785. *The Molecular-weight Distribution in Some Poly(methyl Methacrylates).*

By T. J. R. Weakley, R. J. P. Williams, and J. D. Wilson.

Methods of fractionating poly(methyl methacrylates) have been tested. A column procedure is used to fractionate the three types of polymer: (i) initiated by free radicals which are made by photolysis or by thermal decomposition of initiators; (ii) initiated by anions at room temperature; (iii) initiated by anions at low temperatures. Two anions were used as initiators. The molecular-weight distributions in the polymers are very different and depend on both the nature of the initiator and the conditions of polymerisation. The causes of these differences are discussed. Tung's equation,[1] which is said to be particularly suitable for representing distributions, is analysed.

The distribution of molecular weights in a polymer can be predicted only if the kinetics of formation of the polymer are readily described by simple equations. In preceding papers [2,3] it was shown that the molecular-weight distributions in polystyrenes, polyesters, and polysarcosines, prepared under controlled conditions, are very nearly those expected from different sets of simple rate equations. Polymerisation of methyl methacrylate does not proceed in such a simple way. Radical-initiation was thought to lead to the distribution expected from chain-termination by combination,[4] but more recently it has been shown by an analysis of end-groups [5,6] that both combination and disproportionation of radicals occur. In such circumstances the distribution of molecular weights is likely to vary considerably with the conditions of polymerisation, *e.g.*, temperature and solvent. In an early study [4] an attempt was made to determine the molecular-weight distribution in a radical-initiated polymer, but the methods used can now be shown to be unsatisfactory (see below). Brown and Szwarc [7] prepared a number of poly(methyl methacrylates) by anion-initiation where there is only self-termination. The distribution of the molecular weights in such polymers is calculated [8] to vary between that of the Poisson distribution and that found in radical-polymerisations when termination is by disproportionation. From analogy with work on other polymers [9,10] a totally different molecular-weight distribution is to be expected in isotactic polymers produced in the presence of colloidal catalysts. Isotactic poly(methyl methacrylates) can be prepared by initiation at low temperatures by fluorenyl-lithium.[11] These observations suggest that a wide variety of distributions will be found in poly(methyl methacrylates) and that a knowledge of the distributions will add to the understanding of the kinetics of their formation.

Fractionation.—Three methods have been used: fractional precipitation, fractional extraction in a column,[12] and chromatography.[2,3] In the first two procedures the only variable is the solvent (see Table 1). We used the same solvent systems for all three methods.

Our original chromatographic procedure has been modified for the fractionation of

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[1] Tung, *J. Polymer Sci.*, 1957, **24**, 333.
[2] Baker and Williams, *J.*, 1956, 2352.
[3] Pope, Weakley, and Williams, *J.*, 1959, 3442.
[4] Baxendale, Bywaters, and Evans, *Trans. Faraday Soc.*, 1946, **42**, 675.
[5] Bevington, Melville, and Taylor, *J. Polymer Sci.*, 1954, **12**, 449.
[6] Ayrey and Moore, *J. Polymer Sci.*, 1959, **36**, 41; Bamford and Jenkins, *Nature*, 1955, **176**, 78.
[7] Brown and Szwarc, *Trans. Faraday Soc.*, 1958, **54**, 516.
[8] Gold, *J. Chem. Phys.*, 1958, **28**, 91.
[9] Henry, *J. Polymer Sci.*, 1959, **36**, 3.
[10] Ang, *J. Polymer Sci.*, 1957, **25**, 126.
[11] Glucker, Stiles, and Yancoski, Abstracts of Papers, 135th Meeting Amer. Chem. Soc., 1959, S.14, paper 37.
[12] Desreux, *Rec. Trav. chim.*, 1949, **68**, 789.

polymers of high average molecular weight, for which the earlier method was unsatisfactory in the specific case of poly(methyl methacrylates). The column (Fig. 1) was inverted, so that the solvent flowed up the column, the temperature increasing from top to bottom. With this arrangement it is essential that the solvents are degassed before entering the column. A suitable device is shown in Fig. 1. The advantage of the inverted column is that polymer gel, which is denser than polymer solution in equilibrium with it, will flow, if it flows at all, into column regions of better solvent properties at a higher temperature. In the earlier procedure the gel flowed into cooler regions of lower solvent power and the column sometimes became blocked. The new procedure prevents blocking but we do not know if the method of fractionation is improved in any other way.

TABLE 1. *Solvent systems used in fractionations.*

Polymer class	$10^{-3}M_n$	Poor solvent	Good solvent	Comment
A	5—10	Cyclohexane	50% EtOH–COMeEt	Fractionation satisfactory
A, C	10—25	,,	7 : 3 EtOH–COMeEt	
A, C	25—60	,,	4 : 1 EtOH–COMeEt	
B, C, D	60—125	,, EtOH	COMeEt COMeEt	
D	>125	70% EtOH–COMeEt	COMeEt	Fractionation unsatisfactory

A second and frequent difficulty with the column procedure is that the sequence of molecular weights does not follow the sequence of tube numbers at the end of the chromatogram, undoubtedly owing to a failure of the method. Change of solvent gradient often overcomes this problem. When this difficulty is met the solution leaving the column is not saturated: the procedure cannot then be satisfactory in theory and is unlikely to be so in practice.

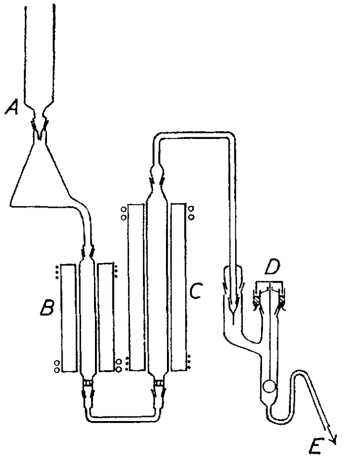

FIG. 1. *Apparatus for upward elution. A, Solvent reservoir and mixing vessel which produce the solvent gradient; B, degassing column, heated at top and cooled at bottom; C, " inverted " chromatographic column; D, syphon; E, to the fraction collector.*

Tests of the Fractionation.—The methods of fractionation of a polymer can be tested by the analysis of a polymer of known molecular-weight distribution or by the demonstration that the fractions are nearly homogeneous, *i.e.*, the weight average to number average molecular weight ratio, $M_w : M_n$, approaches one. There is no simple procedure which leads to a poly(methyl methacrylate) of known molecular-weight distribution. On the other hand, there is a well-defined relation [13,14] between M_w and the intrinsic viscosity in any solvent, $[\eta]$, which is independent of heterogeneity of the fractions. From recorded data it seems that for chloroform solutions the best relation is $[\eta]_{CHCl_3} = 6{\cdot}6 \times 10^{-5}M_w{}^{0{\cdot}77}$.

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[13] Bischoff and Desreux, *Bull. Soc. chim. belges*, 1952, **61**, 10.

[14] Cantow and Schulz, *Z. phys. Chem.* (*Frankfurt*), 1954, **2**, 9; Cantow, Meyerhoff, and Schulz, *J. Polymer Sci.*, 1953, **10**, 7.

From osmometric measurement of M_n and determination of $[\eta]_{CHCl_3}$ the homogeneity of polymers can be estimated. As a standard test polymer for fractionation, which was required in large quantities, we used a commercial product, called below polymer D.1. It has M_n of 68,000 and $[\eta]_{CHCl_3}$ 0·61, whence $M_w : M_n$ is 1·95. This polymer was fractionated several times by all three methods. Thirty-seven fractions prepared by the chromatographic method had $M_w : M_n$ ratios between 1·05 and 1·15, the ratio being independent of M_w. This means that a plot of $[\eta]_{CHCl_3}$ against M_n for these polymers lies very close to, but just above, the calibration curve of $[\eta]_{CHCl_3}$ against M_w. Twenty-seven fractions prepared by fractional solution of a film on glass beads held in a column had $M_w : M_n$ ratios between 1·05 and 1·15. This shows that the method is as efficient as the chromatographic procedure. There was, however, an increase of the ratio with molecular weight, so that at high molecular weights the method appears to be somewhat inferior to the column method. Thirty-three fractions from standard batch fractional-precipitation procedures, applied to polymer in 0·1—1·0 wt. % concentration, had $M_w : M_n$ from 1·10 to 1·40, showing that this method of fractionation is here unsatisfactory. There was a strong correlation of the ratio with molecular weight, the ratio increasing as the molecular weight increased. No dependence of the ratio on dilution of the polymer in the fractionation procedure could be demonstrated in the above concentration range. The batch method of fractional precipitation was used in an early fractionation [4] of poly(methyl methacrylate); there also a calibration curve of $[\eta]_{CHCl_3}$ against M_n determined from batch fractions was used to find the molecular weights of the fractions. The combination of these procedures leads to a distribution for polymer D.1. very different from that obtained by the method used here—fractionation by the chromatographic procedure and molecular-weight determination from a calibration curve of $[\eta]_{CHCl_3}$ against M_n for column fractions. We do not consider that the earlier procedure can give a correct distribution. In Fig. 2 we illustrate this point by giving the distribution of molecular weights in the batch fractions. If instead of a molecular-weight distribution a distribution is given by plotting cumulative weight per cent against $[\eta]_{CHCl_3}$, then we have found that in a number of cases the viscosity distribution is independent of the fractionation procedure. Thus the best available molecular-weight distribution for a polymer can be obtained by batch fractionation if the molecular weights of the fractions are then obtained as weight averages from a good calibration of $[\eta]$ against M_w.

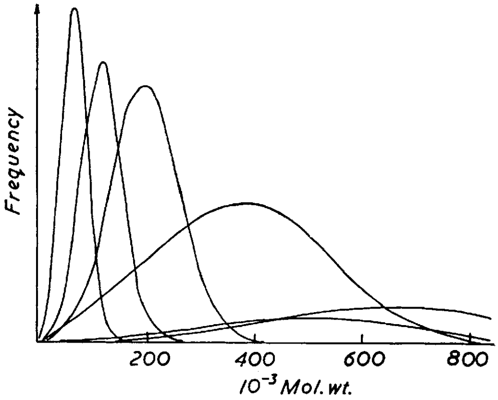

FIG. 2. *The frequency distribution of molecular weights in six batch fractions from an industrial poly(methyl methacrylate).*

Molecular-weight Distributions.—We have analysed the following polymers (Table 2): (A) Polymers of low molecular weight prepared by thermal free-radical initiation in both the presence and the absence of chain-transfer agents; (B) polymers of medium molecular weight prepared by photochemical initiation in the presence of ferric salts; (C) a series of polymers prepared by anion-initiation; (D) two emulsion polymers prepared industrially. (For details see Table 2.) We shall discuss the polymers in each class separately.

(A) The conditions of preparation of these polymers were rather ill-defined (see p. 3971) and we expected the polymers to have broad molecular-weight distributions. In no case was this true. A typical distribution is shown in Fig. 3 and compared with the distribution expected for termination by combination. It will be seen that the polymer has a narrow distribution. This result is the more surprising as the conditions (high initiator concentration, high monomer concentration, presence of chain transfer agents) might all have led in theory to much broadening of the distribution.[15] We do not understand the observations.*

TABLE 2. *The polymers.*

Polymer	$10^{-3}M_n$	$10^{-3}M_w$	Method of preparation		
			Solvent	Regulator	Temp.
A.1	2·5	4·0	CCl_4	$HS{\cdot}CH_2{\cdot}CO_2H$	B. p.
2	2·5	4·0	C_6H_6	,,	,,
3	4·0	6·0	NEt_3	None	,,
4	5·0	10·0	CCl_4	,,	,,
5	5·0	10·0	CCl_4	,,	,,
7	22·0	30·0	CCl_4	,,	,,
8	30·0	38·0	Bulk monomer		100°
B.1	50·0	130·0	Action of light on ferric picolinate at different monomer concentrations		
2	90·0	170·0			
C.1	20·0	110·0	Toluene		−80°
2	25·0	145·0	,,		,,
3	31·0	160·0	,,		,,
4	33·0	190·0	,,		,,
5	21·0	45·0	,,		−35
6	4·5	5·0	,,		20
7	8·5	12·0	,,		20
8	10·5	21·0	,,		−70
9	31·0	67·0	,,		−70
10	30·0	65·0	,,		−70
D.1	58·0	131·1	Industrial emulsion polymerisation		
2	160·0	400·0	,, ,, ,,		

Initiation: A, with azobutyronitrile; C.1 to C.7 with fluorenyl-lithium; C.8 to C.10 with butyl-lithium; D, with benzoyl peroxide.

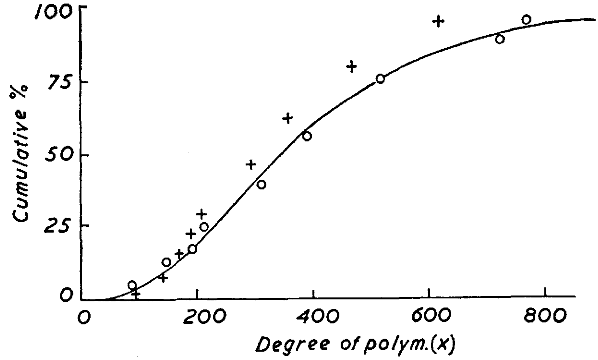

FIG. 3. *The molecular-weight distribution in a polymer low molecular weight,* A.7 *(two experiments), compared with the theoretical distribution for chain-ending by combination.*

(D) The emulsion polymers are also thermally initiated by radicals. They too have relatively narrow distributions, as narrow as that expected for chain termination by disproportionation (see Fig. 4). The distributions are much narrower than that of the industrial polystyrene analysed earlier.[2] It should be noted that these polymerisations

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* One of the Referees pointed out that distributions such as we have observed could be explained for polymerisations in which the rate of reaction was diffusion-controlled. The experimental conditions make such control possible, and methyl methacrylate polymerisations are known to be diffusion-controlled under certain conditions.

[15] Bamford, Barb, Jenkins, and Onyon, " The Kinetics of Vinyl Polymerisation by Radical Mechanisms," Butterworths, London, 1959, p. 295.

were carried to roughly 100% conversion so that a very broad distribution in the polymers was expected.[15]

(B) Photochemical initiation gave polymers with a distribution very close to that for radical chain-ending by disproportionation. This is in satisfactory agreement with the observation from end-group analysis that disproportionation of radicals is more frequent than combination in the polymerisation of methyl methacrylate.[5,6]

(C) The polymers in this group had both very broad and very narrow molecular-weight distributions (Fig. 5) depending upon the polymerisation conditions. Polymer C.7 has a distribution not much broader than that given by the Poisson distribution. Polymer C.2 has a distribution much broader than any we have examined before and is typical of isotactic polymers.[9,10] Polymer C.2, like the other broad-distribution polymers, was prepared at low temperature whereas polymer C.7 was prepared at high temperature. Table 2 also shows that polymerisation with butyl-lithium produces polymers of narrower distribution than polymerisation with fluorenyl-lithium at the same temperature. The narrow distributions are of the kind expected for anion-initiated polymerisation in solution. Thus it seemed likely that high-temperature polymerisations occur in solution, though this is not certain, but that the polymerisations at low temperatures take place in the presence of a suspension of the initiator—the normal condition for obtaining an isotatic polymer. The suspension is easily observed at the low temperatures. The suggestion that the polymerisation may proceed by two paths, perhaps simultaneously, is supported by a more detailed analysis of the distributions and by examination of the end-groups incorporated in the polymers under different reaction conditions.

Tung has shown that the molecular-weight distributions in isotactic polymers are somewhat peculiar. He plots distributions as $\log < \ln \{1/[1 - I(x)]\} >$ against $\log (x/x_n)$ where $I(x)$ is the experimental integral weight fraction at the degree of polymerisation x, and x_n is the average degree of polymerisation of the fraction. Plotted in this form, distributions generally approximate to straight lines.[1] We analyse this statement in the Appendix and show that, although it is a half-truth (no theoretical distribution devised from kinetic schemes gives an exact straight line), most experimentally determined distributions can be represented by a fair straight line with these co-ordinates. For example, as Fig. 4 shows, poly(methyl methacrylates) with narrow distribution, $M_w : M_n \approx 1{\cdot}2$, polymethylacrylates with approximately the "most probable" distribution, $M_w : M_n = 2{\cdot}0$, and polystyrene with very broad distribution, $M_w : M_n = 3{\cdot}5$, give good straight lines though of very different slopes. In most cases that we have studied, the inverse of the slope is related to the ratio $M_w : M_n$. The low-temperature, anion-initiated, isotactic polymers do not give a straight line but give two intersecting lines (cf. refs.[9,10]). In the Appendix we show how such a Tung plot can arise in an experimental distribution which has resulted from the combination of two quite narrow distributions, centred about widely different number-average molecular weights: if the two distributions are both of the Poisson type then the plot breaks down into two almost parallel straight lines. Two parallel lines of infinite slope would be obtained from a mixture of two pure single-component compounds. As the two distributions broaden the region of their overlap (if we assume roughly equal quantities of two polymers of very different M_n) becomes sufficiently important to dominate the plot from about 50% to 95%, giving it a slope, b, in this region of 0·5—0·7. If the polymers both have very broad distributions the plot becomes a single line of about unit slope and this is also true of a polymer built up of a very large number of component distributions of equal weight. Tung's method of plotting polymer distributions indicates therefore that the low-temperature polymers we are examining could be mixtures of two relatively narrow distributions centred about very different molecular-weight averages.

End-group Analysis of Anion-initiated Polymers.—The polymerisation of methyl methacrylate by both butyl- and fluorenyl-lithium was carried out in toluene. The order of acid strengths of these three anions is fluorenyl > tolyl > butyl, so that proton transfer is to be expected from toluene to the butyl anion, but not from toluene to the fluorenyl anion. In a solution polymerisation in toluene initiated by butyl-lithium we might expect to find polymer with tolyl end-groups on the assumption that the reaction of the butyl anion with monomer is not too fast. Tolyl end-groups should not be incorporated if the polymerisation occurs on the surface of the butyl-lithium or in polymerisation initiated by fluorenyl-lithium either in solution or on the surface of a suspension. In the latter case we expect fluorenyl end-groups only. Both tolyl and fluorenyl end-groups are readily detected spectrophotometrically in the presence of the polymer, especially if their concentration is reasonably high as is the case in polymers of low molecular weight. In estimating tolyl end-groups contamination of the polymer by solvent must be reduced. This was accomplished by reprecipitation of polymer from chloroform and drying in an oven overnight at 60°. Table 3 shows that this treatment virtually eliminates contamination by toluene. In

FIG. 4. *Tung plots for molecular-weight distributions in three polymers of greatly differing heterogeneity.* (*Subtract* 1·5 *units from x values for* C.6 *plot and add* 1·0 *to y values for the polystyrene* (*P*) *plot.* D.1 *data illustrate reproducibility.*)

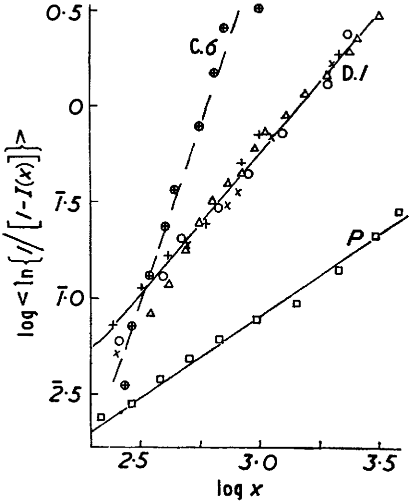
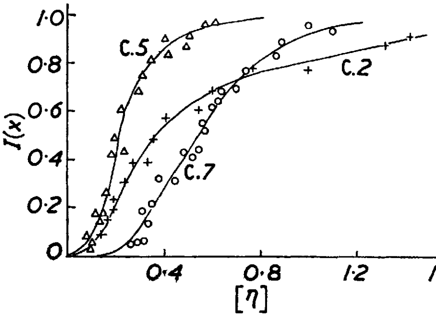


FIG. 5. *The distribution of viscosity in three anion-initiated polymers, produced at different temperatures.*



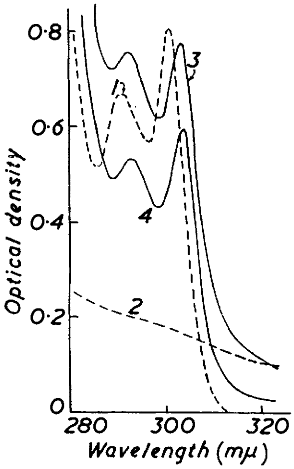


FIG. 6. *The absorption spectra of* (1) *fluorene* (1·09 × 10^{-4} M), (2) *a polymer with no absorbing end-groups* (1·0% *solution*), (3) *and* (4) *typical polymers with fluorenyl end-groups* (0·25% *solution*).

this experiment a polymer of very high molecular weight was used to reduce any contribution from end-groups. The Table also shows that two fractions of high molecular weight from a polymer giving a Tung plot characteristic of isotactic polymers contained fewer tolyl end-groups per polymer molecule than did the whole original polymers, and therefore than the fractions of low molecular weight. This result is in agreement with the supposition that material of high molecular weight is not produced in the same way as that of low molecular weight. The incorporation of tolyl end-groups suggests that the latter polymer is formed in solution.

In the spectrophotometric estimation of fluorenyl end-groups we have had to adopt a special procedure. We observed that, whereas fluorene itself had absorption maxima at 291 and 301 mμ, the absorption maxima in polymers containing fluorenyl end-groups were at 292—295 and 303·5 mμ (Fig. 6). This shift is not due to the polymer background as a spectrum of a mixture of fluorene and polymer with non-absorbing end-groups is merely a sum of the component spectra. The fluorene absorption cannot be used directly as a basis for measuring fluorenyl end-groups. Absorption of a polymer not containing fluorenyl end-groups changed rather considerably, below 305 mμ, but showed little significant change between 305 and 310 mμ. The latter region of the spectrum is where the fluorenyl absorption changes most rapidly with change of wavelength. Thus, if the absorbancy at 305 mμ is D_1 and that at 310 mμ is D_2, then $(D_1 - D_2)/c$, where c is the weight concentration percent, will be proportional to the number of fluorenyl end-groups per gram of polymer and therefore to $1/M_n$ (a constant number of end-groups per polymer molecule being assumed). For sharp fractions $[\eta]_{CHCl_3} = KM_n{}^{\alpha}$ where K and α are constants. Combining this relation with

$$\log [(D_1 - D_2)/c] = A - \log M_n$$

where A is a proportionality constant, we have

$$\alpha A + \log K - \alpha \log [(D_1 - D_2)/c] = \log [\eta]_{CHCl_3} \quad . \quad . \quad . \quad . \quad (1)$$

In Fig. 7 we have plotted log $[\eta]_{CHCl_3}$ against log $[(D_1 - D_2)/c]$ for a series of fractions. In

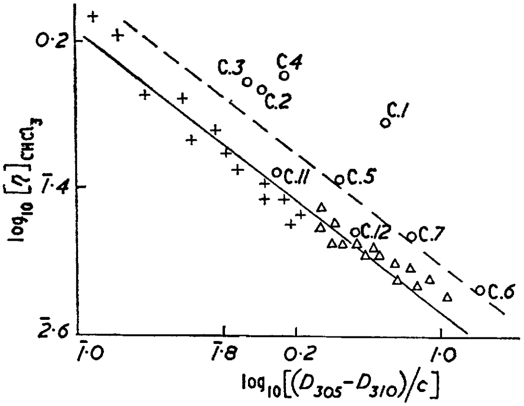


FIG. 7. *Relation between the absorbancy increment and the viscosity of the polymers,* $[\eta]$, *and fractions from these polymers.* + *from* C.2; Δ *from* C.7. C.11 *and* C.12 *were polymers prepared at* 20°.

TABLE 3. *Tolyl end-groups in poly(methyl methacrylates).*

Polymer	M_n	End-groups per polymer mol.
C.9	36,000	1·0 ± 0·1
Fraction from C.9	40,000	0·5 ± 0·1
Fraction from C.9	80,000	0·1 ± 0·1
Low fractions C.9	<30,000	1·0 ± 0·1
Polymer	M_n	Apparent end-groups per polymer mol.
B.3 pptd. from toluene	350,000	25·0 ± 5·0
B.3 repptd. from chloroform		0·1 ± 0·1

order to obtain the number of end-groups per molecule we compare these data with a calculated relationship. In equation (1), K and α are known from the earlier studies on sharp fractions, $[\eta]_{CHCl_3} = 6{\cdot}6 \times 10^{-5}M^{0{\cdot}77}$. We must evaluate A. This can be done by assuming that the polymer fractions all contain material with the same number of end-groups per molecule (1·0 when A is zero or 2 when A is 0·30). The absorption increment per fluorenyl group can be evaluated from the fluorene spectrum by assuming that the difference in extinction coefficient between 303 and 308 mμ for fluorene is the same as that between 305 and 310 mμ for the fluorenyl group, a reasonable assumption as their extinction coefficients are known to be very similar. The theoretical lines on the two possible assumptions about the number of end-groups are plotted on Fig. 7. Over the range of log $[\eta]$ from $-1{\cdot}2$ to $-0{\cdot}2$ there can be little doubt that the polymers contain one (or slightly fewer) fluorenyl end-group per molecule. We have checked this result by determining M_n for a polymer by osmometry and by this method. The results were: by osmometry, 45,000; by the spectrophotometric method, 39,000. At very low viscosities there appears to be a slightly greater number of end-groups per molecule. However, it must be remembered that the viscosity–molecular weight relation has never been adequately tested in this region though there is some evidence suggesting that α in the equation $[\eta] = KM^{\alpha}$ changes from 0·7 towards 0·5 at low molecular weight. This change would create the erroneous impression of a high number of end-groups per molecule from Fig. 7. At very high molecular weights there also appears to be rather more than one end-group per polymer molecule. The scatter of the points prevents a definite conclusion. Summarising, it seems most probable that the number of end-groups per molecule does not exceed one in the high-temperature polymerisations, no isotactic polymer being present. This is expected from the general treatment of anion-initiated polymerisations in solution.[7,8] We also conclude that it is unlikely that there is more than one fluorenyl end-group per molecule in the fractions of low molecular weight from the isotactic polymers. Since our measurements were completed, very similar results have been reported[16] for isotactic polymers in what seem to be more detailed studies. Thus in the case of polymers initiated by fluorenyl-lithium the number of end-groups is the same for all the fractions of the polymer and the end-group analysis does not distinguish between the two parts of the distribution. The marked difference between this result and that obtained in the butyl-lithium polymerisations argues in favour of simultaneous polymerisation by two mechanisms. The end-group analysis also shows that the initiation in the production of these polymers is reaction of a fluorenyl anion with monomer and that the termination probably does not involve such a mechanism. Termination could then be by self-termination,[7] in which case the distribution in the isotactic portion is much the same as that in the non-isotactic portion, moderately narrow, with $M_w : M_n$ from 1·1 to 1·5. The combination of two such distributions with a suitable choice of the two M_n values could give the total distributions we have observed (see above). However, only a much more detailed analysis of the polymers produced by the different anions under different conditions can test this tentative suggestion.

Experimental—Preparation of polymers. Class A polymers were all prepared by the same method. A given weight of freshly redistilled methyl methacrylate was dissolved in a volume of purified solvent containing weighed amounts of initiator and regulator (see Table 4). Oxygen was excluded by bubbling oxygen-free nitrogen through the solutions. Polymerisation was carried out by refluxing the solution and was discontinued at 30—70% conversion.

Photochemical initiation was brought about by irradiating solutions of monomer in water or aqueous alcohol in the presence of a series of ferric salts with ultraviolet light from a mercury-vapour lamp. The reaction vessel was a quartz cell fitted with suitable gas-leads to permit the displacement of dissolved oxygen with oxygen-free nitrogen before irradiation. The details of the apparatus and procedure were in all ways conventional. Under illumination several

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[16] Glusker, Lystoff, and Stiles, Abs. Papers, 136th Meeting Amer. Chem. Soc., 1959, T.8, paper 16; Graham, Dunkelberger, Panchak, and Kampf, *ibid.*, S.14, paper 38.

ferric complexes failed to initiate polymerisation. The order of effectiveness was oxalate > picolinate, and quinaldinate > oxinate; acetylacetonate caused little or no initiation.

Butyl- and fluorenyl-lithium were prepared by recorded methods. Anion-initiated polymers (Table 5) from these salts were made by a method [16] kindly communicated by members of the research laboratory of Röhm and Haas, Philadelphia, U.S.A.

Osmotic measurements were made in a conventional manner.

TABLE 4. *Preparative details of radical polymerisations.*

Polymer	Solvent	Solvent (ml.)	Monomer (g.)	Initiator (g.)	Regulator (g.)	Conversion (%)	Temp.
A.1	CCl_4	35	3·8	0·027	0·479	25	B. p.
A.2	C_6H_6	16	4·5	0·048	0·064	69	,,
A.3	NEt_3	70	4·5	0·089	—	35	,,
A.4	CCl_4	29	3·8	0·030	—	37	,,
A.5	CCl_4	30	2·8	0·037	—	40	,,
A.7	CCl_4	30	2·8	0·041	—	64	,,
A.8	Bulk monomer		4·0	0·034	—		100°

TABLE 5. *Preparative details of anion-polymerisations.*

Polymer	Butyl-lithium		Fluorene (g.)	Suspension (ml.) used in polymn.
	M	Ml.		
C.1	0·76	27	3·4	20
C.2	0·69	29	5·1	25
C.3	0·75	22	3·0	20
C.4	0·76	27	3·4	10
C.5	0·69	29	5·1	25
C.6	0·76	28	0·95	20
C.7	2·6	12	6·0	10
C.8	0·76	10	—	—
C.9	2·6	10	—	—
C.10	2·6	10	—	—

APPENDIX

Tung [1] has suggested that experimental integral weight fraction, $I(x)$, curves for fairly narrow distributions approximate to the equation

$$I(x) = 1 - e^{-ax^b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where x is the degree of polymerisation and a and b are constants. If this expression did represent distributions closely it would provide a way of plotting distributions as straight lines, $\log < \ln \{1/[1 - I(x)]\} >$ against $\log (x/\bar{x}_n)$, and a and b might be expected to define characteristics of the distribution. The purpose of this Appendix is to enquire into the significance of the equation (1).

From eqn. (1), the weight fraction of an x-mer, $W(x)$, is

$$W(x) = ab \,.\, x^{b-1}e^{-ax^b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The expressions for $W(x)$ for radical-initiated polymers where the termination is by (i) combination of radicals [$M_w : M_n = 3 : 2$, equation (3)] or (ii) disproportionation of radicals [$M_w : M_n = 2 : 1$, equation (4)] are:

$$W(x) = x(x - 1)p^{x-2}(1 - p)^{3/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$W(x) = xp_1^{x-1}(1 - p_1)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $p = (1 - 2/\bar{x}_n)$, and $p_1 = (1 - 1/\bar{x}_n)$, and $\bar{x}_n$ is the number-average degree of polymerisation. Now p and $p_1 \approx 1{\cdot}0$ and $x \gg 1$, so that equations (3) and (4) approximate to (5) and (6) respectively:

$$W(x) = x^2e^{x \ln p}(1 - p)^{3/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$W(x) = xe^{x \ln p_1}(1 - p)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Integration of eqns. (5) and (6), by using the approximations $(1 - p) = -\ln p$ or $(1 - p_1) = -\ln p_1$ and then eliminating p or p_1, gives:

$$I(x) = 1 - e^{-2x/\bar{x}_n}(1 + 2x/\bar{x}_n + 2x^2/\bar{x}_n{}^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$I(x) = 1 - e^{-x/\bar{x}_n}(1 + x/\bar{x}_n) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Tung plots log $< \ln \{1/[1 - I(x)]\} >$ against log $(x/\bar{x}_n)$ [cf. equation (1)]. Now, equations (7) and (8) will not give linear plots if these co-ordinates are used (see Fig. 8). However, in practice, the curvature of the plot is slight, and equation (7) can be said to approximate to equation (1) with $b = 2{\cdot}0$ and a dependent on molecular weight average for $x/\bar{x}_n$ from 0·5 to 2·0. Similarly, equation (8) approximates to equation (1) with $b = 1{\cdot}6$ and a dependent on molecular weight average with the same limits for $x/\bar{x}_n$. The actual slopes of (7) and (8) are as tabulated:

$x/\bar{x}_n$	= 0·5	1·0	2·0
Polymer of distribution (3), b	= 2·39	2·05	1·72
Polymer of distribution (4), b	= 1·76	1·63	1·48

It appears that the Tung procedure could supply a quick way of distinguishing between distributions. However, at high $x/\bar{x}_n$, $b \approx 1{\cdot}0$ for both these distributions. It will be very dangerous to draw any conclusions from the value of b at high $x/\bar{x}_n$. Now in certain distributions (see above), even lower values of b have been observed over part of a very broad distribution. When plotted by the Tung procedure these distributions fall into two parts, one with high b at low molecular weights and one with low b at high molecular weights. We shall show now how such a plot can arise from a combination of two distributions of the kind (3) or (4), or for that matter of the kind (1). The two distributions need only differ greatly in $\bar{x}_n$ (average molecular weight); they must not be either very narrow or very broad if they are of kind (1).

FIG. 8. *Tung plots for polymer distributions obeying the formulæ given in the text. Numbers on figure refer to equations in the Appendix.*

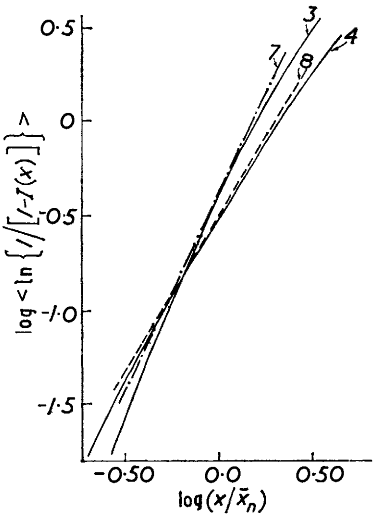
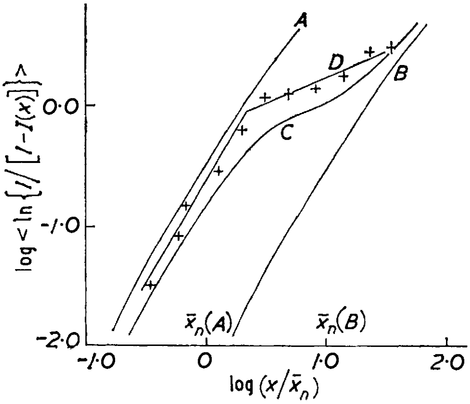


FIG. 9. *Tung plots, A and B, for two polymers having the most probable molecular-weight distribution but of average molecular weights as* 1·0 : 10·0; *and for a polymer, C, composed of equal parts by weight of each of A and B. D is an experimental distribution for the anion-initiated polymer,* C.4.



Consider the artificial 1 : 1 (by wt.) mixture of two polymers each having a distribution given by (4), but with an $\bar{x}_n$ ratio of 10·0 : 1. The Tung plot can be worked out empirically (Fig. 9), log (ln $\{1/[1 - I(x)]\} >$ being plotted against log $[x/\bar{x}_n(c)]$ where $\bar{x}_n(c)$ is the number average degree of polymerisation of the mixture.

The slope b at low x and up to $I(x) = 0{\cdot}4$ is very like that of a narrow-distribution polymer. Above this value there is a sharp change of slope and the best straight line through the points from $I(x)$ 0·55—0·90 is 0·67. This line is obviously rather a rough approximation to the points, but in a real experiment where there are considerable errors in the value of x for each fraction a quite good straight line might well be obtained. Thus the Tung plot for a mixture of two such polymers could apparently give two intersecting straight lines of very different slopes. Such distributions are discussed above.

The Poisson distribution can be written

$$W(x) \doteq \{x \exp [(x - 2) \ln \bar{x}_n] \exp e^{-\bar{x}_n}\}/(x - 1)! \quad . \quad . \quad . \quad . \quad (9)$$

There is no simple form for the integral weight distribution, so that it is hard to compare the expression with equation (1). However, if the distribution is plotted with Tung's co-ordinates one finds that b increases with $\bar{x}_n$. For $\bar{x}_n = 100$, b is 12·0.

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INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

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