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Autoassociative natural polymer derivatives: the alkylchitosans. Rheological behaviour and temperature stability

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Abstract

Chitosan may be chemically modified by reductive amination leading to the grafting of hydrophobic alkyl chains along the hydrophilic macromolecular chain. This allows to obtain amphiphilic polymers whose the hydrophobicity (or the hydrophile–lipophile balance, HLB) may be adjusted according to the length of the grafted alkyl chain or the degree of substitution of the amine functions. The existence of hydrophobic interactions between the alkyl chains will change the physico-chemical properties of the solutions of the modified chitosans. These properties are studied and the study is particularly focused on the influence of the polymer concentration and temperature on them and applications as rheology modifiers. Threshold concentrations, over which the polymer solutions have peculiar temperature behaviour, were defined. According to their structure it is possible to prepare solutions with constant viscosity or increasing one with temperature.

Keywords: Hydrophobic chitosan; Autoassociative; Temperature

1. Introduction

Associative polymers are a class of polymers that have found a widespread use in technical formulations. Their main function is as rheology modifiers (particularly thickening agents) especially in aqueous based formulations within numerous industrial domains such as paints, oil recovery, cosmetics or foods [1–3]. Polymers belonging to this group are amphiphilic, containing hydrophilic as well as hydrophobic parts [4,5]. In an aqueous solution hydrophilic segments are responsible for the hydration and swelling, while the hydrophobic domains of the macromolecular chain minimise the contact with water by assembling in aggregates (as the micellization process of surfactants) [6]. The first studies describing an associative behaviour were in 1951 [7] with a poly(4-vinylpyridine) derivative bearing ethyl and dodecyl groups. From this date, for economic and environment reasons, the interest for these original macromolecules increases as indicated by the numerous books and reviews on this subject [1,8–13]. The architecture of such associative polymers is widely varied from telechelic structure to block copolymers passing through branched macromolecules. It is possible to distinguish four major families of water soluble polymers which associative and thickening properties lead to industrial applications more or less developed:

- poly(ethylene oxide) based polymers modified with hydrophobic groups [14],
- acrylic acid based chains with a small number of laterally grafted hydrophobic blocks [15],
- copolymers from acrylic hydrophile monomer and an hydrophobe monomer [16],
- cellulosic derivatives with hydrophobic substituents [17–19].

According to their structure the aggregation mechanism will be different as the properties. But in any case the basic phenomenon will be the hydrophobic interactions between hydrophobic parts of the polymeric chains leading to junction zones and then a physical gel, which is a loose tridimensional network. Hence a large viscosity increase was observed. Amphiphilic polymers that spontaneously form supramolecular structures in aqueous media mainly

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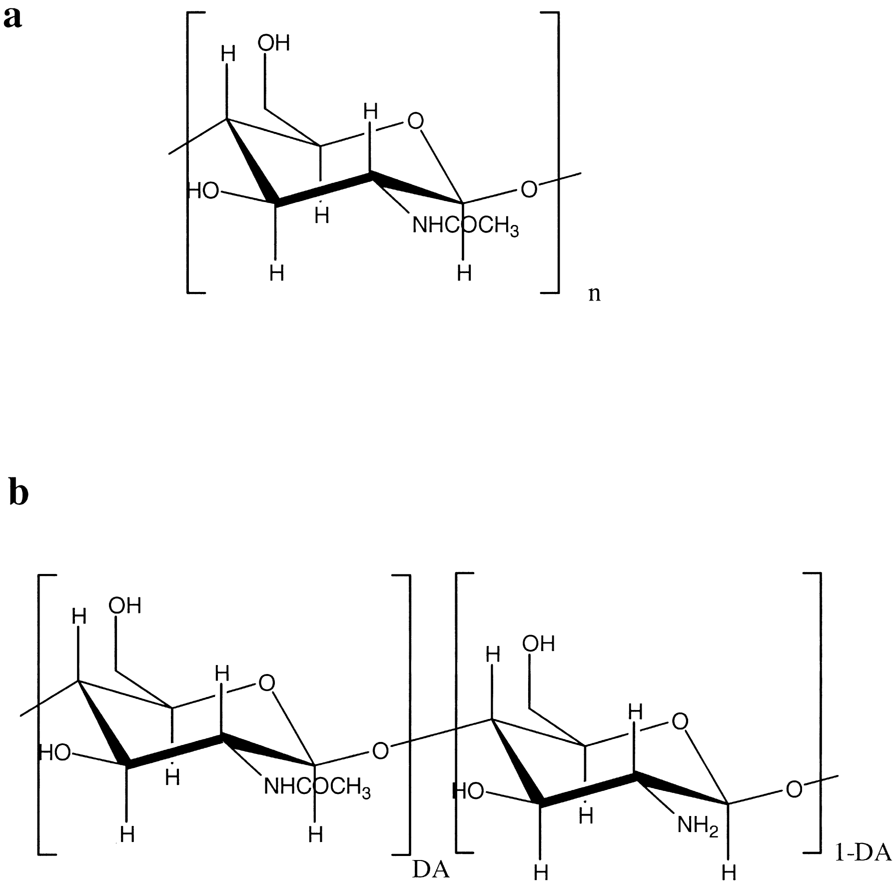

Fig. 1. Chemical structures of chitin (a) and chitosan (b) DA is the degree of acetylation.

due to hydrophobic interactions (also called autoassociative polymers) have attracted a great deal of interest in recent years [20–26]. Hydrophobically modified polyelectrolytes are such systems that belong to this class of self-associating polymers. In these systems, hydrophobic associations through intra- or interpolymer interactions compete with electrostatic repulsions, which operate within the same polymer chain or between different chains. The preference of intra- or interpolymer hydrophobe association depends on the polymer concentration and the structural characteristics of the macromolecule, notably the content and the nature of the hydrophobic groups and the sequence distribution of electrolyte and hydrophobic monomer units along the polymer chain. These effects and the ionic strength of the system are factors that also are important [27,28] for the association efficiency and subsequently the dynamical behaviour of solutions of hydrophobically modified polyelectrolytes. Numerous theoretical studies [29–37] in recent years have been devoted to properties of such polyelectrolyte solutions.

Among all the hydrophobically modified water-soluble polymers a great effort is focused now on the natural polymers (such as polysaccharides) and their derivatives for availability and environment reasons. For some years my work was dedicated to chitin and its derivatives. Chitin is a structural polysaccharide in the exoskeleton of many arthropods and it is the second most abundant polysaccharide in nature. But its applications are limited due to its lack of solubility in major solvents. Its deacetylation, performed in basic medium, leads to chitosan, which is soluble in acidic medium due to the presence of amino groups which may be protonated. This polymer consists of a linear chain of (1 → 4) linked 2-amino-2-deoxy-β-D-glucopyranose and 2-acetamido-2-deoxy-β-D-glucopyranose units (Fig. 1). It is characterised by its degree of acetylation (DA) which is the average molar ratio of *N*-acetyl-D-glucosamine units within the macromolecular chain.

The potential uses of chitosan derive from its unique chemistry: it is a polycation in neutral and acidic solutions (due to the value of pK_a equal to 6.0 [38,39]). Hence it is a biopolymer favourable for a broad variety of industrial and biomedical applications [40–44]. The cationic property of chitosan is exploited in numerous domains such as the recovery of proteins from food processing wastes [45], the chelation of heavy metals from waste water [46], drug delivery and pharmaceutical industries [47], cosmetics and personal care [48], ophtamology [49], textile industries as dye binding [50]. Chitosan may also be modified and hydrophobic chitosans were prepared by grafting alkyl chains [51].

Holme [52] has prepared chitosan derivatives bearing C_{10}-alkyl glycoside branches and mentioned temperature-induced gelling behaviour. However, the solubility properties

Table 1
Physico-chemical characteristics of chitosan and hydrophobic derivatives. (Solvent: AcOH 0.3 M/AcONa 0.05 M; $T = 278$ K)

Sample	Degree of alkyl substitution (DS[a], %)	Intrinsic viscosity ([η], ml/g)	Huggins constant (k')
Chitosan	–	1013	0.45
CC3, 100%	100	911	0.41
CC6, 50%	50	980	0.43
CC8, 5%	5	1030	1.45
CC8, 25%	25	1105	1.65
CC10, 5%	5	1119	1.8
CC12, 5%	5	1179	2.15

[a] Degree of substitution expressed as the molar ratio of substituted amine groups.

were more particularly discussed. Preliminary rheological results were presented by Nyström et al. on the alkylated chitosan [53–56]. They have focused their studies on one type of chitosan derivative, its rheological behaviour and the interactions with surfactant. The effect of the concentration was studied and it is indicated that a temperature rise seems to promote the disengagement of the polymer chains [56].

In this paper the influence of the chemical modification of chitosan on the rheological behaviour of solutions of such derivatives will be studied as a function of the structural parameters (length and number of grafted alkyl chains) and hence the hydrophobicity. Finally the role of temperature and the deduced applications will be presented.

2. Experimental section

The precursor chitosan sample was from Pronova (Norway). The degree of acetylation (DA) was determined by ^{1}H NMR considered to be the most sensitive technique using an AC300 Bruker spectrometer [57] and found to be equal to 0.12. Its viscosity–average molar mass was determined to be equal to 193,000 g/mol from the Mark–Houwink parameters previously found [58] (the intrinsic viscosity in 0.3 M acetic acid (AcOH)/0.2 M sodium acetate (AcONa) at 298 K was equal to 780 ml/g). It was purified by solubilization in 0.5 M acetic acid solution. This solution was filtrated through sintered glass filters and then cellulose nitrate membranes with average pore sizes of 3, 1.2, 0.8 and 0.45 μm successively. The filtrate was neutralised with NaOH up to a pH of 8.5 and the chitosan precipitates. It was then washed with water up to reach the conductivity of distilled water. Finally it was washed with ethanol before drying.

The solvent used for rheological experiments was 0.3 M AcOH/0.05 M AcONa. This electrolyte concentration was chosen to screen electrostatic repulsions and limiting hydrophobic interactions promoted by electrolytes. The polymer sample was dissolved, at the convenient concentration, in the solvent during 48 h at a temperature of 5 °C under magnetic stirring and used immediately.

The determination of the intrinsic viscosity as a function of the temperature was performed with an Ubbelohde capillary viscometer ($\phi = 0.58$ mm). A low shear viscometer (LS40 from Contraves) was used for low polymer concentration solutions (up to 1 g/l). A cone-plate rheometer (AR1000 from TA Instruments) was used for high polymer concentration solutions and steady flow or dynamic experiments. The cones we have used have 2, 4 or 6 cm diameter and angles of 1° (for the 6 cm cone) and 3°59′ (for the other cones) with a cap to avoid vaporisation. The oscillatory shear measurements were performed within the linear viscoelastic regime, where the storage (G') and loss (G'') moduli are independent of the strain amplitude. The temperature range was 278–353 K. The temperature ramp was carried out at a rate of 1 °/min. and a frequency of 0.1 Hz using a cone-plate rheometer (AR 1000 from TA Instruments).

The fluorescence of pyrene used as a marker for hydrophobic domains was determined using a Perkin Elmer LS 50B spectrofluorimeter; pyrene was added at a concentration of 10^{-7} mol l^{-1}. The studied parameter is the I_1/I_3 ratio of the intensities of first and third peaks of fluorescence spectrum of pyrene (respectively, at 373 and 384 nm) in chitosan derivative solutions. The excitation wavelength of pyrene was equal to 334 nm and the bandwidths in emission and excitation were, respectively, of 5 and 2.5 nm. The emission spectrum was registered between 300 and 500 nm.

2.1. Synthesis of alkylchitosans

The alkylated chitosan derivatives were obtained by reductive amination following the procedure described by Yalpani [59]. It is a versatile and specific method for creating a covalent bond between a substrate and the amine function of the chitosan. In our work it involves the reaction between the amine function of the glucosamine unit and an aldehyde function. Generally the reaction of substitution on polysaccharides proceeds in heterogeneous conditions with preferential reactivity of accessible zones thus giving a blockwise distribution of substituents. Hence the derivative is structurally inhomogeneous. We have developed a procedure for performing homogeneous chemical reactions based on the swollen structure of chitosan directly modified after precipitation by basic neutralisation, which allows a better accessibility of reactive sites [51] and an homogeneous repartition of substituted units along the macromolecular chain. The reaction is performed in mild conditions with no modification of the degree of acetylation nor of the polymerisation degree. On the basis of chitosan, one gets cationic amphiphilic polymers in acidic medium (due to the amine protonation).

The prepared derivatives are named according to the alkyl chain length which is grafted (as an example CC8 is a

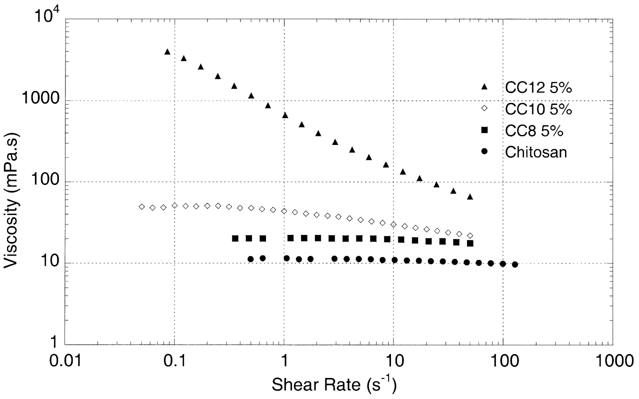

Fig. 2. Influence of the hydrophobicity on rheological curves. (Solvent: AcOH 0.3 M/AcONa 0.05 M; $T = 278$ K; $c = 2$ g/l).

chitosan substituted with C_8 alkyl chain from a C_8 aldehyde). The characteristics are given in Table 1.

3. Results and discussion

3.1. Role of the concentration and the hydrophobicity

The rheological curves (variation of the viscosity as a function of the shear rate) are determined for different polymer concentrations at different temperatures. At a constant temperature when the viscometric behaviour of alkylated chitosan solutions is compared with the one of chitosan solutions at a constant concentration (Fig. 2) the chitosan solution has a newtonian behaviour when the modified chitosan solutions are more and more viscoelastic when the hydrophobicity (related with the length of the alkyl chain) was increased. For the longest alkyl chain a yield stress fluid was observed related to the formation of a gel as it will be shown afterwards and no newtonian plateau was described in the used shear rate range. The higher the hydrophobic properties of the macromolecular chain, the larger the gap to the newtonian behaviour.

Considering the viscosity at a low shear rate (on the Newtonian plateau or extrapolated at zero shear-rate according to Cross or Carreau rheological models for non Newtonian solutions choosing the best fit of the experimental curve) as a function of the polymer concentration (Fig. 3) the viscosity rises with increasing polymer concentration. This increase is stronger as the hydrophobicity of the polymer increases (as the length of the alkyl chain or the degree of substitution). Moreover the concentration at which this increase is marked compared with the chitosan curve decreases when the hydrophobicity increases. This is due to the presence of interactions between polymer chains. Only the CC3 solution has a curve below the chitosan one. It is explained by the presence of intramolecular interactions, related with the large number of C_3 alkyl chains along the macromolecular backbone, compared with other polymers for which intermolecular interactions are predominant. The association effect on the viscosity becomes gradually more marked as the polymer concentration increases. We should note that even for the original chitosan there is a pronounced increase in the viscosity at higher concentration. Previously [60] intermolecular interactions between chitosan chains leading to the formation of a gel were demonstrated. Moreover we have shown [51] that an adequate length (a minimum of five to six carbon atoms) of the grafted chain is necessary for chitosan derivatives to present hydrophobic characteristics and self-association.

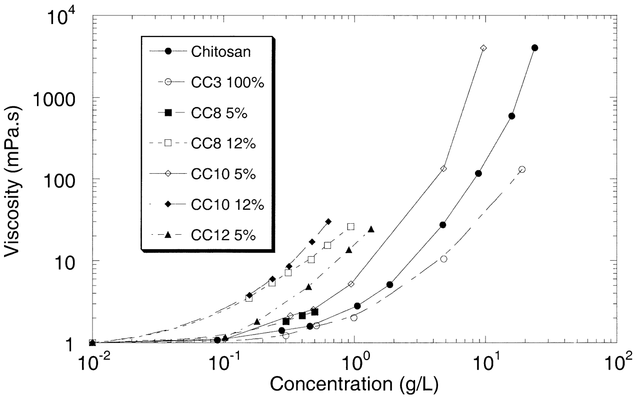

Fig. 3. Role of the polymer concentration on the zero-shear rate viscosity of chitosan and hydrophobic derivatives solutions. (Solvent: AcOH 0.3 M/AcONa 0.05 M; $T = 298$ K).

The intrinsic viscosity of these polymers was also measured for different polymers and at different temperatures. The introduction of hydrophobic groups will affect the intrinsic viscosity and the Huggins constant (k'). The intrinsic viscosities of polymers increase for alkylated samples compared with chitosan in the same time that k' increases. The Huggins constant is higher than that of common random coil polymers. The significance of k' has been investigated both theoretically and experimentally. This quantity may be viewed as a measure of segment–solvent and segment–segment interactions, or practically as a parameter indicating the relative effectiveness of various solvents for a given polymer. It is almost independent of molar mass for linear synthetic polymers. Higher values of the Huggins constant are usually interpreted as enhanced polymer–polymer interactions and indicate poorer solvent quality. The tendency of Huggins constant increase with increasing hydrophobic content reflects the possibility of intermolecular association as observed with synthetic hydrophobic polymer synthetized from acrylamide based polymers or copolymers [61]. With CC3 sample the intrinsic viscosity is decreased compared with chitosan and k' does not change significantly. This is related with intramolecular interactions decreasing the hydrodynamic volume of the macromolecular chain. With alkyl derivatives, the intrinsic viscosity slightly increases compared with the parent polymers in the same time as the Huggins constant (k') also increases. These two characteristics indicate loose interchain interactions even in the dilute regime (the overlap concentration c^* is in the range of 1 g/l

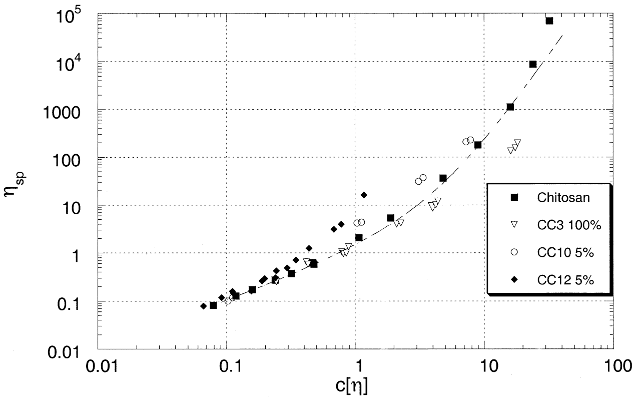

Fig. 4. Dependence of specific viscosity as a function of the overlap parameter ($c[\eta]$) for chitosan and hydrophobic chitosan derivatives. (Solvent: AcOH 0.3 M/AcONa 0.05 M, Temperature from 278 to 298 K, curve: Kwei representation from Ref. [62]).

estimated from the intrinsic viscosity $c^* \sim [\eta]^{-1}$) covered in these experiments. Chitosan, CC3 and CC6 have a close behaviour related with the small length of the hydrophobic chain and the absence of hydrophobic zones (related with an homogeneous distribution of substituents along the macromolecular backbone).

This difference in the behaviour of hydrophobically modified chitosans is more demonstrated when plotting the specific viscosity η_{sp} as a function of the overlap parameter ($C[\eta]$) considering different temperatures (Fig. 4). Each polymer has its own curve, the difference coming for CC10 and CC12 samples from the different values of the Huggins constant. These are related with the hydrophobicity: the higher it is, the larger the difference with the chitosan curve. Indeed CC3 sample presents a peculiar behaviour. It has the same Huggins constant than chitosan sample but it does not follow the Kwei relation [62] relative to macromolecular chains without interactions in a good solvent as observed for precursor chitosan sample:

$$\eta_{sp} = C[\eta]\{1 + k_1 C[\eta] + k_2(C[\eta])^2 + k_3(C[\eta])^3\} \qquad (1)$$

with $k_1 = 0.4, k_2 = k_1^2/2!$ and $k_3 = k_1^3/3!$. As specific viscosities of CC3 sample are lower than the 'theoretical' values, that demonstrates that the macromolecular chains are more compact due to intramolecular interactions. But with other alkylated derivatives (CC10 and CC12 samples) intermolecular interactions prevail.

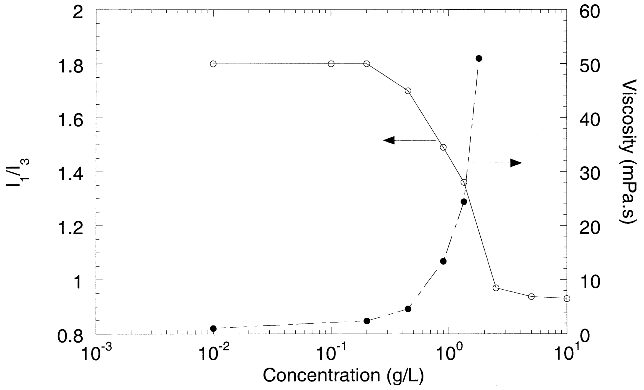

Fig. 5. Influence of the polymer concentration on the fluorescence (I_1/I_3) and the viscosity of CC10, 5% solutions. (Solvent: AcOH 0.3 M/AcONa 0.05 M; $T = 298$ K).

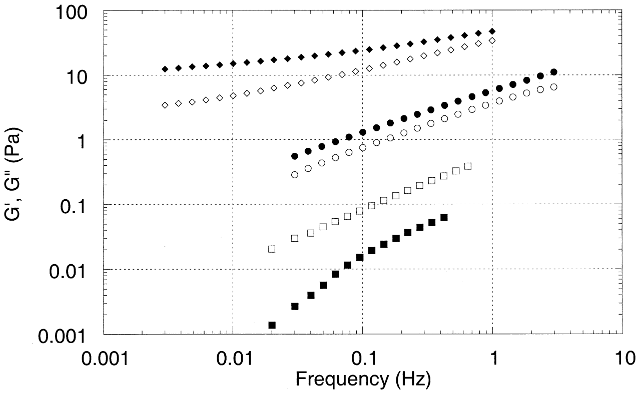

Fig. 6. Influence of concentration and frequency on the dynamic moduli G' (filled symbols) and G'' (open symbols) of CC10, 5% solutions (□) 5 g/l; (○) 15 g/l; (◇) 20 g/l; Solvent AcOH 0.3 M/AcONa 0.05 M; $T = 293$ K).

The nature of these interactions is demonstrated from fluorescence spectroscopy experiments [63]. The pyrene is used in these experiments as a probe whose the vibrational structure of the fluorescence emission spectrum is very sensitive to the polarity of its environment. Particularly it tends to concentrate inside the hydrophobic domains. The variation of the I_1/I_3 ratio indicates that the pyrene molecules are within polar or apolar environment, i.e. the hydrophobic nature of these interactions (in case of the presence of apolar aggregates). The evolutions of the viscosity and the fluorescence as a function of the polymer concentration are shown in Fig. 5 for CC 10, 5% sample. The two series of data point out the existence of a critical concentration $C_{crit} \sim 0.2$ g/l over which viscosity increases rapidly and the fluorescence indicates that pyrene is present in hydrophobic domains; this effect is specific of the presence of the alkyl chains. This critical concentration is largely smaller than the overlap concentration and indicates that even in dilute solutions hydrophobic interactions exist as already demonstrated from the values of intrinsic viscosity and Huggins constants. The junction points for the 3D-network formation are constituted of alkyl aggregates looking like a micellisation.

3.2. Gelation concentration

As the association effect increases with polymer concentration it may be expected to observe a gelation concentration. Increasing the concentration will allow to observe the transition from the rheological behaviour of a solution (the storage modulus G' proportional to ω^2 and the loss modulus G'' to ω^1, $G' < G''$) to which of a gel (G' and G'' independent on the frequency and $G' > G''$ over a wide

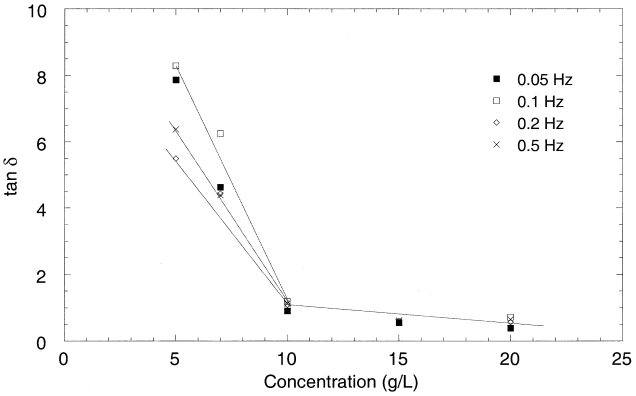

Fig. 7. Determination of the gelation concentration of CC10, 5%. (Solvent: AcOH 0.3 M/AcONa 0.05 M; $T = 293$ K).

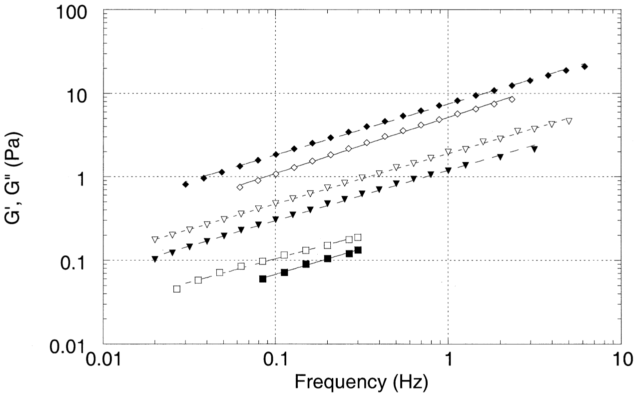

Fig. 8. Mechanical moduli as a function of the frequency (G' in filled symbols, G'' in open symbols) close to gelation concentration. (□) CC8, 25% at 2 g/l; (▽) CC6, 50% at 10 g/l; (◇) CC10, 5% at 15 g/l; Solvent: AcOH 0.3 M/AcONa 0.05 M; $T = 283$ K).

frequency range). This evolution was demonstrated in Fig. 6 for CC10, 5% sample even if the extremal behaviours were not obtained. The dynamic mechanical behaviour at gel point for chemically crosslinking systems is characterised by a scaling relation between dynamic moduli and frequency ($G'(\omega) \sim G''(\omega) \sim \omega^n$) and a frequency independent loss angle ($\tan \delta_c = G''/G' = \tan(n\pi/2)$) [64]. This may be applied to physically crosslinking systems [65,66]. Hence the concentration-induced gel point can be determined by the observation of a frequency-independent value of tan δ obtained from a multifrequency plot of tan δ as a function of the polymer concentration. This type of plot is shown in Fig. 7 for CC10, 5%. The general trend is similar for all the systems: a steady decrease in the loss tangent. This results in values of tan δ becoming independent at a certain gelation concentration, the latter depending on the hydrophobicity of the polymer (Table 2). The gelation concentration decreases with increasing hydrophobicity and this suggests that the hydrophobic interactions play a major role in the gelation process. At the gel point G' and G'' curves become parallel to each other and the power law behaviour ($G' \sim G'' \sim \omega^n$) in frequency is observed (Fig. 8). Previous experimental results on chemical gels from synthetic polymers indicate that the exponent n is not constant but takes values in the range $0 < n < 1$, depending on the species of gelling materials, the stoichiometric ratio between them, the gel preparation method and also on polymer molecular weight. The value of the viscoelastic exponent (n) is larger than for the chitosan precursor ($n = 0.41$ [60], Table 2). This may be due to stronger entanglement couplings for chitosan solutions related to the higher concentration used for precursor. It has been argued [67] that an increasing entanglement density may give rise to lower values of n. For the CC8, 5% sample presenting the highest gelation concentration (35 g/l, close to chitosan one) the n value is not very far from chitosan one. We have previously shown [51] that a minimum value of six carbon atoms is necessary to observe the presence of intermolecular hydrophobic interactions. Hence when chitosan is substituted with a small amount (degree of substitution equal to 5%) of C_8 alkyl chains, it is very difficult to detect intermolecular hydrophobic interactions explaining a behaviour close to chitosan. When interchain hydrophobic interactions are observed the n value seems to increase with hydrophobicity. The values of n observed for these systems are considerably smaller than that (0.7) predicted for percolating networks [68,69]. To rationalise values deviating the percolation value, Muthukumar [70] developed a theoretical model in which it is assumed that the variations in the strand length between crosslinking points of the incipient network gives rise to changes in the excluded volume interactions. The surmise is that increasing strand length will enhance the excluded volume effect. If the excluded volume interaction is fully screened, the relaxation exponent for a polydisperse

Table 2
Rheological characteristics of chitosan and hydrophobic derivatives (Solvent: AcOH 0.3 M/AcONa 0.05 M; $T = 283$ K)

Sample	Gelation concentration (C_{gel}, g/l)	Concentration at maximum activation energy (g/l)	n[a]	d_f[a]	Power law index[a]
Chitosan	40		0.41	2.1	0.553
CC6, 50%	7	5	0.606	1.87	0.396
CC8, 5%	35	30	0.462	2.045	0.540
CC8, 25%	5	3	0.587	1.89	0.595
CC10, 5%	10	6	0.644	1.82	0.491
CC12, 5%	3	3			0.968

[a] Values are obtained close to gelation concentration.

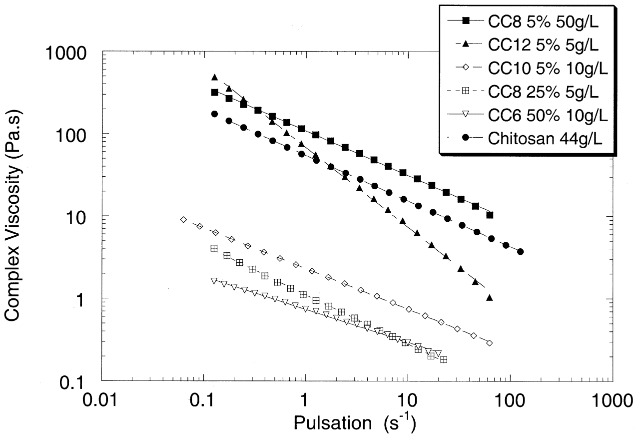

Fig. 9. Influence of pulsation on the viscosity of solutions of chitosan and chitosan derivatives close to gelation concentration. Determination of the power law index. (Solvent: AcOH 0.3 M/AcONa 0.05 M; $T = 283$ K).

system may be written as [71]:

$$n = d(d + 2 - 2d_f)/2(d + 2 - d_f) \quad (2)$$

where d ($d = 3$) is the spatial dimension and d_f is the fractal dimension which relates the mass of a molecular cluster to its radius of gyration by $R^{d_f} \sim M$. The values of the fractal dimension, calculated from Eq. (2) are given in Table 2. The value of the fractal dimension for the chitosan is higher than those of the hydrophobically modified chitosans. These findings indicate [70,72] that the incipient network of the chitosan is more tight than those of alkylchitosans. In this context the values of the intrinsic viscosities of these polymers suggest that the molecules of chitosan are more compact than those of the modified chitosans. It is possible that the introduction of hydrophobic chains produce a gel structure with some branches, giving rise to a more open network structure.

We have observed that the chitosan derivative solutions may have, according the concentration and the hydrophobicity of the polymer, a non-Newtonian behaviour. At low shear rates the viscosity is independent upon the shear rate, the solution is Newtonian. For higher values than a critical shear rate ($\dot{\gamma}_c$), the viscosity decreases and tends towards a power law variation:

$$\eta = K(\dot{\gamma})^{-p} \quad (3)$$

p being the power law index. It may also be obtained from dynamic rheological experiments from plotting the complex viscosity (η^*) as a function of the pulsation ($\omega = 2\pi\nu$, ν being the frequency) considering the Cox–Merz superposition. It is a positive value and the larger its value, the most non Newtonian behaviour it has. Related with this value is the behaviour of the fluid in flow conditions. When the value is high the flow behaviour is as plug flow and the fluid has very good properties of particle transport. It is very interesting in pipe cleaning applications for example or to avoid sedimentation of particles (case of xanthan gum). Values of this index, close to the gelation concentration, are given in Table 2 for chitosan and derivatives (from Fig. 9). At the gelation concentration (where $G'(\omega) \sim G''(\omega) \sim \omega^n$) we have $G^* = k\omega^n$ and hence $\eta^* = k\omega^{n-1}$ ($\eta^* = G^*/\omega$). Thus the values of power law index should be equal to $(1 - n)$. Only two of the samples (CC6, 50% and CC8, 5%) comply with this expectation. For other samples (which appear as the most hydrophobic) the power law index is higher than would be expected from the tabulated values of n. This is related with the presence of larger interactions in these latter (compared with other ones having a behaviour close to parent chitosan) leading to a departure from Cox–Merz superposition (different frequency dependence of η^* compared with the shear-rate dependence of the steady-flow viscosity). For CC12, 5% the very high power law index (0.968) is related with a very small value of the n exponent, the $G'(\omega)$ and $G''(\omega)$ curves being closely horizontal and meaning a gel-like behaviour. There are too much parameters involved (concentration, length of alkyl chain and degree of substitution) to determine a direct relationship between the power law index and the hydrophobicity. For the same alkyl chain, this index is increasing with the degree of substitution (even if the polymer concentration is decreasing) meaning increased transport properties. The CC8, 5% sample has very similar behaviour than chitosan up to their gelation concentration (around 35 g/l). CC6, 50% does not present strong intermolecular interactions at low concentration (see intrinsic viscosity and Huggins constant values in Table 1) but due to the number and the minimal length attained of the grafted chains these hydrophobic interactions increase with concentration to reach a similar behaviour than others at the gelation concentration, even if the power law index stays small. The CC12, 5% sample presents a peculiar behaviour. It is the most hydrophobic sample, from the rheological point of view, and it seems that the length of the grafted alkyl chain is an important parameter in the rheological behaviour of hydrophobically modified polysaccharides. But as the length of the alkyl chain is increasing, the maximal degree of substitution to keep soluble the sample is decreasing. Hence a compromise has to be reach to reach required properties.

3.3. Role of the temperature

It is well known that hydrophobic hydration is exothermic while hydrophobe–hydrophobe interaction is endothermic [73,74]. The results indicate that the interaction of interchain association of polymers is favoured by increasing the temperature, at least to an extent. As a consequence of these observations the role of the temperature on the rheological behaviour of polymer solutions was studied and the consequences on their applications. Newtonian viscosity η_0 may be written as containing at the same time a structure sensitive factor S and a mobility factor F_m [75]:

$$\eta_0 = S(M, \phi_v)F_m(\phi_v, T)$$

where M is the molar mass, ϕ_v the polymer volume fraction and T the temperature. S is related to the characteristics of the molecule and especially its structure when F_m depends upon the relative movement of this molecule to the solvent. The last term includes ξ, the friction coefficient per monomer unit. In all the rheological theories (Rouse [76], Zimm [77], de Gennes [78]) this friction coefficient is concerned. It is governed by the solvent in the dilute regime and by polymeric molecules in semidilute or concentrate regimes. All theories concerning the variation of the newtonian viscosity with the polymer concentration were developed for constant T and ξ parameters. To compare rheological experimental results with theories the experimental viscosities have to be corrected with the mobility effect, i.e. to work at constant ξ and study only topological effects. This correction may be obtained from the variation of ξ with the polymer concentration. Indeed the influence of the temperature on the viscosity may be expressed using the relation [71]:

$$\ln \eta_0 = A + E_a/RT + B/(T - T_\infty) \tag{4}$$

where E_a, B and T_∞ represent, respectively, the activation energy, a parameter depending of the expansion coefficient of the free volume and the Vogel temperature [79]. B is not relevant to the dependence of the viscosity on the temperature for the concentration range studied. The E_a/RT factor depends upon the concentration and contains, if it exists, the variation of the friction coefficient ξ with the concentration. To perform the corrections due to the variations of F_m with the polymer concentration, it is necessary to represent ($\ln \eta_0 - E_a/RT$) as a function of $\ln C$ knowing that E_a varies with the polymer concentration. This correction is valid only if the structure factor, that is to say the conformation does not depend upon the temperature. It was demonstrated previously that chitosan chains do not change their conformation in the studied temperature range [60].

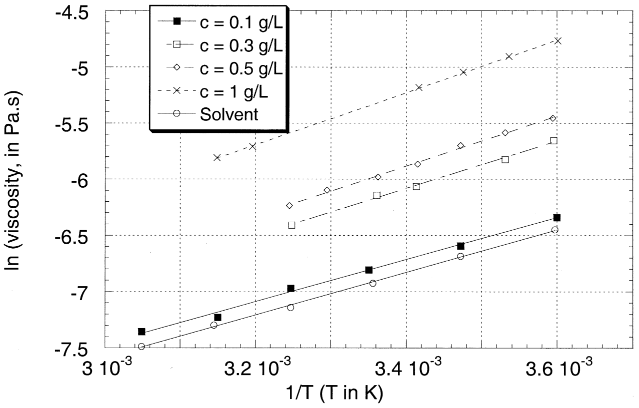

Fig. 10. Arrhenius dependence of the zero shear rate viscosity of CC10, 5% solutions. (Solvent: AcOH 0.3 M/AcONa 0.05 M).

To determine the activation energy at a given concentration the zero-shear rate viscosity has to be studied as a function of the temperature according to the Arrhenius law. Some solutions, depending on the concentration and the nature of the hydrophobically modified chitosan, do not present a Newtonian behaviour. In such cases when steady flow experiments were carried out the zero-shear rate viscosity was calculated from extrapolation using rheological models such as Cross or Carreau ones. When dynamic experiments were performed the complex viscosity at the lowest frequency (0.01 Hz) was considered. In Fig. 10 the variation of η_0 as a function of $1/T$ at constant polymer concentration was plotted for the CC10, 5% sample, as an example. The Newtonian viscosity follows an Arrhenius law in the temperature range from 278 to 323 K and the slope allows the determination of the activation energy. The variation of the activation energy with the polymer concentration was plotted in Fig. 11. For all the hydrophobically modified chitosans the curve $E_a(c)$ presents a maximum and for concentrations higher than this critical concentration the activation energy decreases indicating that the temperature has less influence on the viscosity of the solution. The concentration for maximal activation energy decreases as hydrophobicity increases. This threshold concentration is of the same order of magnitude than the gelation concentration determined from rheological experiments (Table 2). This behaviour may be explained by an increase of the rigidity of the chains or the decrease of their mobility due to an increase of the intermolecular interactions when the polymer concentration increases, as already observed on hyaluronan [80]. In our case the presence of hydrophobic interchain interactions explains the presence of this maximum. As a consequence it may be understood that the evolution of the polymer concentration at maximum activation energy is not monotonous with the length of the grafted alkyl chain. This concentration decreases significantly when passing from CC8, 5% to CC10, 5% and with further increase of the length of the substituted chain the decrease is less pronounced. The ability to build interchain interactions is better when the length of alkyl chains increases, at constant degree of

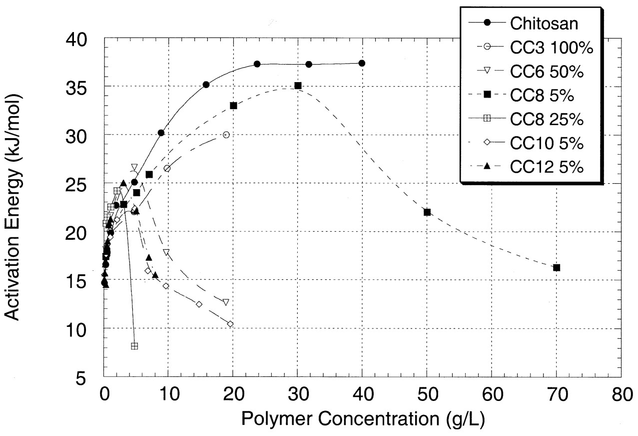

Fig. 11. Variation of the activation energy, E_a, with the polymer concentration. (Solvent: AcOH 0.3 M/AcONa 0.05 M).

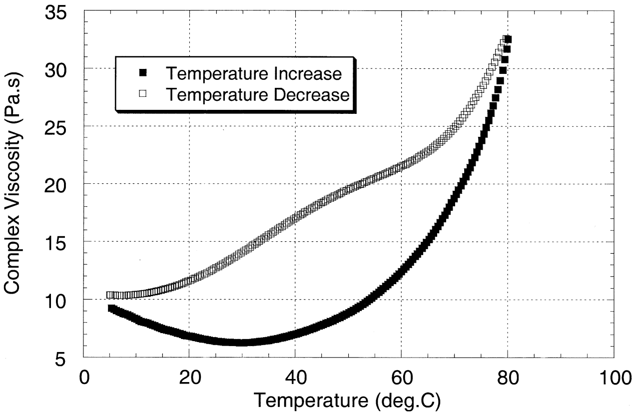

Fig. 12. Thermoreversibility of the evolution of the complex viscosity of CC6, 50% solution. (Solvent: AcOH 0.3 M/AcONa 0.05 M; $c = 2$ g/l; $\omega = 0.1$ Hz).

substitution. But when a critical hydrophobicity parameter is reached this gain is not so large due to the easiness these alkyl chains have to interact, related to their high flexibility making the formation of a physical network easier. For higher concentrations than the threshold concentration a peculiar behaviour with temperature may be expected. With chitosan derivatives bearing C_{10}-alkylglycoside branches Holme and Hall [52] have observed, at very high concentration (50 g/l) temperature-induced gelation (over 50 °C) with increased solution opacity, probably related to the 'cloud point' phenomenon that occurs at the monomeric level. The thermoreversibility of the observed interactions was first studied (Fig. 12). After heating and increase in the viscosity and elastic moduli, solutions recover initial viscosity upon subsequent cooling. A hysteresis appears due to the presence of interactions having a certain lifetime depending upon the considered temperature as already observed with methylcelluloses [81]. According to the structure of the derivative different behaviours may be observed (Fig. 13): an increase of the viscosity with temperature (as observed for CC6, 50%) or a constant value of the viscosity (CC12, 5% as an example), this viscosity value being adjusted with the polymer concentration (Fig. 14). The interest of such derivatives is the very low concentration at which such behaviour was observed (in the range of 5–10 g/l according to the hydrophobicity of the derivative) compared with, as an example, the methylcelluloses (of the order of magnitude of 10–50 g/l according to the molecular weight from 400,000 to 30,000 [82]). This may be due to the higher stiffness of the chitosan compared with the cellulose derivatives.

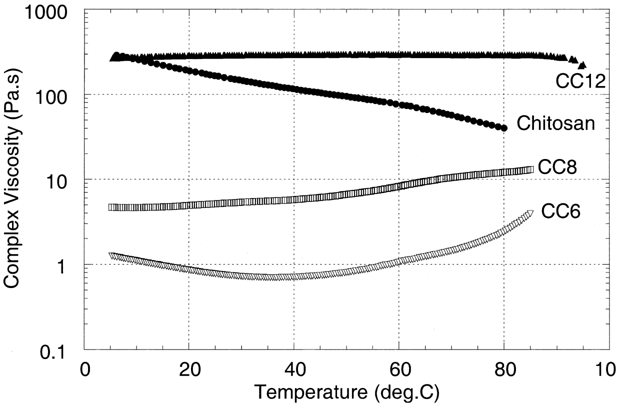

Fig. 13. Role of the structure of the alkylchitosan on the temperature-dependent rheological behaviour of polymer solution (▲) CC12, 5%, $c = 8$ g/l; (□) CC8, 12%, $c = 10$ g/l; (▽) CC6, 50%, $c = 10$ g/l; (●) Chitosan, $c = 53$ g/l; Solvent: AcOH 0.3 M/AcONa 0.05 M; $\omega = 0.1$ Hz.

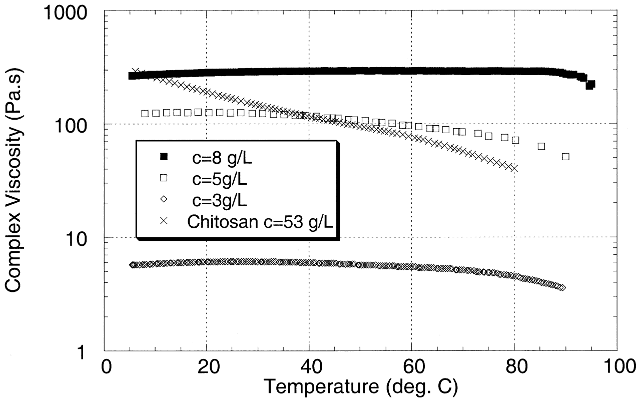

Fig. 14. Influence of temperature on the complex viscosity of CC12, 5% solutions. (Solvent: AcOH 0.3 M/AcONa 0.05 M, $\omega = 0.1$ Hz).

Taking into account this specific behaviour and the properties of natural polymers applications in food industry, cosmetics, but also petroleum ones may be investigated. As demonstrated previously, the chemical structure of the polymer can be adjusted to reach the required properties.

4. Conclusions

Chitosan may be chemically modified by reductive amination leading to the grafting of hydrophobic alkyl chains along the hydrophilic macromolecular chain. This allows to obtain amphiphilic polymers whose the hydrophobicity (or the hydrophile–lipophile balance, HLB) may be adjusted according the length of the grafted alkyl chain or the degree of substitution of the amine functions. The existence of hydrophobic interactions between the alkyl chains will improve the physico-chemical properties of the solutions of the modified chitosans. These properties are studied and the study is particularly focused on the influence of the polymer concentration and temperature on them and applications as rheology modifiers. Threshold concentrations, over which the polymer solutions have peculiar temperature behaviour, were defined. According to their structure it is possible to prepare solutions with constant viscosity or increasing one with temperature and allowing development of such derivatives in cosmetics, food or oil industries, for example, as rheology modifiers. But further work has to be carried out to define the existence of a pertinent parameter which determines the rheological behaviour of alkylated chitosans: is it preferentially the length of the grafted alkyl chain, the degree of substitution or we cannot dissociate these two parameters?

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