456. *A New Chromatographic Procedure and its Application to High Polymers.*

By C. A. BAKER and R. J. P. WILLIAMS.

A new chromatographic method for the fractionation of mixtures is described which may be generally applicable. It employs equilibration between a moving solution and a stationary precipitated phase along the length of a column. The column is virtually a continuous series of filter beds covering a range of temperatures. The application to the fractionation of polystyrenes is described, and the homogeneity of the fractions compared with those obtained by earlier methods. Details of the properties of the fractions are given.

CHROMATOGRAPHIC procedures utilise repeated transfer across phase boundaries to bring about the separation of components in mixtures. The three common forms are known as adsorption, liquid-partition, and vapour-phase chromatography and employ respectively equilibration between (1) an adsorbed film on a solid surface and a flowing solution, (2) a stationary solution and a flowing solution, (3) a stationary solution or an adsorbed film and a flowing gas stream. In each case the static phase is held on a support which is packed in a column. The procedures make use of differences in adsorbability, solubility, and vapour pressure, but no method has been devised which takes advantage of the differences in the specific forces in interaction between like molecules which bring about crystallisation. The method described here fills this gap in so far as it is a chromatographic method based upon the equilibration of substances between a stationary precipitated phase and a moving solution. In essence the method requires a column of inert material, which acts only as a filter bed, in a temperature jacket. The jacket is so designed that at the top it is held at a higher temperature than at the bottom, *i.e.*, the column is made into a continuous series of filter beds covering a continuous range of temperatures. A further requirement is a progressively modified solvent, as used in gradient elution,[1] which is passed down the column. The material to be analysed is applied to the top of the column as in other chromatographic techniques. There is the additional requirement that the substance under examination must have a positive temperature coefficient of solubility.

Consider a simple substance placed at the top of such a column. Initially, the solvent passing down the column is chosen so that negligible quantites of material dissolve even at the highest temperature of the column. This will be called the poor solvent. A progressive change of solvent, brought about by a mixing vessel, leads on to the column a liquid with an increasing solvent power for the substance. At some time after the beginning of an experiment, material will dissolve appreciably at the top and pass down the filter beds to colder parts of the column. Provided the substance has a positive temperature coefficient

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[1] Bannister, Phillips, and Williams, *Analyt. Chem.*, 1954, **26**, 1451; Williams, *Analyst*, 1952, **77**, 905.

of solubility there will be a precipitation of material at these lower temperatures. The precipitated material will be re-equilibrated with the mobile phase as more and further improved solvent passes over it. If the equilibrium of the material between the solid and the liquid phase is rapid, the substance must travel as a saturated solution down the column. It is continuously transferred between the stationary precipitated phase and the mobile solution, and finally passes out from the column into some collecting device, *e.g.*, an automatic fraction collector, as a saturated solution at the temperature of the bottom of the column. If a mixture of two substances is applied to the column and *they form mixed crystals* (or they grossly affect the solubility of one another by interaction in solution) then as they travel through the column they will automatically go through a series of separations by continuous fractional reprecipitation or recrystallisation. Fig. 1 shows the expected shape of the concentration–fraction number diagram for a simple substance (cf. Fig. 4).

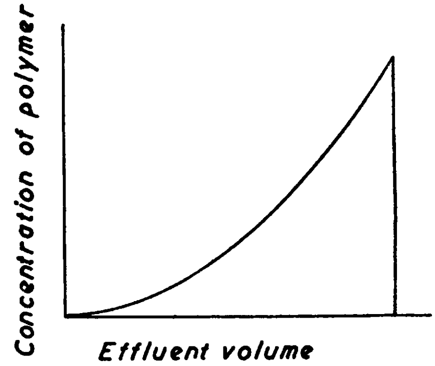


FIG. 1. *The expected peak shape in " crystallisation chromatography."*

FIG. 2*a*. *The apparatus. (Apart from the components described in the text, P is a magnetic stirrer, O a drop capillary.)*

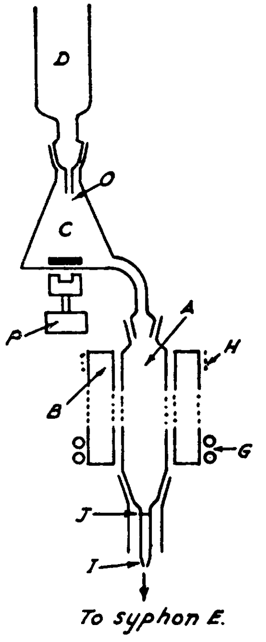
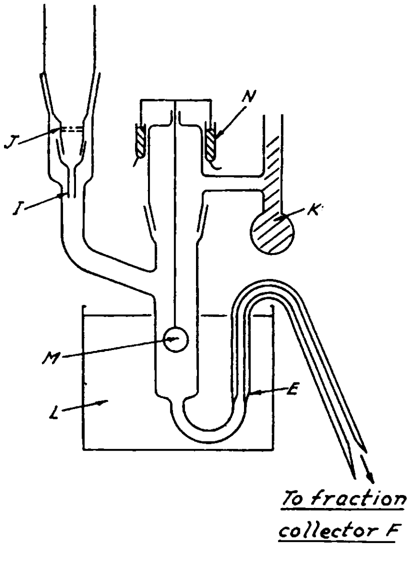


FIG. 2*b*. *The syphon. (The vessel K is filled with cotton-wool soaked in solvent; M, a float, operates the mercury contacts, N, which are connected to the relay of the fraction collector.)*



The Apparatus.—The essential parts of the apparatus (Figs. 2*a* and *b*) are the column *A*, the temperature jacket *B*, the mixing vessel *C* which provides the solvent gradient, the container of good solvent *D*, a syphon *E*, and a fraction collector *F*. The arrangement of these parts is shown in Figs. 2*a* and 2*b*.

The column used is a glass tube, 35 cm. long and 24 mm. wide (external diameter). It is packed with glass beads of average size 0·1 mm. diameter (sold under the name " Ballotine " no. 15 by the English Glass Co.). The glass beads are packed as a slurry in the poor solvent, which is also put in the mixing vessel *C*. Near the bottom of the glass column is fitted a 1 cm. no. 3 sintered-glass disc, *J*, and the column is tapered at the bottom to a fine capillary *I*, which controls the rate of flow of solvent through the column as the glass beads permit too rapid a flow. In later forms of the column the capillary, which became blocked infrequently, was made exchangeable by fitting it to a B. 7 cone and terminating the column in a corresponding Quickfit B. 7 socket (Fig. 2*b*).

The jacket is a cylindrical aluminium block, *B*, of length 30 cm. and external diameter 50 mm., from which has been drilled out a hole of 25 mm. diameter making it a close fit with the external diameter of the glass column. The top of the jacket is heated by an electric heating spiral, *H*, dissipating 60 w. The bottom is cooled by a spiral of 4 turns of copper tubing, *G*, through which cold tap-water is passed. The whole column is well insulated with asbestos string and cotton-wool so that, while the bottom of the column is held close to 10°, the top is at 60—65°. It has been proved that the temperature of the glass-bead packing varies linearly down the jacketed length of the column.

The solvent gradient is supplied by an apparatus already described[1] and illustrated in Fig. 2*a*. The solvent gradient obtained is logarithmic in form.[2] The advantages of this gradient form will be made apparent later (p. 2359). Other gradients[3] may be preferable in different circumstances.

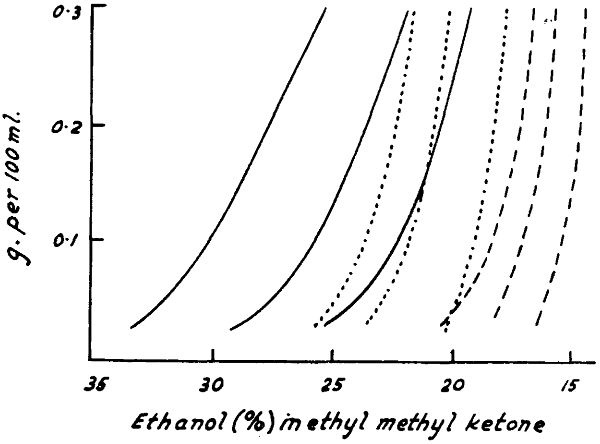


FIG. 3. *The solubility of three polymer fractions. (Continuous line is for a fraction of low molecular weight, the dotted line for one of intermediate molecular weight, and the broken line for one of high molecular weight. The solubility of each fraction is recorded at three temperatures from left to right:* 25°, 45°, *and* 65°.)

The collection of saturated solutions from a column is more difficult than that of unsaturated solutions normally handled in chromatography. Evaporation of solvent in the syphon, used here to cut the fractions as in other volume-fraction collectors, must be prevented, for if it is allowed to take place a second phase will separate in the syphon and may not be cleanly delivered into the fraction-collector tubes. In the experiments described here two precautions were taken. The syphon was connected to a solvent reservoir, *K*, as shown in Fig. 2*b*, so that the air space above the liquid in the syphon was always saturated. The bottom of the syphon was immersed in a small thermostat, *L*, held at 35° so that the liquid was held at a temperature well above that at which a second phase separates. In these circumstances precipitation was never observed in the syphon but it frequently occurred in the test-tubes on the collector.

Choice of Test Substances.—Suitable mixtures for separation on the column must have positive temperature coefficients of solubility and form mixed crystals or solid solutions. High polymers fulfil these conditions (see Fig. 3). They are mixtures of compounds which differ only in the number of identical units in the chains of the molecules. The usual method for their fractionation is a single-stage fractional precipitation brought about by cooling a solution, *i.e.*, a theoretical stage of the column. The method is far from satisfactory[4] and could obviously be

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[2] Alm, Williams, and Tiselius, *Acta Chem. Scand.*, 1952, **6**, 826.

[3] Bock and Ling, *Analyt. Chem.*, 1954, **26**, 1543.

[4] Baxendale, Bywaters, and Evans, *Trans. Faraday Soc.*, 1946, **42**, 675.

improved by an increase in the number of stages. It should be observed that intermolecular forces in many high polymers are often so weak that they are of low crystallinity and are precipitated as highly viscous liquids or gels. The operation of the column is not affected by the absence of solid crystals providing that the polymer gel does not flow through the column.

For testing the method of fractionation, polystyrene was chosen, on the advice of Professor H. W. Melville (Birmingham University). The polymerisation of styrene has been carefully studied, and kinetic analysis of the rate data indicates that the polymer is ideally linear, *i.e.*, there is neither cross-linking nor chain-branching.[5] An appendix to this paper (p. 2361), is concerned with the demonstration of these facts for particular polymers prepared by us. Such polymers have two advantages from the points of view of this study. The solubility of fractions is proportional to chain lengths (Fig. 3), a readily determined parameter, and the simple polymerisation kinetics lead to a determinable molecular-weight distribution which can then be assumed as a check on the method of analysis proposed here (p. 2362).

Three such polystyrenes have been prepared (p. 2361). The number-average molecular weights, M_n, of the polymers as given by the rate expressions were 100,000, 316,000, and 741,000. Their respective osmotic molecular weights were found to be 108,000, 350,000, and 725,000, with a possible error of $\pm 5\%$. The polymers will be referred to in the paper by their osmotic values, *e.g.*, 108,000 polystyrene.

Analysis of Molecular-weight Distribution in Certain Polystyrenes.—The polymers were analysed under the following column conditions: temperature gradient 60—10°; solvent gradient from 100% ethanol in the mixing vessel and the column initially, to 100% ethyl methyl ketone in the top vessel; mixing vessel 150 ml.; flow-rate 5 ml./hr.; 10-ml. fractions were collected. The polymer was applied to the top of the column as follows; 300 mg. of polymer were dissolved in 10 ml. of ethyl methyl ketone; the solution was added to 30 g. of glass beads, and the solvent evaporated with a hot-air fan. The polymer coats the glass beads as a thin film but leaves the beads apparently unaffected, at least to the naked eye. These bead are added to the top of the column in a slurry in the poor solvent and fill a distance of 4 cm. along its length. This is a similar distance to the length of the heating spiral at the top of the column.

In each experiment 50 test-tubes of effluent were collected. The tubes were analysed for polymer by the following procedure. The polymer solution in the tube was transferred with washings with ethyl methyl ketone to a 250-ml. beaker. On occasion, polymer gel was found to have separated in some of the test-tubes owing to evaporation of solvent. This polymer was transferred by dissolving it with additional ethyl methyl ketone. The polymer solution in the beaker may now be some 30 ml. This solution was flooded quickly with 100 ml. of methanol while being stirred rapidly. A fine suspension of polymer resulted, which gradually settled. After at least 3 hr. the clear liquid was decanted. The precipitate was thoroughly washed by decantation with methanol and finally transferred to a watch-glass of known weight. After allowance of a time known to be sufficient for the evaporation of the solvent, the watch-glass were weighed. In this way the amount and thence the concentration of polymer in each test-tube were found. Recovery of polymer invariably exceeded 90% and was usually greater than 95%. The difference from complete recovery is due to the complicated handling of fractions. In separate experiments, designed to test the recovery, it was proved that all the polymer was recovered from the column.

The fractions were analysed by measurement of their specific viscosity (0·5% solution in toluene) in an Ostwald viscometer, and in certain cases by osmotic-pressure determinations at a given concentration. Later in the work a calibration curve of viscosity against osmotic molecular weight was set up by using some of the fractionated material. From this calibration and the information from the fractionation on the column, a cumulative percentage-composition curve against molecular weight can be obtained for any given polymer. A typical analysis of a chromatographic experiment for the 108,000 polystyrene is shown in Fig. 4. It is a plot of concentration of polymer in a given fraction against the tube number of the fraction. All but the last two tubes contained saturated solutions of polymer. The numbers inserted in the Figure refer to the specific viscosity of the fractions. The viscosity increases along the fractions as expected from the decrease of solubility with increase in molecular weight (see Fig. 3). The experiment was repeated four times and shown to be highly reproducible. A detailed discussion of the properties of the fractions is given on p. 2359. Experiments with the 350,000 and 725,000 polymers were carried out with some trivial modifications in method (see p. 2358). From these

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[5] Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, pp. 106 *et seq.*

analyses and the calibration curve of viscosity against molecular weight, molecular-weight distributions in the three polymers have been determined and compared with theory (see Appendix). The agreement, as shown in Figs. 5 and 6, is good. Exact coincidence between experiment and theory could not be expected in view of the number of different assumptions involved in the theory (p. 2361). The experiments confirm the belief that polystyrene is a strictly linear polymer, implying that the kinetics of formation of the polymer involve termination by combination only.

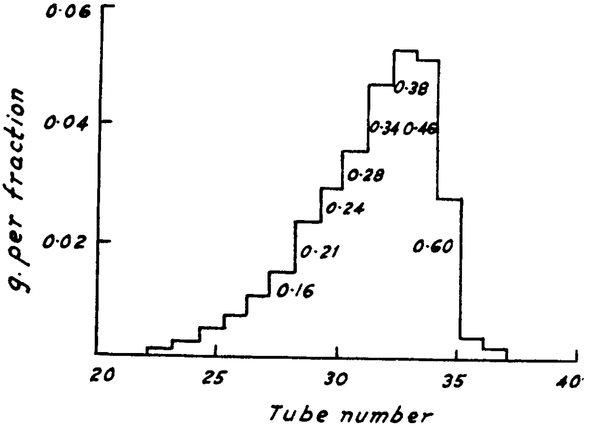

FIG. 4. *The numbers written in the diagram are for the specific viscosity of the fractions* (0·5% *solution in toluene*).

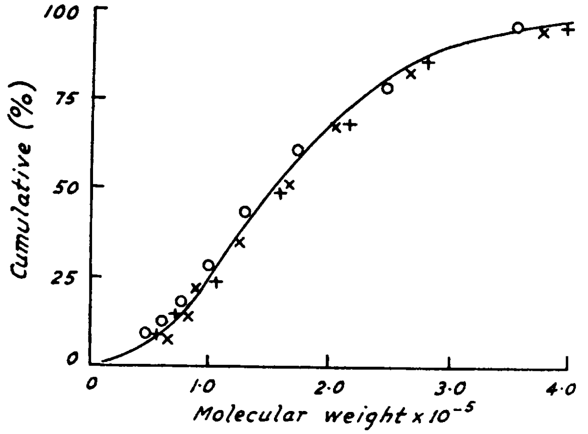

FIG. 5. *The molecular-weight distribution in the* 108,000 *polymer; theoretical curve and experimental points obtained in three different analyses.*

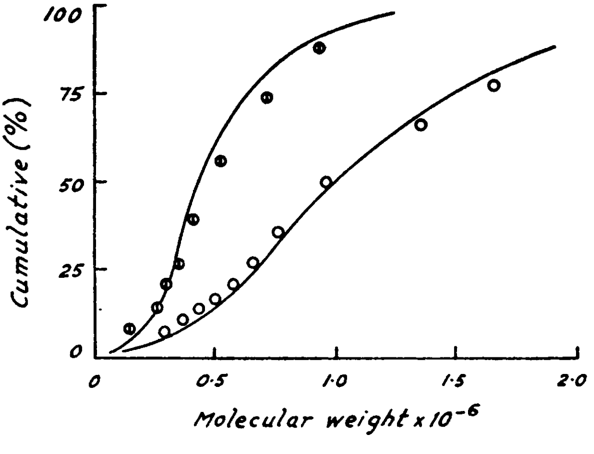

FIG. 6. *The molecular-weight distribution in* 350,000 *and* 725,000 *polymers.*

⦶, 350,000 polymer.
○, 725,000 polymer.

Further Test Experiments.—The experiments with polymers of known molecular-weight distribution were considered to be the best absolute tests of the new method that could be devised. Because of some not altogether satisfactory features of the kinetics of polymerisation (see Appendix), it was however thought better to make a number of experiments on the relative efficiency of our fractionation as compared with earlier techniques. It has been mentioned that, after the saturated solutions from the column have been delivered into the test-tubes of the fraction-collector, where no attempt was made to prevent evaporation, two phases separate. By decanting the supernatant liquid from the gel phase and investigating the properties of the polymer in both phases, the fractionation on the column can be tested as compared with a further one-stage fractionation (by what amounts to a conventional precipitation procedure). The result of the analysis of split fractions from a run with 108,000 polymer (cf. Fig. 4) can be summarised as follows :

Tube no.	30	31		32		33		34		35		36	
	sol	sol	gel	sol	gel	sol	gel	sol	gel	sol	gel	sol	gel
Polymer weight (mg.)	13	17	11	22	15	15	29	17	34	21	23	15	—
$\eta_{sp.}$	0·17	0·21	0·21	0·23	0·23	0·29	0·31	0·35	0·40	0·43	0·53	0·65	—

It can be seen that in no case on further fractionation did the viscosity of a polymer solution (0·5% solution in toluene) of sol material fall below that of the gel in the previous tube and that in most cases the viscosities of sol and gel material from the same tube are very similar.

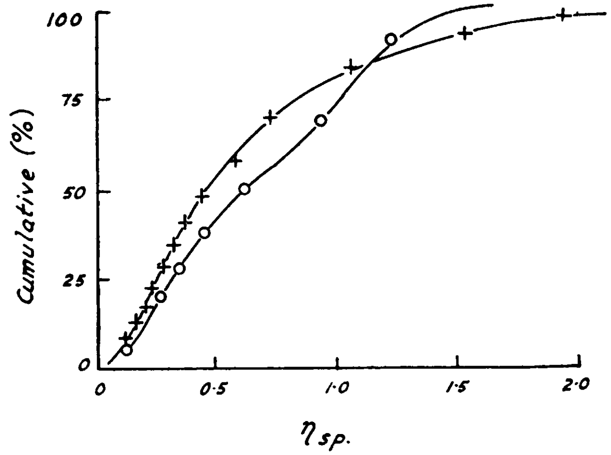

FIG. 7. *Distribution of specific viscosity in an industrial polymer. (The line through the circles is the result from batch fractionation. The other line is the best smooth curve through the* 69 *points from the summed analysis by chromatography of the same seven batch fractions. The crosses on this line represent the chromatographic analysis of the original polymer.)*

The polymers prepared by us under controlled conditions were not available in large quantities, and the continuation of the testing of the new method was made with an industrial polymer produced by Distillers Co. Ltd. under the name of "Distrene." The first test made was a determination of the molecular-weight distribution in this polymer by three methods : (1) by batchwise precipitation into seven fractions using a conventional procedure followed by analysis of the fractions by osmotic-pressure and viscosity measurements; (2) by column analysis followed by determinations of osmotic pressure and viscosity; and (3) by column analysis of all seven batch fractions from method (1) and subsequent examination of the fractions before summing the results to give a composite analysis. The results are shown in Fig. 7. The conventional method gives a result in disagreement with the other two methods. Both column methods give the same result; the line drawn through the crosses on the Figure represents the best smooth curve through 69 points, method (3), from the seven different batch fractions, and the points from method (2) lie on this line. The molecular weights, by osmometry, of the seven fractions from method (1) did not lie on the plot of molecular weight against viscosity which we claim to be a calibration curve for near-homogeneous fractions. The molecular weights of the fractions from the column analyses gave points which lay on the plot within experimental error. Fig. 8 is a plot of the molecular-weight distribution in the seven fractions from method (1) compared with the distribution in the whole polymer.

A usual method for the examination of the efficiency of a chromatographic method is the re-running of material through the column. The method is assumed to be good if the second analysis substantiates the initial one. Such experiments have been performed with polystyrene fractions. They are well illustrated by Fig. 9. The distribution of molecular weight in the material of the fractions was tested by turbidity titration (this test was carried out by Dr. Stead, University of Birmingham, under the guidance of Professor Melville). The method is described by Stead and Melville.[6] A comparison between the titration of a fraction and that of a whole polymer or that of a fraction from batch precipitation shows the narrow range of molecular weights in the column fractions (Fig. 9*c*). There does not appear to be a very large overlap of molecular weight even between material from adjacent test-tubes. This result confirms the impression of the previous experiments and, in particular, it should be considered together with the experiment on the further fractionation of fractions from the column (p. 2357). There it was shown that the viscosity of material from a given test-tube, a given fraction, did not overlap with material from test-tubes on either side of it.

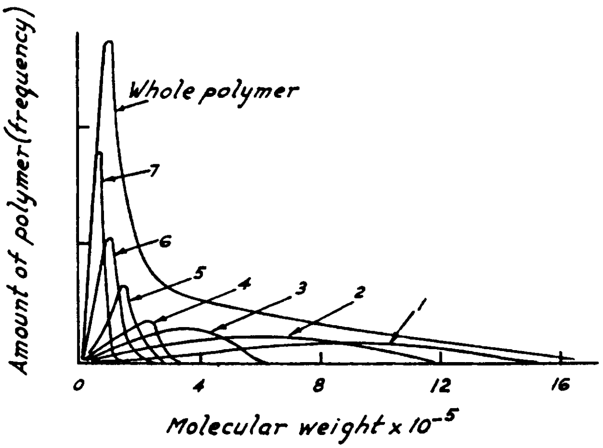

FIG. 8. *Frequency distribution of molecular weight in an industrial polymer and in seven batch fractions obtained from it.*

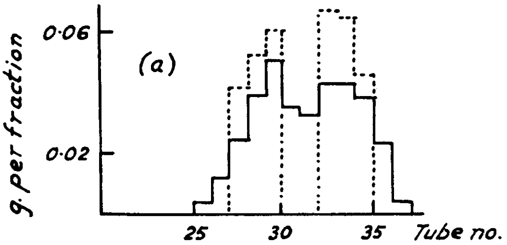

FIG. 9*a*. *Rechromatogram of material from tubes* 27—30 *and* 32—35 *from two different chromatograms of two batch fractions. (The amount of material taken and its original position in the previous chromatographic analyses is shown by the dotted line.)*

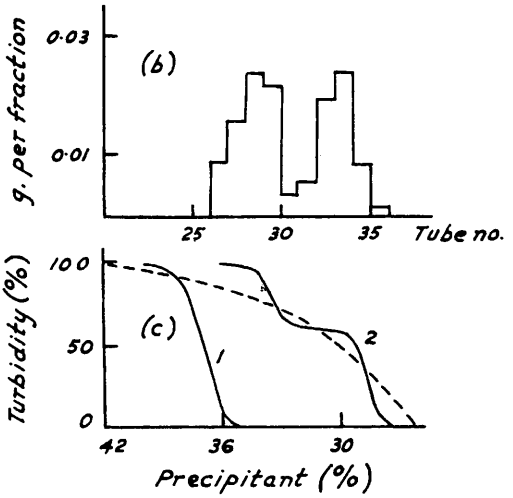

FIG. 9*b*. *Further re-analysis of material recovered from tubes* 26—30 *and* 32—35 *of rechromatogram described in Fig.* 9*a*.

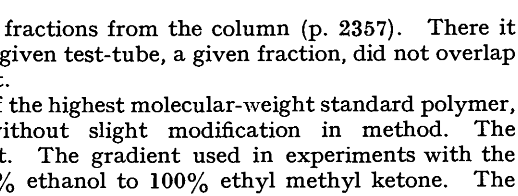

FIG. 9*c*. *Turbidity titrations with methanol, benzene being used as solvent. [Full curves :* (i) *material from tube* 28, *Fig.* 9*b*; (ii) *mixed material from tubes* 29, 30, 32, 33, *Fig.* 9*b*; *broken curve : a typical titration of unfractionated polymer.]*

It was mentioned earlier that fractionation of the highest molecular-weight standard polymer, 725,000, was not altogether satisfactory without slight modification in method. The modification was a change of solvent gradient. The gradient used in experiments with the lower molecular-weight material ran from 100% ethanol to 100% ethyl methyl ketone. The spread of the material of lower molecular-weight in this gradient was satisfactory from the

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[6] Melville and Stead, *J. Polymer Sci.*, 1955, **16**, 505.

point of view of the method (Figs. 3 and 4) but polymer of higher molecular weight tended to be spread over too few tubes so that the solutions were unduly concentrated. It is generally recognised that a high concentration of polymer reduces the fractionating efficiency. It was obvious from experiment that the solvent was being changed too rapidly. Two changes were made. The good solvent was changed to 10% ethanol in ethyl methyl ketone and, in order to shorten the time taken for the experiment, the poor solvent in the mixing vessel was changed to 50% ethanol in ethyl methyl ketone. With this gradient, satisfactory analyses were made of material of high molecular weight. The advantages of the logarithmic form of the solvent gradient in polymer analysis are that it counteracts the change of solubility with solvent composition and molecular weight. The solubility of material of high molecular weight is much more sensitive to changes in solvent composition than that of polymer of low molecular weight (Fig. 3). The logarithmic gradient changes more rapidly over the solvent range in which low polymer is soluble than over the range in which higher polymers dissolve. These factors are important when making adjustments in solvent gradient. For example, a number of experiments have been performed with an American Standard Polymer, a polystyrene, labelled No. III,[7] obtained by batch fractionation of a commercial polymer. It was analysed by the column method described here, the same conditions being used as those described for the 725,000 polymer. Somewhat surprisingly, it was shown to have distribution almost identical with that of an unfractionated 725,000 polymer. This result has been confirmed with two other fraction of high molecular weight from batch precipitation of commercial polymers. The importance of these observations is discussed below.

The Properties of Fractionated Polystyrene.—Three groups of fractions will be discussed here. The first, Y-fractions, were made by the batch-wise precipitation of polystyrenes which had been prepared under carefully controlled conditions such that the ratio of the weight-average molecular weight, M_w, to the number-average molecular weight, M_n, was as 1·5 : 1·0 (see Appendix). The second group, Z-fractions, were prepared by the same procedure from industrial polymers of much wider heterogeneity, $M_w : M_n$ being greater than 2·0 : 1·0. Fractions prepared by Desreux's method [14] are different again: they form a third group of fractions which are obtained by fractional solution. Finally, there are fractions prepared by the method described in this paper. Whereas other methods give fractions of differing heterogeneity depending upon the nature of the original polymer, yet the new chromatographic method gives fractions which cannot be differentiated no matter what the source of the original polymer.

The properties of the fractions which we have studied include osmotic molecular weight, measured in toluene, and intrinsic viscosity in toluene and *cyclo*hexane at 34°. This temperature is the θ-point for polystyrene–*cyclo*hexane.[15] Our studies of these properties call for two comments. The intrinsic viscosity of a polymer solution in one solvent as compared with that in another is independent of molecular-weight distribution but not, of course, of average molecular weight. Secondly, the extrapolation of the osmotic pressure–concentration ratio, π/c, against c was in good agreement with measurements by Krigbaum and Flory [16] but did not agree closely with those by Bawn, Freeman, and Kamalidden [17] at higher molecular weights.

The intrinsic viscosities and osmotic molecular weights of a number of fractions are plotted in Fig. 10. The points for all fractions prepared by the new chromatographic method lie on the same curve no matter what the source of the fractions. The points for whole polymers do not lie on this curve, nor do those for Z- or Y-fractions, which were prepared according to standard recipes. If the osmotic molecular weights of the polymers prepared under controlled conditions (see Appendix) are multiplied by 1·5 to obtain their weight-average molecular weights, then the points for the whole polymers lie very close to the full line. Again, the weight-average molecular weight of the American Standard polymer No. III is known from the literature to be 960,000. This point also falls very near the line. It is concluded from these observations that the line in Fig. 10 is very close to that for homogeneous polymer fractions. This being assumed to be the case, the heterogeneity of other polymers and polymer fractions can be discussed. Several points are of interest: (1) Industrial polymers are of very wide heterogeneity; for " distrene " $M_w : M_n = 3{\cdot}0 : 1{\cdot}0$. (2) Z-Fractions are of considerable heterogeneity; $M_w : M_n$ for those of highest molecular weight is 1·5 : 1·0. All the fractions of this type have not the same heterogeneity, those of lowest average molecular weight having the smallest molecular-weight spread. (3) Polymers prepared according to methods described in the appendix have $M_w : M_n$ ratios of 1·5 : 1·0, which is in agreement with theoretical

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[7] Frank and Mark (I.U.P.A.C. Report), *J. Polymer Sci.*, 1953, **10**, 129.

prediction. (4) Y-Fractions are of low heterogeneity, $M_w : M_n = 1{\cdot}15 : 1{\cdot}0$, but their heterogeneity increases along a series of fractions prepared from one polymer with molecular weight.

It will be appreciated from these comments that the new fractions have a higher number-average molecular weight for any given viscosity than previously described fractions. In support of the contention that they are near-homogeneous fractions, the curve of Fig. 10 falls close to that obtained from the measurement of molecular weight by light-scattering methods.[18]

Fractions can be prepared by fractional solution as well as by the above methods. One particular technique [14] is apparently similar to the chromatographic method described here. It is however a single-stage method. The method yields fractions of very high homogeneity and is probably better than fractional precipitation. It is less satisfactory than the chromatographic method when applied to the fractionation of industrial polymers. It suffers from the further disadvantage that it is a non-equilibrium method.

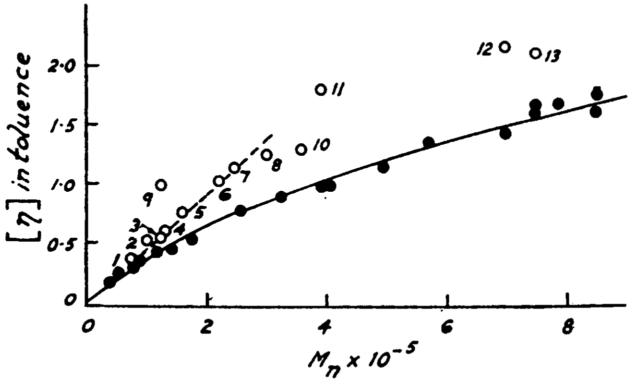
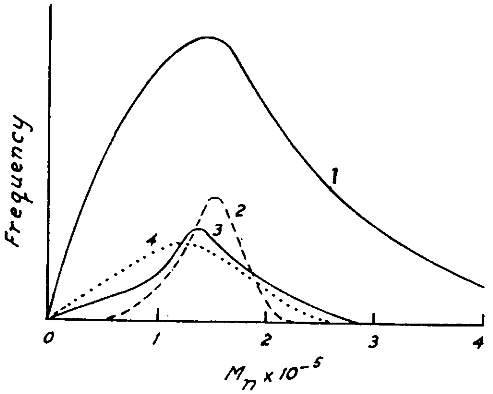


FIG. 10. *The relation between M_n and [η] in toluene. (Filled circles are for chromatographic fractions; 1, 2, 4, 5, 6, 7, 8, and 11 are batch Z-fractions from "Distrene"; 9 is "Distrene" itself; 3, 10, and 13 are the polymers of M_n 108,000, 350,000, and 725,000 respectively; 12 is the Standard polymer No.* III.)

FIG. 11. *Frequency distributions of molecular weight in* (1) 108,000 *polymer,* (2) *a chromatographic fraction,* (3) *a Y-fraction,* (4) *a Z-fraction.*



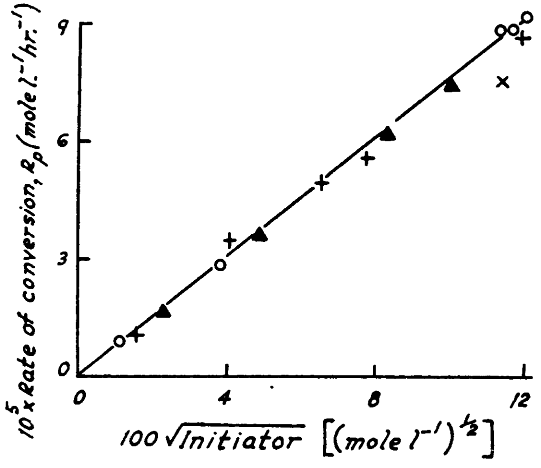
Finally, it is important to note that theories of intrinsic viscosity depend for their verification upon the preparation of near-homogeneous fractions. It is clear from the present work that such fractions cannot be readily prepared by current techniques. The fractionation of polymers of different degrees of heterogeneity leads to fractions of different heterogeneity, and the study of these fractions can lead to a variety of relations between M_n and intrinsic viscosity. Fig. 10 makes this point obvious. In Fig. 11 the molecular weight distribution in various types of fraction is given from their analysis by the present chromatographic method. This and other evidence presented above indicates that the molecular-weight distribution in industrial polymers cannot be found by the earlier methods of fractionation.

Conclusions.—At the outset of this work the analysis of high polymers was undertaken in order to establish a new method of chromatography. The method has now been proved by its ability to fractionate polystyrenes of known molecular-weight distribution. Its subsequent use in the study of the distribution of molecular weights in other polystyrenes of unknown heterogeneity, as described in detail above, may have obscured the general principle on which the fractionations are based. The method that has been described is a form of crystallisation chromatography which should be of value in separating pure components from mixtures whether they be of, for example, salts or proteins.

APPENDIX.

Kinetics of Polymerisation of Polystyrene.—Initiation of the polymerisation of styrene by radicals leads to relatively simple reaction kinetics providing the reaction is carried out in the absence of oxygen and at constant temperature. The three polymers prepared by one of us (C. A. B.), under the guidance of Professor H. W. Melville and Dr. J. C. Bevington at Birmingham University, were made under controlled conditions which are standard practice in this field. 2 : 2′-Azobis*iso*butyronitrile was used as the initiator, and the reaction vessel, a dilatometer, was held at 60°. The rate of reaction was observed in the dilatometer by following the meniscus with a travelling microscope.

FIG. 12. *A plot of the rate of polymerisation against the square-root of the initiator concentration* : ○ *This paper,* + *Melville and Bevington (communicated),* ▲ *Johnson and Tobolsky,*[12] × *Matheson* et al.[13]



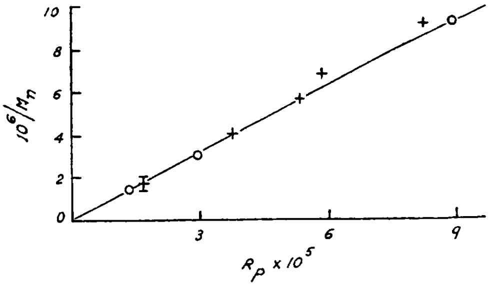


FIG. 13. *The inverse of the number-average molecular weight plotted against the rate of polymerisation* : ○ *This paper,* + *Melville and Bevington (communicated). Molecular weights by osmometry except the point* ⊻ *which was obtained by end-group analysis.*

The rate of polymerisation, R_p, is given by

$$R_p = k_p f k_d[\mathrm{I}]^{\frac{1}{2}}[\mathrm{M}]/k_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k_p, k_d, and k_t are the rate constants of propagation, initiator decomposition, and termination respectively, [I] is the concentration of initiator, [M] the concentration of monomer, and f the efficiency of the initiation step in the polymerisation. The equation is based on assumptions summarised by Flory.[8] The initial rate, found by the extrapolation of rate curves, should be directly proportional to $[\mathrm{I}]^{\frac{1}{2}}$. The experimental results are plotted in Fig. 12.

The kinetic chain length, ν, is given by

$$\nu = (k_p{}^2/2k_t)[\mathrm{M}]_2/R_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence the inverse of the number-average molecular weight, M_n, proportional to ν, should vary with the initial rate. Fig. 13 shows how well this relation is obeyed. From both Figs. 12 and

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[8] Flory, *op. cit.*, ref. 5, p. 106.

13 it can be concluded that the rate of polymerisation in the preparation of the three standard polymers described and analysed here was in no way anomalous and that therefore they are likely to be typical of all styrene polymers prepared in this way in so far as molecular weight distribution is concerned. It will be assumed then that transfer to monomer may be neglected. The kinetic expressions do not differentiate between two mechanisms for chain termination. By using radioactive-labelled initiator, however,[9,11] it has proved possible to show that termination in styrene polymerisation is by combination. This method of termination being assumed it follows that the frequency, M_m, of synthesis of a polymer of m units in a chain is given by [10]

$$\ln M_m = \ln\left\{\frac{\frac{1}{2}A^2\theta^2}{[\mathrm{M}]^2}(m-2)\right\} - \frac{\theta\sqrt{A}}{[\mathrm{M}]}(m-2) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $A = 2fk_d[\mathrm{I}]$ and $\theta = \sqrt{(2k_t)}/k_p$.

In order to use this equation, all the rate constants have to be evaluated : k_d, the rate of decomposition of the initiator, is known to be $10{\cdot}1 \times 10^{-6}$; k_p and k_t can be found from the plots in Figs. 12 and 13. Now with assumption of termination by combination, $2\nu = x_n$, x_n can be measured, for any given polymer, by osmometry. The value 108,000 being taken for the lowest polymer prepared in this work (this is the most accurately known molecular weight), the value of f is found to be 0·61. This value is lower than those in the literature and it must be admitted that its reliability is very sensitive to the other rate constants. Since this work was completed, however, Bevington [11] has shown that a value of 0·60 for f is to be expected.

By using the values derived for the constants in equation (2), the molecular weights of the other two polymers are found to be 316,000 (350,000 by osmometry) and 741,000 (725,000 by osmometry).

The three equations for the molecular-weight distributions are [see equation (3)] :

$$\log M_m/m = -\ 8{\cdot}36 \times 10^{-4}m - 12{\cdot}496 \text{ (108,000 polymer)}$$
$$\log M_m/m = -\ 2{\cdot}86 \times 10^{-4}m - 14{\cdot}357 \text{ (350,00 polymer)}$$
$$\log M_m/m = -\ 1{\cdot}216 \times 10^{-4}m - 15{\cdot}842 \text{ (725,000 polymer}$$

The distributions and their experimental verification are given in Figs. 5 and 6.

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