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SOLUTION STUDIES OF THE CHITIN–LITHIUM CHLORIDE–*N,N*-DIMETHYLACETAMIDE SYSTEM*

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ABSTRACT

Light scattering and viscosity measurements on dilute or moderately concentrated solutions of chitin in *N,N*-dimethylacetamide (DMAc) containing 5% or 8% of LiCl are reported. Chitins with d.p. lower than that of commercial samples were obtained by treatment of these solutions with ultrasound. The curve c/H_0 *vs.* c exhibits a maximum at c values inversely related to the molecular weight of the polymer and is consistent with a model in which, at relatively low concentration, the polysaccharide chains intertwine whereas at high concentration they become hyper-entangled, eventually resulting in an inhomogeneous network. Light scattering measurements on the dilute solutions containing 5% of LiCl allowed an evaluation of the molecular weight, second virial coefficient, and radius of gyration. The values of the Mark–Houwink parameters a and K and the relationship between radius of gyration and molecular weight were obtained. An evaluation of the linear expansion factor, α_s, using the interpenetration function, gives values close to unity. This fact, together with the observed high values of the second virial coefficient, implies that the chitin molecules are rather stiff in this solvent system. The persistence length was evaluated by means of the Yamakawa–Fujii and Benoit–Doty theories for worm-like chains. Derivatives of chitin prepared in DMAc–5% LiCl in a homogeneous phase under mild conditions had high degrees of substitution without main-chain degradation.

INTRODUCTION

Chitin (poly-2-acetamido-2-deoxy-β-D-glucopyranose) is insoluble in common organic solvents but soluble under highly acidic conditions, with simultaneous considerable depolymerization[1,2]. Non-degradative solubilization occurs with the *N,N*-dimethylacetamide (DMAc)–LiCl system[3]. In addition to chitin and aromatic

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polyamides, this system solubilizes cellulose as well[4]. Physicochemical studies[5–7] and derivatization reactions[8,9] using this system have been performed for cellulose, whereas for chitin it was only demonstrated, by n.m.r. spectroscopy, that DMAc–LiCl is a true solvent[10]. As with cellulose, intramolecular hydrogen bonds occur between HO-3 and the ring oxygen of the neighbouring unit[11]. In the present work, the dissolution in DMAc–LiCl of commercial chitin samples has been studied.

EXPERIMENTAL

Materials. — Samples of chitin were obtained from Bioshell Inc. (U.S.A.), Katakura Chikkarin Co. (Japan), and Chugai–Boyeki Co. (Japan), and characterized by i.r. spectroscopy and elemental analysis. The moisture contents were 5–15%. "Soluble chitin" (Table I) was prepared by solubilizing the Katakura chitin in DMAc–5% LiCl, centrifugation (Beckman L8-70 centrifuge: 3 h, 17000 r.p.m., 20°), and dilution of the supernatant solution with water. The precipitate was washed with DMAc, and, after storage for 48 h in DMAc, the polymer was dried for 24 h at 40°. The polymer content was 14%. Complete removal of the organic solvent than gave "soluble dried chitin".

N,N-Dimethylacetamide was dried for 4–5 days over molecular sieves (4 Å) activated for 4 h at 280°, and LiCl was dried at 130°.

The system DMAc–LiCl was prepared by weighing rapidly the salt and adding the solvent required. Complete dissolution was achieved after stirring for 12–16 h. Salt concentrations are given as g of LiCl per 100 g of binary (LiCl and DMAc) solution.

Chitin solutions. — Stock solutions of chitin in DMAc containing 5 or 8% of LiCl were prepared by adding to the weighed polymer a weighed amount of DMAc–LiCl. No activation process was necessary. After initial swelling, the suspension was stirred for several days. Dissolution was rapid at low concentrations of chitin but was more difficult at higher concentrations due to the increasing viscosity of the system[3]. Swollen material, if present, was removed by centrifugation. The concentration of chitin in solution was determined by precipitating the polymer with water, washing with water, lyophilization, and drying. The concen-

TABLE I

VISCOSITIES OF SOLUTIONS OF SAMPLES OF CHITIN IN DMAc–LiCl

Chitin sample	C_p (%)	$[\eta]$ (*dL/g*) *at* C_s 5%
Bioshell	0.04	20.0
Bioshell	0.26	22.8
Bioshell	0.88	21.6
Katakura	0.05	19.1
Chugai–Boyeki	0.04	30.1
Soluble	0.03	19.0
Soluble, dried	0.03	19.4

tration (C_p), given as g of chitin per 100 g of ternary solution, varied between 0.03% and 1%. Stock solutions with different C_p were characterized by intrinsic viscosity $[\eta]$ in DMAc–5% LiCl. These solutions were prepared from weighed amounts of stock solution and DMAc–5% LiCl. After dilution, each solution was shaken for ~1 h to ensure complete homogenization. The $[\eta]$ values reported in Table I did not vary with the C_p of the stock solution and were not affected by the previous precipitation.

Intrinsic viscosity. — Intrinsic viscosity data were obtained using the Huggins equation[12]. Viscosities were determined with a suspended-level Ubbelohde viscometer at 25 ±0.1° having flow times for the solvent of >150 s and relative viscosities between 1.1 and 1.6. Dilutions were made directly in the viscometer. High-polymer viscosities were extrapolated to zero flow velocity gradient[13].

Light scattering. — Light scattering measurements were performed at 25° with a Sofica Model 42000 photometer with cylindrical cells immersed in toluene. Non-polarized light (λ 546 nm) was used covering scattering angles between 30° and 150°. A Rayleigh ratio[14] $R_{90} = 15.8 \times 10^{-6}\ \mathrm{cm}^{-1}$ was used for the calibration of the instrument with benzene. Solutions and solvents were clarified by centrifugation at 17,000 r.p.m. for 3 h. The light scattering data are plotted as c/H_ϑ at given c *vs.* $\sin^2 \vartheta/2$, and as c/H_ϑ at $\vartheta = 0$ (c/H_o) *vs.* c. H_ϑ is defined as

$$H_\vartheta = \frac{(I - I_o)\sin\vartheta}{1 + \cos^2\vartheta}.$$

The molecular weight M_w was calculated from the relationship:

$$\frac{1}{M_w} = \frac{2\pi^2 n_B^2}{\lambda^4 N R_B}\left(\frac{dn}{dc}\right)^2 I_B \left(\frac{c}{H}\right)_{\substack{c=0,\\ \vartheta=0}} = 0.491 \left(\frac{dn}{dc}\right)^2 I_B \left(\frac{c}{H}\right)_{\substack{c=0,\\ \vartheta=0}},$$

where N is Avogadro's number, n_B, R_B, and I_B are the refractive index, the Rayleigh ratio, and the scattered intensity (at 90°) of benzene, respectively. The virial coefficient B can be determined, once M_w is known, from the slope of the c/H_o *vs.* c line

$$B = \frac{1}{2M_w}\,\frac{[(c/H_o)_{c_i} - (C/H_o)_{c=0}]/(c/H_o)_{c=0}}{c_1},$$

whereas the radius of gyration R_G is determined, without knowledge of M_w, from the slope/intercept ratio of the $(c/H_\vartheta)_{c=o}$ *vs.* $\sin^2 \vartheta/2$ line.

$$R_G^2 = \frac{3\lambda^2}{16n^2\pi^2} \cdot \frac{(c/H)_{\vartheta=180} - (c/H)_{\vartheta=0}}{(c/H)_{\vartheta=0}}$$

Proper evaluation of M_w and R_G by light scattering in a multicomponent solution requires dilution with a diluent brought to dialysis equilibrium with the solution[15]. This requirement is especially important for the determination of the refractive index increment (d*n*/d*c*). Unfortunately, most conventional membranes are soluble in DMAc–LiCl. Furthermore, since no alternative methods are available for the determination of M_w of chitin, it is not possible to calculate d*n*/d*c* by fitting the molecular weight to the corresponding diffusion parameter, as has been done for cellulose in the same solvent system[5]. The problem was solved by dialysing for 20 days at 25° solutions of Bioshell chitin *vs.* DMAc–5% LiCl, using a PTFE membrane supported on polyethylene (Fluoropore, 0.5 μm). The d*n*/d*c* value of 0.10 mL/g is at variance with the value of 0.05 mL/g obtained prior to equilibrium dialysis. A Brice Phoenix differential refractometer at λ 546 nm was used.

For the ultrasonic depolymerization, a Branson B-15 sonicator, set to 90 W and 20 kHz, was used.

I.r. measurements were performed on KBr discs, using a Perkin–Elmer model 580B instrument.

Derivatives of chitin. — *(a) Acetate.* Acetic anhydride (20.5 g) and potassium acetate (0.2 g) were added at 60° to a solution of Katakura chitin (45 g) in DMAc–LiCl (C_p 1%, C_s 5%). The solution was kept for 2 h at 110°. After cooling, the material was recovered by precipitation with water and washed with water–ethanol, 1:1 [*Anal.* Calc. for $(C_{12}H_{17}NO_7)_n$: C, 50.17; H, 5.92; N, 4.88. Found: C, 48.69; H, 5.81; N, 4.57%].

(b) Carbanilate. Pyridine (1 mL) and phenyl isocyanate (10 mL) were added at 60° to a solution of Bioshell chitin (45 g) in DMAc–LiCl (C_p 1%, C_s 5%). The temperature was raised to 80° for 3 h, methanol (10 mL) was added after cooling to room temperature, and the polymer was recovered by precipitation with a large excess of methanol [*Anal.* Calc. for $(C_{22}H_{23}N_3O_7)_n$: C, 59.86; H, 5.21; N, 9.52. Found: C, 56.56; H, 5.35; N, 8.94%].

*(c) Toluene-*p*-sulfonate.* Pyridine (6.8 mL) and slowly a solution of toluene-*p*-sulfonyl chloride (17 g) in the reaction solvent (20 mL) were added, at room temperature, to a solution of Bioshell chitin (32 g) in DMAc–LiCl (C_p 1%, C_s 5%). The solution was stirred for 24 h, methanol (10 mL) was added, and the polymer was recovered by precipitation with excess of methanol [*Anal.* Calc. for $(C_{22}H_{25}NO_9S_2)_n$: C, 51.66; H, 4.89; N, 2.74; S, 12.52. Found: C, 44.11; H, 5.0; N, 5.80; S, 1.19%].

RESULTS

Depolymerization of chitin by ultrasound. — Several examples of depolymerization by high-intensity ultrasound have been reported[16]. The depolymerization of solutions of chitin in DMAc–LiCl was studied as a function of C_p, C_s, temperature, and volume. The kinetics were examined by viscosity measurements. Samples sub-

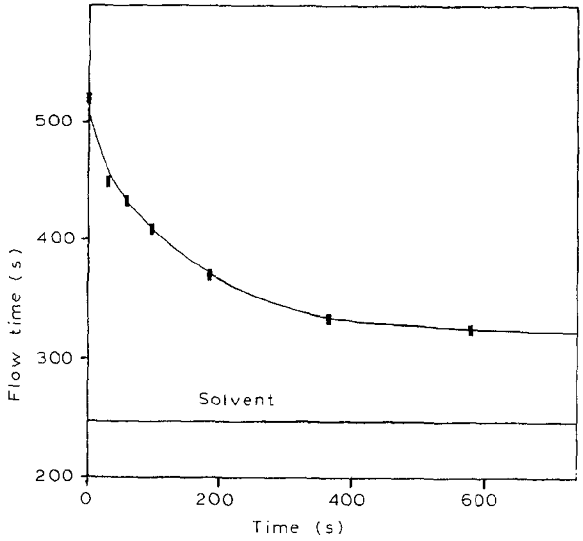


Fig. 1. Solution viscosity (η given by flow-time viscometer) plotted against time of irradiation with ultrasound; Bioshell chitin: C_p 0.88%, C_s 5%, 0°, vol. 100 mL, concentration for viscosity determination 0.042%.

jected to degradation for prolonged times were isolated by precipitation and examined by elemental analysis and i.r. spectroscopy in order to determine chemical modifications other than cleavage of the glycosidic bonds. The results did not reveal any difference between the chitin before and after treatment with ultrasound. Fig. 1 illustrates the depolymerization process. The viscosity flow time decreases progressively to a constant value.

Intrinsic viscosity and light scattering. — Commercial chitins (Table I) and chitins depolymerized by treatment with ultrasound (Table II) were examined by viscometry and light scattering in DMAc–LiCl at C_s 5% and 8%.

The η_{spec}/c *vs. c* data at C_s 5% are illustrated in Fig. 2. Within the concentration range of most viscosity determinations, $0.01<c<0.08$ g/100 mL, these plots are linear, with Huggins constants between 0.3 and 0.4. Extrapolated values of $[\eta]$ are reported in Table II.

Solutions of Katakura chitin in DMAc–8% LiCl gave values of $[\eta]$ much higher than those for solutions in DMAc–5% LiCl.

At C_s 5%, the range of concentrations investigated by light scattering was $0.2–5.0 \times 10^{-3}$ g/mL. Samples at higher concentration could not be examined due to the very high viscosity of the solutions. The low d*n*/d*c* value causes a considerable error of ±10% in the determinations.

The angular dependence of the c/H_θ factor was found to be similar to that observed for other polysaccharide systems[17,18]. At low concentration, qualitatively parallel and linear plots were found. Above a certain concentration, curved and

TABLE II

DILUTE SOLUTION PARAMETERS OF CHITIN SAMPLES IN DMAc–5% LiCl

Sample[a]	$[\eta]$ *(dL/g)*	$M_w \times 10^{-5}$	$B \times 10^3$ *(mol.mL.g^{-2})*	R_G *(Å)*
Bioshell chitin	21.6	5.1	0.9	1100
A	16.5	3.5	1.0	990
B	12.5	2.5	1.0	780
C	11.5	2.2	0.3	850
D	6.5	0.9	0.7	370

[a] Bioshell chitin (C_s 5%, 0°) was depolymerized by ultrasound as follows: A, C_p 0.26%, 20 s; B, 0.88%, 98 s; C, 0.26%, 90 s; D, 0.88%, 590 s.

non-parallel patterns were observed, especially at angles <90°. The corresponding c/H_0 *vs.* c plots are reported in Fig. 3. The intercept with the ordinate is proportional to $1/M_w$; the initial slope is a function of the second virial coefficient B, whereas the following part is related to the concentration dependence of the Rayleigh factor in moderately concentrated solutions[19–22]. A maximum value (corresponding to c_{max}) was found, which was shifted to lower c on increasing $[\eta]$. The c_{max} values are considerably higher than the c^* values (Fig. 3), defined as the concentration at which the hydrodynamic volume of polymer chains equals the

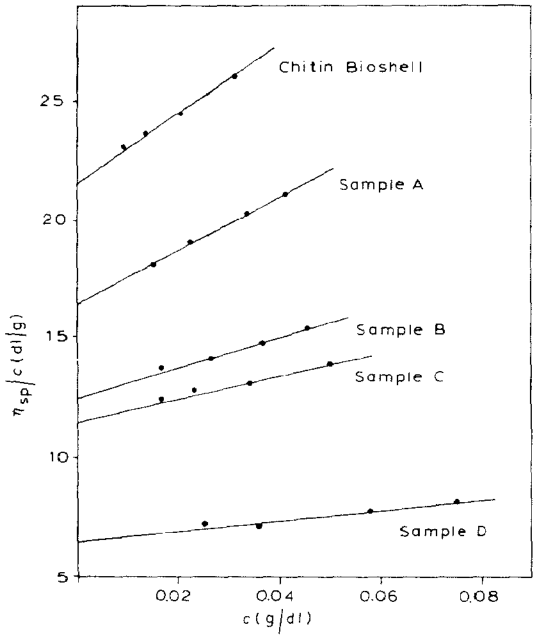


Fig. 2. Viscosity–concentration plots for chitin in DMAc–5% LiCl at 25°.

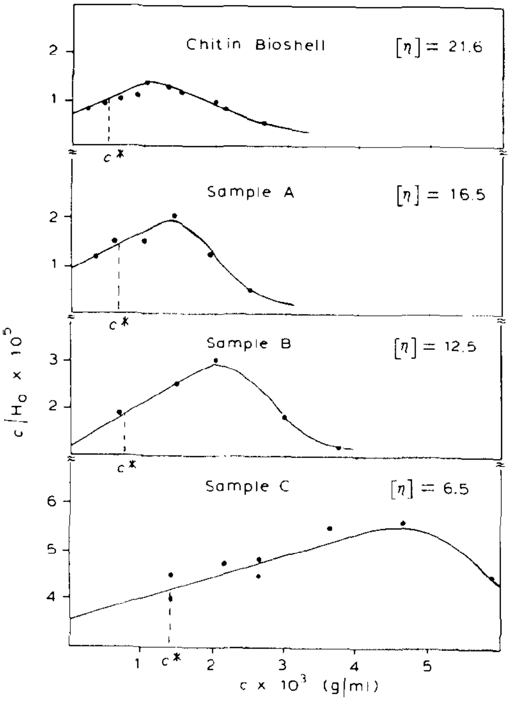


Fig. 3. Concentration dependence of c/H_0 for chitin samples at C_s 5%; c^* can be evaluated by the equation $c^*\,[\eta] = 1$.

solution volume. It is possible to correlate c^* and $[\eta]$ with the relationship[17] $c^* \simeq 1/[\eta]$, and c^* can be also evaluated[17] from R_G. The data obtained for our system according to the above methods are in fairly good agreement. Considering a narrow distribution of molecular weights, the term Kc/R_0 (proportional to c/H_0) is related to the osmotic pressure by the equation[19]

$$Kc/R_0 = \frac{1}{RT} \times \frac{d\pi}{dc}.$$

Thus, the reduced osmotic pressure $\pi M/cRT$ can be evaluated from light scattering measurements. For chitin in DMAc–5% LiCl as well as for hyaluronic acid in aqueous solutions[17], logarithmic plots of $\pi M/cRT$ *vs.* c/c^* show that the reduced osmotic pressure is not a monotonic function of c/c^*, as a drop occurs at c/c^* values of ~2.5. Data reported[19] for vinyl polymers indicate that c/H_0 increases monotonically on increasing c, and that the function lg $\pi M/cRT$ *vs.* lg c/c^* increases in the range (2.5×10^{-2} – 40) of c/c^* examined. Thus, a striking difference between our system and the vinyl polymers is evident even at comparable values of c/c^*.

From the diffusion data at $c < c_{max}$, it is possible to calculate molecular

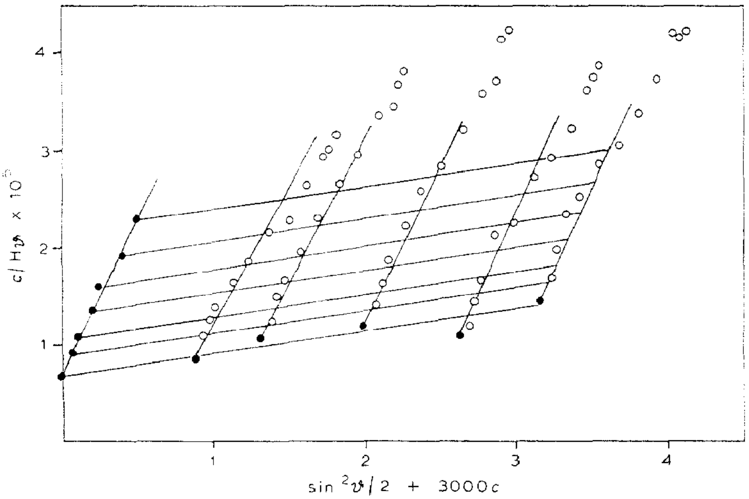


Fig. 4. Zimm plot of Bioshell chitin in DMAc–5% LiCl.

parameters as M_w, R_G, and *B*. Fig. 4 shows as an example the Zimm plot relative to Bioshell chitin at C_s 5%. Table II reports the molecular parameters calculated as indicated in the Experimental.

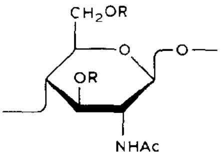
According to previous investigations on stiff and extended macromolecules, the scattering behavior in the high-angle asymptotic domain was analyzed by means of the Holtzer plot[23,24].

The curves for several samples of chitin having a sufficiently high molecular weight, after a monotonic increase, reach a plateau at high ϑ values. From the plateau data, M_L, the mass per unit length, can be determined and we obtained a value of 48 (±15%) Da/Å.

As far as the light scattering measurements at C_s 8% on commercial Katakura chitin and on the depolymerized sample E (depolymerization conditions: C_p 1.00%, 240 s) are concerned, comparable c/H_0 values were obtained on increasing the polymer content up to 1.5×10^{-3} g/mL. At higher concentrations, c/H_0 decreased progressively, eventually reaching very low values. However, unlike other polysaccharide systems[18,19], the plots c/H_ϑ *vs.* $\sin^2 \vartheta/2$ are linear and parallel. This effect can be ascribed to hyper-entanglement of a small percentage of polymer accompanied by a relevant association phenomenon between the polysaccharide chains. These results could be due both to the higher concentration of salt and to the different characteristics of the Katakura and Bioshell chitins. Experiments are in progress to elucidate this point, not yet fully explained even for cellulose in the same solvent system[5].

Derivatization. — Chitin was derivatized in the DMAc–5% LiCl system, to give the acetate (**1**), carbanilate (**2**), and toluene-*p*-sulfonate (**3**).

In the formation of ethers, additional problems occur, related to the difficult activation of the hydroxyl groups[9] and to *N*-alkylation. The esters were prepared



1 R = Ac
2 R = PhNHCO
3 R = Ts

by using a large excess of the acylating reagent at 25–80°. The modified polymer was recovered by precipitation with ethanol–water and characterized by i.r. spectroscopy (Fig. 5) and elemental analysis (see Experimental). The i.r. spectra of the derivatives contained additional bands, attributable to the new functional groups[25]. The degree of substitution (d.s.) calculated from the C, H, N, and S analyses was ~2 for the acetate and carbanilate and 0.15 for the toluene-*p*-sulfonate. The low d.s. in the last derivative probably reflects the fact that the reaction was carried out at 25°. Above this temperature, displacement of tosylate by chloride can occur[9].

As reported in the literature[26] for acetyl-chitins, obtained using acetic anhydride–methanesulfonic acid at 0° overnight or acetic anhydride–perchloric acid for 3 h at 0°, this derivative was insoluble in the common organic solvents (except acidic solvents), preventing macromolecular characterization. Light scattering

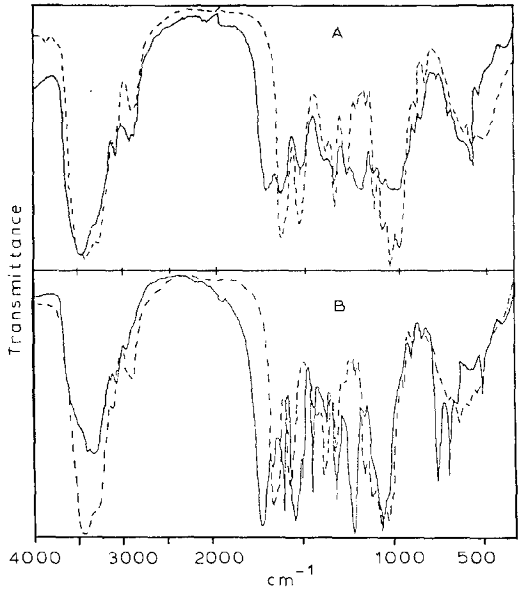


Fig. 5. I.r. spectra of Bioshell chitin (------), chitin diacetate (——, A), and chitin dicarbanilate (——, B).

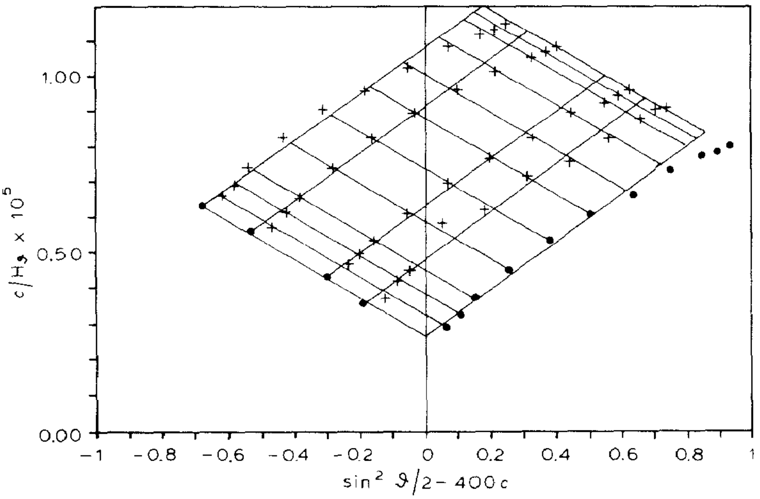


Fig. 6. Zimm plot of chitin carbanilate in DMAc.

measurements on solutions of the carbanilate in DMAc gave the values $M_w = 1.4 \times 10^6$ ($dn/dc = 0.10$ mL/g), $B = 2 \times 10^{-4}$ (mol.mL.g^{-2}), and $R_G = 650$ Å. The intrinsic viscosity $[\eta]$ in DMAc was 4.4 dL/g and a gel was formed at C_p 1%. This polymer was soluble also in methyl sulfoxide and viscosity measurements gave $[\eta] = 3.2$ dL/g.

DISCUSSION

From the above data, it is clear that the DMAc–LiCl system can be utilized to study and derivatize chitin. Solubilization of the polysaccharide is easy and no activation is required, as is the case with cellulose[4]. The commercial samples of chitin dissolved almost completely, even at moderately high concentration ($\leqslant$1%). Solubilization is independent of C_p, as quantitatively verified for the Bioshell chitin, for which the insoluble material is constantly 12%. Treatment of solutions of chitin in DMAc–LiCl with ultrasound gives chitins with a d.p. much lower than that of the commercial samples, without affecting the degree of acetylation. Thus, the process is useful for solution studies and industrial applications of the polymer, since it can be used for characterization, derivatization, or to obtain chitin samples with a desired molecular weight. Moreover, since larger molecules are more rapidly depolymerized than smaller ones[16], this method allows chitin samples with narrow molecular-weight distributions to be obtained.

Dilute and moderately concentrated solutions of chitin with different d.p. were examined by light scattering techniques, but a rationalization of the results is possible at present only for solutions at C_s 5%. The plot c/H_0 *vs.* c (Fig. 3) is a direct measure of the dependence of $(1/M_w)_{app}$ on c (apparent means: calculated from experimental data at finite concentration)[27]. Before c_{max} is reached, $(M_w)_{app}$

decreases, due to non-ideal deviations, and beyond c_{max}, $(M_w)_{app}$ increases dramatically. Thus, irrespective of high values of B (Table II), chitin chains associate at moderately high concentration. The process is a function of molecular weight since c_{max} increases as M_w decreases (Fig. 3). This behaviour is similar to that observed for other polysaccharide systems and indicates that, at $c < c_{max}$, entanglement is present between the polymeric chains, whereas at $c > c_{max}$, self-association causes the formation of large hyper-entangled particles but involves only a minor fraction of the chains in solution. Light scattering measurements on dilute solutions ($c < c_{max}$) allowed an evaluation of the molecular parameters M_w, B, and R_G for the system chitin–DMAc–5% LiCl (see Table II). The calculated values are influenced by the uncertainty of the value of dn/dc (see Experimental). An error in the determination of this value, due to incomplete equilibration of the sample or other factors, strongly affects the values of M_w and B, whereas that of R_G is not modified. The increase of the value of dn/dc after equilibrium dialysis of the solutions is in keeping with data on cellulose in the same solvent system[5] and on polymers in multicomponent systems[28].

Samples A–D, obtained by depolymerization of Bioshell chitin with ultrasound, show molecular weights decreasing regularly with decreasing $[\eta]$. Multimerization phenomena, observed for cellulose in the same solvent[5] or for other polysaccharides (chitosan and its derivatives) in aqueous solvents[29,30], were not observed for the limited number of samples examined. The range of M_w is satisfactorily large ($0.9–5 \times 10^5$) but shifted to higher values in comparison with those ($1–12 \times 10^4$) of cellulose samples. Thus, it is difficult to compare these two polysaccharides since the physico-chemical properties of a polymer are possibly dependent on the range of molecular weights. A better comparison can be made with the cellulose samples studied by McCormick[7] (M_w $1.2–7 \times 10^5$). However, the literature results refer to celluloses in DMAc–9% LiCl at 30°. Comparison of cellulose and chitin at C_s 5% requires an investigation of cellulose samples with higher M_w ($2–5 \times 10^5$) and/or chitin samples with lower M_w ($1–10 \times 10^4$). There are major problems in solubilizing cellulose, even after appropriate activation (cellulose with d.p. 1000, corresponding to M_w 1.6×10^5, dissolves only partially with marked degradation and darkening of the solution). For chitin, it is necessary, for treatment with ultrasound, to extend the irradiation time even if the value (9×10^4) of M_w seems to be near to the limit molecular weight, or adopt enzymic or chemical methods to break the glycosidic bonds.

From the plot log $[\eta]$ *vs.* log M_w, the parameters a and k of the Mark–Houwink equation were obtained and were, respectively, 0.69 and 2.4×10^{-3} dL/g, whereas the dependence of R_G on M_w can be described by the equation: $R_G = 0.24 M_w^{0.64}$ (Å). An evaluation of the linear expansion factor[31] α_s, using the interpenetration function[32], depending on the experimental parameters B, M_w, and R_G, gives a value close to unity for each sample. When taken together with the observed high values of B, this implies[33] that the chitin molecule is rather stiff in DMAc–5% LiCl. A similar explanation probably holds for the relatively high values of the exponent in the R_G–M_w relationship. Indeed, an even higher value (0.74) was found[7] for cellulose in DMAc–9% LiCl. The unperturbed chain dimension A (~4 Å) and the conformation parameter σ (~10) are comparable to those found in cellulose systems[7,34].

The persistence length (q_{YF}) was determined[18] by using the Yamakawa–Fujii expression for the intrinsic viscosity–molecular weight dependence for a worm-like chain[35], namely,

$$[\eta] = \Phi L'^{3/2}/\tau^3 M,$$

where $L' = M/M_L$ is the reduced contour length, M_L is the mass per unit length, $\tau^{-1} = 2\,q$ is the Kuhn segment (q being the persistence length), and Φ is a function of L' and of the reduced diameter d' (tabulated by Yamakawa and Fujii)[35]. Theoretical $[\eta]$–M_w curves have been calculated assuming $M_L = 39.50$ Da/Å, corresponding to a molecular weight of the repeating unit $M_0 = 203$ and to a projection of the repeat unit on the chain axis $L_0 = 5.14$ Å[6,18,35,36].

The unreduced diameter was taken as 6.63 Å, as obtained from the relationship[37]

$$d = (M_0/\rho N L_0)^{1/2},$$

where ρ is the polymer density, taken as 1.49 g/cm, evaluated from X-ray diffraction data[38].

Evaluation of the errors affecting q from the uncertainty of the diameter and M_L values showed that an underestimate of M_L gave a lower value of q of the same order, whereas the uncertainty of d does not significantly influence the q values.

The persistence length was also evaluated by light scattering data. Using the Benoit–Doty treatment of the worm-like chains[39], it is possible to obtain the persistence length (q_{BD}) according to the equation

$$R_G^2 = q^2\{1/3\,(L/q) - 1 + (2\,q/L) - (2q^2/L^2)\,[1 - \exp(-L/q)]\},$$

where L is the contour length, whereas, in the Gaussian coil, the limit (q_{CL}) is given by

$$q_{CL} = 3\,R_G^2/L.$$

The following results were obtained:

$$q_{YF} = 150 \pm 20\ \text{Å},\ q_{BD} = 250\text{–}500\ \text{Å},\ q_{CL} = 200\text{–}400\ \text{Å}.$$

Similar differences in the values of the persistence length evaluated by a viscometric or light scattering method have been observed[6,18,34]. These were correlated with the significant role played by the free draining effect that the Yamakawa–Fujii theory[35] neglects.

The use of the M_L value of 48, derived from light scattering data, gave an increase of ~35% in the value of the persistence length, evaluated from both the Yamakawa and the Benoit–Doty treatment.

The formation of mesophase for a worm-like chain can be evaluated according to the Flory theory for semiflexible polymers, using the relation[37,40]

$$v_2' \simeq \frac{8}{X_K}\left(1 - \frac{2}{X_K}\right),$$

where X_K is the axial ratio of the Kuhn segment ($2\,q/d$) and v_2' is the critical volume fraction necessary for the formation of a stable anisotropic phase. This relation is valid[41] for $X_K > 20$ and is applicable in the absence of interactions of the polymer and solvent[42].

An estimate of v_2', without considering the effect of the solvent, gave a value of 0.17 (using the smaller q value). The formation of a mesophase for concentrated solutions of the Bioshell chitin (C_p 12%) has been verified in preliminary experiments.

Problems in the derivatization of chitin may arise if the reactions are heterogeneous. Homogeneous reactions would result in high degrees of substitution and uniform substitution patterns with high yields and milder conditions. By using chitin in DMAc–5% LiCl, the acetate and carbanilate were obtained readily with high degrees of substitution, although no attempts were made to optimize the conditions. Comparison of the d.p. of the carbanilate and the starting chitin showed similar values, indicating that, as with cellulose[43], the complete substitution was obtained without breaking the main chain. Determination of the molecular weight of the carbanilate in DMAc, where equilibrium dialysis is not required, confirmed the M_w value found for the starting chitin in DMAc–5% LiCl.

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