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Thermoreversible gels of chitin

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Gels of chitin have been obtained by heating solutions of the polymer in dimethylacetamide containing 5% of LiCl at $T > 90°C$. The sol–gel transition is reversible and its temperature depends on the polymer concentration and, to a lesser extent, on the molecular weight. Pretransitional effects were observed by viscometry. A possible interpretation of the results, in terms of polymer–solvent interaction and the thermodynamics of the transformation, is suggested. © 1997 Elsevier Science Ltd

INTRODUCTION

In this note we will deal with the gelation of chitin solutions in dimethylacetamide–5%LiCl (DMAc–5LiCl). The sol–gel transformation takes place reversibly on raising the temperature. Gelation phenomena due to both an increase or a decrease of temperature are known for different polysaccharides: for example, aqueous solutions of hydroxypropylcellulose at relatively high polymer concentration, give thermoreversible gels when T increases above 40°C (Werbowyj & Gray, 1980; Werbowyj & Gray, 1984; Làrez *et al*., 1995; Guido, 1995). On the other hand, amylose in dimethylsulfoxide–water mixtures gelifies reversibly at T lower than 30°C (Takeyama *et al*., 1993). Therefore, the influence of T on the stability of the sol phase depends on the polymer–solvent system. When the solvent power improves by increasing T, gelation may occur on cooling; the opposite, when the solvent power decreases with increasing T, gelation may occur on heating.

In any case, gelation depends on the development of a tridimensional network in the liquid phase. Intermolecular aggregates, crystalline or glassy microareas may act as crosslinking points of macromolecular chains. Gelation may also arise from a liquid–liquid demixing [spinodal mechanism (Olabisi *et al*., 1979) or, for mesogenic polymers, in the region of a wide biphasic gap (Flory, 1985)]. A high level of phase interconnectivity, together with the development of crosslinks inside the most concentrated phase, assures gel formation. However, the superimposition of several of the previously described phenomena often makes it difficult to interpret the gelation mechanism.

A few years ago we studied very dilute chitin solutions in DMAc–5LiCl: on uptake of moisture, of the order of 1%, gelation occurs (Bianchi *et al*., 1990). Further moisture absorption causes the formation of a film, which progressively shrinks. As the polymer concentration inside the film increases, chitin tends to organize spontaneously to a grandjean cholesteric structure, that is a structure having the cholesteric helix axis perpendicular to the surface of the sample. It was suggested that the self-assembly is due to the solvent, which gradually becomes poorer.

The possibility of obtaining gels of chitin using different methods of decreasing the solvent power is reported in this note.

MATERIALS AND METHODS

Two samples of chitin, obtained by steam explosion of a Chitobios Crangon-crangon commercial product, have been supplied by Stazione Sperimentale Cellulosa, Carta e Fibre (Milano, Italy).

Their characteristics are:

(1) Sample 1: $M_v = 300.000$; $[\eta]$ 15.3 dl/g in DMAc–5LICl at 25°C.
(2) Sample 2: $M_v = 480.000$; $[\eta]$ 21 dl/g in DMAc–5LiCl at 25°C.

Solutions of chitin at different concentrations have been prepared at room temperature under a nitrogen atmosphere, by mixing suitable amounts of polymer and solvent. After 2–3 days the solutions were purified by centrifugation at 15 000 rpm for 10–30 h in order to separate insoluble material (about 0.3%), Then the final polymer concentration was determined by a gravimetric method.

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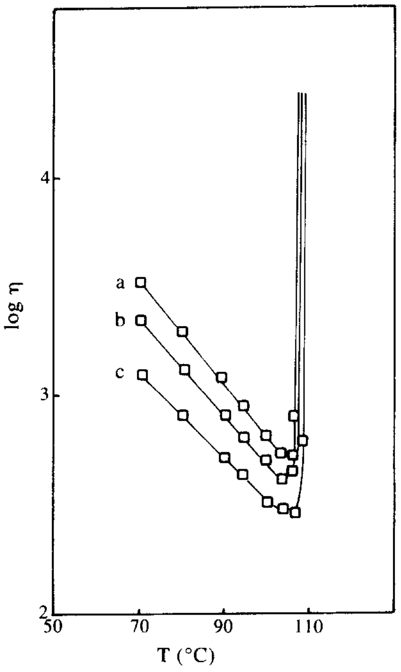

Fig. 1. Trend of η vs T for sample 2 ($C_p = 0.9\%$.w/w); a,b,c: first, second and third heating cycles, respectively.

Absolute kinematic viscosity η, as a function of the temperature, was measured using Cannon-Fenske viscometers. Depending on the η value, two viscometers having $k = 2.198$ and $k = 14.85$ were employed: the capillary diameters were 2.2±0.05 and 4±0.05 mm, respectively. The product kt (with t = flux time in seconds) gives the kinematic viscosity in centistokes. The flux time at the upturn of the η/T curves (a,b,c in Fig. 1) was: (a) 222.5 s; (b) 177 s; (c) 129.6 s. Temperature was varied between 30 and 130°C. Each experience lasted about 1–3 h.

Alternatively, tubes having diameter ~10 mm and length ~10 cm and containing about 3 ml of solution may be used for determining gelation temperatures at higher concentrations. The tubes were tilted up and down observing the flow of the solutions as T increases. T_{gel} was defined as the temperature at which the flow stops and the shape of the sample, inside the tube turned upside down, does not change after 1 h.

Thermal analysis has been performed by using a Perkin-Elmer DSC7 calorimeter. Heating rate was 20°C/min.

RESULTS AND DISCUSSION

When a solution of chitin in DMAc–5LiCl is progressively heated, its absolute viscosity η decreases to a minimum and then starts to increase and the complete gelation of the solution rapidly follows. No more than 2°C separates the minimum of T (incipient, gelation temperature $T_{i,g}$) from the temperature corresponding to the block of the solution inside the viscometer (T_{gel}). The maximum polymer concentration C_p which can be used is, in our case, about 3% (w/w). At higher C_p values, a calorimetric method may be used.

When a second and a third heating–cooling cycles are performed and observed by viscosimetry, a progressive shift of the η–T curve towards significantly lower η values occurs due to depolymerization, while T_{gel} decreases no more than 1–2°. Thus, M_v has little effect on T_{gel} (Fig. 1).

This point is substantiated by the data in Table 1. From these data, the trend T_{gel} vs C_p is shown in Fig. 2. Again it is seen that T_{gel} is influenced little by M_v. When C_p increases T_{gel} decreases, a ΔC_p of about 4% causes a ΔT_{gel} of about−25°C. T_{gel} values obtained by using different techniques fall on the same curve, confirming the consistency of the different experimental methods.

Figure 3 shows the endothermic peaks (a) and (b), concerning the first and the second heating processes of a solution of sample 2 at $C_p = 4.9\%$, respectively.

The cooling curve between two successive heating scannings was registered. A broad exothermic peak, spread on a range of about 40°, appears at about 60° below T_{gel}. It further confirms the reversibility of the sol–gel transition. Also evident from the figure is a good reproducibility of the endothermic peaks. The range of

Table 1. Trend of T_{gel} vs C_p

Sample	C_p (w/w, %)	T_{gel} (°C)	Method
1	0.6	115	Viscometer
1	0.98	108	Viscometer
1	1.7	103	Viscometer
1	2.7	97	Viscometer
1	2.7	96	Tube
2	0.9	109	DSC
2	0.9	107	Viscometer
2	1.1	104	Tube
2	4.9	94	DSC

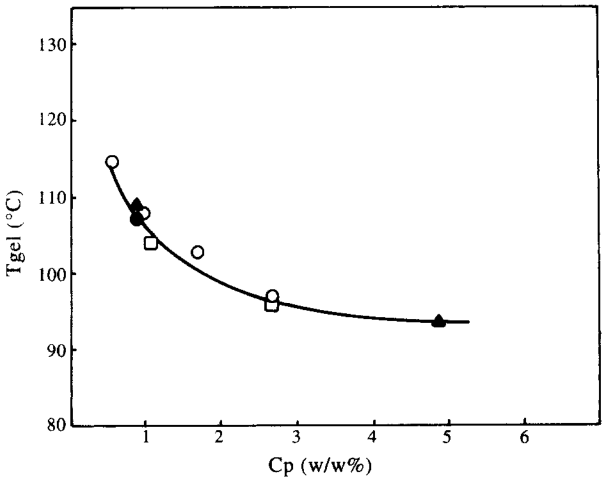

Fig. 2. T_{gel} vs C_p: ○, □, △, viscosymetric measurements, test tube and calorimetric analysis, respectively. Sample 1 open points, sample 2 full points.

T of the transformation is relatively wide and superimposes the narrow range observed by viscosimetry. However, we have to take into account that the calorimetric heating lasts about 6 min, against 1–3 h of the viscosimetric experiments.

The area under the two peaks, on Fig. 3 ($C_p = 4.9\%$), gives the variation of enthalphy associated with the transition: $\Delta H = 15.1\,\mathrm{J/_{g\text{-}chit}}$ and $\Delta H = 14.3\,\mathrm{J/_{g\text{-}chit}}$ correspond to the peak (a) and (b), respectively. When C_p is lowered, ΔH increases: at $C_p = 0.9\%$, $H = 20\,\mathrm{J/_{g\text{-}chit}}$. A similar result has been obtained by Robitaille *et al.* (1991) during the heating process of isotropic and biphasic solutions of hydroxypropylcellulose in water. The phase transition observed at 40°C shows positive ΔH values which increase as C_p decreases. According to the authors the phenomenon only concerns the isotropic phase and reflects the melting of the water structure around the hydrophobic regions of the chains.

By analogy we believe that the the breaking of the links between the DMAc–LiCl complex and the chitin repetition units causes the endotermicity of the sol–gel transition.

The last result concerns the existence of pretransitional sol–gel phenomena. When the viscosity of a solution, maintained at a few degrees below $T_{i,g}$, was measured as a function of time, a progressive increase of its initial value occurred. Table 2 reports, as an example, the data for a solution of sample 2 at C_p 0.9% and $T = 104.5$°C.

A quicker increment of η occurs when T is closer to $T_{i,g}$. In order to attempt a hypothetical explanation of these complex results, it is useful to recall some properties of chitin: light scattering measurements performed a few years ago by some of us (Terbojevich *et al.*, 1988, 1996) demonstrated that chitin is a semirigid polymer with a persistence length of about 200 Å, that is about twice the value of cellulose (Bianchi *et al.*, 1985). Moreover, the polymer shows two peculiar properties: at low M_v ($[\eta] < 10\,\mathrm{dl/g}$) intermolecular aggregates are always present, even at $C_p \rightarrow 0$ (Terbojevich *et al.*, 1996). Notwithstanding the chain rigidity, we never found a trace of mesophase in DMAc–7LiCl, even at C_p close to the solubility limit ($C_p \sim 15\%$) (Bianchi *et al.*, 1995), which is about 25–30% higher than the limit concentration for the mesophase appearance in the case of cellulose.

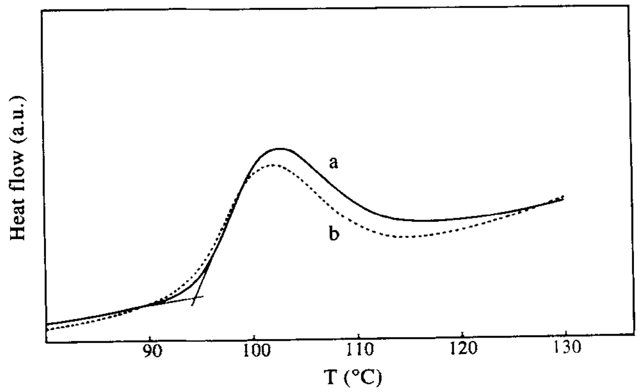

Fig. 3. DSC analysis of sample 2, $C_p = 4.9\%$ w/w, scanning rate 20 K/min. a and b first and second heating cycle, respectively.

Table 2. Viscosity of sample 2 at $C_p = 0.9\%$

Time (min)	η (centistokes)	Log η
0	309	2.49
20	316	2.50
40	355	2.55
60	417	2.62
80	501	2.70
100	603	2.78
120	776	2.89
140	977	2.99
160	1175	3.07
180	1202	3.08
200	1260	3.10
220	1260	3.10
240	1260	3.10
260	1260	3.10
280	1260	3.10
300	1260	3.10
320	1260	3.10
340	1260	3.10

While the tendency to give aggregates at low M_v is common to other polysaccharides, the lack of mesophase formation cannot so easily be explained. In the mentioned reference (Bianchi *et al.*, 1995), we suggested the development of side to side aggregation as the polymer concentration increases, with a concomitant reduction of the chain axial ratio and the impossibility of observing any mesophase. If we now try to relate these behaviours with our last results, the simplest sequence of events during heating process could be the following: increase of T causes, first of all, a decreasing of the solvent power. In fact, as previously observed,the complex between DMAc and LiCl which solubilizes chitin is progressively destroyed by increasing T. This fact enhances the tendency to form intermolecular aggregates, which are consequently stabilized from an increase of T. The increasing of polymer concentration acts, of course, in the same way.

A given chitin chain may participate in the aggregation at different points: when a partial crystallization occurs, the tridimensional network becomes stable and self-supporting. In any case, dimension of crystalline areas must be very small, as the gels are transparent.

A qualitative interpretation of the endotermicity of the gelation may be attempted. When gelation is characterized by $\Delta H > 0$, ΔS must be positive for $\Delta G < 0$. During the network formation, polymer–polymer interactions become dominant and solvent molecules are released, accounting for the increase of entropy during the transformation. This provides an endothermic term which may overcome the exothermic contributions to ΔH.

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