

EFFECT OF SUPERMOLECULAR PARTICLES IN CHITOSAN SOLUTIONS ON THE CORRELATION OF INTRINSIC VISCOSITY AND DEGREE OF POLYMERIZATION

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ABSTRACT

Large differences in some reported relationships between the intrinsic viscosity $[\eta]$ and the weight-average degree of polymerization P_w of chitosans are discussed in terms of a simple model based on the assumption that the P_w values estimated by light scattering can be significantly increased by large supermolecular particles which have not been removed from solutions and which do not affect significantly $[\eta]$. The effect depends on their content and size. Various shapes of the plots of $[\eta]$ vs P_w can be explained. The hypothesis is presented that the supermolecular particles are residues of crystalline structures of chitosans.

Keywords: Chitosan, Mark-Houwink-Kuhn-Sakurada equation, Supermolecular particles.

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INTRODUCTION

Chitosans, i.e., products of deacetylation of chitin, have received wide attention from both the academic and practical points of view^{1,2}. Their chains consist of (1-4) linked 2-acetamide-2-deoxy- β -D-glycopyranose (N-acetyl glucosamine) and 2-amino-2-deoxy- β -D-glycopyranose (glucosamine) units. The composition is characterized by the degree of acetylation F_A (mole fraction of N-acetyl glucosamine units). It depends on conditions of the deacetylation process. Chitosans with $F_A < 0.6$ are soluble in aqueous solution of acids. In such media the amino groups are protonated and the polymer is transformed into a polycation where electrostatic repulsion of charged groups affects the chain conformation and dimensions.

In many studies of chitosans the chain conformation was deduced from the value of the exponent a of the Mark-Houwink-Kuhn-Sakurada equation correlating the intrinsic viscosity $[\eta]$ with the molecular weight M_w or the degree polymerization P :

$$[\eta] = K \cdot M^a \quad (1)$$

$$[\eta] = K' \cdot P^a \quad (1a)$$

The reported plots of $[\eta]$ vs M , based mainly on the weight-average molecular weights M_w estimated by light scattering, display unusually large differences frequently attributed to differences in chain conformation. However, several authors have shown that chitosan solutions usually contain supermolecular particles (associates, aggregates, microgel)³⁻⁹. If these particles have not been removed from solutions they deform the Zimm plots of light scattering data, rendering the molecular weights very high. On the contrary, the intrinsic viscosity is not sensitive to such species, provided they are present in small quantities, so differences in the relationships between $[\eta]$ and M_w can result from inaccuracy of M_w values.

These differences are largely reduced if light scattering is applied to chitosan fractions prepared by SEC and the solutions are cleared with extreme care^{4, 5, 7-10}. We have obtained a very good correspondence of results obtained by other authors^{4, 5, 11, 12}. In the former papers the molecular weights were estimated by light scattering, in the last named by a combination of the sedimentation and diffusion coefficients. As is typical with stiff chain polymers the bi-logarithmic plot of $[\eta]$ vs P_w covering the range of $M_w \times 10^{-3}$ from 13 to 400 is non-linear and can be fitted by equation

$$[\eta] = P^2 / (A_\eta + B_\eta \cdot P^{1/2})^3 \quad (2)$$

with $A_\eta \cong 8$ and $B_\eta = 1.35$. This equation is a simple approximation to exact formulae derived by Yamakawa and Fujii for the intrinsic viscosity of the worm-like cylinder model¹³⁻¹⁵. The parameters A_η and B_η are characteristics of the strength of the intramolecular hydrodynamic interaction and the chain stiffness, respectively. They are independent of the degree of acetylation for $F_A < 0.3$.

In the present paper we discuss the relationships between $[\eta]$ and P_w which strongly deviate from those described by Eq (2) with the above parameters^{7, 8, 16-19}. The analysis is based on a simple model where solutions comprise dispersed chitosan molecules and a small amount of supermolecular particles.

RESULTS AND DISCUSSION

Experimental results to be discussed are plotted in Fig. 1. In order to reduce the effect of differences in the degree of acetylation and to make the analysis easier we characterize the samples by the degree of polymerization instead of the more common molecular weight²⁰. As various cleaning methods of polymer solutions before light scattering were used in the papers in question, the results are divided into panels containing data of the same origin. This presentation reveals differences in the slopes of the plots of $[\eta]$ vs P_w as well as in position with respect to the reference curve calculated with Eq (2).

Intrinsic viscosity of systems comprising supermolecular particles

The intrinsic viscosity $[\eta]$ and the weight average degree of polymerization P_w of systems comprising supermolecular particles and dispersed macromolecules are assumed to be additive on the weight fraction basis. Adopting the nomenclature introduced by Elias & Bareiss, we denote the former as „multimers“ and the latter as „unimers“. Assuming, for simplicity, that both of them are homogenous in the degree of polymerization, we can write²¹

$$P_w = P_1(1 - w_2) + P_2 w_2 \quad (3)$$

$$[\eta] = [\eta]_1(1 - w_2) + [\eta]_2 w_2 \quad (4)$$

$$w_1 + w_2 = 1 \quad (5)$$

where w_1 and w_2 are the weight fractions of unimers and multimers, respectively, and P_1 and P_2 are the corresponding degrees of polymerization. The size of supermolecular particles is characterized by the multimerization factor K_a

$$K_a = P_2 / P_1 \quad (6)$$

From Eqs (2) to (6) we obtain

$$[\eta] = \left[P_w^2 f^2 w_1 / (A_\eta + B_\eta P_w^{1/2} f^{1/2})^3 \right] + [\eta]_2 w_2 \quad (7)$$

where

$$f = w_1 / (w_1 + K_a w_2) \quad (8)$$

The use of Eq (7) is simplified if the term $[\eta]_2 w_2$ can be neglected in comparison with the first term:

$$[\eta] \cong P_w^2 f^2 w_1 / (A_\eta + B_\eta P_w^{1/2} f^{1/2})^3 \quad (9)$$

We assume that this is possible with $[\eta]_2 w_2 / [\eta] < 0.05$. Most w_2 values are lower than 0.1^{5, 8}. Higher values (0.18-0.19) have been obtained in two cases only. Simple calculation shows that the contribution to $[\eta]$ by multimers is negligible if $w_1 < 0.1$ even if the $[\eta]$ values are of the order of unity. Thus

multimers may be compact spheres (with $[\eta]_2 = 0.025$ dL/g) or cross-linked spherical microgel swollen by the solvent or similar to branched macromolecules with many long chain branches²².

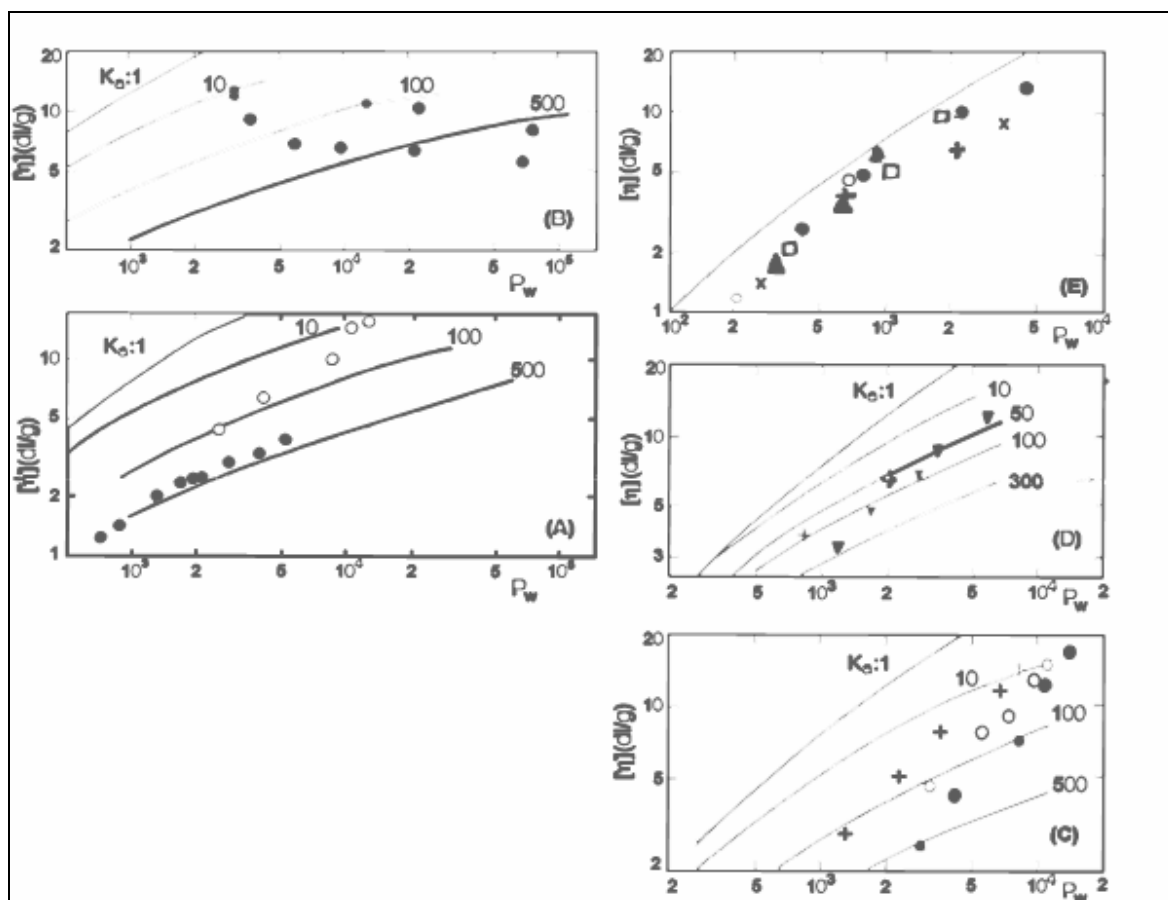


Fig.-1: Correlation of $[\eta]$ vs P_w for chitosan solutions.

Experimental results. Panel A: ● “filled circle” (Tsai et al.¹⁷), ○ “empty circle” (Kasaai et al.¹⁶). Panel B: ● “filled circle” (Berth et al.⁵). Panel C: ($F_A = 0.31$) ● “filled circle”, (0.16) ○ “empty circle”, (0.09) + “cross” (Wang et al.¹⁸). Panel D: ($F_A \cong 0$): ▼ “reverse filled circle” (Wang et al.¹⁸), + “cross” (Ottoy et al.⁷). Panel E: ($F_A = 0.15$) ○ “empty circle” □ “empty square”, (0.32) ● “filled circle” ▲ “filled triangle” (Ottoy et al.⁷), ($F_A \approx 0$) + “cross”, (0.6) × “multiplication sign” (Anthonsen et al.⁸). Symbols □ “empty square” and ▲ “filled triangle” in panel E denote samples where the content of supermolecular particles has been assessed (Ottoy et al.⁷). Curve 1 (for solutions without supermolecular particles) has been calculated using Eq (2). Curves in panels (A) to (C) have been calculated for $\beta = 0.15$ and $N^* = 5$, curves in panel D for $\beta = 0.03$ and $N^* = 3$. The K_a values are given by attached numbers.

It follows from Eq. (9) that the intrinsic viscosity of such systems and its correlation with P_w depend on the pair of w_2 and K_a values, i.e., the content and size of multimers. Since the effects of these factors cannot be resolved without additional information (e.g., content of multimers), the individual cases will be characterized by a pair of w_2 and K_a values denoted by p_a .

Fig. 2 presents a few typical results of calculations in the form of plots of r vs P_w where

$$r = [\eta]/[\eta]_1 \quad (10)$$

$[\eta]$ stands for the intrinsic viscosity of solution containing supermolecular particles and $[\eta]_1$ is the intrinsic viscosity of unimers of the same degree of polymerization. The former were computed using Eq (9), the latter with Eq (2). Some curves have a shallow minimum at $P_w < 50$ but all of them have an increasing branch in the range of current interest ($P_w > 50$). However, similar or even almost identical curves correspond to largely different p_a values. Curves for $p_a = (0.05, 10)$ and $(0.02, 2)$ may serve as an

example. Nevertheless, comparison of experimental plots of r vs P_w with theoretical curves computed for the same range of p_a values can provide qualitative information on the variation of p_a with P_w .

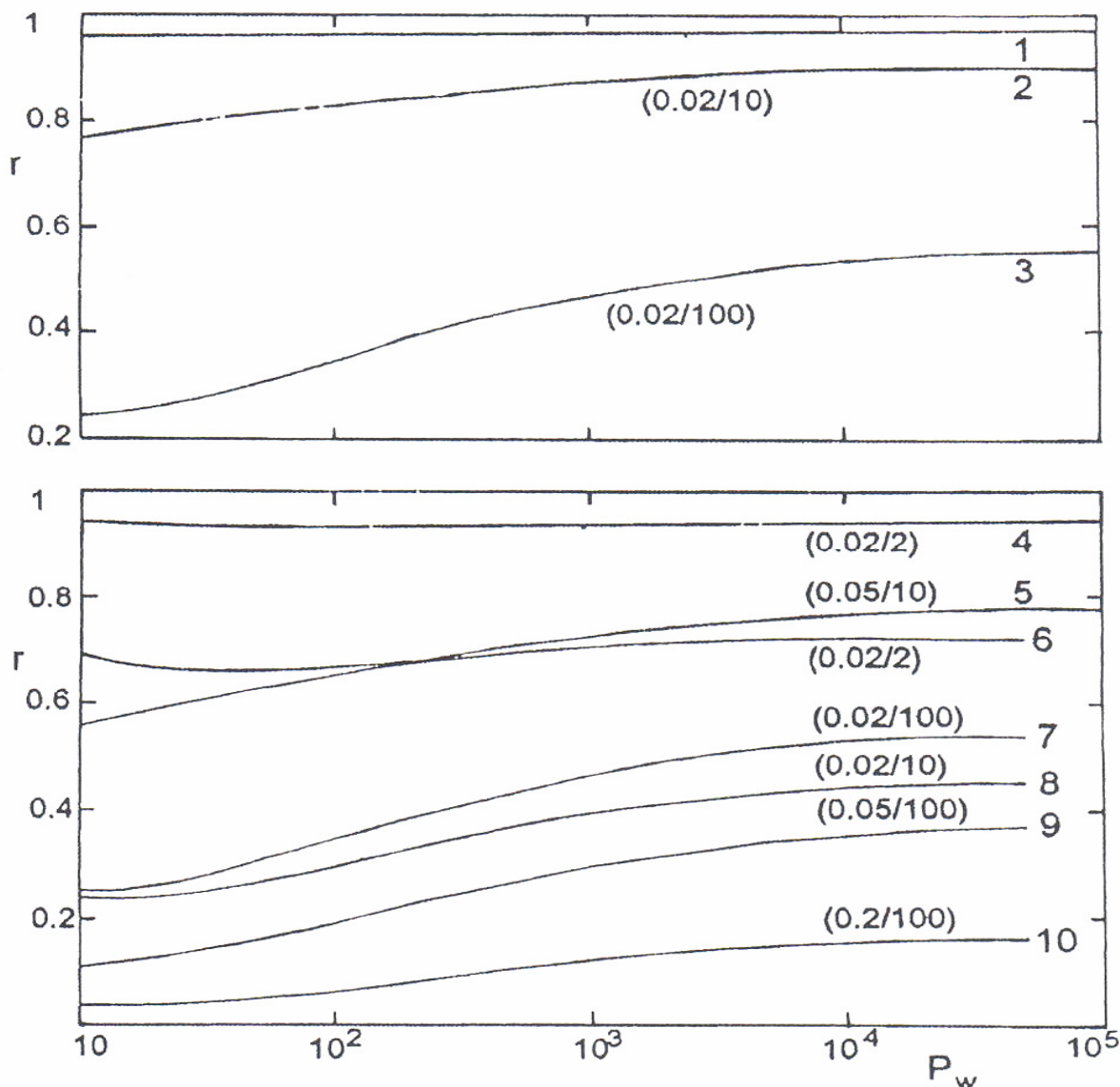


Fig.-2: Effect of supermolecular particles on the ratio r defined by Eq (10).
Curves 1 to 10 calculated using Eqs (2), (9) and (10) with p_a values attached.

Application of Eqs (10), (9) and (2)

In Fig. 3 the r values computed from experimental data have been plotted against $\log P_w$. The decreasing trend such as observed in panels (E) and (G) indicates an increase of p_a values with increasing P_w . In the other panels, the plots have an increasing trend and some exhibit a sharp upturn at the highest P_w values. This can be attributed to a transition from high p_a values to lower ones, in other words, a decrease of p_a with increasing P_w .

Panels (A) to (D) in Fig. 3 have been constructed for samples differing in the degree of acetylation F_A^{18} . The r values are the lower the higher F_A . This finding supports the conclusion by Ottoy

et al. that the tendency towards formation of supermolecular particles is stronger at higher degrees of acetylation⁷. However, low r values (0.4-0.5) have surprisingly been obtained with samples with very low degree of acetylation ($F_A \approx 0$, panel (D) and two data points in panel (G)). They show that supermolecular particles may occur even with highly de-acetylated chitosans. Thus, acetyl groups do not seem to be *conditio sine qua non* of the formation of these particles.

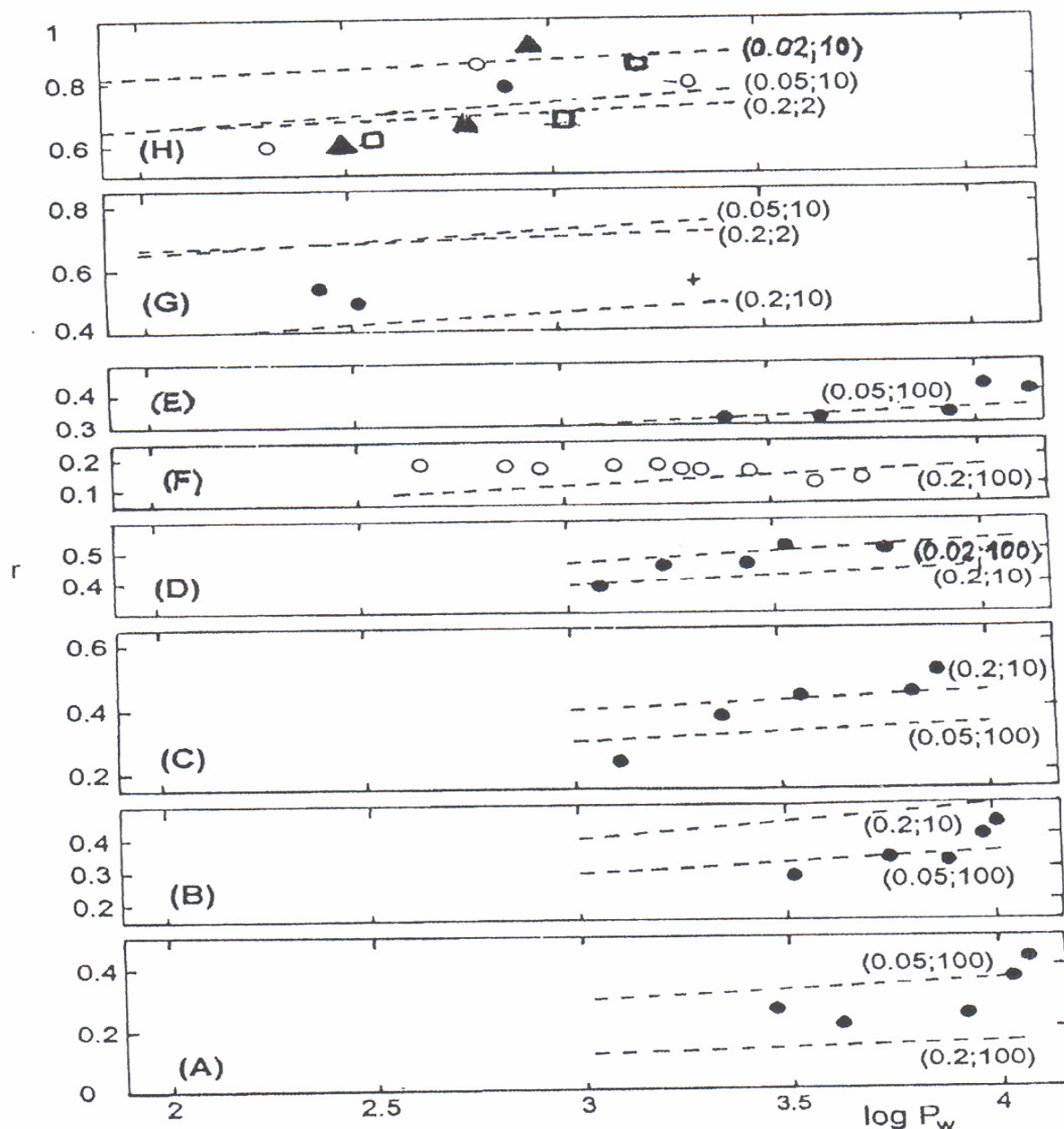


Fig.-3: Effect of supermolecular particles in chitosan solutions on the ratio r defined by Eq (10). Experimental data for given F_A values: Panels A to D ● “filled circle” 0, 0.09, 0.16, 0.31 (Wang et al.¹⁸). Panel E ● “filled circle” 0.24 (Kassai et al.¹⁶). Panel F ○ “empty circle” 0.17 (Berth et al.⁵). Panel G + “cross” 0, ● “filled circle” 0.6 (Anthonsen et al.⁸). Panel H ● “filled circle” 0.15, ○ “empty circle” 0.52 (Ottoy et al.⁷). Symbols □ “empty square” and ▲ “filled triangle” denotes data where the content of supermolecular particles has been assessed by SEC (Ottoy et al.⁷). Dashed curves were calculated using Eqs (2), (9) and (10) for attached p_a values.

Multimerization factor K_a

The multimerization factor, which is characteristic of the size of multimers, can be assessed only if the content of multimers has been obtained from an independent experiment or predicted from an acceptable model of aggregation. These points will be illustrated using, respectively, the experimental results by Ottoy et al. and theoretical data based on the model by Fox & Schnecko^{7, 23}.

The paper by Ottoy et al. provides estimates by SEC of the content of supermolecular particles in solutions of six chitosan samples⁷. To assess the K_a values we have first calculated theoretical dependences of $[\eta]$ vs K_a for the degrees of polymerization of the respective samples (Fig. 4) and estimated K_a by interpolation for experimental $[\eta]$ values. The accuracy of K_a values is not high because the w_2 values are “rough estimates” only. We obtained $K_a = 1.1, 10$ and 25 for $w_2 = 0.16, 0.07$ and 0.08 , respectively, for samples with $F_A = 0.15$, and $K_a = 1, 13$ and 28 for $w_2 = 0.16, 0.05$ and 0.03 , respectively, for samples with $F_A = 0.52$. The result is surprising in that the multimerization factor K_a is the higher the lower the content of multimers.

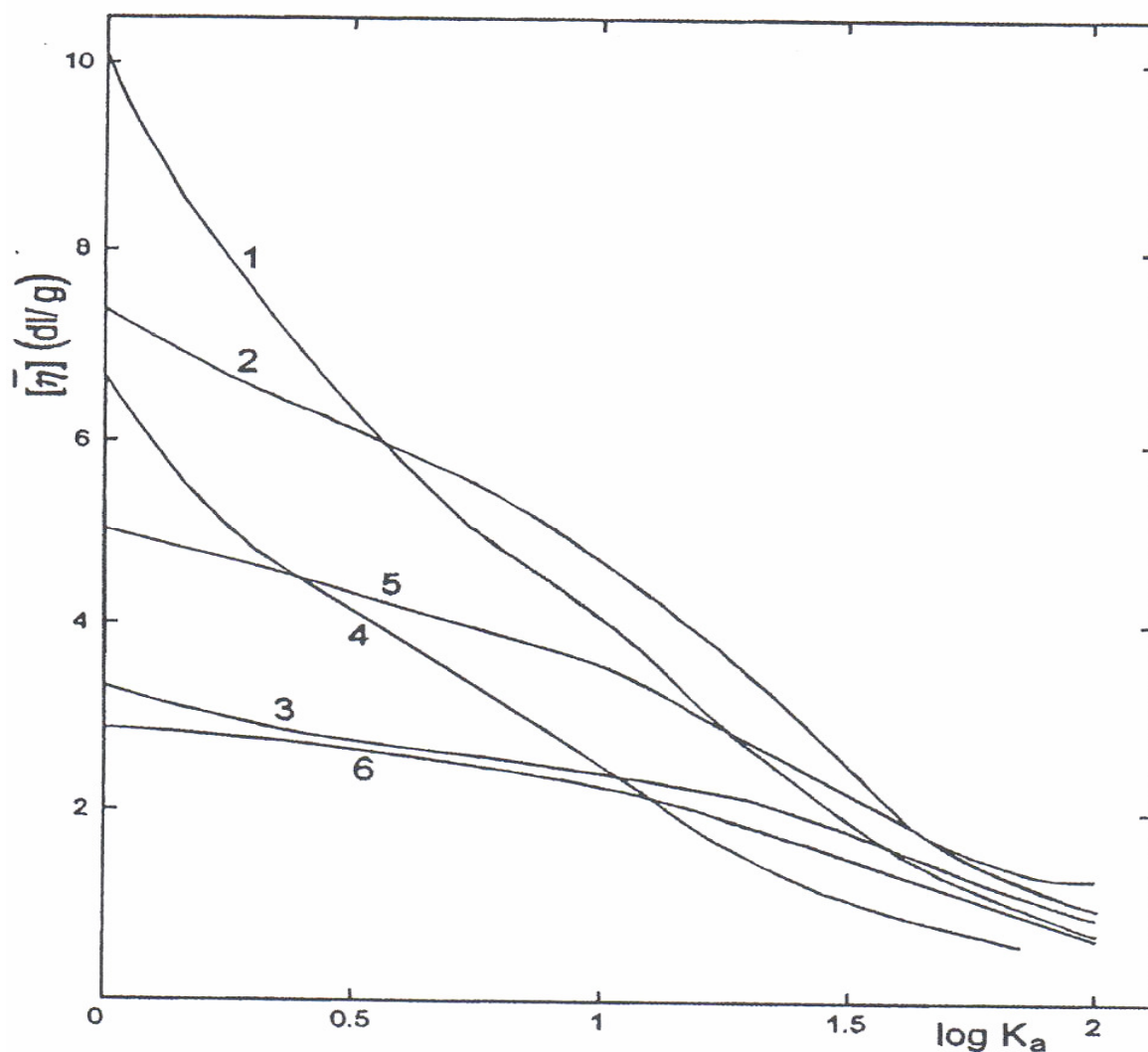


Fig.-4: Theoretical effect of supermolecular particles on the intrinsic viscosity of chitosans.
Curves 1 to 6 calculated for P_w and w_2 values from Ottoy et al.⁷

Anthonsen et al. have advanced a qualitative model where multimers of chitosan are aggregates where aggregation sites are long sequences of acetylated units⁸. The model is similar to that proposed, long ago, by Fox et al. to explain some solution properties of semicrystalline poly (methyl methacrylates) where limited solubility is caused by long sequences of syndiotactic units²³. An experimental procedure based on this model has been applied to separate semicrystalline and amorphous components of poly (vinyl chloride)²⁴. Basing on this model and using Eq (9) we calculate the dependence of $[\eta]$ vs P_w .

The assumptions are as follow: The Flory-Huggins polymer – solvent interaction parameter χ is lower than $1/2$. In spite of that, the solution contains multimers in addition to unimers. The latter are homogenous in the degree of polymerization. The multimers are compact particles. All molecules comprising at least one sequence of length N^* are capable of aggregation and are incorporated into the multimers. Thus the condition of molecular dispersion in solution is absence of sequences of length higher than N^* . The solubility expressed by the weight fraction w_1 of a P-mer is calculated by Fox et al.²³:

$$w_1 = (1 - \beta^{N^*})^{(P - N^* + 1)} \quad (11)$$

It depends on the critical length N^* , the degree of polymerization of the unimer P_1 , and the probability β of occurrence of several consecutive units capable of aggregation or association.

We first calculate the w_1 values for various β (Fig. 5). Included into this figure are the w_1 values computed from rough estimates of the fraction of aggregates formed in chitosan solutions at concentration 0.1%^{7, 8}. They are plotted against the number average degree of polymerization P_n . This is preferred here to P_w because it is not affected by aggregation. Comparison with calculated curves indicates N^* to be $4 < N^* < 5$ and $10 < N^* < 15$ at $F_A = 0.15$ and 0.52 , respectively. By means of Eq (2) we calculate the intrinsic viscosity $[\eta]_1$ of unimers for $100 < P_1 < 5 \times 10^3$, and using Eq (11) with $N^* = 5$ and $\beta = 0.15$ and 0.4 we compute the weight fraction w_1 of soluble material. The last step is the calculation of $[\eta]$ for several values of the multimerization factor ($10 < K_a < 500$). The results are displayed in Fig. 6.

Curve 1 in Fig. 6 represents the dependence of $[\eta]$ vs P_1 for unimers. The other curves represent plots of $[\eta]$ vs P_w for systems comprising multimers of constant K_a . Generally they are shifted with respect to curve 1 and diverge from it, the more so the higher the multimerization factor. The flattening of plots at high P_w and K_a values may be such that the quotient $d \ln [\eta] / d \ln P_w$ is close to $1/2$ or even lower than this⁵.

Fig. 6 enable us to qualitatively explain various types of the plots of $[\eta]$ vs P_w found with chitosans (Fig.1). If the initial part is close to curve 1 and flattens at high P_w values the K_a parameter is probably constant or increases with increasing P_w . The same holds for the case where the dependence has a maximum or a very low slope (panel B). If the plot is approximately parallel to, or steeper than, curve 1, but shifted to the right (panels A, C, D), one can say that the K_a parameter decreases with increasing P_w .

Panel E in Fig. 1 is of particular interest because the content of supermolecular particles has been assessed for several samples by SEC⁷. Data points for these samples are distinguished by different symbols. It can be seen that data for samples with the highest content of supermolecular particles and the lowest K_a values are close to curve 1 whereas those for samples with low values of w_2 and high values of K_a are more remote. For this reason the plot of experimental data is steeper than curve 1. It also turns out that the multimerization factor has a more pronounced impact on the correlation than the content of multimers.

Let us return to the finding that supermolecular particles occur in solutions of chitosans with $F_A \approx 0$. If acetylated units were the only site of multimerization, the plot of $[\eta]$ vs P_w for $F_A = 0$ would have to be identical with curve 1 in Fig. 1. However, the estimation of low F_A values is inaccurate, so we have to consider the possibility that F_A is slightly higher than zero⁷. Therefore, we repeat the calculation of w_1 and $[\eta]$ for $\beta = 0.33$ setting $N^* = 3$ and 5 . In the latter case w_1 is unity over the whole span of P values. At $N^* = 3$ the solubility decreases with increasing P_w and the plot of $[\eta]$ vs P_w has a typical shape for systems comprising multimers. Low r values (Fig. 3, panel D) for samples with a very low degree of acetylation can be accounted for in this way. However, this would imply that the critical chain length N^* is surprisingly low.

Supramolecular particles in chitosan solutions

The presence of supramolecular particles in solutions of chitosans has been well established by light scattering^{3-9,25, 26}. The trend to association or aggregation is also manifested in rheological properties, gelation or cholesteric mesophase formation at higher concentrations or time instability (ageing) of solutions^{20, 22, 27-31}.

Some authors believe that equilibrium depending on concentration is rapidly established between supramolecular particles and dispersed macromolecules^{7, 8, 25}. Contrary to that, Berth et al. have found that, once removed, these particles do not reform⁵. However, this contradiction may be an apparent one because the solution of cellulose in *N,N*-dimethylacetamide/LiCl contains dispersed macromolecules or stable aggregates persisting even at $c \approx 0$ or concentration dependent associations³⁰.

The chemical and physical character of supramolecular particles in solutions of chitosans is not well known. Van Duin & Hermans assumed that divalent cations present as impurities in chitosans interact with the chains to form branched or cross-linked particles of large size⁶. In view of insolubility of chitin ($F_A \approx 1$) and poor macroscopic solubility of chitosans with $F_A > 0.5$, some authors concluded that the supramolecular particles contain organized structures formed by hydrophobic association of acetylated units, particularly if the latter occur in long sequences or blocks^{8, 9}. Indeed, Amiji and Philippova et al. have revealed hydrophobic domains by fluorescence spectrometry^{32, 33}.

However, Philippova et al. have also found that some hydrophobic domains were stable and resisted to substances (urea, salts, and ethanol) which usually destroy them³³. Furthermore, ageing phenomena, supramolecular species and high crystalline order in solid state were observed with samples with very low degree of acetylation ($F_A < 0.01$)^{7, 20, 31, 34}. Thus, it appears that association or aggregation of chitosans in aqueous solutions is not exclusively due to hydrophobic effects and that another mechanism should also be considered.

Berth et al. proposed the opinion that aggregates of chitosans are survivors of the native structure⁵. Terbojevich et al. proposed a similar explanation for the aggregation of some cellulose samples and related the differences in aggregation to differences in crystallinity³⁰. Long ago, Domard et al. advanced the hypothesis that aggregation of chitosans is a sort of crystallization²⁰. We return to this hypothesis because a similar explanation has been used with success in studies of anomalies in dilute solution properties of some semicrystalline vinyl polymers such as poly (vinyl chloride) (PVC) or poly (vinyl alcohol) (PVA)^{24, 35}. The problem of aggregation will tentatively be treated as a problem of solubility of crystalline polymers.

As shown by electron and X ray diffraction, chitin and chitosans are crystalline and their crystalline structure is stabilized by strong hydrogen bonding^{32, 36-40}. While intramolecular bonding links oxygen atoms of glucosamine units in the same chain, intermolecular bonding links the oxygen and nitrogen atoms of neighboring chains. In hydrated polymorphs, which appear in contact with aqueous media, new intermolecular hydrogen bonds form and connect the chains with water molecules situated in the space between the chain sheets.

In view of decomposition of chitin and chitosans at high temperatures the melting temperatures T_m^0 are not known^{38, 40}. However, the results of DTA measurements indicate the T_m^0 values to be high, probably above 500 K^{34, 40}. As follows from the theory by Flory the solubility of a crystalline polymer at temperature T , that is lower than the melting temperature T_m^0 of the pure polymer, depends, among others, on the ratio $\tau = T_m^0 / T$ and the Flory-Huggins interaction parameter χ . The higher τ and χ , the lower the solubility⁴¹.

If the temperature T of solution is not high enough to completely destroy the crystalline structure, some chains are not molecularly dispersed and the system contains supramolecular particles consisting of organized and inorganized domains. The organization of the former is similar to that in the crystalline state. Since some chains belong to both types of domains, the boundary between the domains is diffuse and the supramolecular particles are swollen microgels. In aqueous solutions of amphiphilic polymers, the particles can also be stabilized by hydrogen and hydrophobic bonding.

Chitosans are copolymers of acetylated and deacetylated units. As their crystalline structure is less compact than that of chitin, the T_m^0 values of chitosans are probably lower, the more so the lower degree of acetylation⁴². Anyway, crystallinity does not vanish at $F_A = 0$ ³⁴. Better solubility at room temperature of chitosans with lower F_A values may be connected with a lower melting temperature. The solubility in aqueous media of such samples is further enhanced by protonation of amino groups resulting in a lower χ value.

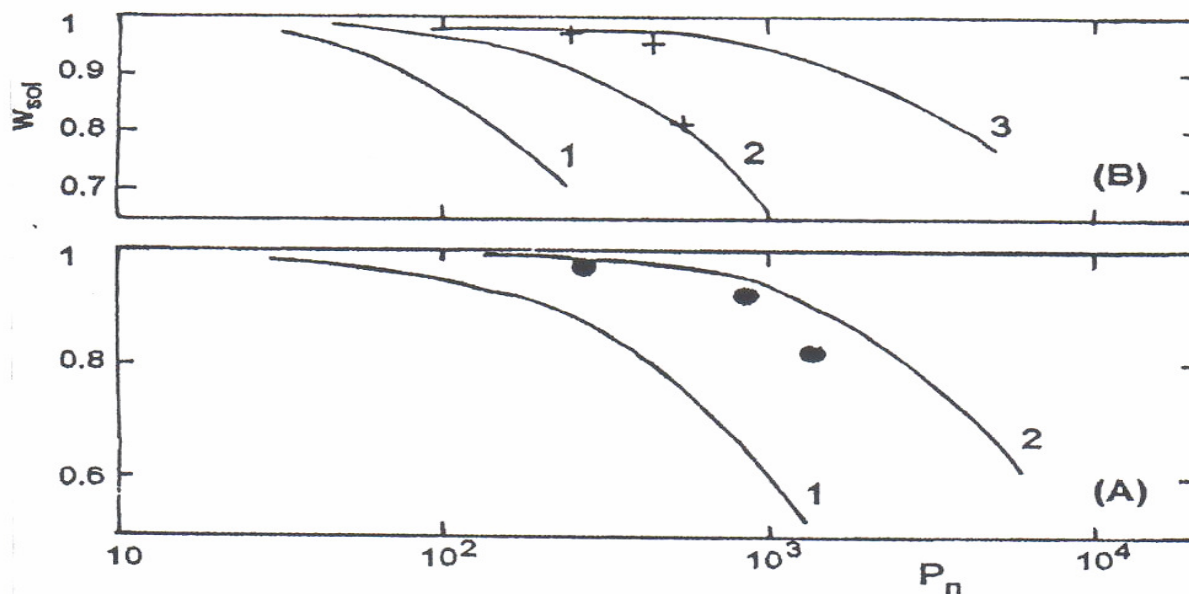


Fig.-5: Results of calculations according to Eq (11).
Panel A for $\beta = 0.15$, curves 1 and 2 for $N^* = 4$ and 5. Panel B for $\beta = 0.052$, curves 1 to 3 for $N^* = 10, 12$ and 15, respectively. Experimental data from Anthonsen et al.⁸.

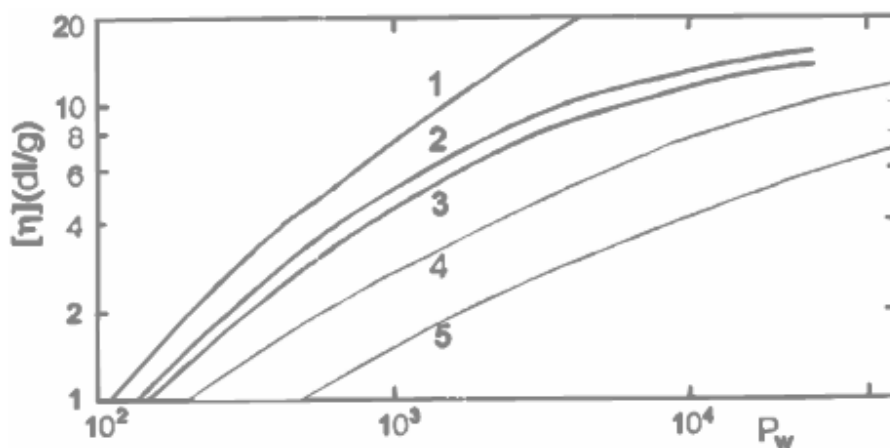


Fig.-6: Theoretical correlation of $[\eta]$ vs P_w for chitosan solutions comprising supermolecular particles.
Curves 1 to 5 calculated for $K_a = 1, 10, 20, 100$ and 500 with $\beta = 0.15, N^* = 10$.

Remarks on the efficiency of filtration

It is amazing that the same method of solution cleaning is successful with some samples and unsuccessful with others. There emerges the question about the reason of this difference. We believe that the following simple calculation can offer a qualitative answer. We calculate the radii of compact spheres $R_{g,s}$ and the root mean square radii of gyration $\langle S^2 \rangle_0^{1/2}$ of chitosan molecules in the unperturbed random coil limit. The former are given by equation

$$R_{g,s} = (3vM_0 / 4\pi N_A)^{1/3} P^{1/3} \quad (12)$$

which, with $v = 0.57$ mL/g and $M_0 = 165$, is transformed into¹²

$$R_{g,s} = 3.4 \times 10^{-4} P^{1/3} \quad (\mu\text{m}) \quad (13)$$

The $\langle S^2 \rangle_0^{1/2}$ values are obtained from⁹

$$\langle S^2 \rangle_0^{1/2} = 1.28 \times 10^{-3} P^{1/2} \quad (\mu\text{m}) \quad (14)$$

Fig. 7 presents the plots of these dimensions against P . Horizontal lines 1 and 2 denotes the lowest radii r_m of pores of membranes used by Berth et al. and Rinaudo et al.^{4, 5}. It can be seen that the radii of compact spheres approach these lines at $P > 10^6$. This indicates that in spite of very small size pores, these membranes need not efficiently remove aggregates whose degree of polymerization is lower than 10^6 . Contrary to this, chitosan random coils approach the r_m values at $P \approx 1500$ and 20000 , respectively, and therefore they can be separated by filtration. Thus, the cleaning operation may change the distribution of dispersed molecules and aggregates in favour of the latter.

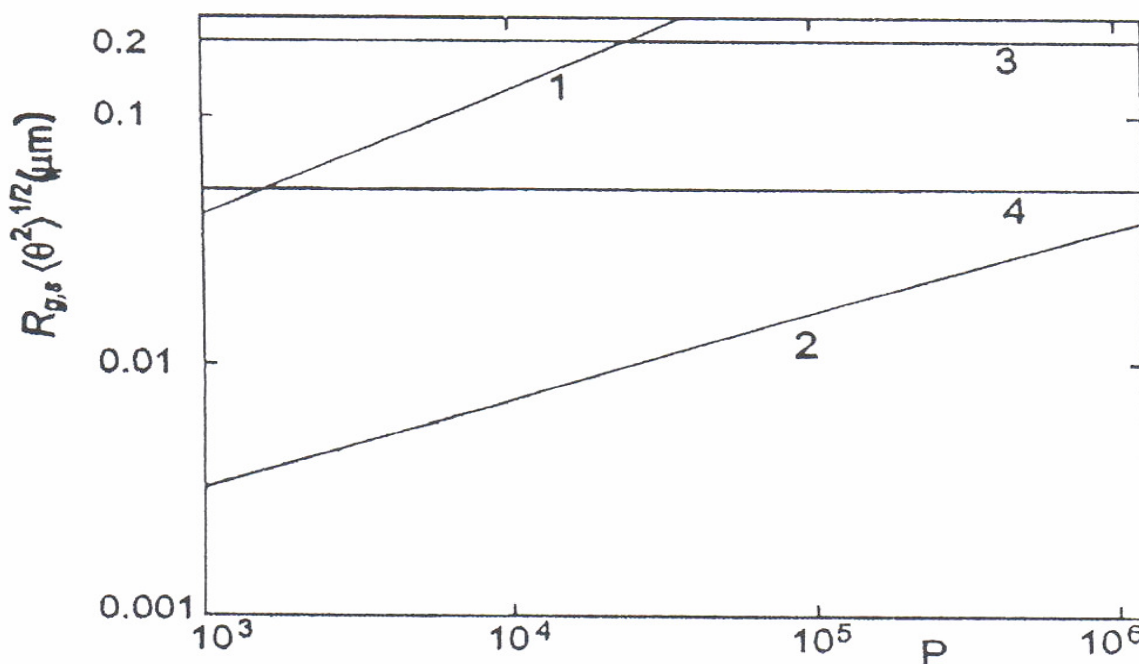


Fig.-7: Filtration efficiency of membranes for chitosan random coils and aggregates

Curves 1 and 2 calculated dependence on P of the radii of gyration of random coils and compact spheres, respectively. Lines 3 and 4 represent the lowest pore size of membranes used by Rinaudo et al. and Roberts et al. respectively^{1,4}.

Compact spheres present, no doubt, an extreme case. It is probable that real particles are swollen by the solvent. Their penetration through membranes will be more difficult for compact spheres but easier than

for random coils. Hence, filtration through membranes with small pore size will be less efficient than it would be with compact spheres.

The result of this simple calculation can account for the finding that, in many cases, the deviations from curve 1 in Fig. 1 are larger and the r values lower (Fig. 2) at lower average degrees of polymerization. However, it cannot explain the opposite trends where the r values decrease with increasing P_w . This may follow from another size distribution of aggregates where aggregates with lower P values are absent and those with high P 's prevail.

The differences in the size distribution of aggregates probably depend on the origin and preparation of chitosans, namely, on conditions (homogenous or heterogeneous process, time) and degree of deacetylation, distribution of units (random or block-like), etc. This information as well as a detailed description of cleaning operations before light scattering measurements are lacking in many papers, particularly those where commercial samples were studied.

CONCLUSIONS

The paper presents a simple model which, we believe, can help to understand large differences in the relationships between the intrinsic viscosity and weight-average degree of polymerization of chitosans which are attributed to aggregation of polymer molecules. The bimodal distribution underlying the model calculation consists of two monodisperse components (unimers and multimer) with large differences in the degree of polymerization. However, as the real systems are polydisperse in P values, in size and shape of multimers, and may be multimodal, the information obtained on this basis is qualitative only. Nevertheless, the model may be of use with other aggregating systems provided a good reference correlation of $[\eta]$ vs P_w is available for solutions without aggregates.

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