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Comparative studies on molecular chain parameters of chitosans and poly(diallyldimethylammonium chloride): the stiffness *B*-parameter and the temperature coefficient of intrinsic viscosity

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Abstract

The empirical coefficient *B*, a measure of polyelectrolyte chain stiffness was estimated for two types of polycations: chitosans with F_A (mole fraction of *N*-acetyl-D-glucosamine units) ranging from 0.09 to 0.21 (determined by ^{1}H NMR method) and poly(diallyldimethylammonium chloride) (PDADMAC), in the presence of different counterions (Cl^-, Br^-, NO_3^-, ClO_4^-).The method relies on the measurements of the intrinsic viscosity, $[\eta]$, of polyelectrolyte chains at different solution ionic strength (I). Thus, the *B*-parameter shows the response of the hydrodynamic volume of polyelectrolyte molecules to the salt concentration in solution (the so-called *salt tolerance*) referred to the $[\eta]$ at $I = 0.1$ M. The temperature coefficient of intrinsic viscosity of PDADMAC and chitosan was also determined. The comparison of the *B*-parameters indicates lower flexibility of chitosan than PDADMAC. The reasons for this difference are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Chitosan; Poly(diallydimethylammonium chloride); Chain stiffness

1. Introduction

Many natural and synthetic cationic polyelectrolytes have found a wide spectrum of practical applications. In this group water soluble polyelectrolytes are of significant importance, especially in the field of environmental protection, e.g. as flocculants and coagulants, and also in paper making, the petrol industry, or in cosmetics and medicine (Dautzenberg, Jaeger, Kötz, Phillip, Seidel & Stscherbina, 1994; Brand, Dautzenberg, Jaeger & Hahn, 1997; Shigemasa & Minami, 1995).

Chitosan is commercially produced from chitin — the second-most important polysaccharide after cellulose in the world — using deacetylation processes (Roberts, 1992a). Because the deacetylation is usually not complete, chitosan can be considered as a binary heteropolysaccharide containing (1 → 4) linked 2-acetamide-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose residues. The chemical composition of different chitosans is characterised by the F_A value (molar fraction of acetylated units) or by the deacetylation degree: $100(1 - F_A)\%$. Chitosan chloride structure is shown in Fig. 1.

Poly(diallyldimethylammonium chloride) (PDADMAC) is a synthetic polymer (Fig. 2) easily obtained by radical polymerisation (Negi, Harada & Ishizuka, 1967; Wandrey, Jaeger & Reinisch, 1982; Jaeger, Hahn, Lieske & Zimmermann, 1996).

Commercial PDADMAC samples were shown to be branched (Xia, Dubin, Edwards & Havel, 1995; Wandrey, Hernándes-Barajas & Hunkeler, 1999).

Chitosan and PDADMAC are polyelectrolytes and have cyclic structures in their backbone. It seemed interesting to compare the parameters characteristic of chain stiffness and their dependence on the type of counterion and on temperature. The Smidsrød-Haug parameter *B* (1971) has been chosen as characteristics of stiffness. Its use is based on the fact that the chain dimensions and the intrinsic viscosity of polyelectrolytes are related to the salt tolerance in solution. Smidsrød and Haug (1971) have found that the more

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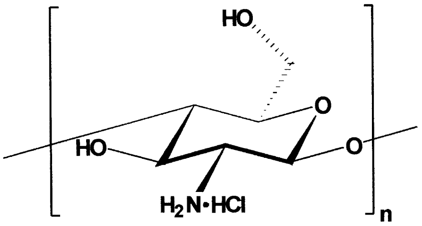

Fig. 1. Structure of chitosan chloride ($F_A = 0$).

flexible the chain, the higher the response of the intrinsic viscosity on the ionic strength, and higher is the B value. Though the B values are relative characteristics only, they are suitable for comparative studies as they are easy to estimate.

The determination of the B-parameter requires the knowledge of two dependencies: (1) $[\eta]$ vs. $1/\sqrt{I}$, where $[\eta]$ (dL/g) is the intrinsic viscosity of a polymer in a solution at a given ionic strength I (M), and (2) $\log S$ vs. $\log[\eta]_{I=0.1}$, where S is the slope of the plot obtained from

$$S = \mathrm{d}[\eta]/\mathrm{d}(1/\sqrt{I}) \tag{1}$$

The B-parameter is then related to S by equation

$$S = B[\eta]^{\nu}_{I=0.1} \tag{2}$$

where ν is a factor found to range between 1.2 for polyphosphates (flexible chains) and 1.4 for DNA (stiff chains) (Smidsrød & Haug, 1971; Smidsrød & Christensen, 1991). The ν factor can be obtained also as a slope, simultaneously with B

$$\log S = \log B + \nu \log[\eta]_{I=0.1} \tag{3}$$

when measurements with samples varying in molecular weight are performed.

Theoretical foundations for this procedure based on the theory of Fixman (1964) are discussed by Smidsrød and Haug (1971). The results obtained for pectin and polyacrylate (Smidsrød & Haug, 1971) support the idea that some variation in the stoichiometric charge density of polyelectrolytes does not lead to variation in B.

The temperature quotient of the intrinsic viscosity dln $[\eta]$/dT consists of three contributions (Reddy & Bohdanecký, 1987)

$$\mathrm{d}\ln[\eta]/\mathrm{d}T = (3/2)\,\mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T + \mathrm{d}\ln \Phi_0/\mathrm{d}T + \mathrm{d}\ln \alpha_\eta^3/\mathrm{d}T \tag{4}$$

The first contribution is due to the effect of temperature on the ratio $(\langle R^2\rangle_0/M)_\infty$ of the unperturbed mean-square end-to-end distance and the molecular weight in the random coil limit, the second to the effect of temperature on the Flory viscosity function Φ_0 (strength of the hydrodynamic interaction) of chains which are not expanded by the excluded-volume effect, and the third to the temperature dependence of the viscosity radius expansion factor α_η (i.e. strength of the excluded-volume interaction). The analysis of d ln$[\eta]$/dT values is rather easy with random coils in the non-draining limit where the second term is negligible (i.e. with flexible chain polymers of high molecular weights) but becomes difficult with short and/or stiff chains, where the second term comes into play (Reddy & Bohdanecký, 1987), and is still more difficult, if the third term is significant or unknown (Reddy, Bohdanecký, Staszewska & Huppenthal, 1988).

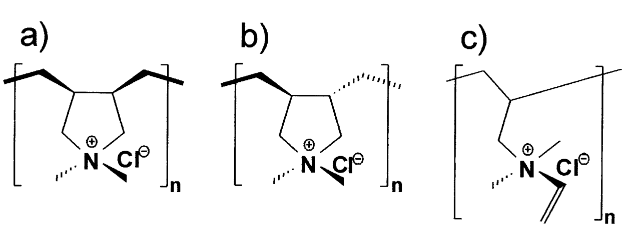

Fig. 2. Structure of: (a) linear *cis*- (84%), (b) linear *trans*- (14%), (c) branched (≤2%) PDADMAC (e.g. Jaeger et al., 1996).

2. Experimental

Chitosan was obtained from Fluka (Switzerland) and from the Sea Fisheries Institute in Gdynia (Poland). Some commercial chitosan samples were degraded heterogeneously with H_2O_2 to obtain samples with lower degree of polymerization (Trzciński, Lewandowska, Szulc, Kowalczyk & Staszewska, 2000). Chitosan samples not converted and converted (sample 1, 2, 3) to the chloride form by the method described elsewhere (Anthonsen, Vårum & Smidsrød, 1993) were used. The F_A values were determined by the ^{1}H NMR method (Vårum, Anthonsen, Grasdalen & Smidsrød, 1991) using a Jeol DPX 300 (300.13 MHz) spectrometer and by the 1DUV method (Muzzarelli & Rocchetti, 1985; Tan, Khor, Tan & Wang, 1998) using a Schimadzu UV 2401 PC spectrophotometer. The characteristics of the used chitosan samples are given in Table 1.

Commercial PDADMACs, p. a. (high, medium and low molecular weight) as ~20 wt% water solutions were obtained from SIGMA (Germany). PDADMAC solutions of desired concentrations were prepared by dilution of the stock, ~20 wt% water solution. The exact concentration was checked by weight.

Viscosity measurements were carried out using the Schott–Geräte Ubbelohde capillary viscometer (type 531 01/0a) at 293 K. To get the desired solution ionic strengths, simple electrolytes as NaCl, NaBr, $NaNO_3$ and $NaClO_4$ were used. The intrinsic viscosity values were calculated using the Hagenbach correction. Chitosan samples dried to a constant weight were taken for measurements.

Table 1
The characteristics of chitosan samples

Producer/source	$\overline{M}_v{}^a \times 10^3$	d-degraded; n-not degraded	F_A (^{1}H NMR)	Sample No.
Sea Fisheries Institute, Gdynia, Poland/anctartic krill	46.3	d	0.21	1
	36.9	d	0.21	4
Fluka/crab	55.8	d	0.17	2
	47.1	d	0.09	3
	300	n	0.18	5
	490	n	0.10	6
	313[b]	n	0.28[c]	7
	31.1	d	0.09	8

[a] On the basis of method of Anthonsen et al. (1993).

[b] On the basis of method of Roberts and Domszy (1982) and recalculation for Anthonsen's et al. (1993) constants K and a in a Mark–Houwink–Sakurada equation.

[c] 1DUV method (Muzzarelli & Rocchetti, 1985; Tan et al., 1998).

3. Results and discussion

3.1. Chitosan salts

The following effects on the B parameter were investigated: (i) degree of acetylation ($0.09 \leq F_A \leq 0.21$), (ii) type of counterions (NO_3^-, Cl^-, ClO_4^-), (iii) temperature. The first effect was studied with chitosan chloride. As can be seen in Table 2, the B parameter ($B \cong 0.1$) is independent of $F_A \leq 0.21$. This finding cannot be generalized inasmuch as Anthonsen et al. (1993) have shown that $B = 0.02$ at $F_A = 0.6$. This is in line with the finding of other authors that chitosan molecules with a high degree of acetylation are more rigid (Terbojevich, Cosani, Scandola & Fornasa, 1986).

Measurements of the intrinsic viscosity in aqueous solutions of NaCl, $NaNO_3$ and $NaClO_4$ were performed with chitosan sample No. 2 in the acetate form. The procedure of preparing solutions adopted by Domard and Rinaudo (1983) was used: required amounts of salts were added to the chitosan sample dissolved by addition of stoichiometric quantity of acetic acid. The pH value of chitosan solutions did not change after addition of electrolytes.

The $[\eta]$ values are listed in Table 2. The values of $[\eta]$ of chitosan acetate in the presence of chloride, nitrate and perchlorate anions are systematically higher than those of chitosan chloride in the presence of chloride anions. The difference may be attributed to differences in the procedure of preparing the solutions. A similar effect has also been observed by Roberts (1992b).

The S values of sample No. 2 in both forms (acetate and chloride) in the presence of chloride counterions are identical but the B value of chitosan acetate is lower. That arises from the higher value of $[\eta]_{I=0.1}$ being used in Eq. (2). The $[\eta]$ values of chitosan acetate somewhat depend on the type of the counterions but the B values are almost equal for all system investigated. The differences amount to less than 5%, thus the conclusion is, that there is no significant effect

Table 2
Intrinsic viscosities (dL/g) at different ionic strength, salt tolerances S, viscosity average molecular weights, $\overline{M}_v$, and experimental values of the B-parameter for chitosan chloride (in NaCl aqueous solution) and chitosan acetate (in NaCl, $NaNO_3$ and $NaClO_4$ aqueous solutions); $T = 20°C$

	Chitosan chloride			Chitosan acetate		
Sample No.	1	2	3		2	
$\overline{M}_v \times 10^{-4a}$	4.6	5.6	4.7		5.6	
F_A	0.21	0.17	0.09		0.17	
Counter ions		Cl^-		Cl^-	NO_3^-	ClO_4^-
$[\eta]_{I=0.02}$	3.76	4.39	4.19	5.28	5.13	5.04
$[\eta]_{I=0.03}$	–	–	–	4.88	4.58	4.43
$[\eta]_{I=0.05}$	2.84	3.42	3.01	4.47	4.07	4.35
$[\eta]_{I=0.07}$	2.58	3.06	2.78	–	–	–
$[\eta]_{I=0.10}$	2.49	2.82	2.70	3.75	3.55	3.70
$[\eta]_{I=0.20}$	–	–	–	–	3.24	3.37
$[\eta]_{I=1.0}$	1.92	2.14	1.96	–	2.61	–
S	0.3	0.38	0.36	0.37	0.4	0.33
B^b	0.092	0.10	0.10	0.064	0.078	0.059
R^2	0.995	0.998	0.992	0.989	0.999	0.976

[a] Calculated according to the K and a values in the Mark–Houwink–Sakurada equations in Anthonsen et al., 1993.

[b] $v = 1.3$.

Table 3
The temperature coefficient, d ln[η]/dT (I) and d ln[η]/d(1/T) (II) of chitosan

No.	Experimental conditions			$\overline{MW}\times10^{-5}$	Reference
		(I)	(II)		
1	0.1 M CH_3COOH/0.2 M NaCl; $F_A = 0.10$–0.28 (samples No. 5, 6, 7)	-5.0×10^{-3}, $R^2 = 0.947$	(480)	3.0–4.9 ($\overline{M}_v$)	This paper
2	0.1 M CH_3COOH/0.2 M NaCl; $F_A = 0.09$–0.21 (samples No 4, 8)	-4.5×10^{-3}, $R^2 = 0.945$	(429)	0.3 ($\overline{M}_v$)	This paper
3	0.33 M CH_3COOH/ 0.3 M NaCl; $F_A = 0.2$	-5.3×10^{-3}	(488)	1.34 ($\overline{M}_w$)	Pogodina et al. (1986)
4	0.2 M CH_3COOH/0.1 M NaCl/4 M urea; $F_A = 0.21$	-3.2×10^{-3}		1.35-4.92 ($\overline{M}_v$)	Lee (1974)
5	0.2 M CH_3COOH/0.1 M CH_3COONa; $F_A = 0.21$	4×10^{-3}		1.35–4.92 ($\overline{M}_v$)	Lee (1974)
6	0.01 M HCl; $F_A = 0.17$		(1334-666)	0.78–9.14 ($\overline{M}_w$)	Chen and Tsaih (1998)

of the radius of the counterion on the B parameter. This is in line with the results of Rodriguez-Sanchez, Kienzle-Sterzer and Rha (1982).

The temperature coefficient d ln[η]/dT of chitosan acetate solutions is negative. The values obtained in the present study (cf. Table 3) are independent of the chitosan molecular weight ($3.0 \leq M_v \times 10^{-5} \leq 4.9$) (item No. 1, Table 3) and are close to that obtained by Pogodina et al. (1986) (item No. 3, Table 3). The values found by Lee (1974) (items 4 and 5, Table 3) are also independent of the molecular weight but are lower, contrary to that, the quotients obtained by Chen and Tsaih (1988) are higher and decrease with increasing M.

These results can be discussed in terms of the theory of hydrodynamic properties of the worm-like chain model advanced by Yamakawa and Fujii (1974). Based on this theory, Reddy & Bohdanecký, 1987 derived the equation

$$(M^2/[\eta]_0)^{1/3}\mathrm{d}\ln[\eta]_0/\mathrm{d}T = S_1 + S_2(M^2/[\eta]_0)^{1/3} \qquad (5)$$

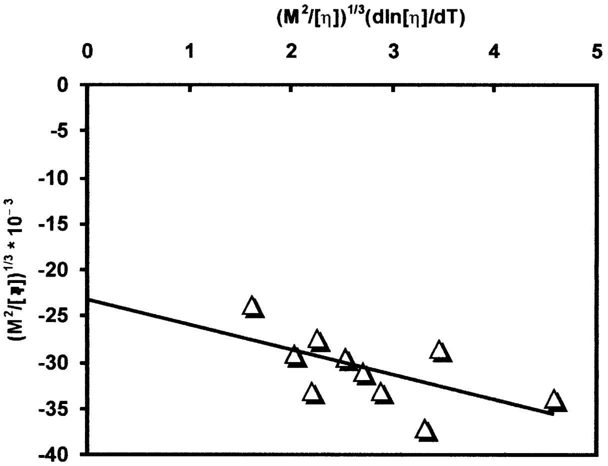

Fig. 3. Plot of d ln[η]/dT of chitosan according to Eq. (5). Data from paper by Chen and Tsaih (1988).

where

$$(2/3)S_2 = Q = \mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T \qquad (6)$$

and S_1 is characteristic of the temperature effect on the hydrodynamic parameters. The ratio of the unperturbed mean-square end-to-end distance and the molecular weight in the random coil limit, $(\langle R^2\rangle_0/M)_\infty$, reflects the effect of the temperature on the conformation (flexibility) of polymer chains. If $S_1 = 0$, the quotient d ln[η]/dT is independent of molecular weight

$$\mathrm{d}\ln[\eta]/dT = (3/2)\,\mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T \qquad (7)$$

and in this case may be simply converted into Q. Note that Eqs. (5) and (6) are valid only if the temperature dependence of the excluded volume effect is negligible. They are used here because this condition is usually met with polysaccharides.

Using Eq. (7) with data sub 1, 4 and 5 in Table 3, where the quotient d ln[η]/dT is independent of molecular weight, we obtain $Q \times 10^{-3}(\mathrm{deg}^{-1}) = -3.3$, -2.1 and -2.7, respectively. Unlike the results sub 1, 4 and 5, the values of d ln[η]/dT reported by Chen and Tsaih (1988) for solutions in 0.01 M HCl ($F_A = 0.17$) (item 6 in Table 3) decrease with an increase in molecular weight. In Fig. 3 they are plotted according to Eq. (5). From the slope, S_2, we obtain $Q \cong -1.8 \times 10^{-3}\mathrm{deg}^{-1}$. It may seem amazing that, in this case, the absolute $|Q|$ value is much lower than the quotient $|\mathrm{d}\ln[\eta]/\mathrm{d}T|$. The difference may be attributed to a strong temperature effect on the parameters of hydrodynamic interaction. It illustrates the limits imposed on the simple conversion of the quotient d ln[η]/dT into Q. The Q values for chitosan are similar to those for cellulose derivatives (Reddy & Bohdanecký, 1987).

We have observed with sample No. 8 ($M_v = 0.3 \times 10^5$) at $c = 0.3$ g/dL that the plot against temperature of the relative viscosity obtained on heating was situated above that obtained by cooling. The phenomenon was absent at lower concentrations ($c = 0.1$ g/dL, sample Nos. 5 and 6).

Table 4
Intrinsic viscosities (dL/g) at different ionic strength, salt tolerances S, viscosity average molecular weights,$\overline{M}_v$, and experimental values of B and ν for PDADMAC (in NaCl, NaBr and $NaNO_3$ aqueous solutions); $T = 20°C$

Counter ion	Cl^-			Br^-			NO_3^-		
$\overline{M}_v \times 10^{-4}$	7.93	11.2	20.1	7.93	11.2	20.1	7.93	11.2	20.1
$[\eta]_{I=0.02}$	1.80	3.08	4.32	–	–	–	–	–	–
$[\eta]_{I=0.05}$	1.22	2.04	2.61	0.905	1.84	2.03	0.888	1.58	2.25
$[\eta]_{I=0.07}$	1.06	1.80	2.50	–	1.67	–	–	–	–
$[\eta]_{I=0.08}$	–	–	–	0.719	–	1.71	0.757	1.19	1.68
$[\eta]_{I=0.10}$	0.846	1.58	2.27	–	1.26	–	–	–	–
$[\eta]_{I=0.15}$	–	–	–	0.532	–	1.23	0.564	0.911	1.26
$[\eta]_{I=0.30}$	–	–	–	0.403	–	0.865	0.427	0.687	0.904
$[\eta]_{I=0.50}$	0.546	0.892	1.17	–	0.644	–	–	–	–
$[\eta]_{I1=1.0}$	0.513	0.751	1.06	0.381	0.633	0.790	0.345	0.514	0.683
S^a	0.217	0.383	0.533	0.159	0.370	0.385	0.162	0.301	0.450
ν^b		1.07			1.12			1.21	
B^b		0.24			0.25			0.26	
B^c	0.24	0.24	0.24	0.25	0.26	0.24	0.26	0.26	0.26
R^2		1.000			0.994			1.000	

[a] From Eq. (1) cf. Fig. 3.
[b] From Eq. (3).
[c] From Eq. (2).

The same has been found by Rinaudo and Domard (1989) at $c = 0.8$ g/dL ($F_A = 0.18$, $M_v = 11 \times 10^5$). The authors attributed it to the presence of aggregation, which they had previously demonstrated by light scattering, and suggested that higher values of the relative viscosity in the heating cycle were due to the disintegration of aggregates. It is noteworthy that Anthonsen, Vårum, Hermansson, Smidsrød and Brant (1994) also detected concentration dependent aggregation.

3.2. PDADMAC chains

The effect of the type of counterions (Cl^-, Br^-, NO_3^-) and the effect of temperature on the B parameter were investigated.

The intrinsic viscosities of PDADMAC depend on the type of counterion (Table 4) but the B parameters are practically independent of them. Some of the ν values obtained as the slope S of the plot according to Eq. (3) and shown in Table 4 ($1.07 \leq \nu \leq 1.21$) are lower than the value 1.2 usually found with flexible polymer chains (Smisrød and Haug, 1971). From the $[\eta]$ values reported by Dautzenberg, Görnitz and Jaeger (1998) for linear PDADMAC we obtained $B = 0.20$ and $\nu = 0.97$. Increasing chain branching of PDADMAC with the increase of its molecular weight was shown (Zia et al., 1995; Dauztenberg et al., 1998; Wandrey et al., 1999). The occurance of such structural deviations would change the stiffness of PDADMAC molecules, thus the higher B value ($B = 0.26$) obtained in this paper for commercial PDADMAC samples might be an indication of polymer chain branching.

The quotient d ln$[\eta]$/dT of PDADMAC (Table 5) is positive and is not influenced by the ionic strength of solution at $I > 0.1$ M, irrespective of the molecular weight. At low ionic strength it is lower by about 30% than at $I \geq 0.1$ M.

3.3. Comparison of chitosan and PDADMAC

The stiffness parameters B of chitosan and PDADMAC estimated in the present paper, as well as those reported by other authors, are given in Table 6. The values for chitosan ($0.02 \leq B \leq 0.1$) are lower than those of PDADMAC ($0.17 \leq B \leq 0.28$). According to the correlation established by Smidsrød and Haug (1971), the Kuhn statistical segments length l_K are in the range from 5 to 20 nm for chitosan (depending on the degree of acetylation) and about 2 nm for PDADMAC.

The difference in l_K values reflects several factors. The chain repeating units of chitosan and PDADMAC are nearly of the same length (0.57 and 0.55 nm, respectively), but differ in the distances between groups at which rotation around the main chain bonds is possible. Rotation in the chitosan chain can occur at the glycosidic oxygen atoms only. Their separation is larger than the separation of two methylene groups (denoted by 0 and 3 in Fig. 4a) adjacent to the same monomer unit in PDADMAC. The second factor to be taken into consideration is that the number of groups connecting the rings is lower with chitosan (one glycosidic oxygen) than with PDADMAC (two methylene groups). Thus small distances between the substituents on two neighbouring repeating units of chitosan conduce steric or energetic interferences that restrict rotation at the oxygen atom. Such interferences are less severe with PDADMAC.

Possible interactions in PDADMAC can be deduced from Fig. 4a. The bonds one and three are coplanar, so it is possible to replace bonds one, two and three by a pair of virtual

Table 5
The temperature coefficient, d ln[η]/dT (I) and d ln[η]/d(1/T) (II) of PDADMAC

No.	Ionic strength, I (M)	The temperature coefficient of [η]		R^2	$\overline{M}_v \times 10^{-4}$	Reference
		(I)	(II)			
1	0.0032	2.5×10^{-3}	(−238);	0.803	20.1	This paper
2	0.0065	2.2×10^{-3}	(−208)	0.954	7.93	This paper
3	0.1	3.4×10^{-3}	(−328);	0.909	20.1	This paper
4	0.1	3.5×10^{-3}	(−329);	0.978	7.93	This paper
5	0.5	3.5×10^{-3}	(−339);	0.986	20.1	This paper
6	0.5	3.5×10^{-3}	(−337);	0.967	7.93	This paper

bonds *a* and *b* intersecting at the point *P*. These bonds are located in the plane of the paper and the ring is inclined by 60°. It is expedient to compare the *cis*-PDADMAC unit with that of *cis*-polyisoprene (PIP) (Fig. 4b). The possibility of rotation about bonds *a* and *b* is similar with both polymers. However, a difference exists between them due to the presence of the $(CH_2)^{**}$ group in PDADMAC. Rotation about bond *c* into the *cis* or *gauche* position would bring the *B* ring into proximity to ring *A* and the group (CH_2^{**}) to (CH_2^{*}) and would produce strong overlaps. Thus these conformations are disfavoured and the *trans* conformation of bond 4 is preferred. The chains assume larger end-to-end distances and the Kuhn segment is longer than the *cis*-PIP where this interference does not exist. Both polymers are examples of molecules in which rotation of bonds in separate units are mutually independent (Flory, 1966). Thus the increase in stiffness brought about by incorporating a ring into a chain of methylene groups can be understood.

To further illustrate this point, we have calculated the Kuhn segment lenghts of *cis*-PIP from the characteristic ratio C_∞ (Flory, 1966) with resort to equations

$$C_\infty = (\langle R^2\rangle_0/M)_\infty (M_b/l_b^2) \tag{8}$$

and

$$l_\mathrm{K} = (\langle R^2\rangle_0/M)_\infty M_\mathrm{L} \tag{9}$$

where l_b^2 and M_b are, respectively, the mean square length and the mean molecular weight per main chain bond, and M_L is the shift factor usually set equal to the molecular weight per unit contour length of the chain at full extension ($M_\mathrm{L} = M_0/l_0$; M_0 and l_0 are the molecular weight and the length of the repeating unit, respectively). Combining

Table 6
The B-parameter of chitosan and PDADMAC determined (this paper), calculated (this paper) on the basis of data in the literature (*) and the B value reported

B-parameter of chitosan	Experimental conditions	Reference
0.10	Chloride salt form in aq. NaCl; samples No 1, 2, 3	This paper
0.064	Acetate salt form in aq. NaCl; sample No 2	This paper
0.078	Acetate salt form in aq. $NaNO_3$; sample No 2	This paper
0.059	Acetate salt form in aq. $NaClO_4$; sample No 2	This paper
0.05–0.13*	Acetate salt form in aq. NaCl; $0.15 \le F_\mathrm{A} \le 0.22$	Lyubina, Strelina, Nud'ga, Plisko and Bogatova (1983)
0.02–0.10	Chloride salt form; $0 \le F_\mathrm{A} \le 0.6$	Anthonsen et al. (1993)
0.08		Roberts (1992b)
0.043–0.091	$0.12 \le F_\mathrm{A} \le 0.52$	Terbojevich et al. (1986)
0.023	Acetate salt form in aq. NaCl; $F_\mathrm{A} = 0.18$	Rinaudo and Domard (1989)
B-parameter of PDADMAC		
0.24	Aqueous NaCl (cf. Table 3)	This paper
0.25	Aqueous NaBr (cf. Table 3)	This paper
0.26	Aqueous $NaNO_3$ (cf. Table 3)	This paper
0.28*	Aqueous NaCl	Negi et al. (1967)
0.22*	Aqueous NaCl	Maxim, Dimitriu, Ioan and Carpov (1977)
0.17*	Aqueous $NaNO_3$	Bowman and Cha (1979)
0.20*	Aqueous NaCl	Dautzenberg et al. (1998)

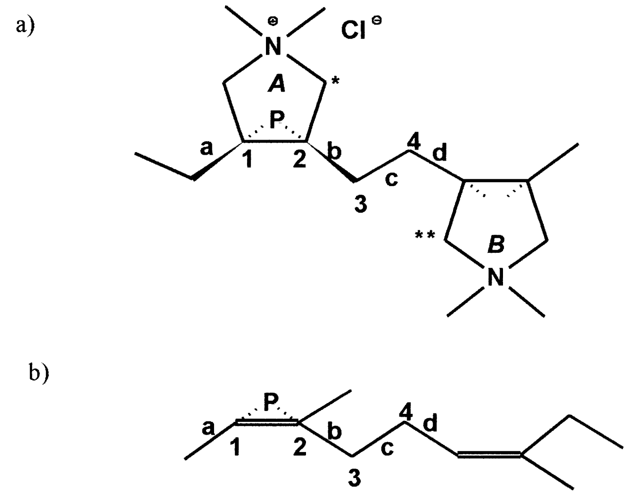

Fig. 4. PDADMAC in *cis*- configuration (a), *cis*-polyisoprene (b). Notation of real bonds 1–4, notation of virtual bonds *a* and *b*, notation of rings *A* and *B*.

these equations we have

$$l_K = C_\infty(l_b^2/l_0)(M_0/M_b) \tag{10}$$

The chain repeating unit is assumed to consist of two virtual bonds and one C–C bond (Flory, 1966), so $M_0/M_b = 3$ and $l_b^2 = 0.056\ \text{nm}^2$. With $C_\infty = 4.7$ (Flory, 1966), $M_0 = 68$ and $l_0 = 0.55$ nm we obtain $l_k = 1.4$ nm for *cis*-PIP. This is lower than the value for PDADMAC found in this paper and much lower than the value for PDADMAC ($l_k = 5$ nm) estimated by Dautzenberg et al. (1998) by means of osmometry and light scattering.

The stiffness of chitosan chains is explained in different ways, e.g. by hydrogen bonding between C(6′)OH and C(2)NHCOCH$_3$ groups (Terbojevich et al.,1986) or by hydrogen bonded water in the hydration sphere of the chain (Noguchi, 1981). As heating destroys hydrogen bonds, hindrances to rotation at the glycosidic oxygen atom are relieved at higher temperatures and the chain become more flexible. This can explain negative values of the quotient *Q*.

The d ln[η]/dT values for PDADMAC were estimated with two samples only and seem to be independent of molecular weight. The positive value is indicative of an increase of chain dimensions on heating. We hesitate, however, to make use of Eq. (7). In view of lower stiffness (in comparison with chitosan) the chains of PDADMAC are more liable to the excluded-volume interactions. So the quotient d ln[η]/dT need not reflect the temperature effect on the unperturbed dimensions only but may contain a contribution from the change of the polymer–solvent interaction with temperature. In order to resolve these effects, we would need more experimental data.

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