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Reactions of Polyunsaturated Fatty Alcohols. IX. Molecular-Weight Distribution of Some Conjugated Soybean Vinyl Ether Homopolymers[1]

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The molecular-weight distributions of several conjugated soybean vinyl ether homopolymers were studied by means of the integral fractionation technique. Polymers having number-average molecular weights of 2,200, 4,800, and 10,000 prepared with stannic chloride as catalyst as well as a polymer having a molecular weight of 3,400 prepared with boron trifluoride as catalyst were included in the study. The observed distributions for all the polymers were found to approximate the so-called "most probable" distributions expected theoretically for polymers obtained by simple difunctional polymerization.

THE MOLECULAR-WEIGHT distribution of a polymer is an important characteristic to which many of its physical and chemical properties are related. Polyunsaturated fatty vinyl ether polymers and copolymers (12) have been under investigation at this laboratory because of their promising properties as coatings, especially for metal. Knowledge of their molecular-weight distribution might contribute to a better understanding of their drying behavior and of the properties of their films. Since the functionality of a polyunsaturated fatty vinyl ether polymer molecule towards oxygen varies with the number of monomer units in the chain, knowledge of the molecular-weight distribution would provide information on the maximum and minimum functionalities to oxygen available in the polymer and on the relative amounts of material having these and intermediate functionalities.

This paper reports the results of an investigation of the molecular-weight distribution of several conjugated soybean vinyl ether homopolymers. These were selected to permit comparison of polymers that had different number-average molecular weights or that were prepared with different polymerization catalysts.

Discussion of Fractionation Methods

Because of the physical and chemical properties of polyunsaturated fatty vinyl ether polymers, special problems are encountered in their fractionation. Reasonably quantitative recovery of fractions is difficult because these polymers are liquid. Because these polymers and the fractions separated from them are sensitive to oxygen and because this sensitivity increases with molecular weight, handling in an inert atmosphere is necessary. Furthermore the molecular weights of the polymers and their fractions lie in ranges such that only very approximate values can be obtained.

In view of these problems, simple fractional precipitation of the polymers was considered impractical. The integral fractionation method (10) and the cumulative volume technique (1,2) appeared more suitable for investigation.

The principle of the integral fractionation method is illustrated by Figure 1. A very dilute solution of polymer is divided into a number of aliquots of equal volume. (For simplicity only five aliquots are shown in the figure; in practice a large number are required.) To each aliquot is added an increasingly large volume of nonsolvent. This results in precipi-

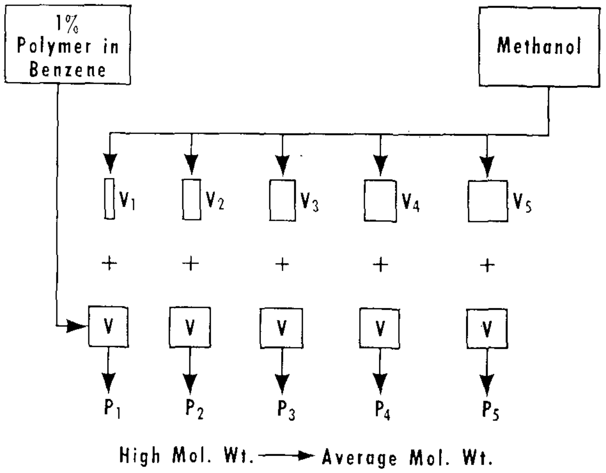

FIG. 1. Simplified representation of the integral fractionation method.

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TABLE I

Preparation and Properties of Conjugated Soybean Vinyl Ether Polymers

Preparation[a]			Polymer properties					
Catalyst	Monomer sample no.	Solvent ratio	Viscosity (Gardner)	Iodine value	Free vinyl ether	Conjugation		Molecular weight
						Diene	Triene	
					%	%	%	
$SnCl_4$	1	1	Z6	90.9	0.61	33.2	0.32	10,000
$SnCl_4$	2	4	Z3	90.2	2.30	34.6	0.26	4,800
$SnCl_4$	2	10	Z2	89.1	4.95	33.7	<0.10	2,200
BF_3	2	3	Z3–Z4	94.6	0.23	.. ...	......	3,400

[a] See text.

tation of a series of polymer fractions. The fraction precipitated by the least amount of nonsolvent will have the highest molecular weight. As the amount of nonsolvent is increased, the molecular weight of the precipitated polymer will approach the average molecular weight of the unfractionated polymer.

In each precipitation it is assumed that all material having a molecular weight greater than a certain value, M_s, is precipitated while all material having a lower molecular weight remains in solution. If the weight fraction and number-average molecular weight for each fraction are designated by C and $\overline{M}_{nc}$, respectively, it can be shown that:

$$M_s = dC/d\ (C/\overline{M}_{nc})$$

By plotting values of C against $C/\overline{M}_{nc}$ for each precipitated polymeric fraction and by differentiating the resulting curve, values of M_s corresponding to any value of C can be determined. A plot of M_s against 1-C corresponds to the usual integral or cumulative weight-distribution curve. Differentiation of the integral curve yields the differential weight-distribution curve, showing, as a continuous function, the weight fraction (w_x) of polymer corresponding to all values of molecular weight (usually expressed as degree of polymerization to facilitate comparison with theoretically calculated curves).

Sources of error in application of the integral fractionation procedure include failure to achieve complete separation and quantitative recovery of precipitated polymer, contamination of precipitated polymer with soluble polymer, and limitations on molecular-weight determination. These sources of error are, of course, magnified for polyunsaturated fatty vinyl ether polymers for the reasons described, but an even more serious source of error lies in the requirement for double differentiation of an experimentally determined curve. As such differentiation must be accomplished graphically, the results must be regarded as only approximate.

The cumulative volume method utilizes a single closed vessel containing a dilute solution of polymer to which successive increments of nonsolvent are added. After the addition of each increment, the system is equilibrated and the total volume of the precipitated polymer is determined. This method offers several obvious advantages for use with polyunsaturated fatty vinyl ether polymers; for example, isolation of fractions is eliminated and maintenance of an inert atmosphere is simplified. However preliminary experiments showed that only a low percentage (30–50) of the fractionation of vinyl ether polymers could be achieved by this method before difficulties were encountered, resulting from the adherence of the precipitated polymer to the walls of the vessel. Since relatively complete precipitation is needed for interpretation of the results, no further study was made of this method.

Discussion of Results

Four conjugated soybean vinyl ether homopolymers are included in the present study (Table I). Three of these were prepared with stannic chloride as catalyst and had number-average molecular weights ($\overline{M}_n$) of 2,200, 4,800, and 10,000. The fourth was prepared with boron trifluoride as catalyst and had a number-average molecular weight of 3,400.

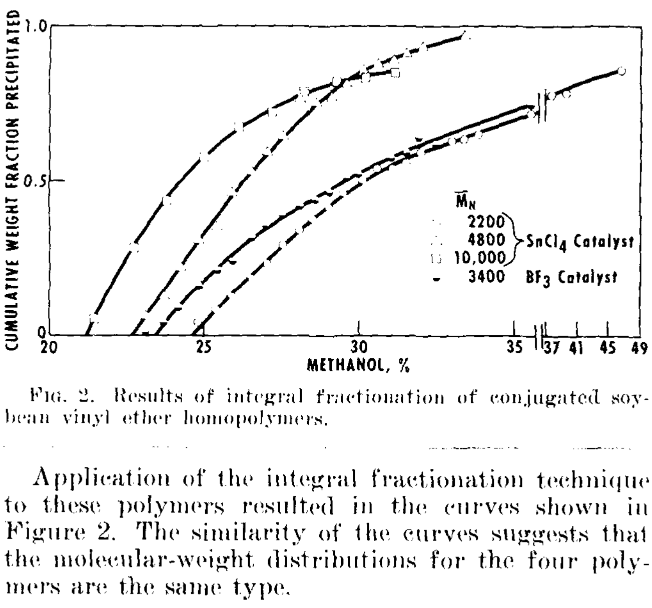

FIG. 2. Results of integral fractionation of conjugated soybean vinyl ether homopolymers.

Application of the integral fractionation technique to these polymers resulted in the curves shown in Figure 2. The similarity of the curves suggests that the molecular-weight distributions for the four polymers are the same type.

Molecular weights were obtained on fractions from the three polymers prepared with stannic chloride as catalyst. Typical results for the polymer having $\overline{M}_n$ = 4,800 are given in Table II. Theoretically mo-

TABLE II

Molecular Weights of Fractions Obtained by Integral Fractionation of a Vinyl Ether Polymer[a]

Fraction	Methanol	Cumulative weight fraction (C)	Molecular weight (M_{nc})
	%	%	
1	23.10	6.9	23,500
3	24.22	23.9	14,500
4	24.80	30.7	13,000
5	25.39	35.4	11,000
7	26.49	52.7	10,000
8	27.00	59.7	9,400
9	27.53	64.8	7,600
11	28.59	75.7	7,800
12	29.09	77.4	7,800
13	29.59	81.4	7,800
16	31.03	89.0	7,000
17	31.50	91.8	6,800
18	31.99	93.2	6,000

[a] M_n = 4,800.

lecular weights for the 18 fractions should decrease smoothly and approach the value of $\overline{M}_n$ for the whole polymer at C = 100. In all experiments irregularities, such as are evident in Table II, were encountered. These apparently resulted from the inevitable difficulties in removing the solvent completely from fractions, avoiding oxidation, and determining molecular weights. In plotting C *vs.* $C/\overline{M}_{nc}$, since two points of the curve were known (*i.e.*, the origin, corresponding to C = 0, and $C/\overline{M}_n$, corresponding to C = 100), usually the irregularities did not seriously complicate the problem of drawing a smooth curve to represent the experimental data adequately. An exception was encountered with the polymer having $\overline{M}_n = 10{,}000$. Because a large percentage of this polymer was comprised of species with a molecular weight above 10,000, only very approximate results were possible.

Integral weight distributions, obtained by plotting C *vs.* $C/\overline{M}_{nc}$ for each polymer and differentiating the resulting curves, are shown in Figure 3.

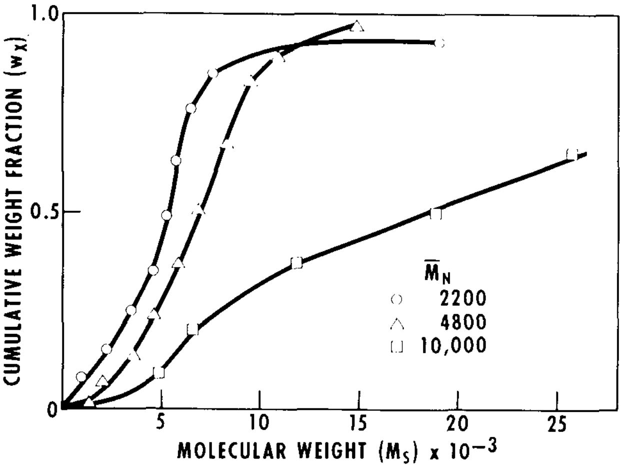

FIG. 3. Integral weight distributions for conjugated soybean vinyl ether homopolymers.

From these distributions it is evident that by weight half of the polymer of $\overline{M}_n = 2{,}200$ consists of species having molecular weights above 5,000, that half of the polymer of $\overline{M}_n = 4{,}800$ consists of species exceeding 7,000, and that half of the polymer of $\overline{M}_n = 10{,}000$ consists of species exceeding 18,000.

Differential distributions for the three polymers were determined by differentiation of the integral curves. Figure 4 shows a comparison of these differential distributions with the so-called "most probable" distributions calculated for polymers of corresponding values of $\overline{M}_n$ by means of Flory's equation (4):

$$w_x = x\,(1 - p)^2\,p^{x-1}$$

In this equation $p = (\bar{x}_n - 1)/x_n$, w_x is the weight fraction of polymeric species composed of x monomeric units, and $\bar{x}_n$ is the number of monomeric units contained in the number-average molecular weight for the whole polymer.

Flory's equation, originally derived for condensation polymerization (*e.g.*, polyester formation from an ω-hydroxy acid), is also applicable to vinyl polymerization if nearly all molecules are terminated by chain transfer and if the ratio of concentration of chain transfer agent to monomer concentration is constant. The latter condition will be met if conversion is low or if rates of propagation and transfer are equal.

Cationic polymerization, which is involved in polymerization of vinyl ethers, does not appear to have been analyzed mathematically to determine the theoretical shape of the differential molecular weight distribution curve.

However proposed mechanisms for, and kinetic studies on, cationic polymerization (6) suggest that the relationship between reaction kinetics and molecular distribution should be analogous to that for vinyl polymerization, terminated by chain transfer, and also suggest that Flory's equation should therefore be applicable.

This view appears to be confirmed by the agreement between experimental and calculated distributions (Figure 4) which, if limitations of the fractionation method are taken into account, is reasonably good. At least as a first approximation, Flory's equation should be satisfactory for calculating molecular distributions for polyunsaturated fatty vinyl ether polymers.

If the polyunsaturation of the fatty vinyl ether is conjugated, a possibility exists that the conjugated systems might participate in cationic polymerization. In this event the vinyl ether could no longer be regarded as a purely difunctional molecule, and the polymer produced would be cross-linked to some degree. Since the diene content of a monomeric vinyl ether is about the same as that of its polymer, it is evident that little participation of the diene system in the polymerization could have occurred. Thus, for the polymer of molecular weight 10,000, conjugated diene content was 33.2% compared with 35.4 for the monomer. This loss, which amounts to only 6.2% of the original diene content of the monomer, could have resulted from participation of the diene in polymerization. If only 7.6% of the original diene had actually entered into the polymerization, according to Flory's equations (5) for calculation of the extent of reaction at gelation in a polyfunctional condensation, gelation should have taken place at molecular weight 10,000.

It has been observed in related work (13) that a polymer of molecular weight 24,500 containing 35.5% of conjugated diene was obtained from a monomer containing 39.5% diene. Since this loss in diene is far in excess of the loss required to produce gelation at this high molecular weight it is probable that the loss in diene during polymerization of a polyunsaturated fatty vinyl ether is not caused by participation in polymerization. In considering the molecular-weight distribution of the polymer, effects caused by cross-linking through conjugated diene may therefore be neglected.

Experimental

Analyses. Vinyl ether content of polymers and monomer purity were determined by an iodometric method (11). Conjugated diene and triene were estimated spectrophotometrically.

Molecular Weights. Molecular weights up to 10,000 were determined cryoscopically in cyclohexane. Molecular weights above 10,000 were determined by extrapolation of the relationship between molecular

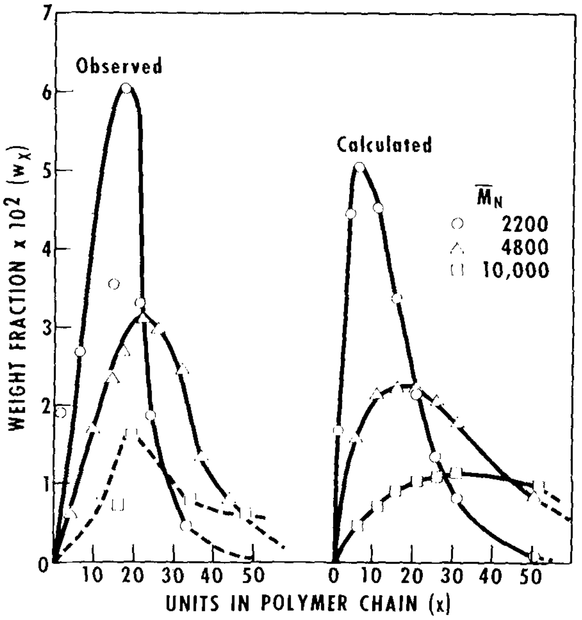

Fig. 4. Differential distributions for soybean vinyl ether homopolymers.

weight and intrinsic viscosity of benzene solutions of polymers having molecular weights below 10,000 (7).

Preparation of Monomer. Conjugated soybean vinyl ether was prepared by the method of Mustakas *et al.* (8). Two samples were used, having the following analyses:

Monomer Sample 1. Purity: 98.2%. Conjugation: diene, 35.4%; triene, 0.3%.
Monomer Sample 2. Purity: 99.5%. Conjugation: diene, 36.0%; triene, 0.3%.

Preparation of Polymers. Polymerizations with stannic chloride as catalyst were conducted in benzene solution and initiated at 25°C. as described by Dufek *et al.* (3). The ratio of solvent to monomer was varied to obtain polymers of the desired molecular weight. Polymerization with boron trifluoride as catalyst were conducted in methylene chloride solution and initiated at −37° as described by Schneider *et al.* (9). Other experimental details and properties of the polymers are given in Table I.

Fractionation of Polymers. The method of integral fractionation (10) was employed. In the following operations precautions were taken to minimize contact of the solutions and polymeric materials with air. Commercial C. P. solvents were used without further purification. Approximately 5 to 10 l. of a 1% solution of polymer in benzene were prepared. Portions (500 ml.) of this solution were transferred to a number of 1-liter Erlenmeyer flasks (stoppered with corks wrapped in aluminum foil; referred to hereafter as flasks 1, 2, 3, etc.). Flask 1 was titrated with methanol until permanent turbidity developed. The volume (V) of methanol was noted, and to each of the remaining flasks, Nos. 2, 3, 4, etc., increasing volumes, for example, V + 5 ml., V + 10 ml., V + 15 ml., etc., of methanol were added, respectively. The bottles were stoppered and allowed to stand (2 to 3 days) until the precipitated polymer had settled to the bottom, leaving a clear supernatant liquid.

The supernatant liquid in each flask was then carefully decanted, and the precipitated polymer was immediately dissolved in benzene. About 20 to 50 ml. of benzene were required for each flask to insure solution of all the polymer that might have adhered to the walls of the flask. The benzene solutions were then transferred quantitatively with the aid of additional benzene to tared 100-ml., round-bottom, one-necked flasks. The bulk of the benzene was removed from each solution by distillation *in vacuo* on a steam bath, and the final traces of solvent were removed *in vacuo* by means of a rotating evaporator. Residual polymer from each flask was weighed. Fractionation of each polymer is shown graphically in Figure 1. Molecular weights of selected fractions of each polymer were determined as described. Data obtained on fractions of the polymer of molecular weight 4,800 (Table II) are typical.

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Erratum

Eric Jungermann of Armour and Company, Chicago, Ill., writes: "In our article, 'Quantitative Gas Chromatography of Fatty Derivatives,' which appeared in the September 1960 issue (*37*, 456) a line was omitted from the text. The error occurs between the eighth and ninth lines from the bottom of the right-hand column of p. 457, where the following should be inserted: 'methyl esters have the relative magnitudes required. This line has the.' "