

DILUTE SOLUTION BEHAVIOUR OF AMYLOSE TRIBUTYRATE

LIGHT SCATTERING, VISCOSITY AND OSMOTIC PRESSURE MEASUREMENTS IN NON-IDEAL SOLVENTS*

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Abstract—Amylose tributyrates have been prepared and fractionated; the dilute solution behaviour of the polymer has been studied in four solvents, ethyl acetate, methyl ethyl ketone, carbon tetrachloride and tetrahydrofuran. The Mark-Houwink relations have been established for each solvent and the exponent ν varies between 0.72 and 0.86, for different solvents. Perturbed dimensions have been measured for the polymer dissolved in two solvents and an estimate of the unperturbed dimensions has been made; the latter appear to be solvent dependent. Heterogeneity corrections were applied using data established by gel permeation chromatography measurements. Values of the effective bond length b of between 17 and 19.5×10^{-8} cm and the Kuhn statistical segment A_m of 70 to 180×10^{-8} cm, indicate that amylose tributyrates behave like a moderately stiff coil in good solvents, with a chain stiffness intermediate between the vinyl and cellulosic polymers.

INTRODUCTION

The hydrodynamic properties of cellulose and several of its derivatives have been studied in some detail by a number of workers [1–5]. Considerably less attention has been directed towards the related polysaccharide amylose. This is partly due to the increased difficulties encountered in isolating this polymer in large quantities and uncontaminated with the amylopectin component associated with it in the starch granule.

Small-scale fractionation procedures are capable of producing amylose free from amylopectin [6] but Banks and Greenwood [7] have also drawn attention to the possibility that chains with limited branching may be present in such preparations. These authors have stressed that the amylose must be leached out of the starch granule if only linear chains are to be removed for examination. This precaution has been rigorously adhered to so that samples suitable for hydrodynamic studies be obtained for the present study.

EXPERIMENTAL

Isolation of linear amylose

The method was essentially that outlined by Greenwood *et al.* [8]. Fresh starch was isolated from potatoes (*var.* Golden Wonder) as described previously [6]. A slurry of starch was added to water (2.5 dm^3) to give a suspension with a concentration of about 20 g dm^{-3} . This was stirred

for 1 hr at 335 K under nitrogen, then allowed to cool. After standing overnight, the swollen granules settled, leaving a supernatant containing soluble amylose, which was removed. The amylose was precipitated from this supernatant and recrystallized several times with butan-1-ol. To ensure complete removal of any non-linear amylose, the highest molecular weight portion was precipitated, from a 3 per cent solution in dimethyl sulphoxide, by controlled addition of butan-1-ol and discarded. The remaining amylose was recrystallized from aqueous solution twice more, using butan-1-ol.

Analysis of amylose

The linearity of the product was established by reacting the amylose with the enzyme β -amylase. A β -amylase hydrolysis limit of >98 per cent of the amylose was found, indicating that the amylose chains were completely linear. Treatment with a mixed ($\beta + Z$) enzyme preparation gave 100 per cent hydrolysis, confirming that no amylopectin was present either [9]. We are indebted to Dr W. Banks for carrying out these analyses.

Preparation of amylose tributyrates

Method 1. Amylose–butanol complex (9.4 g) was added to a mixture of pyridine (200 cm^3) and butyric anhydride (250 cm^3). The mixture was agitated for 1 hr at 313 K to aid dissolution, then left stirring for 7 days at room temperature. The resulting solution was filtered and injected into cold methanol (243 K) to precipitate the ester which was washed with cold methanol, redissolved in equal volumes of pyridine and butyric anhydride, and stirred for another 2 days at room temperature. The final product was isolated and coded B.

Method 2. Amylose (9.3 g) was dispersed in a mixture of butyric anhydride (450 cm^3) and pyridine (450 cm^3) and heated on a water bath under reflux at 373 K for 2 hr. After

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cooling, the ester was separated by precipitation in methanol at 243 K, washed, dissolved in chloroform, reprecipitated and washed with methanol, and finally dried in a vacuum oven. The product was coded X.

Degree of substitution

The success of the esterification was estimated by measuring the degree of substitution of the product. This was carried out both by a saponification method described earlier [10] and by examining the infra-red spectrum of the ester. Infra-red spectra were measured by dissolving the dry ester (0.1 g cm^{-3} concentration) in silica gel dried chloroform and spreading the solution between two sodium chloride plates. The chloroform was removed in a current of dried nitrogen and the spectrum of the film taken. The absorption region corresponding to the hydroxyl group stretching was used; after calibration with samples of known degrees of substitution, the method enabled a rapid estimation of the degree of esterification of each sample to be made. Both methods of preparation gave esters with a degree of substitution > 2.9 compared with a degree of substitution of 3.0 for a completely substituted polymer.

Fractionation

Amylose tributyrates were dissolved in toluene (concentration about 15 g dm^{-3}) and the solution thermostatted at 298 K. The precipitating agent was petrol ether (60–80). After the initial precipitation of each fraction, the solution was warmed to about 308 K to redissolve the fraction, then allowed to cool slowly to 298 K overnight. This reduced the effects of occlusion during precipitation. Twelve fractions were separated from batch X and five fractions from batch B.

Molecular weight measurements

Values of the number average molecular weight \bar{M}_n were obtained using a Melabs recording osmometer, model CSM-2. Pecel 600 membranes were conditioned, in a step-wise manner, to the solvent methyl ethyl ketone (MEK). The temperature of measurement was 295.5 K. Solution concentrations between 1 and 6 g dm^{-3} were used and both the solutions and the solvent were passed through G3 sintered glass filters to remove any extraneous material which might affect the osmometer performance.

Weight average molecular weights \bar{M}_w were measured in a Sofica PGD model 42000 using blue light ($\lambda = 436 \text{ nm}$). Both \bar{M}_n and the Z-average mean square radius of gyration $\langle S^2 \rangle_z$ were calculated from Zimm plots constructed from data at 298 K. Two solvents were used, MEK and ethyl acetate (EA), and \bar{M}_w had the same value (within 5 per cent) in both solvents.

The refractive index increment (dn/dc) was measured for $\lambda = 436 \text{ nm}$ in a Brice-Phoenix differential refractometer. Values were $0.0915 \text{ cm}^3 \text{ g}^{-1}$ and $0.0978 \text{ cm}^3 \text{ g}^{-1}$ for amylose tributyrates in MEK and EA, respectively.

Limiting viscosity number

The limiting viscosity number $[\eta]$ for each fraction was measured in a Cannon-Ubbelohde viscometer at 298 K. The viscosities of the higher molecular weight fractions were also measured in a P.C.L. zero shear viscometer but no shear dependence was detected for samples with $\bar{M}_w < 1.5 \times 10^6$. Concentrations were in units of g cm^{-3} .

Gel permeation chromatography

The molecular weight distributions of the fractions were estimated by gel permeation chromatography (GPC). The

measurements were carried out by kind courtesy of Mr. J. Maisey and Dr. J. Evans at the Rubber and Plastics Research Association of Great Britain. The solvent used was tetrahydrofuran and the molecular weights were calculated on the basis of the equations

$$[\eta] = 1.2 \times 10^{-2} \bar{M}^{0.71} \text{ for polystyrene} \\ \text{and } [\eta] = 1.66 \times 10^{-3} \bar{M}^{0.86} \text{ for amylose tributyrates.}$$

RESULTS

Sample heterogeneity

Experimental values for \bar{M}_n and \bar{M}_w are given in Table 1 where they can be compared with the corresponding values calculated from GPC data. The molecular weights obtained from GPC are consistently lower than the values obtained by direct measurement, but the agreement improves as M decreases. However, the (\bar{M}_w/\bar{M}_n) ratios from both techniques compare favourably and this allowed \bar{M}_w to be estimated from osmotic \bar{M}_n values with confidence, when required. The \bar{M}_w 's calculated in this way are shown in brackets in Table 1 and were found to fit the experimental Mark-Houwink relations extremely well.

The (\bar{M}_w/\bar{M}_n) ratio can also be used to provide a basis for estimating the heterogeneity corrections which are so necessary to ensure a realistic appraisal of dilute solution data. A particular distribution function must also be selected and the Zimm-Schulz distribution whose form is

$$W(M) = [y^{h+1}/\Gamma(h+1)] M^h \exp(-yM) \quad (1)$$

is believed to be a good approximation for many polymer fractions. Here $y = h/\bar{M}_n = (h+1)/\bar{M}_w = (h+2)/\bar{M}_z$ and Γ represents the gamma function. The approximate value of (\bar{M}_w/\bar{M}_n) is 1.6, which corresponds to h of 1.7, and as the GPC data also showed that a number of fractions had (\bar{M}_z/\bar{M}_n) ratios of 2.0 to 2.6, the use of the Zimm-Schulz distribution appears justified.

Heterogeneity corrections, using the relation

$$\langle S^2 \rangle_w^{\frac{1}{2}} = [(h+1)/(h+2)]^{\frac{1}{2}} \langle S^2 \rangle_z^{\frac{1}{2}} \quad (2)$$

can be applied to the Z-average root mean square radius of gyration $\langle S^2 \rangle_z^{\frac{1}{2}}$ calculated directly from light scattering measurements. Similarly, corrections to the Flory "universal" parameter Φ_0 can be assessed by writing the Flory-Fox equation in the form

$$[\eta] = \frac{\Phi_0 \cdot \langle r^2 \rangle_z^{3/2}}{q \bar{M}_w} \quad (3)$$

where

$$q = \frac{(h+2)^{3/2} \Gamma(h+2)}{(h+1)^2 \Gamma(h+1.5)} \quad (4)$$

and the mean square end to end distance $\langle r^2 \rangle = 6 \langle S^2 \rangle$.

The theoretical limiting value of $\Phi_0 = 2.87 \times 10^{-23}$ (in the unperturbed state) derived from the Kirkwood, Riseman [11], Auer and Gardner [12] theory, was chosen for this study.

Table 1. Number and weight average molecular weights for amylose tributyrate obtained from osmometry, light scattering and GPC

Fraction	$10^{-5} \bar{M}_n$	$10^{-5} \bar{M}_n$ (GPC)	$10^{-5} \bar{M}_w$	$10^{-5} \bar{M}_w$ (GPC)	$\left(\frac{\bar{M}_w}{\bar{M}_n}\right)$	$\left(\frac{\bar{M}_w}{\bar{M}_n}\right)$ GPC
B2	—	—	15.6	—	—	—
B3	3.91	2.50	6.13	5.77	1.57	2.31
B4	1.88	1.36	2.75	2.09	1.46	1.53
X9	1.06	0.87	(1.76)	1.45	—	1.66
B5	0.90	0.75	1.50	1.25	1.67	1.67
X10	0.67	0.48	(1.05)	0.76	—	1.57
X11	0.65	0.47	(1.00)	0.71	—	1.52
X12	0.49	0.38	(0.78)	0.60	—	1.60

Mark-Houwink equations

Limiting viscosity numbers were measured in four solvents EA, MEK, tetrahydrofuran (THF) and carbon tetrachloride (CT). As there are slight differences in sample heterogeneity the Mark-Houwink equations $[\eta] = K \bar{M}^\nu$, have been reported for both \bar{M}_n and \bar{M}_w at 298 K. The relations found are

$$\begin{aligned} \text{EA} \quad [\eta] &= 5.59 \times 10^{-3} \bar{M}_w^{0.74} \\ &= 9.86 \times 10^{-3} \bar{M}_n^{0.72} \\ \text{MEK} \quad [\eta] &= 3.39 \times 10^{-3} \bar{M}_w^{0.77} \\ &= 4.88 \times 10^{-3} \bar{M}_n^{0.77} \\ \text{CT} \quad [\eta] &= 3.46 \times 10^{-3} \bar{M}_w^{0.79} \\ &= 6.24 \times 10^{-3} \bar{M}_n^{0.77} \\ \text{THF} \quad [\eta] &= 1.66 \times 10^{-3} \bar{M}_w^{0.86} \\ &= 3.24 \times 10^{-3} \bar{M}_n^{0.83} \end{aligned}$$

In each case the solvent is thermodynamically "good" and the large values of the exponent ν indicate that the polymer coil is in a highly expanded state. Solutions of cellulose tributyrate also have very high values of ν and two which have been reported for the system, cellulose tributyrate-MEK, are $\nu = 0.80$ [13] and $\nu = 0.87$ [14]. Both are larger than the value obtained for the amylose derivative, suggesting that the cellulose ester has a more extended conformation in this solvent. The conclusion is substantiated when we compare the respective perturbed dimensions.

Perturbed dimensions of amylose tributyrate

An estimate of the coil size in EA and MEK was obtained from measurements of $\langle S^2 \rangle_z^{1/2}$ derived from the Zimm plots for the higher molecular weight fractions. These are shown in Table 2 together with the corresponding values of $\langle r^2 \rangle_z^{1/2}$ and $[\langle r^2 \rangle_z / \bar{M}_w]^{3/2}$. The corresponding dimensions reported for cellulose tributyrate [15] indicate that the chain extension of the cellulose derivative is about 1.5 times larger than the amylose tributyrate chain when both are dissolved in MEK.

Perturbed coil dimensions can also be calculated from Eqn. (3) if a reliable value of Φ for the perturbed state is known. As this parameter is subject to the influence of both solvent and sample heterogeneity, it is more instructive here to estimate Φ using the experimental coil dimensions. This leads to an average value of $\Phi = 2.18 \times 10^{23}$ in EA and MEK, which is a reasonable value for expanded coils in good solvents.

Coil dimensions can be estimated from other hydrodynamic theories, notably those proposed by Kirkwood and Riseman [11] and Kuhn and Kuhn [16]. Both theories introduce parameters which measure the rigidity of the polymer coil.

In the Kirkwood-Riseman approach, which is based on a "pearl necklace" model for the polymer chain, the effective bond length b measures the chain flexibility

Table 2. Coil sizes of amylose tributyrate measured by light scattering

Fraction	$10^8 \cdot \langle S^2 \rangle_z^{1/2}$ (cm)	$10^8 \cdot \langle r^2 \rangle_z^{1/2}$ (cm)	$10^{24} \cdot \left[\frac{\langle r^2 \rangle_z}{\bar{M}_w} \right]^{3/2}$ (cm ³)	$10^{23} \cdot \Phi$
Solvent MEK				
B2	550	1347	1.253	2.08
B3	311	762	0.921	2.34
B4	201	492	0.826	2.05
B5	131	320	0.566	2.52
Solvent EA				
B2	574	1406	1.420	1.89
B3	320	784	1.000	2.22
B4	204	500	0.870	1.94

and is related to the dimensions by

$$\langle r^2 \rangle^{\frac{1}{2}} = bx^{\frac{1}{2}}, \quad (5)$$

where x is the degree of polymerization. The parameter b can be derived from the relation

$$b^3 = \left[\frac{28.6M_0}{(6\pi^3)^{1/2}N_A} \right] \lim_{x \rightarrow \infty} ([\eta] \cdot x_w^{-1/2}) \quad (6)$$

by plotting $[\eta]x_w^{-1/2}$ against $x_w^{-1/2}$.

The corresponding Kuhn statistical segment length A_m , can be obtained from viscosity data using

$$[\eta] = \frac{N_A b_0^2 A_m}{M_0} \left[\frac{0.43x}{-1.6 + \ln(A_m/d_h) + (xb_0/A_m)^{1/2}} \right] \quad (7)$$

In these equations, N_A is Avogadro's number, M_0 is the monomer molecular weight, b_0 is the length and d_h is the hydrodynamic thickness of the monomer unit.

The coil dimensions follow from

$$\langle r^2 \rangle_w = b_0 x_w A_m, \quad (8)$$

and have been derived using the suggested [17] value of $b_0 = 4.25 \times 10^{-8}$ cm, which is the distance between two glycosidic bridge oxygens in the chain. The $\langle r^2 \rangle_w^{\frac{1}{2}}$ values calculated from both theories are shown in Table 3 with the corresponding values of b and A_m . In general, the methods give similar results but tend to overestimate the coil dimensions, especially for lower molecular weights.

Dependence of $\langle r^2 \rangle_w$ on \bar{M}_w . When a polymer coil in solution obeys random flight statistics, $\langle r^2 \rangle$ is directly proportional to the molecular weight, and any departure from random coil statistics can be estimated by determining ϵ in the equation.

$$\langle r^2 \rangle_w = K_r \bar{M}_w^{(1+\epsilon)} \quad (9)$$

Ptitsyn and Eisner [18] have used this parameter to account for deviations in Φ_0 and suggest an experimental value of $\Phi(\epsilon)$ can be obtained from

$$\Phi(\epsilon) = \Phi_0(1 - 2.63\epsilon + 2.86\epsilon^2). \quad (10)$$

The experimental data shown plotted in Fig. 1 indicate a dependence of $\langle r^2 \rangle_w \propto \bar{M}_w^{1.18}$. This leads to $\epsilon = 0.18$ and $\Phi(\epsilon) = 1.78 \times 10^{-23}$, which is slightly lower than the average experimental value obtained from

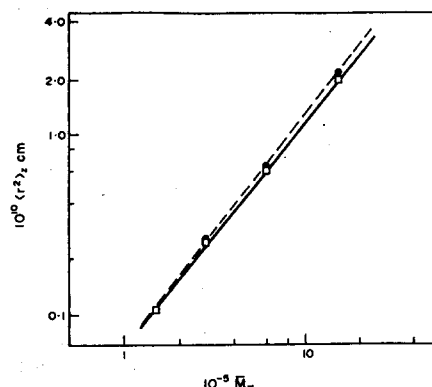


Fig. 1. Dependence of coil dimensions on \bar{M}_w for amylose tributyrates in —●— ethyl acetate and —□— methyl ethyl ketone.

Eqn. (3). This value of ϵ agrees with that expected on the basis of the Mark-Houwink exponent where

$$\epsilon = (2\nu - 1)/3. \quad (11)$$

Equation (11) gives $\epsilon = 0.16$ in EA and $\epsilon = 0.18$ in MEK.

Second virial coefficient and unperturbed dimensions

The second virial coefficients A_2 , obtained from light scattering and osmometry are collected in Table 4, and the dependence of A_2 on M is shown in Fig. 2. The suggested theoretical dependence is

$$A_2 = \text{constant } M^{-\gamma}, \quad (12)$$

where the maximum value of γ in the original development [19] was 0.15, but this is now believed to be closer to 0.25 in very good solvents, according to Berry and Casassa [20]. Lines of slope -0.15 and -0.25 have been drawn but the data are insufficiently accurate to allow any conclusion to be drawn concerning the best fit.

The second virial coefficient can also be used in conjunction with the perturbed dimensions to gain an estimate of the unperturbed dimensions of the polymer. Berry [20] has pointed out that there is rapid conver-

Table 3. Coil dimensions and statistical segment lengths calculated from the Kirkwood-Riseman and Kuhn-Kuhn theories

Fraction/Solvent	$10^8 A_m$ (cm)	$10^8 b$ (cm)	$10^8 \langle r^2 \rangle_w^{\frac{1}{2}}$ (cm) (K-R)	$10^8 \langle r^2 \rangle_w^{\frac{1}{2}}$ (cm) (K-K)	$10^8 \langle r^2 \rangle_w^{\frac{1}{2}}$ (cm) (L.S.)
B2			1182	1113	1198
B3 Ethyl acetate	69.6	18.3	743	698	668
B4			498	467	426
Carbon tetrachloride	102	19.6	—	—	—
B2			1211	1130	1148
B3 Methyl ethyl	71.7	18.7	759	709	649
B4 ketone			508	474	419
B5			376	351	273
Tetrahydrofuran	182	20.6	—	—	—

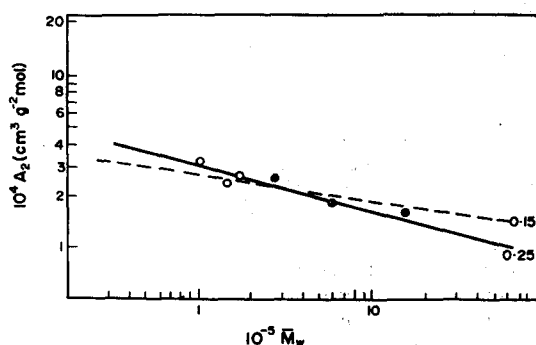


Fig. 2. Molecular weight dependence of A_2 with lines of slope -0.15 and -0.25 drawn as best fit to the data. Average values of A_2 measured from light scattering and osmometry are shown as \circ .

gence of the series for $A_2 \bar{M}^{1/2}$ expressed as a function of the expansion coefficient $(\alpha^2 - 1)$ and that

$$A_2 \bar{M}^{1/2} = \left\{ \frac{4\pi^{3/2} N_A}{a_1} \right\} \left[\frac{\langle S^2 \rangle_0}{\bar{M}} \right]^{3/2} (\alpha^2 - 1) + \dots \quad (13)$$

is a reasonably good approximation for $\alpha^2 < 5$, where $a_1 = (134/105)$. Equation (13) can be recast as

$$A_2 \bar{M}^{1/2} = 1.05 \times 10^{25} A \frac{\langle S^2 \rangle}{\bar{M}} - 1.05 \times 10^{25} A^3 \quad (14)$$

where $A = [\langle S^2 \rangle_0 / \bar{M}]^{1/2}$.

The data for amylose tributyrate in both ethyl acetate and methyl ethyl ketone are shown plotted according to Eqn. (14) in Fig. 3. Inaccuracies in A_2 lead to a scatter of points but the best common line through them all gives a value of $[\langle S^2 \rangle_0 / \bar{M}]^{1/2} = 212 \times 10^{-11}$ cm.

A more reliable method for estimating the unperturbed dimensions from those measured in a good solvent has been suggested by Baumann [21]. If the Fixman closed expression for α as a function of the excluded parameter z is assumed, namely $\alpha^3 - 1 = 2z$, then the following relation ensues

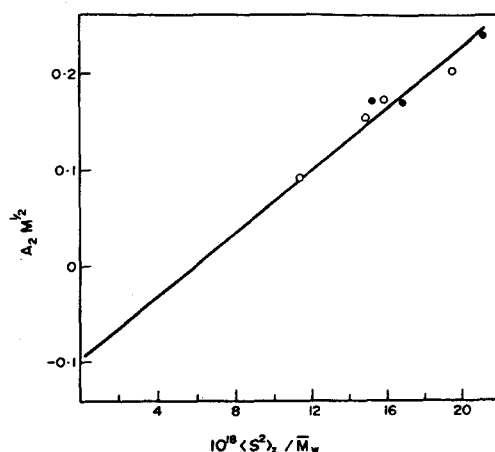


Fig. 3. Estimation of unperturbed dimensions from A_2 and perturbed dimension measurements.

$$\left[\frac{\langle r^2 \rangle}{\bar{M}} \right]^{3/2} = \left[\frac{\langle r^2 \rangle_0}{\bar{M}} \right]^{3/2} + 0.66 B \bar{M}^{1/2}, \quad (15)$$

where B is a solvent-polymer interaction parameter. As shown in Fig. 4, two distinct lines can be obtained and separate intercepts for each solvent. In EA the value is $[\langle r^2 \rangle_0 / \bar{M}_w]^{1/2} = 712 \times 10^{-11}$ cm and in MEK it is 654×10^{-11} cm. If heterogeneity corrections are applied, then $[\langle r^2 \rangle_{\text{ow}} / \bar{M}_w]^{1/2}$ is 595×10^{-11} cm in EA and 557×10^{-11} cm in MEK.

The corrected value of 443×10^{-11} cm, calculated from Eqn. (14) in terms of $\langle r^2 \rangle^{1/2}$, is somewhat lower.

Unperturbed dimensions can also be calculated from viscosity measurements using a variety of extrapolation procedures, and these are examined in more detail in the following paper.

DISCUSSION

Linear polyglucan derivatives are believed to behave as stiff extended molecules in solution. This is particularly true of the cellulose derivatives which have been

Table 4. Second virial coefficients for amylose tributyrate in EA and MEK

Sample	$10^{-6} \bar{M}_w$	$10^4 A_2$ ($\text{cm}^3 \text{g}^{-2} \text{mol}$)	$A_2 \bar{M}_w^{1/2}$	$10^{18} [\langle S^2 \rangle_z / \bar{M}_w]$
Methyl ethyl ketone				
B2	1.56	1.65*	0.206	19.4
B3	0.613	1.93*	0.177	15.8
B4	0.275	2.61	0.156	14.7
B5	0.150	2.34	0.090	11.4
X9	0.175	2.64	—	—
X10	0.105	3.13	—	—
Ethyl acetate				
B2	1.56	1.96	0.245	21.1
B3	0.613	2.24	0.175	16.7
B4	0.275	3.36	0.176	15.1

* Average of A_2 from light scattering and osmometry.

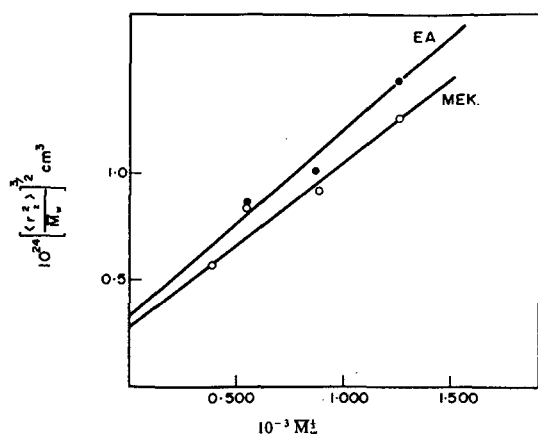


Fig. 4. Baumann plot to estimate unperturbed dimensions of amylose tributyrates. Solvents are—●—ethyl acetate and —○—methyl ethyl ketone.

studied extensively. However, concepts of the existence of rigidly extended structures in solution have been modified somewhat since it has been demonstrated [22,23] that both amylose and cellulose derivatives can exist in randomly coiled conformations in, poor solvents, and it is now more realistic to regard these polymers as stiff coils in very good solvents.

The hydrodynamic data presented here for amylose tributyrates tend to substantiate this picture. When the polymer is dissolved in any of the four solvents studied, it behaves like a highly expanded coil, with the solvent power increasing in the order ethyl acetate < methyl ethyl ketone < carbontetrachloride < tetrahydrofuran. Only in THF does the Mark-Houwink exponent exceed 0.8, the Flory-Fox limit for random coil behaviour.

Other data, however, support the idea that the coil is less flexible than vinyl polymers. The Kuhn statistical segment A_m varies from 70×10^{-8} cm to 180×10^{-8} cm, depending on the solvent, and this corresponds to a segment size of between 15 and 41 monomer units. This is much greater than comparable values of $A_m = 12 \times 10^{-8}$ cm for poly(methylmethacrylate), of $A_m = 33 \times 10^{-8}$ cm for polystyrene. Similarly, b is significantly longer than that recorded for vinyl polymer coils. The high value of ϵ also indicates that the excluded volume effect is substantial and suggests that the chain is highly expanded and extended in both ethyl acetate and methyl ethyl ketone. The

value of $\epsilon = 0.18$ is larger than ϵ measured for a number of cellulose derivatives, e.g. for cellulose carbanilate [1] $\epsilon \approx 0.1$ in good solvents and $\epsilon = 0.08$ for cellulose tributyrates in MEK [15].

One method of assessing coil flexibility is to calculate the ratio of the fully extended chain $(r^2)_{\max}^{\dagger} = x b_0$, with the experimental dimension. If this ratio exceeds 10, then the polymer should behave like a random coil [24].

The results for amylose tributyrates are shown in Table 5, and it can be seen that the ratio drops below 10 when the polymer decreases below \bar{M}_w of about 5×10^5 , implying that only the very long chains will approximate random coils in solution. A similar trend is observed for cellulose tributyrates, but the cellulose polymer also exhibits larger A_m and b values. Furthermore, the cellulose tributyrates chains are found to be much more extended in MEK [15] than the corresponding amylose tributyrates molecules. These observations are in keeping with the concept that amylose and cellulose should be considered as *cis* and *trans* geometric isomers [25], by analogy with poly 1, 4 dienes, where the glucose ring now plays a role similar to the double bond in the polydiene chain. It is interesting, then, to compare the solution behaviour of both amylose and cellulose derivatives with trends observed in *cis* and *trans* polydienes. As the amylose chains are the *cis* form, they should be less extended than the *trans* cellulose; this is confirmed here, and also for the carbanilate derivatives [1].

This analogy will be examined further in the next paper, when steric parameters for the derivatives will be compared.

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REFERENCES

1. W. Burchard and E. Husemann, *Makromolekul. Chem.* **44-46**, 358 (1961).
2. W. Brown, *Ark. Kemi* **18**, 227 (1961).
3. D. Henley, *Ark. Kemi* **18**, 327 (1961).
4. W. Brown, D. Henley and J. Öhman, *Makromolekul. Chem.* **62**, 164 (1963).
5. V. P. Shanbhag, *Ark. Kemi* **29**, 1 (1968).
6. J. M. G. Cowie and C. T. Greenwood, *J. chem. Soc.* 4640 (1957).

Table 5

Fraction	$10^8(r^2)_{\max}^{\dagger}$ (cm)	$[(r^2)_{\max}^{\dagger}/(r^2)_{\text{exp}}^{\dagger}]$ (MEK)	$[(r^2)_{\max}^{\dagger}/(r^2)_{\text{exp}}^{\dagger}]$ (EA)
B2	17823	15.5	14.9
B3	7004	10.8	10.5
B4	3141	7.5	7.4
B5	1713	6.3	—

7. W. Banks, C. T. Greenwood and J. Thomson, *Makromolek. Chem.* **31**, 197 (1959).
8. W. Banks, C. T. Greenwood and D. J. Hourston, *Trans. Faraday Soc.* **64**, 363 (1968).
9. W. Banks and C. T. Greenwood, *Stärke* **7**, 197 (1967).
10. J. M. G. Cowie, P. M. Toporowski and F. Costaschuk, *Makromolek. Chem.* **121**, 51 (1969).
11. J. G. Kirkwood and J. Riseman, *J. chem. Phys.* **16**, 565 (1948).
12. P. L. Auer and C. S. Gardner, *J. chem. Phys.* **23**, 1545 (1955).
13. L. Mandelkern and P. J. Flory, *J. Am. chem. Soc.* **74**, 2517 (1952).
14. L. Huppenthal and S. Claesson, *Roczn. Chem.* **39**, 1867 (1965).
15. L. Huppenthal, *Roczn. Chem.* **42**, 1705 (1968).
16. W. Kuhn, H. Kuhn and A. Silberberg, *J. Polym. Sci.* **14**, 193 (1954).
17. A. Hybl, R. E. Rundle and D. E. Williams, *J. Am. chem. Soc.* **87**, 2779 (1965).
18. O. B. Ptitsyn and Yu. E. Eizner, *Zh. tekhn. Fiz.* **29**, 1117 (1959).
19. M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym. Forsch.* **3**, 196 (1963).
20. G. Berry and E. F. Casassa, *J. Polym. Sci.* **D4**, 1 (1970).
21. H. Baumann, *J. Polym. Sci.* **B3**, 1069 (1965).
22. W. Banks and C. T. Greenwood, *Europ. Polym. J.* **4**, 377 (1968).
23. V. P. Shanbhag and J. Öhman, *Ark. Kemi* **29**, 163 (1968).
24. S. Newman, W. R. Krigbaum, C. Laugier and P. J. Flory, *J. Polym. Sci.* **14**, 451 (1954).
25. J. M. G. Cowie, in *Light Scattering from Polymer Solutions* (Edited by M. B. Huglin), p. 581. Academic Press (1972).

Résumé—On a préparé et fractionné le tributyrat d'amylose; on a étudié le comportement de ce polymère en solution diluée dans quatre solvants, l'acétate d'éthyle, la méthyl éthyl cétone, le tétrachlorure de carbone et le tétrahydrofurane. On a établi les relations de Mark-Houwink pour chaque solvant, l'exposant γ est compris entre 0,72 et 0,86. On a mesuré les dimensions perturbées pour le polymère dissout dans deux solvants et on a estimé ses dimensions non perturbées; ces dernières semblent dépendre du solvant. On a effectué des corrections d'hétérogénéité en utilisant les données obtenues par chromatographie par perméation de gel. Les valeurs de la longueur effective de liaison b comprise entre 17 et $19,5 \times 10^{-8}$ cm et du segment statistique de Kuhn A_m , comprise entre 70 et 180×10^{-8} cm indiquent que le tributyrat d'amylose se comporte dans de bons solvants comme une pelote légèrement rigide avec un rigidité de chaîne intermédiaire de celles des polymères vinyliques et cellulosiques.

Sommario—Si è preparato e frazionato del tributirrato di amilosio. Si è studiato il comportamento in soluzione diluita di tale polimero in 4 solventi: etil-acetato, tetracloruro di carbonio, metil-etil-chetone e tetraidrofuran. Per ciascun solvente si sono stabilite le relazioni Mark-Houwink e l'esponente ν varia tra 0,72 e 0,86 per i vari solventi. Si sono misurate le dimensioni perturbate del polimero disciolto in due solventi e se ne sono stimate le dimensioni non perturbate; sembra che quest'ultime dipendano dal solvente. Si sono applicate delle correzioni d'eterogeneità impiegando i dati stabiliti mediante misurazioni di cromatografia di permeazione di gel. I valori dell'effettiva lunghezza di legame b , compresi tra 17 e $19,5 \times 10^{-8}$ cm, e il segmento statistico di Kuhn, da 70 a 180×10^{-8} cm, indicano che il tributirrato di amilosio si comporta, in buoni solventi, come un'elica moderatamente rigida, compresa tra quelle dei polimeri vinilico e celluloso.

Zusammenfassung—Amylosetributyrat wurde hergestellt und fraktioniert. Das Verhalten dieses Polymeren in verdünnter Lösung wurde in vier verschiedenen Lösungsmitteln untersucht: in Äthylacetat, Methyläthylketon, Tetrachlorkohlenstoff und in Tetrahydrofuran. Die Mark-Houwink-Beziehung wurde für jedes Lösungsmittel aufgestellt, wobei der Exponent ν zwischen 0,72 und 0,86 für die verschiedenen Lösungsmittel variiert. Die gestörten Dimensionen wurden für Lösungen des Polymeren in zwei Lösungsmitteln gemessen und daraus die ungestörten Dimensionen abgeschätzt; diese scheinen lösungsmittelabhängig zu sein. Korrekturen der Heterogenität wurden vorgenommen unter Benutzung von Werten, die aus der Gelpermeationschromatographie gewonnen wurden. Die Werte für die effektive Bindungslänge b zwischen 17 und $19,5 \times 10^{-8}$ cm und das Kuhn'sche statistische Kettensegment A_m zwischen 70 und 180×10^{-8} cm zeigen, daß sich Amylosetributyrat in guten Lösungsmitteln wie ein mäßig steifer Knäuel verhält, wobei die Kettensteifigkeit zwischen derjenigen für Vinylpolymere und der für Cellulosepolymere liegt.