} \frac{F_2 - F_1}{r_2 - r_1}$ becomes the tangent at the point $\frac{r_2 + r_1}{2}$ of the integral weight distribution curve. Thus the two methods are practically identical, but the latter involves no trial solution. Incidentally, it may also be noted that the integral distribution function and the differential molecular weight distribution equation are functionally related as

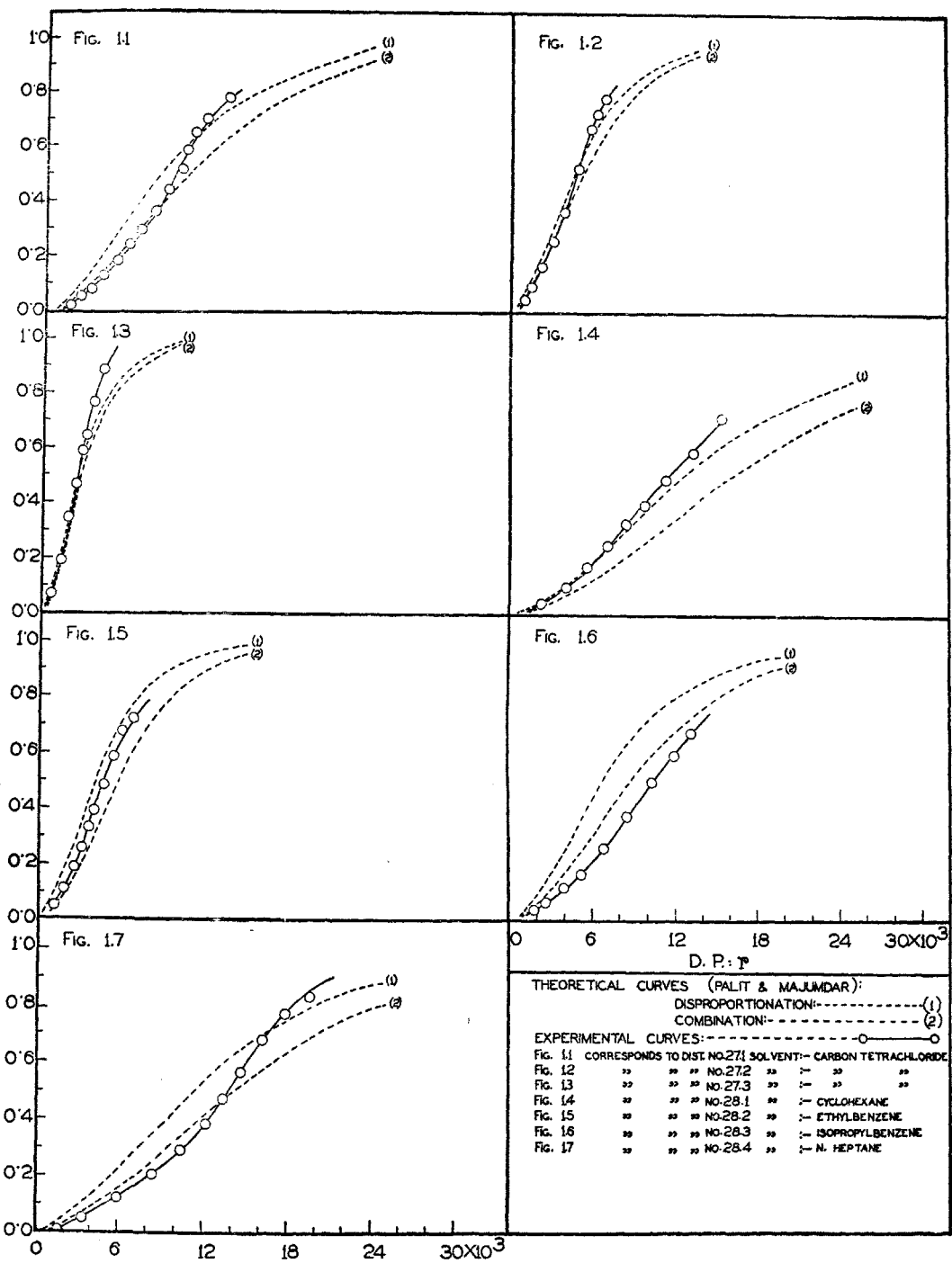
$$F_r = \sum_{r=2}^r W_r \simeq \int_0^r W_r dr.$$

So that

$$W_{r_k} = \left[\frac{d}{dr} \cdot F_r \right]_{r=r_k},$$

i.e. W_{r_k} is the tangent at the point $r = r_k$ of the integral weight distribution curve. This justifies the method of procedure described above. All the values of $W_1, W_2 \dots$ of the weight fractions are obtained by differencing process and plotted against the corresponding D.P.s $\frac{r_1 + r_2}{2}, \frac{r_2 + r_3}{2} \dots$. The molecular weight distribution curves obtained by joining the plot of the points are shown in Fig. 2.

The molecular weight distribution curves can also be drawn from experimental data by the method of Herden (1949) and Schulz (1950). Herden's method gives only the relative values of the weight fractions of the distribution curves, while Schulz's method is an approximate one and is less reliable when distribution becomes extremely narrow.



THEORETICAL CURVES (PALIT & MAJUMDAR):			
	DISPROPORTIONATION:-	(1)	
	COMBINATION:-	(2)	
EXPERIMENTAL CURVES:-			
Fig. 11	CORRESPONDS TO DIST. NO. 271	SOLVENT:-	CARBON TETRACHLORIDE
Fig. 12	" " " NO. 272	" " "	" "
Fig. 13	" " " NO. 273	" " "	" "
Fig. 14	" " " NO. 28-1	" " "	CYCLOHEXANE
Fig. 15	" " " NO. 28-2	" " "	ETHYLBENZENE
Fig. 16	" " " NO. 28-3	" " "	ISOPROPYLBENZENE
Fig. 17	" " " NO. 28-4	" " "	N. HEPTANE

FIG. 1 : INTEGRAL WEIGHT DISTRIBUTION OF POLYSTYRENE POLYMERISED AT 60 °C.

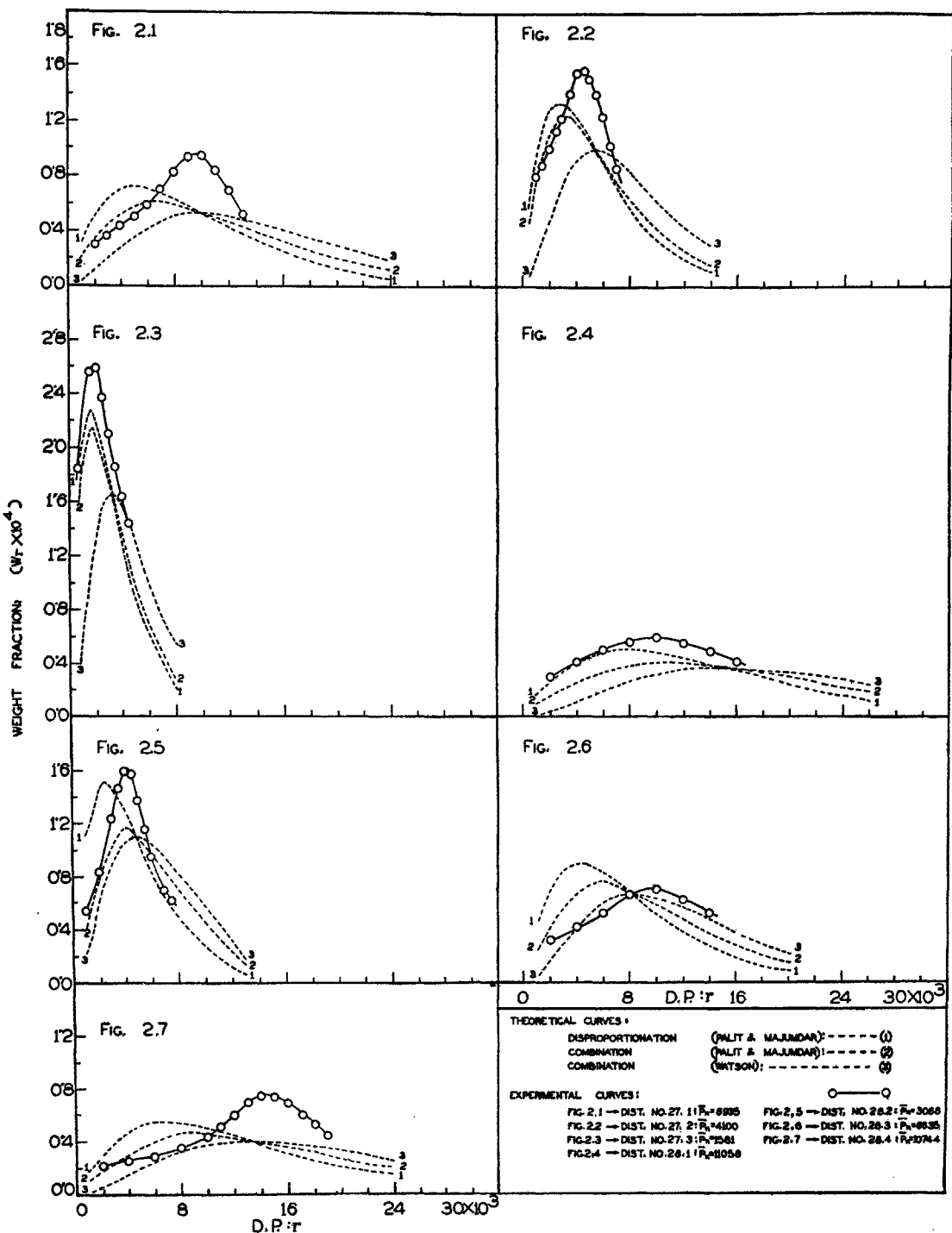


FIG. 2: DIFFERENTIAL MOLECULAR WEIGHT DISTRIBUTION CURVES OF POLYSTYRENE POLYMERISED AT 60°C

RESULTS AND DISCUSSIONS

Our primary object has been to find out the experimental molecular weight distribution curves and then compare them with the theoretical ones using the equations of Palit and Majumdar, who have taken into consideration all sorts of transfer, namely by monomer, solvent, catalysts and termination by combination or disproportionation. For the same purpose some theoretical relations deduced by Palit and Majumdar (1954) from their distribution equations are also tested from the experimental data. At the end of the section Watson's (1953) theoretical distribution curves for termination when combination is predominant have been compared with the experimental ones. Relations similar to those mentioned above which follow from Watson's equation have also been tested.

Before making a detailed comparison as set out above, we might mention that even an agreement in the order of values of W_r and other quantities is a remarkable triumph of theory because k_p and k_t and other constants are obtained from independent experiments involving quite different experimental procedure, hardly related to the present method of experimentation. In fact, most previous experimental workers had to remain satisfied with a crude comparison of the shape of the theoretical and experimental curves and very few ventured to test an absolute agreement. As far as the order of values is concerned it would be seen that the agreement between the theory and experiment is satisfactory beyond expectation which will be regarded as a striking success of recent theory and technique of this field.

In drawing the theoretical distribution curves for styrene polymerized at 60°C. the rate constant data as given below were taken from the work of Matheson, Auer, Bevilacqua and Hart (1951).

$$C_M = 0.60 \times 10^{-4}, k_p = 176, k_t = 7.20 \times 10^7.$$

The solvent transfer coefficients, C_S , were determined from our own experiments.

These together with the solvent: monomer ratio by weight, the values of $C_S \frac{[S]}{[M]}$

and $t = Rp \frac{k_t}{M^2 k_p^2}$ are given in Table I. The C_S values obtained by us agree fairly with those of Gregg and Mayo (1947).

TABLE I

Experimental Values of C_S , $\frac{[S]}{[M]}$, $C_S \frac{[S]}{[M]}$ and t

Distribution No.	Solvent	$C_S \times 10^4$	$\frac{[S]}{[M]}$	$C_S \frac{[S]}{[M]} \times 10^4$	$t \times 10^4$
27.1	Carbon tetrachloride	86.00	0.0063	0.5439	0.8128
27.2	"	"	0.0257	2.2133	0.8558
27.3	"	"	0.0529	4.5485	0.9823
28.1	Cyclohexane	0.09	0.5710	0.0491	0.6895
28.2	Ethyl benzene	0.70	0.4950	0.3469	3.1242
28.3	Isopropyl benzene	1.29	0.4520	0.5835	1.2571
28.4	n-Heptane	0.40	0.4220	0.1689	0.7208

In calculating different quantities, viz. $t = R_p \frac{k_t}{M^2 k_p^2} C_S \frac{[S]}{[M]}$ and $q = C_M + C_S \times \frac{[S]}{[M]} + t$, with which we shall compare our experimental results based on

the total extent of polymerization, we used \bar{M} for M given by $\bar{M} = \frac{1}{2} (M_0 + M_f)$ where M_0 and M_f are the initial and final monomer concentration, as it is neither justified to use M_0 nor M_f in the instantaneous distribution considered owing to the fact that as polymerization proceeds the instantaneous distribution may change progressively throughout the course of polymerization. The true distribution would be, however, the overall integrated distribution in which the change throughout the extent $\Delta M = M_0 - M_f$ of polymerization is taken into account as considered by Watson (1953), and Hulbert, Harman, Tobolsky and Eyring (1943). But, unfortunately, these overall distribution equations contain incomplete

integrals of the form $\int_x^{x_0} \frac{e^{-x}}{x} dx$ rendering its study extremely difficult. Further

simple relationships connecting the various characteristics of the distribution (number average D.P., most probable D.P., etc.) cannot be obtained from these overall distribution equations. The use of \bar{M} in the instantaneous distribution equation, on the other hand, account for the mean overall effect of the whole extent of polymerization. We have, therefore, taken this intermediate course by using \bar{M} for M . In the last section, we have, however, studied the change of the theoretical distributions as affected by change of monomer concentration from initial to final values.

Comparison of the Integral Weight Distribution Curves.—The experimental integral weight distribution curves obtained by the method laid down in the previous section are shown in Fig. 1. In the same figure are also drawn the corresponding theoretical curves using the following equations of Palit and Majumdar (1954).

$$F_r = 1 - (1 + qr)e^{-qr} \text{ for termination by disproportionation} \quad \dots (3)$$

$$F_r = 1 - (1 + qr + \frac{1}{2} qtr^2)e^{-qr} \text{ for termination by combination} \quad \dots (4)$$

where

$$t = R_p \frac{k_t}{M^2 k_p^2} \text{ and } q = C_M + C_S \frac{[S]}{[M]} + t.$$

The nature and shape of the theoretical and experimental curves are in general in good agreement though they are not wholly coincident and such an agreement is somewhat unique in case of Figs. 1.2, 1.4, 1.5 and 1.6. In Fig. 1.5, the experimental curve runs uniformly through the two theoretical curves. In Fig. 1.4, the experimental curve is more close, and akin to the curve due to the termination by disproportionation than due to the termination by combination, while in Fig. 1.6 it is just the reverse. In Figs. 1.1 and 1.2 the experimental curves are found to be coincident in the lower regions of the theoretical curve due to combination, the upper parts being more nearer to the theoretical curves due to disproportionation.

Comparison of the Differential Molecular Weight Distribution Curves.—The differential instantaneous molecular weight distribution curves are obtained from the experimentally found integral weight distribution curves (Fig. 1) by differencing process as already described. These curves are shown in Fig. 2 along with the corresponding theoretical distribution curves from the equations of Palit and Majumdar (1954) which are given below :

$$W_r = q^2 r e^{-qr} \dots \text{ for termination by disproportionation} \quad \dots (5)$$

$$W_r = q^2 r e^{-qr} \left[1 - t \left(\frac{1}{q} - \frac{r-1}{2} \right) \right] \text{ for termination by combination} \quad \dots (6)$$

The nature and shape of the theoretical and experimental curves are exactly identical, the modes of the experimental curves lying slightly to the right of those of the theoretical curves. Even this minor discrepancy is practically absent in Fig. 2.3 for both termination processes and in Figs. 2.4 and 2.5 for termination by combination. The most striking feature is that the order of the weight fraction of the experimental curves are exactly the same as those of the theoretical ones, the maximum weight fraction being slightly higher in the experimental curves except in the case of Fig. 2.6. In all cases except this the maximum theoretical weight fractions for termination by disproportionation are more nearer to the experimental values. In case of Fig. 2.6, the maximum theoretical weight fraction for termination by combination is almost equal to the experimental value. These results in general indicate that the theoretical and the experimental distribution curves are in good agreement.

Most Probable D.P. r_0 and Maximum Weight Fraction W_{r_0} .—The most probable D.P. r_0 is the D.P. corresponding to the mode of the distribution curves while the maximum weight fraction W_{r_0} is the weight fraction corresponding to r_0 . These are readily read off from the curves of Fig. 2. The corresponding theoretical values are, however, obtained from the relations of Palit and Majumdar. The theoretical and experimental values of r_0 and W_{r_0} are given in Table II.

The experimental values of r_0 are slightly higher than the theoretical values indicating that the peak of the experimental distribution curves are shifted more towards the right as already mentioned. In two cases of disproportionation, however, the experimental values are double the theoretical values, while in four cases for combination the experimental and theoretical values are almost the same.

The maximum weight fractions obtained experimentally are about 1.1 to 1.4 times (10 to 40 per cent) higher than the theoretical values in case of termination by combination while in one case the values are almost the same. In case of termination by disproportionation the experimental values are 1.1 to 1.3 times (10 to 30 per cent) greater than the theoretical values. For distribution No. 28.3 the theoretical value is greater than the experimental value by only 9 per cent in case of combination and by 22 per cent in case of disproportionation while for distribution No. 28.2 the experimental value is greater than the theoretical value by 26 per cent in case of combination and by 7 per cent in case of disproportionation.

Number Average D.P. \bar{P}_n .—The number average D.P. \bar{P}_n has been obtained experimentally by viscometric method from the unfractionated samples, and the theoretical values are computed from the relation of Palit and Majumdar. These are also shown in Table II. The experimental values are more closer to the theoretical values in case of termination by combination. In some cases they are almost identical. The theoretical values for termination by disproportionation are, however, not very wide apart from the experimental values and actually in one case they are almost the same.

Interquartile Range Δr .—The interquartile range Δr , the concept of which was first introduced by Palit and Majumdar (1954), can be directly obtained from the integral weight distribution curves without constructing the differential molecular weight distribution curves, and as such it is subjected to less experimental error. These have been calculated from the experimental integral weight distribution curves (Fig. 1) by taking difference of D.P. corresponding to $F_r = 0.75$ and 0.25. The theoretical values of Δr are also calculated from the relations of Palit and Majumdar (1954) and shown in the last column of Table II. The agreement between the theoretical and experimental values of Δr is quite satisfactory. This shows that the spread of the experimental and theoretical distribution curves is not much different.

It can be seen from Table II that all characteristics excepting the maximum weight fraction W_{r_0} have a tendency to decrease as polymerization proceeds. But the final increased value is in general 7 per cent lower than the values obtained by

TABLE II
Experimental and Theoretical Values of Number Average $D.P. \bar{P}_n$, Weight Average $D.P. \bar{P}_w$, Most Probable $D.P. \tau_0$, Interquartile Range Δr , and Maximum Weight Fraction W_{r_0} , based on Equations of Pait and Majumdar (P & M) and of Watson, using Initial M_0 , Final M_f and Average \bar{M} Values of the Monomer Concentration

Characteristics of distribution	Dist. No.	Expt. values	Theoretical Disproportionation (P & M) using			Theoretical Combination (P & M) using			Theoretical Combination Watson's using		
			M_0	\bar{M}	M_f	M_0	\bar{M}	M_f	M_0	\bar{M}	M_f
$\bar{P}_n \times 10^{-4}$	27.1	0.69	0.52	0.51	0.50	0.66	0.64	0.63	1.03	1.02	1.01
	27.2	0.41	0.28	0.26	0.32	0.31	0.30	0.30	0.56	0.55	0.53
	27.3	0.16	0.17	0.15	0.19	0.18	0.17	0.17	0.34	0.33	0.32
	28.1	1.11	0.75	0.74	1.01	1.01	1.00	1.00	1.49	1.49	1.49
	28.2	0.31	0.25	0.24	0.41	0.39	0.39	0.39	0.49	0.49	0.48
	28.3	0.66	0.42	0.40	0.57	0.55	0.53	0.53	0.84	0.82	0.80
	28.4	1.07	0.68	0.66	0.89	0.88	0.87	0.87	1.35	1.34	1.33
	27.1	*	1.04	1.01	1.23	1.23	1.22	1.22	1.55	1.53	1.51
$\bar{P}_w \times 10^{-4}$	27.2	*	0.56	0.54	0.63	0.61	0.59	0.59	0.84	0.82	0.80
	27.3	*	0.34	0.33	0.37	0.35	0.33	0.33	0.51	0.49	0.47
	28.1	*	1.50	1.49	1.89	1.88	1.87	1.87	2.23	2.23	2.23
	28.2	*	0.50	0.48	0.69	0.68	0.67	0.67	0.73	0.73	0.72
	28.3	*	0.84	0.82	1.06	1.06	1.03	1.00	1.26	1.23	1.20
	28.4	*	1.35	1.34	1.33	1.68	1.67	1.65	2.02	2.01	1.99

*Experimental values of \bar{P}_w could not be determined.

TABLE II—*contd.*

Characteristics of distribution	Dist. No.	Expt. values	Theoretical Disproportionation (P & M) using			Theoretical Combination (P & M) using			Theoretical Combination Watson's using		
			M_0	\bar{M}	M_f	M_0	\bar{M}	M_f	M_0	\bar{M}	M_f
$\tau_0 \times 10^{-4}$	27.1	0.95	0.52	0.51	0.50	0.69	0.67	0.66	1.03	1.02	1.01
	27.2	0.43	0.28	0.26	0.33	0.31	0.30	0.30	0.56	0.55	0.53
	27.3	1.00	0.17	0.15	0.19	0.18	0.18	0.18	0.34	0.33	0.31
	28.1	0.41	0.75	0.74	1.07	1.07	1.07	1.07	1.49	1.49	1.49
	28.2	0.97	0.25	0.24	0.44	0.43	0.43	0.43	0.49	0.49	0.48
	28.3	1.41	0.42	0.41	0.40	0.61	0.59	0.57	0.84	0.82	0.80
	28.4		0.68	0.67	0.66	0.95	0.94	0.92	1.35	1.34	1.33
	27.1	0.61	0.88	0.87	0.85	1.04	1.02	1.01			
$\Delta r \times 10^{-4}$	27.2	0.36	0.48	0.45	0.56	0.54	0.53	0.53			
	27.3	0.22	0.29	0.26	0.34	0.32	0.31	0.31			
	28.1	0.95	1.27	1.27	1.50	1.49	1.49	1.49			
	28.2	0.43	0.42	0.41	0.50	0.49	0.48	0.48			
	28.3	0.79	0.71	0.68	0.84	0.82	0.80	0.80			
	28.4		1.15	1.13	1.35	1.34	1.33	1.33			
	27.1	0.96	0.71	0.74	0.63	0.64	0.65	0.65			
	27.2	1.58	1.31	1.41	1.36	1.27	1.23	1.32	0.52	0.53	0.54
$W_{r0} \times 10^{-4}$	27.3	2.60	2.16	2.37	2.07	2.17	2.28	2.28	0.96	0.99	1.03
	28.1	0.59	0.49	0.50	0.43	0.43	0.43	0.43	1.58	1.65	1.73
	28.2	1.62	1.49	1.54	1.17	1.19	1.22	1.22	0.36	0.36	0.36
	28.3	0.70	0.88	0.93	0.75	0.77	0.80	0.80	1.08	1.09	1.12
	28.4	0.75	0.55	0.56	0.47	0.48	0.48	0.48	0.64	0.66	0.67
									0.40	0.40	0.41

Δr values cannot be calculated from Watson's equation

considering the initial concentration of the monomer except in distribution No. 27.3 where the difference between the initial and final values is in some cases about 10 per cent. While on the other hand in a few other cases, e.g. distribution No. 28.1, the difference is practically insignificant. The theoretical values of all the above characteristics obtained by using \bar{M} are midway between the initial and final values using M_0 and M_f respectively and as such the difference between the values with \bar{M} and those with M_0 or M_f lies below 5 per cent. In case of distribution No. 28.1 in which the yield is about 14 per cent the distribution can be taken to have remained constant from theoretical consideration throughout the course of polymerization. Thus the above findings justify the use of \bar{M} instead of M_0 or M_f in the theoretical calculations and conclusions of the preceding paragraphs.

Test of the Theoretical Relationships.—The theoretical relations involving the number average D.P. \bar{P}_n , the maximum weight fraction W_{r_0} , the interquartile range Δr , the most probable D.P. r_0 and the solvent transfer coefficients C_S which we propose to test from the experimental data are given in Table III.

TABLE III
Theoretical Relations involving \bar{P}_n , r_0 , W_{r_0} , Δr , $C_S \frac{[S]}{[M]}$ (Palit and Majumdar)

Serial No.	Relationship between	For termination by	
		Combination	Disproportionation
1	\bar{P}_n and W_{r_0}	$W_{r_0} = 0.37\bar{P}_n + 0.085t$	$W_{r_0} = 0.37/\bar{P}_n$
2	\bar{P}_n and Δr	$\frac{1}{\Delta r} = 0.50/\bar{P}_n + 0.25t$	$\frac{1}{\Delta r} = 0.59/P_n$
3	\bar{P}_n and r_0	$\bar{P}_n \geq r_0 \geq 1.08\bar{P}_n$	$\bar{P}_n = r_0$
4	$C_S \frac{[S]}{[M]}$ and W_{r_0}	$W_{r_0} = 0.37 C_S \frac{[S]}{[M]} + 0.37 C_M + 0.27t$	$W_{r_0} = 0.37 C_S \frac{[S]}{[M]} + 0.37 C_M + 0.37t$
5	$C_S \frac{[S]}{[M]}$ and Δr	$\frac{1}{\Delta r} = 0.50 C_S \frac{[S]}{[M]} + 0.50 C_M + 0.50t$	$\frac{1}{\Delta r} = 0.59 C_S \frac{[S]}{[M]} + 0.59 C_M + 0.59t$

All these relations involve quantities which are directly obtained from the same experiments except in case of termination by combination where $t = R_p \left(\frac{k_t}{M^2 k_p^2} \right)$ depending on the rate of initiation, termination and propagation is also involved.

Relation between \bar{P}_n and W_{r_0} .—The relations (1) between \bar{P}_n and W_{r_0} are uniquely tested from the experimental data of Table II. For this purpose W_{r_0} is plotted against $\frac{1}{\bar{P}_n}$ in case of termination by disproportionation while $(W_{r_0} - 0.085 \times t)$ is plotted against $\frac{1}{\bar{P}_n}$ in case of termination of combination. Most of the points are found as in Figs. 3.1 and 3.2 to lie on straight lines in both cases, the slopes as

calculated by least square method being 0.37 and 0.36 respectively. These are remarkably in agreement with the theoretical values, viz. 0.37.

Relation between \bar{P}_n and Δr .—The relations (2) between \bar{P}_n and Δr are obtained by plotting $\frac{1}{\Delta r}$ and $\left(\frac{1}{\Delta r} - 0.25t\right)$ against $\frac{1}{\bar{P}_n}$ in case of disproportionation and combination respectively. The plot of the points in this case also are found as in Figs. 3.3 and 3.4 to lie in straight lines with slope 0.61 and 0.57 respectively which are

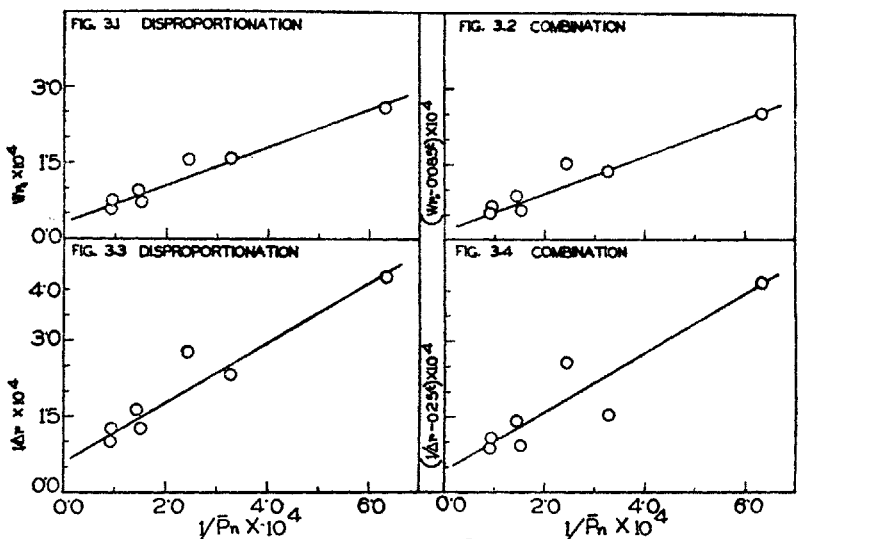


FIG. 3. RELATION BETWEEN NUMBER AVERAGE D. P. \bar{P}_n AND MAXIMUM WEIGHT FRACTION, W_n & INTERQUARTILE RANGE

also in very good agreement with the theoretical values, viz. 0.59 and 0.50 respectively. In case of combination, however, two points are found to lie somewhat away from the straight line but in a symmetrical manner, which can be attributed to chance variation. Relations (1) and (2) also predict that the smaller the number average D.P. \bar{P}_n the narrower and sharper is the distribution curve. This is readily verified from the data of Table II as well as from Fig. 2.

Relation between \bar{P}_n and r_0 .—Theoretically r_0 and \bar{P}_n should be almost equal for both termination processes. Experimentally such relations are also found to hold good except in a few cases where r_0 is greater than \bar{P}_n but not by more than 1.3 times (30 per cent). In one case, however, r_0 has been found to be less than \bar{P}_n but by only 10 per cent.

Relation between $C_S \frac{[S]}{[M]}$, W_{r_0} and Δr .—To test the relations (4) and (5) of $C_S \frac{[S]}{[M]}$ with W_{r_0} and Δr we have plotted $(W_{r_0} - 0.37t)$ and $(W_{r_0} - 0.27t)$ against $C_S \frac{[S]}{[M]}$ while $\left(\frac{1}{\Delta r} - 0.59t\right)$ and $\left(\frac{1}{\Delta r} - 0.50t\right)$ against $C_S \frac{[S]}{[M]}$ in case of disproportionation and combination respectively using the values of $C_S \frac{[S]}{[M]}$ given in Table I. In all these cases the points are found to lie on straight lines with only one or two points lying slightly away from the lines. The slopes obtained in these cases

by the least square method are 0.43 and 0.42 in the case of former relations and 0.75 and 0.75 in the case of latter relations for termination by disproportionation and combination respectively. The slopes obtained in the latter cases are, however, a bit higher than the theoretical values which might be due to the limitation in the use of the values of the rate constant involved in 't' for the sample considered in our experiment. These also seem to be the cause for the lack of exact coincidence of the experimental distribution curves with the theoretical ones.

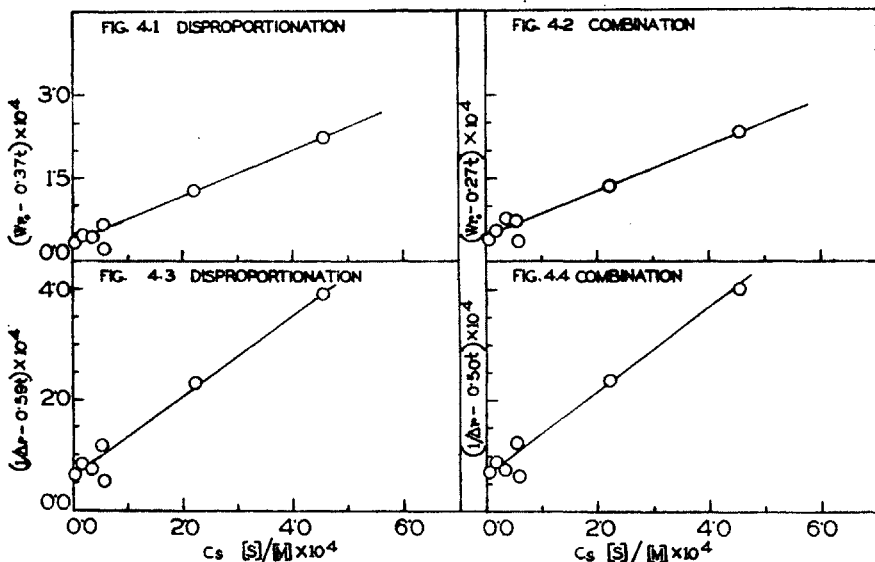


FIG. 4. RELATION BETWEEN $C_s \frac{[S]}{[M]}$ AND MAXIMUM WEIGHT FRACTION, W_r , & INTERQUARTILE RANGE, Δr .

Watson's Equation and its Consequences.—The theoretical differential weight distribution equation in case of termination by disproportionation as deduced by Watson (1953) when converted to our terminology is exactly equivalent with the corresponding equation of Majumdar and Palit (1954), and hence it has not been discussed. We, therefore, discuss Watson's instantaneous distribution equation when termination by combination is predominant as given below after transforming to our notations:

$$W_r = \frac{1}{2} q^3 r^2 e^{-qr} \dots \dots \dots (7)$$

The curves obtained by this equation are also shown in Fig. 2. These curves also agree fairly in order with the experimental curves but the peaks of the curves are lower than those of the experimental ones as well as of the theoretical curves of Palit and Majumdar. This can also be readily seen from the values of W_{r_0} given in Table II.

Following the procedure laid down by Majumdar and Palit (1954) it can be easily seen that Watson's distribution equation (7) satisfies the following relations:

$$\bar{r}_0 = \bar{P}_n = 2 / \left(C_M + C_S \frac{[S]}{[M]} + t \right) \dots \dots \dots (8)$$

$$W_{r_0} = 0.54 / P_n = 0.27(C_M) + 0.27t + 0.27C_S \frac{[S]}{[M]} \dots \dots (9)$$

Relation (8) shows that r_0 and \bar{P}_n are same as in the case of termination by disproportionation. The values of r_0 and \bar{P}_n obtained from Watson's equation are also given in Table II. Watson's theoretical values for \bar{P}_n and r_0 are in general in good agreement with the corresponding experimental values. The theoretical values of \bar{P}_n are, however, higher than the experimental values being almost double in case of distribution No. 27.3. In case of distribution Nos. 27.1 and 28.4 the agreement between the experimental and Watson's theoretical values of r_0 are in better agreement than those of Palit and Majumdar while in other cases it is just the reverse. But the difference is so subtle that the present experimental techniques are not sufficiently precise to make any decisive conclusions on such points of difference.

The relation (9) suggests a linear relationship between (i) W_{r_0} and $\frac{1}{\bar{P}_n}$ and (ii) W_{r_0} and $CS \frac{[S]}{[M]}$ with slopes 0.54 and 0.27 respectively. The corresponding slopes obtained by Palit and Majumdar are in both cases 0.37 which agree better with the experimental results as described above.

CONCLUDING REMARKS

In the preceding sections we have noticed the striking agreement between the experimental results and the theoretical findings of Palit and Majumdar, which shows the soundness of the present concept of polymerization on the basis of which their relations are obtained, *vis-à-vis* this also gives us confidence in the accuracy of the existing absolute values of the rate constants obtained by Matheson and others. The agreement between Watson's theory for combination and experimental result is also quite satisfactory excepting the fact that Watson's theoretical slopes of the linear relationships between W_{r_0} and $\frac{1}{\bar{P}_n}$ and between W_{r_0} and $CS \frac{[S]}{[M]}$ differ appreciably from the experimental slopes. It has, however, not been possible from our experimental results to establish definitely which of these two termination mechanisms—disproportionation or combination—is predominating. Some of the experimental results are closer to combination while others favour disproportionation. It seems that it would be rather impossible to distinguish decisively between the two terminating processes, because the differences in the various characteristics of the distribution and the relationship connecting them due to the two terminating processes are so small and subtle that they cannot be detected within the experimental error with the present experimental techniques. Moreover, the molecular weight determination by viscometric method does not give accurate result (Cleverden and Laker, 1951) in all cases of polymerization. Further, the experimental fractionation techniques used to obtain distribution are not sufficiently precise and the error involved in the assumption made with regard to plotting F_j against \bar{r}_j instead of r_j in drawing the experimental integral weight distribution curves cannot be avoided. It is also likely that not one but both the termination mechanisms can operate simultaneously. The only other relation of Palit and Majumdar that could be used for discriminating the two termination processes is the relation between \bar{P}_w and \bar{P}_n . The ratio of \bar{P}_w and \bar{P}_n is 2.0 in case of disproportionation while it varies from 1.5 to 2.0 in case of combination but in most cases it is not less than 1.8 except when CM is too low in bulk polymerization. Such a small difference of this ratio for the two terminating processes cannot be experimentally detected with confidence with the existing technique. If some experimental method could be found out in which the ratio $\frac{\bar{P}_w}{\bar{P}_n}$ can itself be directly obtained a decision between the two proposed modes of termination could be easily reached.

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ABSTRACT

Experiments were carried out to find the molecular weight distribution curves of polystyrene, polymerized in different solvent media and to compare them with those obtained theoretically by Palit and Majumdar (1954) and Watson (1953) for termination processes in the former case by both combination and disproportionation and in the latter case by combination only. A few linear relations involving different characteristics of the distributions as deduced by Palit and Majumdar and as follows from Watson equation were also tested from experimental data.

In respect of the order of weight fractions, the general nature, shape and spread of the curves, slopes of the linear relations, the theoretical distribution equations and the relationship connecting the different characteristics according to the equations of Palit and Majumdar are in perfect accord with experimental data. Watson's distribution equations are also found to be equally satisfactory but the slopes of the linear relations in this case differ appreciably from the experimental values.

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