

495. *The Fractionation of Polyisobutene by Gradient Elution.*

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Difficulties in the fractionation of elastomers of high molecular weight with a gradient elution column have been overcome for polyisobutenes of molecular weight (M.W.) up to 10^6 by (a) applying the polymer to the column adsorbed on to a solid of high specific surface, and (b) using a bad solvent and a precipitant both with a high boiling point ("mixed xylenes" and n-propanol). The factors affecting the efficiency of fractionation and the causes of "inversion" are discussed. M.W. distribution curves are given for polyisobutenes prepared under a wide variety of conditions.

THE gradient elution method for the fractionation of polymers, introduced by Baker and Williams,¹ has been used in various modified forms to fractionate amorphous polymers,² crystalline polymers,³ and elastomers;^{4,5} only one Paper deals with the fractionation of polyisobutene by gradient elution.⁶ The present work is concerned with the analytical fractionation of polyisobutenes of molecular weight (M.W.) up to 10^6 .

EXPERIMENTAL

Apparatus.—This was very similar to that previously described.⁷ The column consisted of a Pyrex tube, 100 cm. long and 4 cm. in diameter, filled with Ballotini of diameter 0.1 mm. The head temperature of the column was set according to the eluant in use; the temperature gradient down the column was linear. Fractions were collected in test-tubes carried in a gravity-driven turntable at 45 min. intervals.

Materials.—Polyisobutenes prepared as previously described⁸ were used without further purification (see Table 1). Hexane and industrial ethanol were used without purification, and

TABLE I.

Preparative details for the polyisobutenes.

Solvents: A, methylene dichloride; B, ethyl chloride; C, ethylidene dichloride; D, ethylene dichloride.

Expt.	T_1 *	[i-C ₄ H ₈] (mm)	[TiCl ₄] (mm)	[H ₂ O] † (mm)	Expt.	T_1 *	[i-C ₄ H ₈] (mm)	[TiCl ₄] (mm)	[H ₂ O] † (mm)
A 16	-90.8°	67	0.35	Excess	B N89	-78.2	175	0.25	Excess
A 122	-64.2	369	1.79	0.01	B N90	-77.6	175	0.72	Low
A 103	-61.5	96	1.18	0.18	B N88	-73.9	174	0.50	Excess
A 92	-38.3	93	0.46	0.02	B N85	-73.4	173	2.5	Excess
A 116	-11.7	176	1.10	0.23	C 142	-91.3	98	1.35	0.13
A 128	+17.5	370	1.05	0.23	D 165	-14.6	90	0.49	Excess

* T_1 is the initial temperature of the polymerisation. † Excess of water; in these experiments [H₂O] was larger than the minimum required for complete conversion of monomer (Biddulph, Plesch, and Rutherford, Internat. Symp. on Macromolecules, Wiesbaden, 1959, Paper III. A.10; *J.*, 1964, in the press).

di-isobutene, mixed xylenes, n-butanol, and n-propanol were distilled before use. New Ballotini were washed in hot solvent and then in non-solvent before use.

Preparation of the Polymer for Fractionation.—Polyisobutenes to be fractionated by the hexane-ethanol system were prepared by evaporating a hexane solution of the polymer mixed with about 10 times its weight of Ballotini. This resulted in a lumpy, sticky conglomerate

¹ Baker and Williams, *J.*, 1956, 2352.

² Weakley, Williams, and Wilson, *J.*, 1960, 3963; Schneider, Loconti, and Holmes, *J. Appl. Polymer Sci.*, 1960, 3, 251.

³ Guillet, Combs, Slonaker, and Coover, *J. Polymer Sci.*, 1960, 47, 307; Wijga, van Schooten, and Boerma, *Makromol. Chem.*, 1960, 36, 115.

⁴ Hulme and McLeod, *Polymer*, 1962, 3, 153.

⁵ Cooper, Vaughan, and Yardley, *J. Polymer Sci.*, 1962, 59, S2.

⁶ Cantow, Porter, and Johnson, *Nature*, 1961, 192, 752.

⁷ Pepper and Rutherford, *J. Appl. Polymer Sci.*, 1959, 2, 100.

⁸ Biddulph and Plesch, *Chem. and Ind.*, 1958, 1448.

which was roughly broken down before being placed on the column. In later fractionations, the polymer was precipitated on to Chromosorb (a crushed firebrick of large specific surface) instead of on to Ballotini. This procedure improved the fractionation by facilitating the initial extraction of the polymer. Since Chromosorb adsorbs some of the polyisobutene in an almost irreversible manner, it was pretreated with a separate sample of polyisobutene by Hulme and McLeod's method.⁴ The isotherm for the adsorption of polyisobutene on Chromosorb at 70° under the operating conditions showed that about 2% by weight was adsorbed from a "mixed xylenes"-*n*-propanol solution and about 6% from a di-isobutene solution. An intrinsic viscosity determination on the polymer remaining in solution showed that polymer of high molecular weight was retained preferentially.

Recovery and Treatment of Fractions.—The volume of eluant collected in the tubes was measured. The appearance of polymer was detected as a turbidity when methanol was added to selected tubes. The polymers eluted with the hexane-ethanol system were recovered by evaporating off the liquid at about 50° under reduced pressure. Steam-distillation was the most efficient way of recovering polyisobutene fractions from the higher-boiling mixtures. The weight of polyisobutene recovered was never less than 90% of the initial weight, and the normal recovery was 93–98%. Some experiments with polyisobutene supported on Chromosorb gave recoveries slightly greater than 100%, probably owing to incomplete removal of unadsorbed polyisobutene from the Chromosorb during its pretreatment. The fractions were weighed, and their intrinsic viscosity was determined in di-isobutene at 25° with Craig-Henderson dilution viscometers; ⁹ the molecular weights were calculated from Flory's equation.¹⁰

Solubility Limits and the Choice of Solvent-Non-solvent System.—The elution of polyisobutene at the hot, upper end of the column does not start until a certain percentage of solvent is present in the eluant. The composition of the eluant at this stage is known as the upper solubility limit. Similarly, precipitation of the polymer at the cold end of the column does not start until a certain percentage of non-solvent is present; the corresponding composition is known as the lower solubility limit. The limits can easily be determined by test-tube experiments for polyisobutenes of various molecular weights in a variety of solvent-non-solvent mixtures. The difference between the limits is the solubility gap. The importance of the solubility limits to the efficiency of column fractionation has been discussed.^{4,7} The composition of the liquid initially placed in the mixer (the precipitant) is that corresponding to the upper solubility limit, and that of the liquid in the reservoir (the extractant) corresponds to the lower solubility limit.

Polyisobutenes were first fractionated with the hexane-ethanol system, but this was later replaced by the di-isobutene-*n*-butanol system. We hoped that this would increase the efficiency of fractionation by giving a wider solubility gap, and by permitting us to raise the head temperature of the column from 50°, used with the previous system, to 90°. However, we abandoned the di-isobutene-*n*-propanol system, as it gave a very small solubility gap for a polyisobutene of M.W. = 10⁶. We studied eleven solvent-non-solvent systems to find one of high boiling point with a sufficiently large solubility gap for polyisobutenes of M.W. = 10⁶. The system "mixed xylenes"-*n*-propanol gave the best solubility gap (36%) and a minimum boiling point of 106°. For this combination the head temperature of the column was set at 35° below this in order to eliminate gassing of the eluant.

Treatment of Fractionation Results.—The Schulz-Dinglinger¹¹ method of plotting the cumulative weight percentages of the fractions against their corresponding molecular weights was used to obtain the integral weight distribution curves for all our polyisobutenes. The differential weight distribution curves were obtained by plotting the slopes of these curves at specific molecular weights against those molecular weights. These curves are shown in Figs. 1–9.

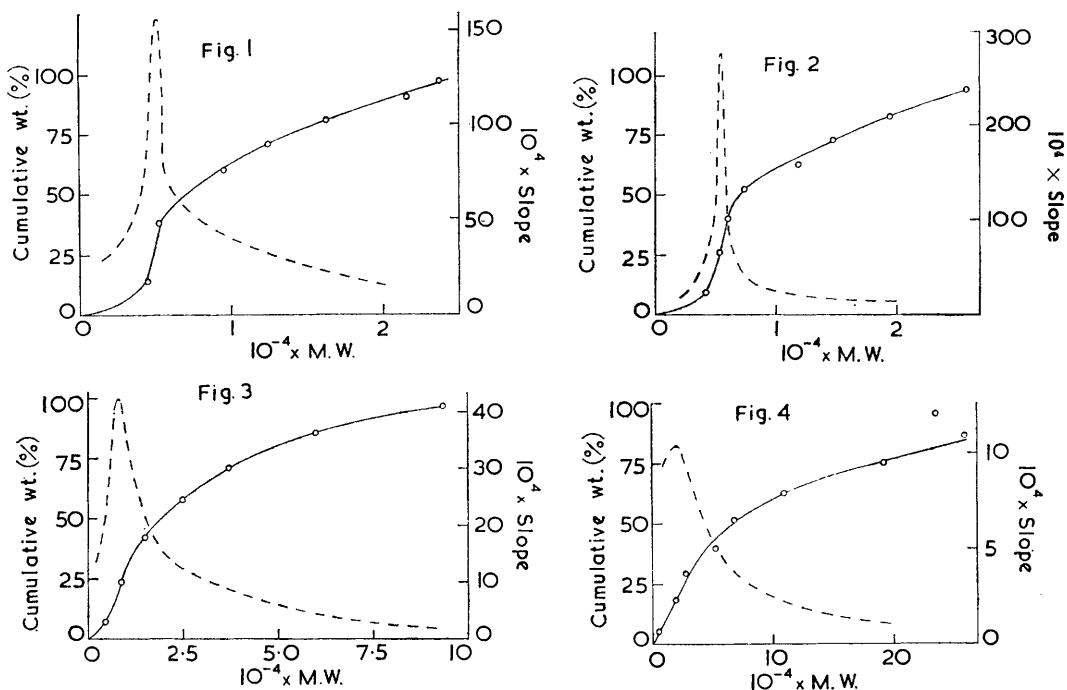
RESULTS AND DISCUSSION

In the discussion of our results we will attempt to correlate the extent of success of our fractionations with the parameters α and β which were defined by Pepper and Rutherford⁷ (see also footnotes to Table 2). Ideally, α should be as large as possible, and unity is about the optimum practical value, taking the operating time into consideration. From

⁹ Craig and Henderson, *J. Polymer Sci.*, 1956, **19**, 215.

¹⁰ Flory, *J. Amer. Chem. Soc.*, 1943, **65**, 771.

¹¹ Schulz and Dinglinger, *Z. phys. Chem.*, 1939, **B43**, 47.



FIGS. 1—4. Weight distribution curves for a series of polyisobutenes.

Full line, integral curve; broken line, differential curve.

TABLE 2.

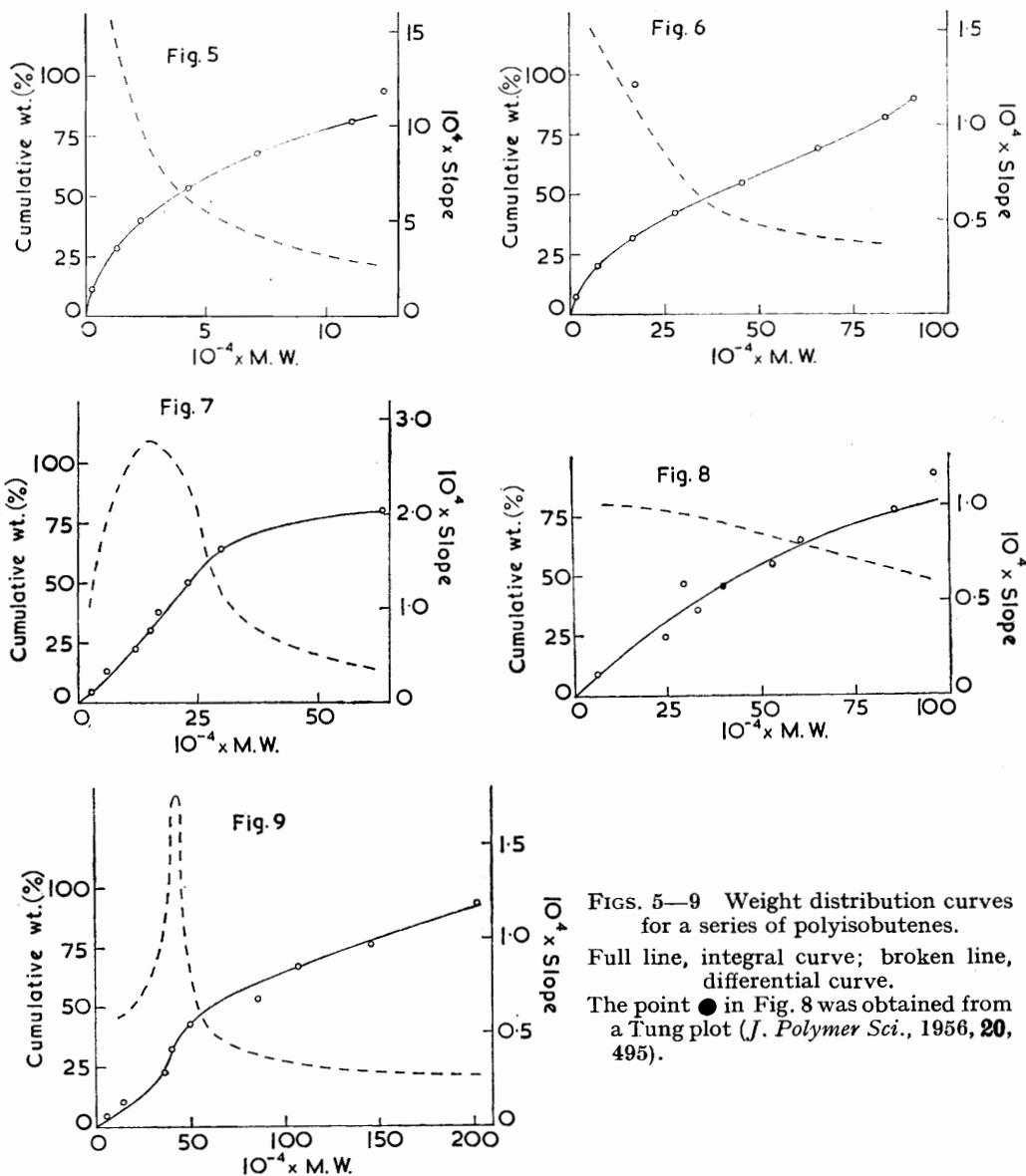
Fractionation of polyisobutenes.

No.	Unfractionated polymer 10 ⁻³ M.W.	Column loading (g.)	Vol. in mixer (ml.)	Concn. of polymer in eluant (wt./vol. %)		10 ⁻³ M.W. Flow rate of highest fraction		α	β	Result †	Fig.
				Av.	Max.	(ml./hr.)					
The hexane-ethanol system *											
128	7.65	0.76	350	0.06	0.10	12.0	24.0	0.37	1.06	S	1
165	15.0	0.43	600	0.08	0.14	5.8	26.0	0.78	1.01	S	2
116	26.1	0.64	300	0.08	0.20	15.0	93.4	0.30	1.00	S	3
92	126	0.45	600	0.13	0.29	7.6	259	0.82	1.20	S	4
142	128	0.29	600	0.08	0.16	6.6	124	1.21	1.78	S	5
103	473	0.43	600	0.20	0.33	7.9	909	0.84	1.09	PS	6
122a	1450	0.94	400	0.10	0.20	12.0	1530	0.38	1.30	F	—
122b	1450	0.56	600	0.03	0.11	8.0	998	0.33	0.94	F	—
The "mixed xylenes"-n-propanol system.											
16	340	0.40	650	0.07	0.14	9.2	640	0.41	1.30	S	7
N85	470	0.30	650	0.04	0.08	8.9	975	0.65	0.96	S	8
N89	970	0.30	550	0.05	0.10	11.1	600	0.55	1.11	PS	—
N90a	1030	0.30	500	0.07	0.16	12.6	303	0.50	1.16	PS	—
N90b *	1030	0.30	500	0.11	0.20	11.3	327	0.50	0.81	F	—
N88a	1047	0.30	1500	0.02	0.04	9.2	516	1.50	1.03	S	—
N88b	1047	0.30	1500	0.02	0.04	10.0	2030	1.50	0.96	S	9

* Chromosorb not used. † S = success, PS = partial success, F = failure.

 $\alpha = V_e/V_t$, where V_e = actual volume in the mixer, V_t = theoretical volume in mixer required to keep average concn. of polymer in eluant at the maximum permissible value. $\beta = v_e/v_t$, where v_e = actual volume of eluant passed through column from first appearance of polymer in eluant to completion of elution, v_t = theoretical volume of eluant required to keep the average concn. of polymer in eluant at the maximum permissible value.

the same point of view the optimum practical value of β is unity. Values of β greater than unity mean that the eluant is undersaturated, and although this need not be detrimental it may extend the time of the fractionation unnecessarily. If β is less than unity the eluant is supersaturated, and this invariably leads to fractionation failure. A fractionation is considered to have failed if the fractions do not come off the column in order of



FIGS. 5—9 Weight distribution curves for a series of polyisobutenes.

Full line, integral curve; broken line, differential curve.

The point ● in Fig. 8 was obtained from a Tung plot (*J. Polymer Sci.*, 1956, **20**, 495).

ascending molecular weight; this phenomenon is known as "inversion," and will be discussed below.

Fractionations with Hexane-Ethanol.—The results of the fractionation of polyisobutene with the hexane-ethanol system are given in Table 2. Some of the successful fractionations show an inversion of the last fraction. Partly successful fractionations show inversion of the last two or three fractions. The failures displayed extensive inversion.

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Polyisobutenes 128, 165, and 116 were all fractionated without complication. The wide variety of conditions, concentrations, and parameters shown in Table 2 indicates that polyisobutenes of low molecular weight may be fractionated under less rigorously controlled conditions than are required for their counterparts of high molecular weight. Fractionation of polymer 92 was successful in spite of the low value for α which caused the maximum concentration of polyisobutene in the eluant to reach 0.29%. The fractionation of polymer 142 was also successful, although the value of β was as high as 1.78, implying considerable unsaturation of the eluant.

However, the adjustment of operating conditions is much more critical for the fractionation of polyisobutenes of relatively high molecular weight; the fractionation of polymer 103 was only partly successful, although the values of α and β were reasonably close to the optimum. We believe that the unfractionated polyisobutene 103 (M.W. = 473×10^3) is probably the compound of highest molecular weight that can be fractionated by the hexane-ethanol system. This conclusion is supported by the two abortive attempts to fractionate a polyisobutene of higher molecular weight (Expt. 122a and b). Indeed, the system seemed incapable of removing molecules of molecular weight greater than 1.5×10^6 . One fault was obviously an insufficiently large mixer volume, as shown by the low value of α . However, later work showed that in this case an increase in this volume would have served little purpose, because the solubility gap for polyisobutene of very high molecular weight in the hexane-ethanol system is very small.

Fractionations with "Mixed Xylenes"-n-Propanol.—The remaining fractionations listed in Table 2 (except Expt. N90b) were carried out with the polymer spread on Chromosorb. The fractionation of polymer N90 with Chromosorb (Expt. N90a) was partly successful, but for the same polymer without Chromosorb (Expt. N90b) it was a total failure, showing the potential of Chromosorb as a means for more efficient fractionation.

In order to study the adsorption effect of Chromosorb *in situ*, the specimen of Chromosorb used in the fractionation of polyisobutene N89 was not pretreated, and after fractionation it retained some 10% by weight of the polymer. From the molecular weights of the fractions it appears that mainly the species of high molecular weight were adsorbed.

No difficulty was encountered in the fractionation of polyisobutenes 16 and N85, both of molecular weight corresponding approximately to the limiting value tractable by the hexane-ethanol system. Fractionation of the higher polymers N90a and N89 was only partly successful, no doubt because the volume of precipitant (500 and 550 ml., respectively) in the mixer was inadequate. The success of fractionation N88a we attribute to our using a volume of 1500 ml. in the mixer; unfortunately the fractions from this experiment suffered some thermal degradation by being dried in air at 50°. In the following fractionation (N88b) the fractions were dried after steam-distillation without being heated in air, and the fractionation of this polyisobutene (unfractionated M.W. just over 10^6) was completely successful. An examination of the parameters shows that β was just less than unity and α was considerably greater than in the earlier experiments with this system.

Thus, we can attribute the successful fractionation of a polyisobutene sample of M.W. $\sim 10^6$ to four main factors. (a) The choice of a suitable solvent-non-solvent pair with a wide solubility gap. (b) The use of Chromosorb. (c) The use of an extremely large volume of precipitant. (d) Reasonable loading of the column. Of these factors, (c) and (d) are directly concerned with keeping the concentration of polymer in the eluant as low as possible. When Chromosorb is used in a fractionation the extent of success is rather insensitive to the flow-rate of the eluant.

Inversion.—A fractionation is classified as a failure when certain of the fractions show "true" inversion. This phenomenon occurs when the fractions are not eluted in ascending order of molecular weights, *i.e.*, if fractions of low molecular weight occur in the region of high molecular weight (Fig. 6). True inversion can be attributed to an imbalance of the extraction-precipitation equilibria down the column (*e.g.*, polyisobutene N90b).

However, there also exists a type of inversion characterised by the inversion of only the last fraction in an otherwise successful fractionation (Figs. 4, 5, 7, and 8). This is generally not an inversion to low molecular weight, but to a molecular weight about the same as that of the second-last or third-last fraction. This phenomenon was observed by other workers,^{4,12,13} but we find that the theories put forward to explain this are inadequate or totally inapplicable to our column. We suggest the following explanation. Consider the clean Ballotini at the start of a fractionation to adsorb firmly, but not irreversibly, from the eluant a monolayer of the species of lowest molecular weight. Eventually, when all the polymer has been eluted and the coated spheres are perfused with the pure extractant, the monolayer will be removed. On combining the contents of the collecting tubes the polymer of low molecular weight will now appear in the last fraction and lower its molecular weight. An approximate calculation showed that 2 kg. of Ballotini covered to a thickness of 20 Å would hold 0.01 g. of polymer, and this quantity is of the correct order of magnitude to account for the effect. Our theory is supported by the fact that if the last fraction weighed about 0.01 g. or less, its molecular weight was usually of the same order as that of the first fraction.

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¹² Jungnickel and Weiss, *J. Polymer Sci.*, 1961, **49**, 437.

¹³ Schneider, Loconti, and Holmes, *J. Appl. Polymer Sci.*, 1961, **5**, 354.
