

ing molecular weight. While this possibility cannot be ruled out it seems much less likely than the first interpretation. It is concluded that the Archibald data are in complete accord with the interpretation that this fraction consists of a reasonably normal distribution of polymer species of  $\bar{M}_w$   $2.44 \times 10^6$  and  $\bar{M}_z/\bar{M}_w$  of the order 1.3.

It must be pointed out that the above discussion is based on the assumption that the second virial

coefficient of amylose in 0.5 *N* aqueous KCl is zero at 25°. This must be essentially true as shown by the virial coefficients at 28 and 31° given earlier in this paper. Any concentration dependence will induce a downward curvature into the plot and would give anomalously low molecular weights and erroneously narrow molecular weight distributions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

## The Conformation of Amylose in Solution<sup>1,2</sup>

BY WILBUR W. EVERETT<sup>3</sup> AND JOSEPH F. FOSTER

RECEIVED JANUARY 2, 1959

The limiting viscosity numbers of subfractions of amylose were determined in dimethyl sulfoxide, 0.33 *N* aqueous KCl and 0.5 *N* aqueous KOH. These results were correlated with the weight-average molecular weights previously reported for these fractions by means of log-log plots and constants in the modified Staudinger equation were determined. The results showed the polymer to be in a coiled conformation in each of the solvents used. Correlation of the radii of gyration from light scattering with the weight-average molecular weights and plots of the angular dependence of scattering intensity also agreed with a coiled conformation. Aqueous KCl solution has been shown to be a  $\theta$  solvent for amylose near 25°. Under such conditions the exponent in the Staudinger viscosity equation was found to be 0.50 and current theories for unperturbed random coils were shown to be applicable to the data. Some implications of the results with regard to the behavior of aqueous solutions of amylose were discussed.

### Introduction

Very few attempts have been made to determine the molecular shape of amylose in solution. Foster and Hixon<sup>4</sup> reported constants in the modified Staudinger equation for unsubstituted amylose in ethylenediamine and for amylose acetates in chloroform. They obtained results which indicated that the amylose behaved essentially as a rod in these cases; however, this work was not carried out on sub-fractionated polymer. Dombrow and Beckman<sup>5</sup> carried out sedimentation and diffusion studies on amylose triacetates in chloroform and concluded that the results were compatible with a helical configuration. Goodison and Higginbotham<sup>6</sup> carried out viscosity and molecular weight studies on subfractions of amylose. These subfractions were acetylated, and the number-average molecular weights and limiting viscosity numbers of the acetates were determined in nitroethane. The values determined for the exponent  $a$  in the modified Staudinger equation were for sago amylose acetate 0.44, for tapioca amylose acetate 0.65, and for maize amylose acetate 0.87. The large variation in these values was explained by assuming the presence of branching in at least two of the amyloses. These values would suggest a coiled conformation in these cases.

Others have evaluated the constants for the

(1) This research was supported in part by grants from the Corn Industries Research Foundation and the National Science Foundation (Grant G-1953).

(2) Presented in part before the Division of Carbohydrate Chemistry, American Chemical Society, Chicago, Ill., September, 1958.

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(4) J. F. Foster and R. M. Hixon, *THIS JOURNAL*, **65**, 618 (1943); **66**, 557 (1944).

(5) B. Dombrow and C. Beckman, *J. Phys. and Coll. Chem.*, **51**, 107 (1947).

(6) D. Goodison and R. Higginbotham, *J. Textile Inst.*, **42**, T248 (1951).

modified Staudinger equation on fractionated and unfractionated amyloses in aqueous KOH and amylose acetates in chloroform; however, no attempt was made in these cases to interpret the results as to molecular shape, as the values lay in the range where unambiguous conclusions concerning conformation are impossible.

This lack of information concerning the shape of unsubstituted amylose in various solvents renders difficult any interpretation of various observations made on the behavior of amylose in solution. This is particularly true in respect to the spontaneous precipitation of amylose from aqueous solutions (retrogradation). Since it is quite well known that amylose may exist in several conformations in the solid state, depending on the conditions under which the amylose is precipitated from solution, it is possible that it could exist in either a coiled form or alternatively as a rod (helix) in solution. In order to decide between these possibilities, the subfractionation of a potato amylose sample into seven subfractions has been achieved and the molecular weights and viscosities of these subfractions have been studied in 0.5 *N* KOH, dimethyl sulfoxide, and aqueous KCl solutions. The constants in the modified Staudinger equation were determined, and these constants were compared with theoretical constants for models of different molecular shape. The conformation of the amylose in the various solvents is deduced from these comparisons. Correlation of various data obtained from light scattering lead to conclusions which agree with those obtained from viscosity-molecular weight relations.

### Experimental

**Materials.**—The amylose subfractions used here are those described in a previous paper.<sup>7</sup> The solvents used are those

(7) W. W. Everett and J. F. Foster, *THIS JOURNAL*, **81**, 3459 (1959).

previously described.<sup>7</sup> All other reagents used were reagent grade unless otherwise indicated.

**Molecular Weight Determinations.**—The molecular weights used in this paper are those previously reported and the root-mean-square  $Z$ -average radii of gyration and angular data on the fractions were determined in the light scattering experiments described in that paper.<sup>7</sup> The  $P_{\theta}^{-1}$  values were calculated for the various angles on the fractions by dividing  $(C/R_{\theta}^*)_{\theta=0}$  by the intercept of the zero angle and zero concentration lines,  $(C/R_{\theta}^*)_{\theta=0, C=0}$ , which gives  $(R_0^*/R_{\theta}^*) = P_{\theta}^{-1}$ . The  $P_{\theta}^{-1}$  used here are those obtained at 436  $m\mu$ .

**Determination of Limiting Viscosity Numbers.**—The limiting viscosity number of fractions I through V were determined in dimethyl sulfoxide, 0.5 *N* KOH and 0.33 *N* KCl at 25.0  $\pm$  0.01°. The viscosities in dimethyl sulfoxide were determined in an Ostwald-Fenske viscometer which had a flow time for solvent of about 117 sec. Some of the viscosity measurements were repeated in a Cannon-Ubbelohde dilution viscometer obtained from the Cannon Instrument Co. and were found to be the same within experimental error. There is essentially no kinetic energy correction in the latter viscometer. The viscosities in 0.5 *N* KOH and 0.33 *N* aqueous KCl were determined in the Cannon-Ubbelohde viscometer which had a flow time of about 56.5 seconds for 0.5 *N* KOH and about 53.7 seconds for 0.33 *N* KCl. The viscosity of a few of the samples were obtained in a Cannon-Ubbelohde viscometer with a longer flow time.

The procedure used for determining the time of flow in the Ostwald-Fenske viscometer was to add 6 ml. of solvent or solution to the viscometer and to place the viscometer in the constant temperature bath and allow about 10 minutes for temperature equilibrium to be established. The flow time was then determined three times and the average taken. In general the deviation of any reading from the average did not exceed 0.1%. The time of flow was determined with a stop watch to the nearest 0.1 second. The flow time was determined in this way for several concentrations of a given sample, and the viscosity numbers,  $(\eta - \eta_0)/\eta_0 C$ , were determined. The different concentrations were made up by repeated dilution of a stock solution or by repeated addition of the stock solution to solvent and solutions of lower concentration than the stock. Thus either dilution or concentration procedures were used. The dilution procedure was more convenient in the case of the Ostwald-Fenske viscometer, and a wider range of concentrations could be covered with the use of the dilution procedure in the Cannon-Ubbelohde viscometer, although the concentration procedure was more convenient. Since the same results were obtained for either procedure in the Cannon-Ubbelohde viscometer the dilution procedure was usually used. The concentration of the stock and of the final solution were obtained by optical rotation measurements. The specific rotations used were reported in a previous paper.<sup>7</sup> Dilutions were made volumetrically, and the concentration obtained for the final solution agreed within 1% in all cases with that calculated from the concentration of the stock and the known dilution factor.

The limiting viscosity numbers were determined by plotting  $(\eta - \eta_0)/\eta_0 C$  versus  $C$  and extrapolating to zero concentration. The relation obtained was linear within experimental error in all cases.

**Preparation of Solutions.**—The amylose samples were dispersed in dimethyl sulfoxide in the same manner as previously described.<sup>7</sup> This procedure consisted of allowing a mixture of the sample and dimethyl sulfoxide in a glass stoppered flask stand in a desiccator over anhydrous calcium chloride until solution was essentially complete. It was sometimes necessary to stir the solution with a magnetic stirrer for a short while to complete the dispersion. The solution was clarified for viscometric measurements by passing it rapidly through a medium Corning sintered glass filter. The solvent was clarified in a similar manner. Dimethyl sulfoxide will absorb water from the atmosphere; absorption of large amounts of water will raise the viscosity of the dimethyl sulfoxide a few per cent. Under the conditions employed here this did not cause a measurable error in the viscosities determined in dimethyl sulfoxide.

Dispersion in alkaline solution was effected by stirring with a magnetic stirrer under high purity nitrogen which had been passed through a vanadyl sulfate train to remove the last traces of oxygen. Details of this procedure have been described previously.

The aqueous KOH solutions of amylose were clarified by centrifuging for about 30 minutes at 20,000  $\times$  G. in a Servall angle centrifuge. This procedure for preparation of the alkaline solutions made it possible to obtain agreement between limiting viscosity numbers obtained on the same sample, in repeated determinations involving separate preparations of the solutions.

The 0.33 *N* aqueous KCl solutions were prepared by neutralizing a 10-ml. portion of the 0.5 *N* aqueous KOH solutions to pH 7, prepared as described above, with 1 *N* HCl. Both the stock and solvent of aqueous 0.33 *N* KCl were clarified by filtering through a medium-porosity sintered glass filter. No loss in concentration was detected on filtering the stock.

All pipetting of aqueous solutions was carried out using pipetting bulbs in order to avoid introduction of  $\alpha$ -amylases into the solutions.

## Experimental Results

The results of viscosity experiments and light scattering experiments carried out on the amylose subfractions are shown in Table I. The light

TABLE I  
LIGHT SCATTERING AND VISCOSITY RESULTS IN AMYLOSE FRACTIONS<sup>a</sup>

Fraction	$M_w \times 10^{-5}$	$[\eta]$		$[\eta]$ KCl	$\sqrt{R_g^2}$ DMSO
		DMSO	0.5 <i>N</i> KOH		
AFIA	22.2	350	595	173	935
AFIB	13.5	262	435	152	724
AF II	10.5	210	320	126	656
AF III	8.47	190	290	115	610
AF IV	5.52	135	207	90.0	543
AF V	2.70	89.5	118	60.0	425
AF VI	1.52	...	..	...	334

<sup>a</sup> Viscosity numbers in ml./g.

scattering results have been reported previously.<sup>7</sup> Figures 1, 2 and 3 show the plots of the viscosity

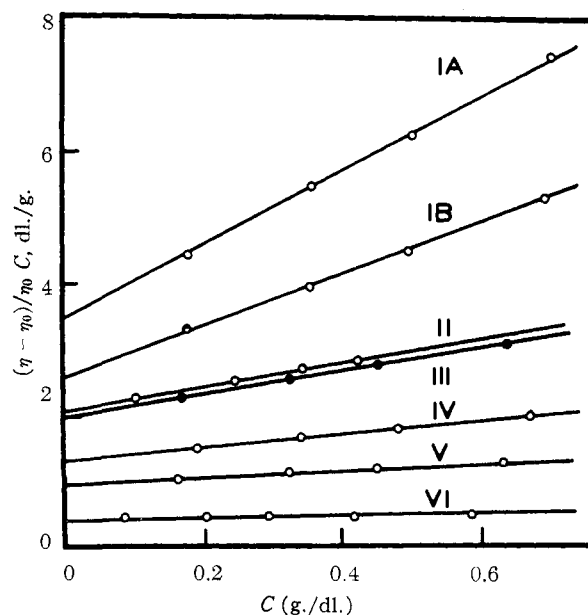


Fig. 1.—Evaluation of the limiting viscosity numbers of the amylose fractions in dimethyl sulfoxide at 25°.

number,  $(\eta - \eta_0)/\eta_0 C$ , versus the concentration of the various fractions in the three solvents. The extrapolations to infinite dilution to give the

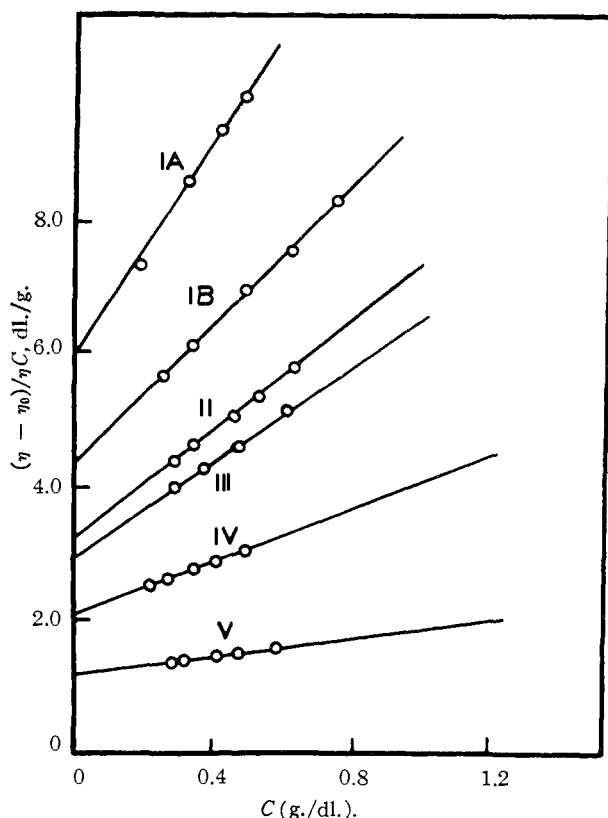


Fig. 2.—Evaluation of the limiting viscosity numbers of the amylose fractions in 0.5 *N* aqueous KOH at 25°.

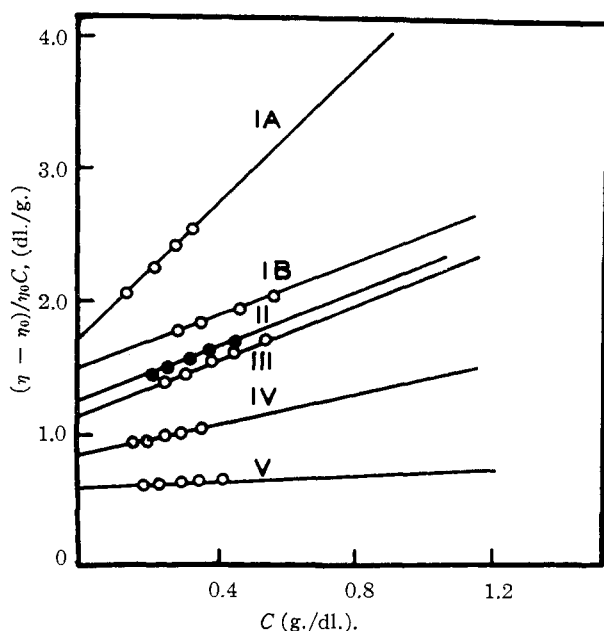


Fig. 3.—Evaluation of the limiting viscosity numbers of the amylose fractions in 0.33 *N* aqueous KCl at 25°.

limiting viscosity number,  $[\eta]$ , agree with Huggins equation<sup>8</sup>

$$(\eta - \eta_0)/\eta_0 C = [\eta] + [\eta]^2 k' C \quad (1)$$

Thus the intercept gives the limiting viscosity

(8) M. L. Huggins, *THIS JOURNAL*, **64**, 2716 (1942).

number  $\lim_{C \rightarrow 0} (\eta - \eta_0)/\eta_0 C = [\eta]$ , and the slope divided by the square of the intercept gives  $k'$ , the Huggins' constant. The Huggins' constant in DMSO was  $0.431 \pm 0.012$ , in 0.33 *N* aqueous KCl  $0.653 \pm 0.055$  and in 0.5 *N* aqueous KOH  $0.433 \pm 0.008$ . The value in aqueous KOH did not include the data for AFIA and AFIB which were determined in a different viscometer. The fairly large variation in  $k'$  in 0.33 *N* KCl was probably due to the fact that the same viscometer was not used in all runs.

### Discussion

The constants in the modified Staudinger equation

$$[\eta] = K' M^a \quad (2)$$

were determined by plotting the log of the intrinsic viscosity *versus* the log of the weight-average molecular weight. This is shown in Fig 4 for the data obtained in the three solvents. The molecular weights used were those determined in dimethyl sulfoxide. These were shown previously to be in good agreement with the molecular weights determined in aqueous KCl and in aqueous KOH.<sup>7</sup>

The equations determined from the graph in Fig. 4 are

$$[\eta]_{\text{KOH}} = 8.50 \times 10^{-3} \bar{M}_w^{0.76} \quad (3)$$

$$[\eta]_{\text{DMSO}} = 3.06 \times 10^{-2} \bar{M}_w^{0.64} \quad (4)$$

$$[\eta]_{\text{KCl}} = 1.13 \times 10^{-1} \bar{M}_w^{0.50} \quad (5)$$

where DMSO indicates dimethyl sulfoxide and limiting viscosity numbers are in ml./g. The molecular weights which should be used in these equations are the viscosity-average values. These fractions are not completely monodisperse; therefore, there must be a difference between the weight-average and viscosity-average molecular weights. This would introduce an error into the value observed in  $K'$ , but the value determined for  $a$  would be correct if the molecular weight distributions for all the fractions are the same. The distributions must be approximately the same or a straight line would not have resulted (Fig. 4).

The viscosity-average molecular weight is defined by the equation

$$\bar{M}_v = \left[ \sum_i W_i M_i^a \right]^{1/a} \quad (6)$$

and the weight-average molecular weight by

$$\bar{M}_w = \sum_i W_i M_i \quad (7)$$

where  $W_i$  are weight fractions of species  $i$ . Thus the viscosity-average molecular weight approaches the weight-average molecular weight as the value of  $a$  approaches one. For linear polymers having a "most probable" distribution  $\bar{M}_v/\bar{M}_n$  goes from 1.67 to 2.00 when  $a$  goes from 0.5 to 1.00.<sup>9</sup> The ratio of  $\bar{M}_w/\bar{M}_n$  for such a distribution is 2.00. Therefore for a linear polymer with a "most probable" distribution  $\bar{M}_v$  is always nearer to  $\bar{M}_w$  than to  $\bar{M}_n$ . For a fractionated polymer the viscosity-average and weight-average values are even closer. Therefore the values obtained for  $K'$  must not be greatly in error. From this dis-

(9) J. R. Schaefgen and P. J. Flory, *ibid.*, **70**, 2709 (1948).

discussion it can be seen that the molecular weights calculated from equation 3, using viscosities in 0.5 *N* KOH, would be nearer the viscosity-average molecular weight, for any distribution, than those which would be calculated from the other equations. Experimentally, however, it is much easier to determine viscosities in dimethyl sulfoxide, and therefore equation 4 will probably be more useful in determining molecular weights of amylose samples by viscosity measurements.

The reason that dimethyl sulfoxide is preferred for obtaining viscosities is that no observable degradation of amylose occurs in this solvent over a long period of time. It has been possible to reproduce the viscosity measurements on solutions of amylose fractions in dimethyl sulfoxide which have been stored for 5 months in a desiccator. It also seems to be easier to dissolve an amylose sample in dimethyl sulfoxide than in 0.5 *N* KOH. The solution may be heated for a short period of time without any obvious degradation occurring. The second virial coefficient is approximately the same for the fractions in the two solvents; however in 0.5 *N* KOH the amylose must contain many ionized hydroxyl groups, and therefore the solvents are not comparable.

The primary purpose of this viscosity-molecular weight correlation was not, however, to provide equations for calculating molecular weights from viscosities but to determine the conformation of the amylose molecule in solution. This can be accomplished by comparing the exponent *a* determined by experiment with those obtained by theory for several models. According to the most refined treatments the value of *a* for a coiled linear polymer should vary between 0.5 and 0.8<sup>10</sup> depending on the swelling of the polymer in a given solvent, and the value for a rod should be around 1.7.<sup>11</sup> The values of *a* in the three solvents are seen to fall within the theoretical range for coiled linear polymers. The applicability of the theory to amylose in 0.5 *N* KOH is rather doubtful, since the amylose must behave as a polyelectrolyte at this concentration of base. It still seems, however, that the amylose in 0.5 *N* KOH would probably be only a somewhat expanded coil. This expansion is probably less isotropic, however, than that which occurs from only solvent polymer interaction. This conclusion is arrived at from the fact that, although equations 3 and 4 for the dependence of  $[\eta]$  on molecular weight indicate a greater expansion in aqueous KOH than in dimethyl sulfoxide, the measured radius of gyration of a given sample in 1 *N* KOH is somewhat smaller than that obtained in dimethyl sulfoxide. This could be explained by a non-isotropic expansion giving a molecule whose radius of gyration does not agree with that of a coil.

Correlation of properties of the molecule derived from light scattering measurements also may lead to a knowledge of the conformation of the amylose molecule in solution. Figure 5 shows a plot of the root-mean-square radii of gyration of the amylose fractions in dimethyl sulfoxide against the square root of the molecular weights. It can be seen that

there is a fairly good correlation. Here we are comparing *Z*-average quantities, the root-mean-square radii of gyration, with weight average quantities, the molecular weights. The dependence here should actually be higher than obtained since the dependence of viscosity on molecular weight is higher than a square root dependence. An equa-

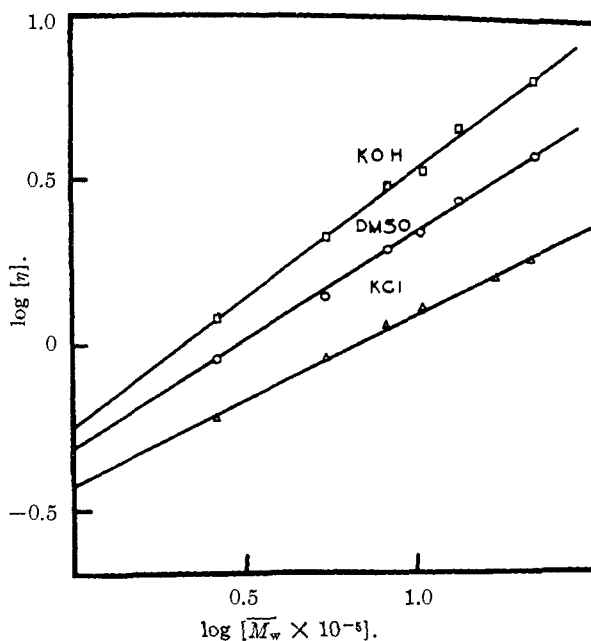


Fig. 4.—Evaluation of  $K'$  and  $a$  in the modified Staudinger equation by plots of  $\log [\eta]$  versus  $\log M_w$ . The units of  $[\eta]$  are here in dl./g.

tion, analogous to the modified Staudinger equation, may be written for the dependence of  $\sqrt{R_z^2}$  on molecular weight

$$\sqrt{R_z^2} = kM_w^b \quad (8)$$

where  $\sqrt{R_z^2}$  is the *Z*-average root-mean-square radius of gyration and  $k$  is a constant. The exponent,  $b$ , in equation 8 should be nearer 0.5 than the value obtained in equation 4 for  $a$ . Therefore the variation of  $\sqrt{R_z^2}$  with  $M_w^{1/2}$  is further evidence for a coiled conformation of the amylose molecule in dimethyl sulfoxide.

There is one further relation from light scattering which is of interest in connection with the conformation. This is the "particle scattering factor"  $P_\theta$ . The reciprocal of this factor,  $P_\theta^{-1}$ , may be obtained by dividing the intercept of a given angular extrapolation line with the zero concentration line in a Zimm plot,  $C/R_{\theta,0}^*$ , by the intercept  $C/R_{0,0}^*$ . This gives  $R_{0,0}^*/R_{\theta,0}^* = P_\theta^{-1}$  where  $R_{0,0}^*$  is the Rayleigh scattering factor at zero concentration and zero angle and  $R_{\theta,0}^*$  is this factor at zero concentration and the angle  $\theta$ . The solid line in Fig. 6 is the  $P_\theta^{-1}$  factor versus  $\sin \theta/2$  for AFIA in dimethyl sulfoxide calculated from data obtained with light of 436  $\mu$ . The curves for all samples in the solvents used for light scattering were of this same general nature. The dashed lines have been calculated for the indicated models

(10) T. G. Fox and P. J. Flory, *THIS JOURNAL*, **73**, 1904 (1951).

(11) J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951).

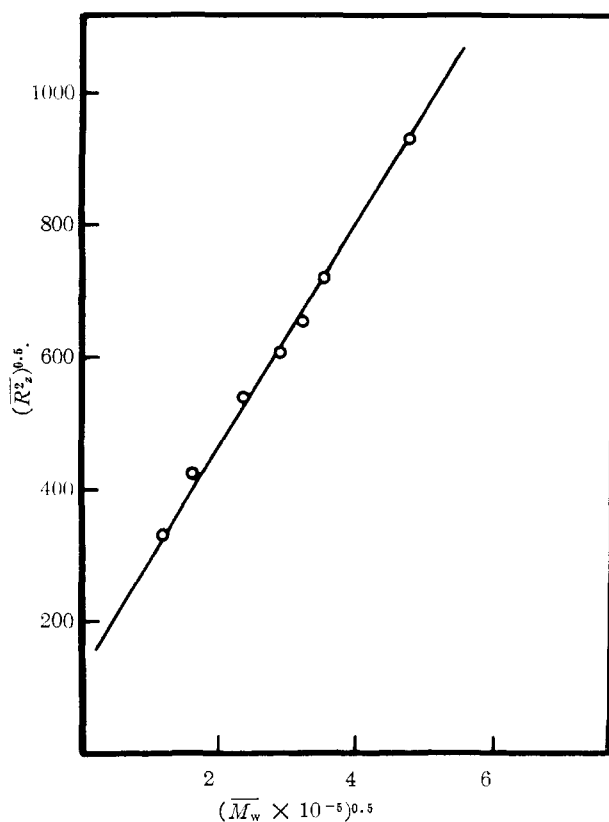


Fig. 5.—Plot of root-mean-square radii of gyration of amylose samples dissolved in dimethyl sulfoxide versus the square-root of  $\bar{M}_w$ . The radii of gyration were determined from light scattering data at 4360 Å. (ref. 7).

from equations developed by Debye.<sup>12</sup> The actual calculations were made with the aid of tables given by Doty and Steiner.<sup>13</sup> If polydispersity is taken into account the theoretical curves for both rods and coils will be shifted downward. Therefore the agreement between the  $P_\theta^{-1}$  curve obtained experimentally and that calculated from theory is extremely good. This evidence also indicates that the amylose molecule is a coil in these solvents.

The value of  $\alpha$  obtained for amylose in aqueous KCl was 0.50. This is the value that a coil should have at the  $\theta$  point (the temperature at which the second virial coefficient is zero). It was pointed out in another paper<sup>7</sup> that the second virial coefficient was very low at around 30° and it was estimated that it would go to zero at a temperature close to 25°. The viscosity equation at the  $\theta$  point is then  $[\eta]_0 = KM^{0.5}$ , as shown in equation 5, where  $K$  is  $1.13 \times 10^{-1}$ . At the  $\theta$  point  $K = \Phi (\bar{r}_0^2/M)^{3/2}$ , where  $\bar{r}_0^2$  is the mean-square end-to-end distance for the random cell coil,  $M$  is the molecular weight and  $\Phi$  is a universal constant for all polymers in all solvents.<sup>10,14</sup> The value of  $(\bar{r}_0^2/M)$  obtained from this relation is a number average. Thus if the limiting viscosity number in a  $\theta$  solvent and the number average molecular weight are

(12) P. Debye, *J. Appl. Phys.*, **15**, 338 (1944); *J. Phys. Coll. Chem.*, **51**, 18 (1947).

(13) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).

(14) T. G. Fox and P. J. Flory, *THIS JOURNAL*, **73**, 1913 (1951).

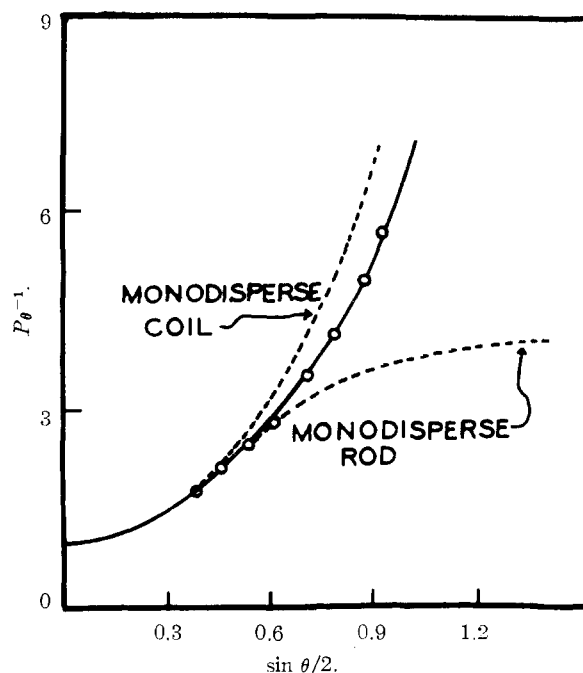


Fig. 6.—Plot of  $P_\theta^{-1}$  versus  $\sin \theta/2$  for fraction AFIA dissolved in dimethyl sulfoxide.

known for a polymer, the unperturbed root-mean-square end-to-end distance may be calculated for the coiled polymer.

If a distribution of  $\bar{M}_n:\bar{M}_w:\bar{M}_z$  of 1:1.5:1.92 is assumed then a value of  $2.33 \times 10^{21}$  is obtained for  $\Phi$ . This compares with the best average value of  $2.1 (\pm 0.2) \times 10^{21}$  for  $\Phi$ .<sup>14</sup> The distribution used was not completely arbitrary, but was constructed from the value of  $\bar{M}_z/\bar{M}_w$  of 1.3 for AFIA estimated previously<sup>7</sup> and from preliminary osmotic pressure data on the lower fractions which indicates that  $\bar{M}_w/\bar{M}_n$  is near 1.5. The value of  $\Phi$  is in remarkably good agreement with theory considering that the  $\sqrt{\bar{r}_0^2}$  enters as a cubed term and  $\bar{M}_n$  enters to the 3/2 power. The value used for  $\sqrt{\bar{r}_0^2}$  was obtained from  $\sqrt{\bar{R}_z^2}$  equal to 745 Å. determined for AFIA in 0.5 N KCl by light scattering at a temperature slightly above the  $\theta$  point.

The value of  $\alpha$ , the molecular expansion factor, may be calculated from a knowledge of  $[\eta]_\theta$  and  $[\eta]$  in a given solvent by the relation  $\alpha^3 = [\eta]/[\eta]_\theta$ . The  $\alpha$ -values for the amylose fractions in dimethyl sulfoxide calculated for samples AFIA, IB, II, III, IV and V are 1.26, 1.20, 1.19, 1.18, 1.15 and 1.14, respectively. The radius of gyration of any sample in dimethyl sulfoxide may then be determined from the relation

$$\sqrt{\bar{R}_z^2} = \alpha \sqrt{\bar{R}_{z,\theta}^2} \quad (9)$$

Using the value of  $\alpha$  for AFIA in dimethyl sulfoxide and the value of  $\sqrt{\bar{R}_{z,\theta}^2} = 745$  Å. obtained in 0.5 N KCl by light scattering we obtain a value for  $\sqrt{\bar{R}_z^2}$  in dimethyl sulfoxide of 939 Å. This compares with the value of  $\sqrt{\bar{R}_z^2}$  obtained by light scattering on AFIA in dimethyl sulfoxide of 935 Å.

Thus it is seen that amylose behaves as a coil in the solvents used and as a nearly ideal random coil in aqueous KCl near room temperature. If the  $\theta$  temperature of amylose in neutral aqueous solution is indeed near  $25^\circ$  it would be anticipated that precipitation should take place from such solutions at significantly lower temperature. Under some conditions amylose does indeed precipitate reversibly at temperatures near the freezing point. However, it is normally impossible to maintain any appreciable concentration of polymer at a temperature even a few degrees below the  $\theta$  temperature. It is suggested as a possible explanation that amylose, in view of its known propensity for adopting a helical conformation in various complexes, may revert to a helix at temperatures below the  $\theta$  point in water, thus satisfying polymer-polymer contacts intramolecularly. Attempts have been made to find evidence for such a change in conformation by measuring the optical rotation of an amylose solution over the temperature range  $9$  to  $41^\circ$  in  $0.5 N$  KCl. No evidence for any transition was seen, the specific rotation (sodium d line) decreasing almost linearly with increasing

temperature, by about  $0.5^\circ$  per degree centigrade, over the entire range. This result is in accord with the expected behavior for a coil.<sup>15</sup> The fact that amylose slowly crystallizes (retrogrades) at temperatures even above the  $\theta$  temperature is, at first thought, somewhat surprising. However, the usual treatment of polymer precipitation and the concept of the  $\theta$  temperature are based on amorphous phase separation and are not strictly applicable to crystallization phenomena.<sup>16</sup> It seems possible that polymer-polymer interactions are increased through slowly attained preferential contacts so that nucleation and crystallization may ensue at temperatures appreciably above the  $\theta$  temperature. In a general way the difficulty of dissolving amylose in water and the instability of aqueous solutions of amylose are compatible with the fact that water is a relatively poor (indifferent) solvent for this polymer.

(15) J. Schellman, *Compt. rend. trav. Lab. Carlsberg. Serie Chim.*, **30**, 363 (1958).

(16) P. J. Flory, "Principles of Polymer Chemistry," Chap. 8, Cornell University Press, Ithaca, N. Y., 1953.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

## The Controlled Thermal Decomposition of Cellulose Nitrate. VI. Other Polymeric Nitrates<sup>1,2</sup>

BY M. L. WOLFROM, ALAN CHANEY AND K. S. ENNOR

RECEIVED DECEMBER 17, 1958

The reduced pressure ignition products (formaldehyde, formic acid, glyoxal, hydrogen cyanide,  $\alpha$ -hydroxynitrile, and volatile and total acid) of amylose and amylopectin nitrates were found to correspond in identity and yield with those produced by cellulose nitrate. Under the same conditions, the nitrates of polyvinyl alcohol and dextran afforded similar products but the yields were distinctively altered. These alterations in yield are correlated with the variations in structure of the polymeric nitrates ignited. The general mechanistic sequences previously utilized to interpret the ignition decomposition of cellulose nitrate appear to be applicable with minor variations to the interpretation of all polymeric nitrate ignition reactions. The intrinsic viscosity and optical rotation of dextran nitrate were determined.

Our investigations<sup>2-6</sup> of the ignition of cellulose nitrate under reduced pressure indicated that additional valuable information might result from similar studies employing other polymeric nitrates. It has been found that the pyrolytic method employed, in which the polymeric nitrate sample is subjected to a nearly instantaneous increase in temperature of several hundred degrees, institutes a self-sustaining, normally non-luminous,<sup>5</sup> decomposition reaction. The initial reaction products, which are expelled violently from the hot

reaction zone, are cooled as rapidly as possible in an attempt to quench secondary reactions between the several substances formed. The investigation, herein described, was initiated in the belief that a study of the products of ignition of the nitrates of dextran, starch and polyvinyl alcohol would provide further insight concerning the important initial decomposition reactions of polymeric nitrates.

The recent commercial availability<sup>7</sup> of two starch fractions, amylose and amylopectin, simplified the study of two considerably different polymeric carbohydrate nitrates. Although similar starch fractions have been nitrated previously,<sup>8,9</sup> the methods appeared experimentally tedious or afforded products that required considerable effort to stabilize. In the current work, both amylose and amylo-

(1) This work was carried out under contract (DA-33-019-ord-2025, technical supervising agency, Ballistic Research Laboratories, Aberdeen Proving Ground, Md.) between the Ordnance Corps and The Ohio State University Research Foundation (Project 675). Preliminary communication: *Abstracts Papers, Am. Chem. Soc.*, **134**, 10E (1958).

(2) Previous communication in this series: F. Shafizadeh, M. L. Wolfrom and P. McWain, *THIS JOURNAL*, **81**, 1221 (1959).

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