

Thermogelation of methylcelluloses: new evidence for understanding the gelation mechanism

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Methylcelluloses are widely used for industrial purposes due to their peculiar properties. These are the consequence of associative behaviour due to hydrophobic interactions involving highly substituted units. The properties of commercial samples with heterogeneous distribution of the substituents and laboratory-made samples, with a more homogeneous distribution, are compared to allow a better understanding of the thermogelation process of methylcelluloses. Whatever the structure (degree of substitution, repartition of substituents and presence or not of highly substituted units) the same steps occur during this process, but the physicochemical observations (critical temperatures of physical changes for example) depend upon this structure.
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INTRODUCTION

Natural or synthetic hydrophobically modified water-soluble polymers are widely used to control the rheological properties of aqueous-based formulations in numerous industrial domains, such as paints, oil recovery, cosmetics or foods^{1–3}. Their associative properties arise from intermolecular interactions between the hydrophobic substituents which are usually in the form of side chains or terminal groups. A loose tridimensional network may develop leading to a large viscosity increase.

For synthetic polymers, the large variety of behaviours observed are now qualitatively understood in terms of nature, number and length of the hydrophobic substituents and also in terms of distribution along the backbone.

In contrast natural derivatives such as hydrophobically modified cellulose, which belong to this class of associating polymers, suffer from a lack of fundamental physico-chemical studies. The difficulty arises mainly in the absence of model polymer with a precise distribution of the substituents. Nevertheless a large number of investigation was done on the commercially available polymers to characterize their ability to form a gel on heating which melts again on cooling. Methylcellulose (MC) is the simplest cellulose derivative known for a long time. Commercial methylcellulose (MC) is a heterogeneous polymer consisting of highly substituted zones called 'hydrophobic zones' and less substituted ones called 'hydrophilic zones'⁴. Due to these unusual properties, most of the experimental works reported in the literature was dedicated to the evolution of viscosity and turbidity of MC solutions during heating and cooling cycles in a small polymer concentration range (10–25 g/l)^{5,6}. The behaviour of this polymer is not monotonous when the temperature varies: the viscosity of a semi-dilute solution decreases

when temperature is increased up to a critical value over which the viscosity increases. Then, the formation of a gel may be observed and this phenomenon is associated with a turbidity, indicating phase separation⁵. All these phenomena are thermoreversible.

Very few studies have been performed on the evolution of the methylcellulose solutions and their thermodynamic behaviour with temperature, in a large concentration range. As a consequence it remains some controversy regarding the mechanism of gelation and specially on the nature of junctions involved during this gelation. Moreover, it is not known how the chemical structure (repartition of the substituents along the macromolecular chain) plays a role on the solution behaviour. Finally the weak knowledge of relations between the molecular structure and the macroscopic behaviour of these polymers prevents the improvement of these industrial products.

In this work, the properties of commercial samples with heterogeneous distribution of the substituents and laboratory-made samples, with a more homogeneous distribution, are compared to allow a better understanding of the thermogelation process of methylcelluloses.

EXPERIMENTAL

Commercial samples of methylcelluloses were kindly supplied by Dow Chemical company under the trade name Methocel A4C. Laboratory made methylcellulose samples (M12, M15, M18, M22, M29 and S23) were prepared according to an original procedure⁷ based on a previously proposed methylation method⁸.

The aqueous solutions were prepared by dissolution of freeze-dried methylcelluloses in water at 5°C during 24 h to assure a complete dissolution.

The cloud point is determined visually using solutions which are heated in a thermostated bath to the required

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temperature⁹. As the process of separation can be very slow, tubes were left in the bath for about 1 week at each temperature. The onset of the appearance of slight turbidity was visually determined by comparison with a tube containing a cold solution at the same concentration. After these observations the bath temperature was increased and the process was repeated. The cloud point temperature we have determined in this way corresponds in fact to the temperature for which about 95% of the light is transmitted as checked on a spectrophotometer at 600 nm.

The rheological measurements are performed with a Couette type rheometer (Contraves Low Shear 40) or a stress-controlled rheometer (Carrimed CS50) according to the concentration and the temperature of the sample.

From these techniques the phase diagram was determined.

The calorimetric experiments were carried out with a Micro DSC III calorimeter from Setaram. The temperature rate is 0.5°C/min.

The fluorescence spectra were obtained using a LS50B luminescence spectrometer from Perkin-Elmer. The experiments were carried out in the temperature and concentration domains where no turbidity was observed. The pyrene concentration was 10^{-7} M due to its low solubility in water and the excitation wavelength was 334 nm.

The quasi-elastic scattering measurements were performed using the ALV apparatus equipped with an automatic goniometer table, a digital ratemeter and a temperature-controlled cell. The scattered light of a vertically polarized 488 nm argon laser (from Spectra Physics model 2020, 3 W operating around 0.3 W) was measured.

Steric exclusion chromatography (SEC) experiments were carried out at controlled temperatures on methylcellulose (MC) aqueous solutions using pure water as eluent and the multidetection equipment described previously¹⁰.

¹³C n.m.r. measurements were realized on a Bruker AC300 spectrometer using DMSO-d₆ as solvent at a temperature of 80°C when the structural determination was done. For studying the gelation mechanism (Figure 6) the A4C methylcellulose was dissolved in D₂O.

RESULTS AND DISCUSSION

Behaviour of the A4C commercial sample

The repartition of the different units of the A4C commercial sample is presented in Table 1. Due to

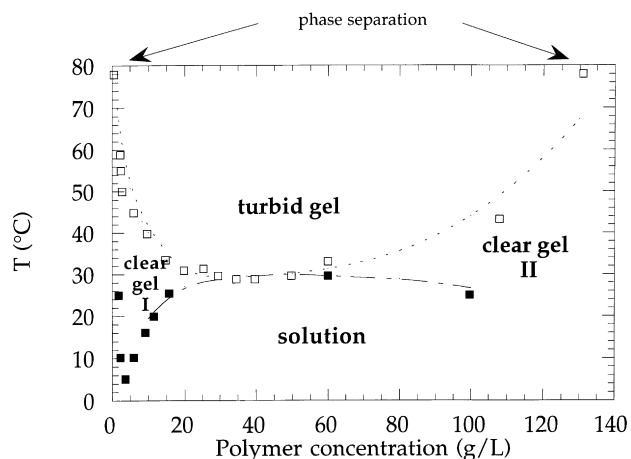


Figure 1 Phase diagram of an aqueous A4C methylcellulose (DS = 1.7) solution including the cloud point curve (□) and the sol-gel line (■) determined from oscillatory measurements

heterogeneous reaction and non-equireactivity of the three hydroxyl groups to the reagent, methylation was different from one monomeric unit to another, along the chain but also from one chain to another. Hence the degree of substitution (DS) which is one of the parameter characterizing the structure of the macromolecular chain was an average value. This heterogeneity was detected by different authors^{11,12} who have revealed properties which can be explained only by heterogeneous structure of MC. This was demonstrated by Arisz *et al.*⁴ who concluded the presence of highly and weakly substituted units along the chain from the comparison of the degree of substitution (DS) of oligomers obtained by MC fractionation and the DS of oligomers calculated from the assumption of homogeneous reaction and equireactivity of hydroxyl groups. MC cannot be considered as a statistical copolymer but as a complex multiblock copolymer. Moreover, it was found the presence of few carboxylic groups along the chain at a concentration of 2.9×10^{-3} equivalent per monomeric unit meaning three carboxylic groups per 1000 monomeric units¹³.

Phase diagram. The phase diagram⁹ (Figure 1) is very complex. A cloud point curve was observed, indicating that the aqueous MC solution presents a LCST-type phase separation and this curve can be considered as the binodal curve with a minimum corresponding to the critical point ($T_c = 29 \pm 2^\circ\text{C}$, $C_c = 45 \pm 5$ g/l). A well-known system presenting a LCST is poly(ethylene oxide) in water¹⁴. Relations between LCST temperature and hydrophobic interactions were examined in literature¹⁵. By using the critical concentration determined from the phase diagram and from Flory theory¹⁶ developed for monodisperse polymer solutions the number of monomers per chain can be calculated using the critical volume fraction and hence, taking into account the polymolecularity index, the weight average molecular weight is found in good agreement with Sarkar⁶ ($M_w = 140\,000$ g/mol) and Hirrien *et al.*⁷ ($M_w = 149\,000$ g/mol) values. Below this curve a clear homogeneous phase was present, while above, the phase separation was incomplete due to the superposition of a gelation process. The gelation was all the more slowed down because the gap to the binodal curve was small. From a structural point of view the phase separation associated to the gelation led to a large increase of the small-angle neutron intensity which expresses the formation of aggregates. Using a Debye and Bueche approach it seemed that, at 55°C, the size of the domain first increased in the low concentration range then decreased when the concentration still rises¹⁷. This phenomenon demonstrates the competition between the phase separation leading to polymer-rich regions, and the gelation which prevents the mobility of chains, hence the growth of dense zones. From these results, a large part of this upper domain seemed to be a macroscopic homogeneous

Table 1 Characterization of some methylcelluloses prepared

	Sample						
	A4C	M22	M15	M12	M29	M18	S23
DS ^a	1.7	1.2	1.3	1.5	1.7	2.2	1.3
% NonS	10	9	9	5	4	9	16
% MonoS	29	68	63	51	45	12	47
% DiS	39	19	21	29	32	36	36
% TriS	22	4	7	15	19	43	—

DS, degree of substitution; NonS, non-substituted; MonoS, monosubstituted; DiS, disubstituted; TriS, trisubstituted

^aDetermination by ¹³C n.m.r. in DMSO-d₆ (353 K)

turbid gel. An actual phase separation was observed only for low concentration and at a temperature higher than 70°C.

This LCST behaviour is similar to ethylhydroxyethylcellulose (EHEC) for which a minimal critical temperature of 34°C was found¹⁸. As was observed from light scattering and rheological experiments¹⁹ our system, above the LCST, is always evolving due to the gelation process which increases the time necessary to reach the equilibrium. Even with a rate of 0.016 deg/min, a gap of 10° was observed, the trouble point for a polymer concentration of 26 g/l being equal to 42°C with a temperature ramp and only 31.5°C when the temperature is fixed during 1 week.

Moreover, the homogeneous domain appeared to be very complex. It was constituted by two gel phases separated by a sol phase. In the dilute regime there was no gel formation, or for very high temperatures there was direct phase separation. From dynamic light scattering experiments we have demonstrated¹⁹ that there was only one population of isolated molecules with a hydrodynamic radius of 20 nm for temperatures lower than a critical value for which another type of molecules with a hydrodynamic radius larger than 200–300 nm appears. For a polymer concentration of 0.2 g/l this critical temperature was around 55°C, and at 60°C the aggregation number was estimated to 200, indicating that around 5% by weight of the material is aggregated¹³. As a consequence the MC solution is, at low temperature and low polymer concentration, an actual solution without any aggregate and this observation was confirmed from SEC experiments¹⁹.

Rheological experiments at equilibrium. We have studied the evolution of the system with the temperature using different techniques, such as n.m.r., rheometry, calorimetry and fluorescence spectroscopy. For low concentration solutions ($c < 20$ g/l) rheological experiments were carried out on MC solutions at equilibrium and within the linear regime in order to determine the sol–gel transition temperature. For a given concentration it was found⁹ that the sol–gel transition observed as temperature increased was well described by a percolation process²⁰. Indeed, at low temperatures, the mechanical spectra was characteristic of a pure viscous solution: the storage modulus $G'(\omega)$ increased like ω^2 and the loss modulus $G''(\omega)$ like ω^1 . At higher temperature, $G'(\omega)$ initiated a plateau in the low frequencies range and intercepted $G''(\omega)$ at a cross-over frequency ω_0 where $G''(\omega_0)$

$= G'(\omega_0) = G_x$. As temperature increased, G' increased and ω_0 went to higher frequencies. The $G_x(\omega_0)$ follows a power law with an exponent Δ equal to 0.76 ± 0.04 (Figure 2) and $\omega_0 = f(T)$ was described by the power law:

$$\omega_0 = (T - T_{\text{gel}}/T_{\text{gel}})^z$$

with a z value equal to 2.6 ± 0.2 and $T_{\text{gel}} = 6 \pm 1^\circ\text{C}$. The Δ and z values were close to values obtained with other systems as different as silica alkoxide²¹ or pectins²². At high concentration (89 g/l) the sol–gel transition was a time-dependent process. It is no longer possible to determine the transition, because the mechanical spectra in the frequency range tested were complex and dominated by the relaxation time of entangled molecules.

Within the intermediate concentration range, whatever the temperature below the phase separation temperature, the viscoelastic behaviour was governed by only one relaxation time in the frequencies range observed, as shown in Figure 3a, the solid line corresponds to the fit by the simplest model of viscoelastic behaviour: the Maxwell model. From the temperature dependence of η_0 (viscosity on Newtonian plateau) an activation energy of 14 kJ at 298 K was obtained which is lower than the value obtained with HEUR²³, but of the same order of magnitude of non-associative polymers. It may be assumed that this activation energy is related with non-associative blocks of the polymer chain.

The increase of the concentration in these systems leads to the appearance of a second relaxation mode at low frequencies, and at high frequencies to the appearance of a distribution of the relaxation times as shown in Figure 3a,c where the solid line corresponds to the fit with a Cole–Cole distribution²⁴. The maximum of $\eta''(\omega)$ evolves towards higher frequencies as the polymer concentration increases in contradiction with the evolution, predicted by the reptation theory for polymer in the semi-dilute regime²⁵. These results may be interpreted as the signature of more and more inhomogeneities which superpose to chain entanglements in semi-dilute regimes and which appear when the temperature and/or the concentration increased. Then the gel(I)/sol transition would be due to the appearance of the heterogeneities which, generating high local concentrations, lead the system below the percolation threshold of the former aggregates. This transition was completely reversible in temperature as well as in concentration at a fixed temperature.

Rheology during temperature sweep. Oscillatory shear experiments at a fixed frequency (1 Hz) were carried out during temperature sweep, and a typical curve for A4C sample is presented in Figure 4. For a concentration larger than 2.5 g/l the evolution of the storage modulus G' showed two distinct waves. At low temperature the solution was clear, and in the range 30–50°C a weak gel appeared. In this temperature range, the solution became progressively turbid (depending upon the polymer concentration). Then, an elastic, turbid gel with a large increase of viscosity was observed over 60°C within the experiment time scale. The second wave, at high temperature, was more pronounced with the highest polymer concentration solutions. The 2.5 g/l concentration (which corresponds to $c[\eta] = 1.27$ at 25°C) may be considered for the A4C sample as the critical polymeric concentration needed for gelation. Curiously, the magnitude of G' within the first wave at low temperature was apparently independent of the polymer concentration.

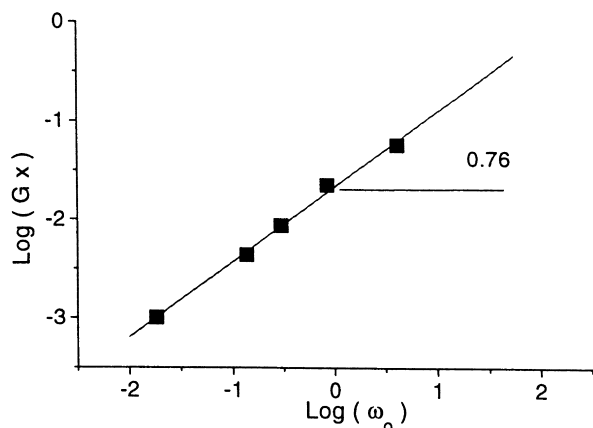


Figure 2 Shear modulus $G_x = G''(\omega_0) = G'(\omega_0)$ with respect to the cross-over frequency ω_0 . The straight line has a slope $\Delta = 0.76 \pm 0.04$ (A4C; DS = 1.7; $c = 9$ g/l)

The gelation phenomenon was time dependent¹⁹ and reversible. After gelling upon heating, aqueous methylcellulose solutions were recovered upon subsequent cooling and the values of the moduli were the same at 20°C before and after the thermal treatment (Figure 5). A large hysteresis was observed, meaning that the redissolution of

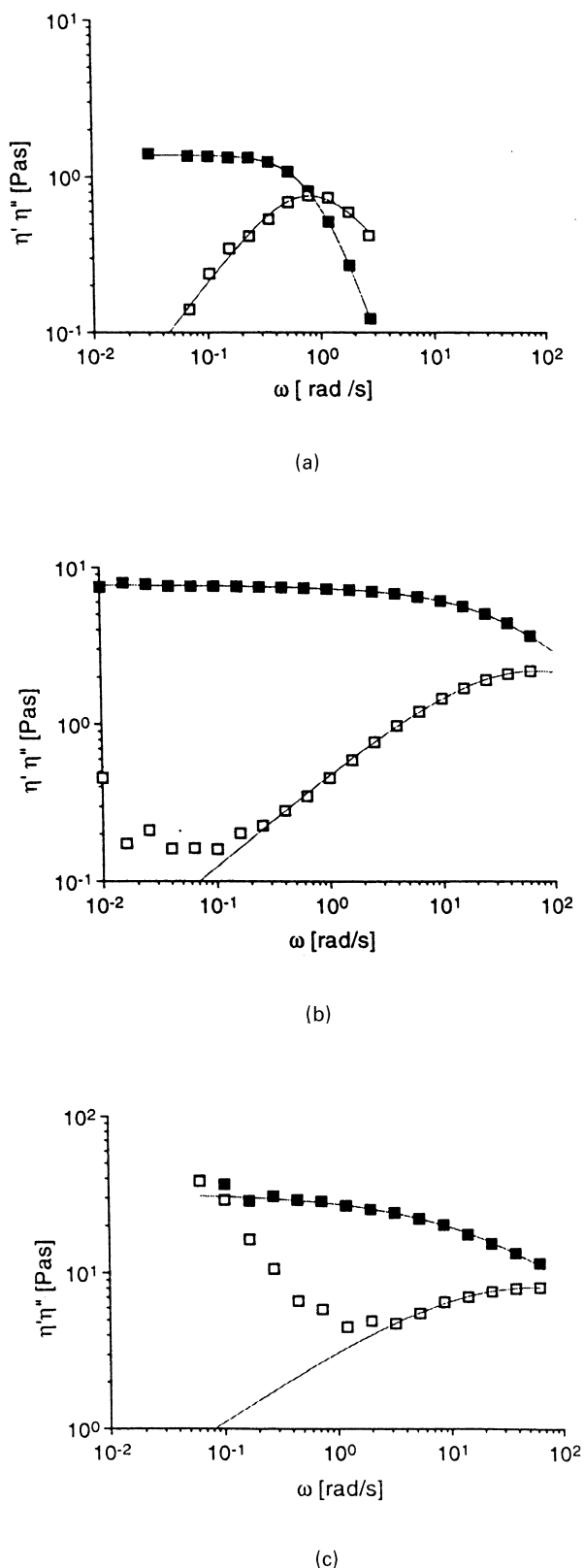


Figure 3 Dynamic viscosity curves for A4C sample: η' (■), η'' (□). (a) $c = 25.67$ g/l, $T = 10^\circ\text{C}$; (b) $c = 40$ g/l, $T = 12^\circ\text{C}$; (c) $c = 60$ g/l, $T = 15^\circ\text{C}$

the polymer network at a fixed temperature was less favourable than gelation from an energetic point of view. This hysteresis appeared only when the maximum heating temperature was higher than 35°C for a polymer concentration of 20 g/l. The larger this maximum heating temperature, the larger the hysteresis. Over this critical temperature (around 40°C for a polymer concentration of 20 g/l) interactions occur leading to gelation. As a consequence of the increase of these interactions when the temperature is increased we can assume that these interactions are hydrophobic in nature.

Clues for hydrophobic interactions. When ¹³C n.m.r. experiments were carried out (Figure 6) on an A4C solution at a concentration of 44.6 g/l, a decrease of the peak intensities was observed for temperatures higher than 50°C, which was characteristic of a progressive decrease of the mobility of the chains. The peaks for which the intensity decrease was firstly observed correspond to signals attribu-

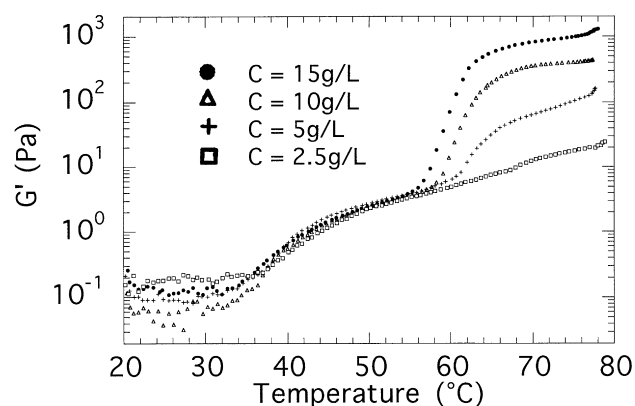


Figure 4 Influence of the polymer concentration and the temperature on the elastic modulus of A4C solutions (G' (Pa) modulus at 1 Hz; DS = 1.7; solvent, water)

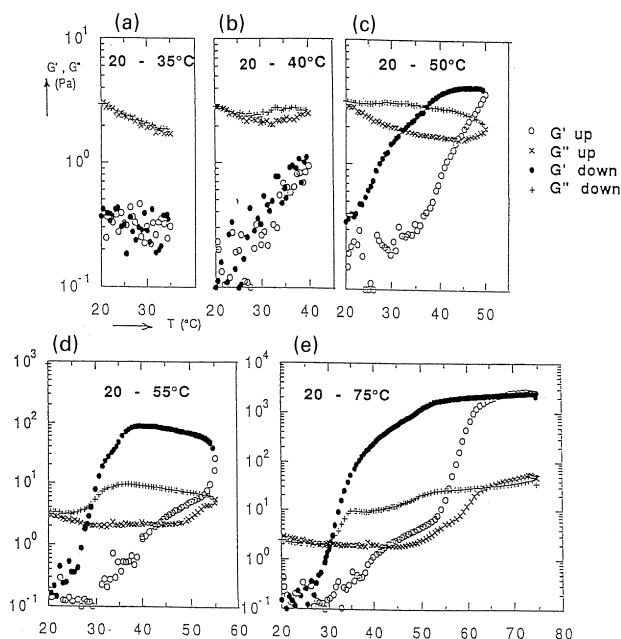


Figure 5 Evolution of G' and G'' for A4C solutions ($c = 20$ g/l) for different temperature cycles (temperature rate, 0.5 deg/min). (a) 20–35–20°C; (b) 20–40–20°C; (c) 20–50–20°C; (d) 20–55–20°C; (e) 20–75–20°C

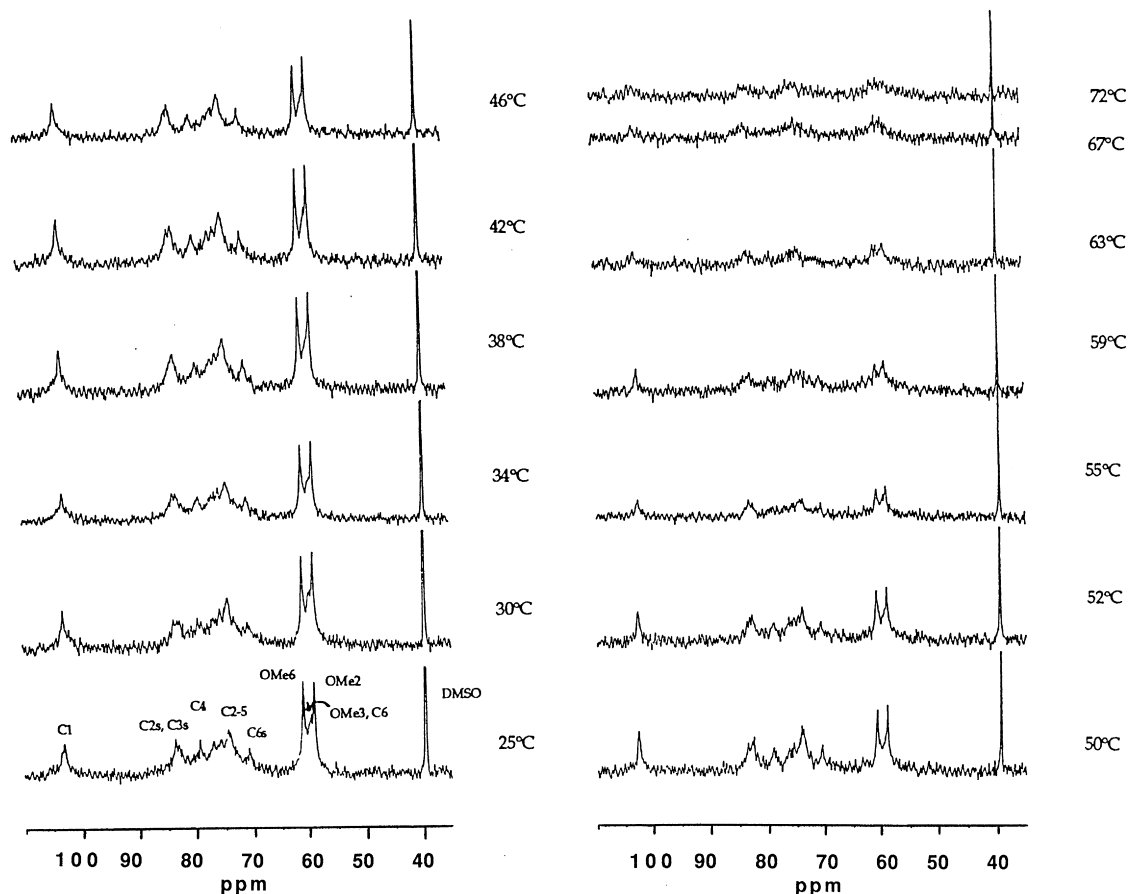


Figure 6 Evolution of ^{13}C spectra as a function of temperature for A4C solutions ($c = 44.6 \text{ g/l}$) in D_2O (DMSO as reference)

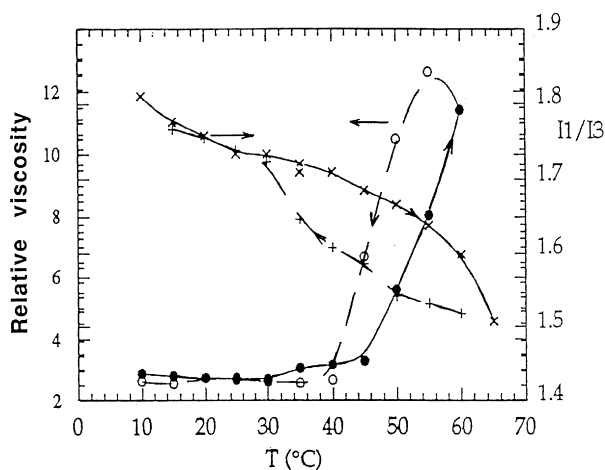


Figure 7 Influence of temperature on fluorescence (I_1/I_3 ratio) and relative viscosity for A4C methylcellulose (DS = 1.7; solvent, water; $c = 2 \text{ g/l}$) during a temperature cycle: ● and ×, on heating; ○ and +, on cooling)

ted to carbon atoms from methyl groups. This confirms interactions between hydrophobic groups.

The presence of interactions has been observed also using fluorescence spectroscopy. Pyrene was used as a probe, as the vibrational structure of its fluorescence emission spectrum is very sensitive to the polarity of its environment²⁶. The ratio between I_1 and I_3 , respectively, the intensities of the first (at 373 nm) and third (at 383 nm) peaks of the fluorescence emission spectrum is equal to 0.6

in hexane and 1.9 in water. Experiments were performed up to a temperature at which turbidity was observed. For A4C in water this ratio was equal to 1.8 at 10°C, meaning that pyrene was in a polar environment, and decreased quickly for temperatures higher than 50°C, indicating the formation of hydrophobic domains in which pyrene remains (Figure 7). A hysteresis was present on cooling as a consequence of these interactions. The rheological behaviour of this solution was compared with the fluorescence data, and interactions were demonstrated from the increase of viscosity during heating (Figure 7). There is a 10°C displacement in the departure of the observation of interactions due to shear in rheology which disrupts weak interactions.

Calorimetric experiments were carried out on the A4C sample. When heating, an endothermic peak was observed and two exothermic peaks were present during cooling (Figure 8). Only the energy of interaction associated with the phase separation (and the large increase in viscosity) was observed on heating. It was necessary to heat up first to 50°C to observe a peak at 30°C on cooling, and to 65°C to observe a peak at 40°C. The position of these peak maxima change rapidly for the lowest heating temperatures and stabilize for highest temperatures. It showed that there is a defined temperature for which interactions occur and develop in good relation with the rheological observations. The number of these interactions increases with temperature as revealed by the increase of G' . These two peaks on cooling seemed to correspond to interactions of different nature: the peak at 30°C being related with interactions involving highly substituted units and the other one to less substituted units.

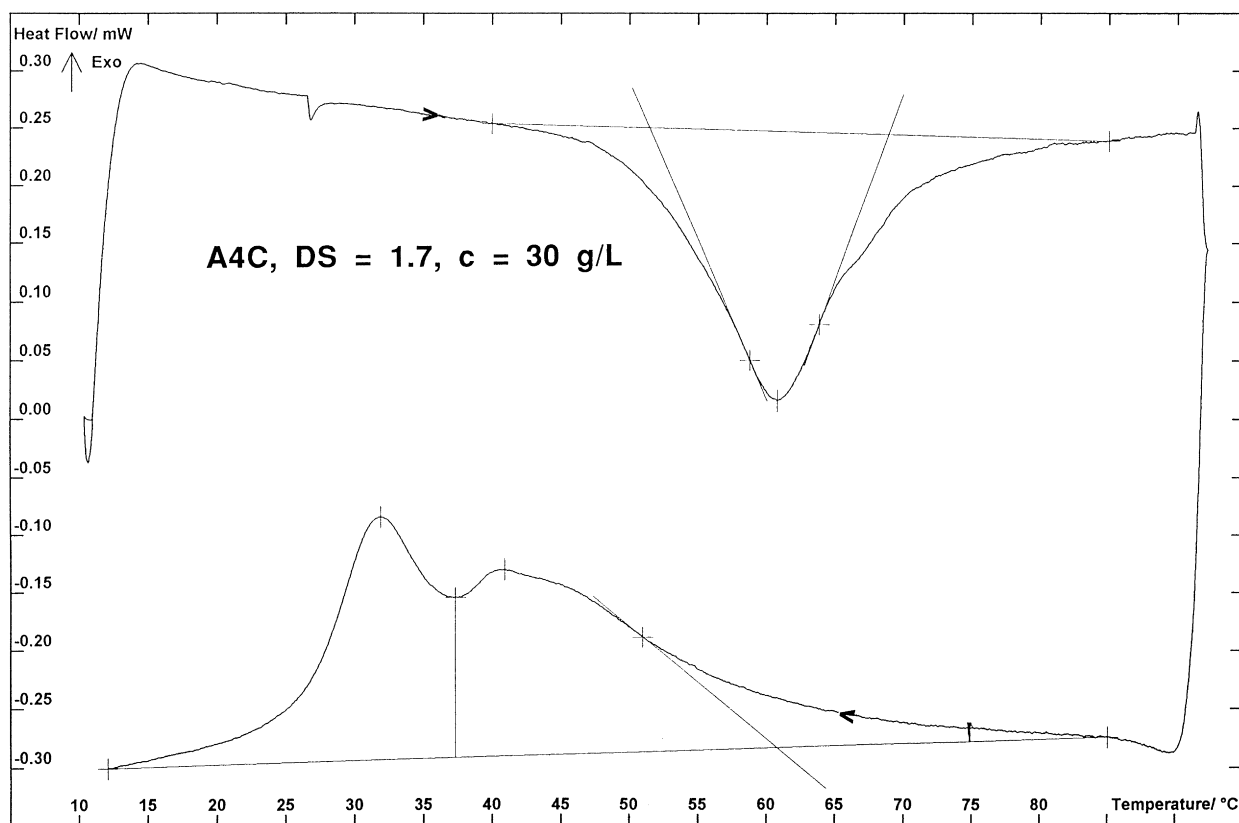


Figure 8 Calorimetric thermograms of aqueous solution of A4C methylcellulose (DS = 1.7; $c = 14.75$ g/l; temperature rate, $0.5^\circ\text{C}/\text{min}$)

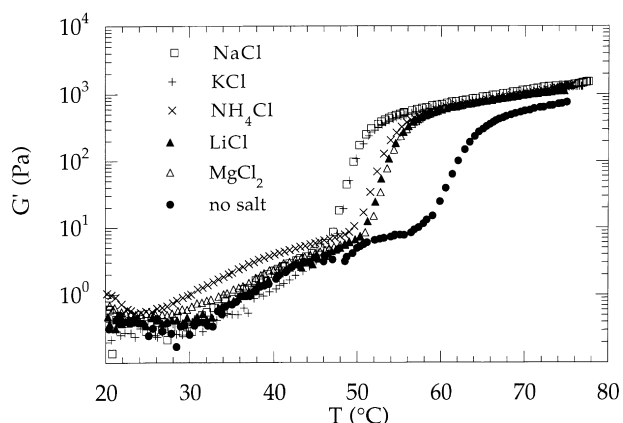


Figure 9 Influence of the nature of the salt on the G' evolution of A4C aqueous solution ($c_{\text{polymer}} = 10$ g/l; $c_{\text{salt}} = 0.5$ M)

The hydrophobic nature of the interaction is finally proven by the influence of salts (Figure 9). The gelation temperature depends on the nature of cations and anions used according to the Hofmeister series²⁸.

Comparison with homogeneous MC systems

Influence of the degree of substitution (DS). From steric exclusion chromatography experiments performed on different MC samples, several peaks reflecting the presence of different types of molecules in solution¹⁹ were observed. The quantity of polymer really eluted through the columns is indeed a good indication of the formation (or not) of aggregates retained at the front of the column when the temperature increases. The ratio between m_c , the eluted weight calculated from the area of the refractive index peak and the refractive index increment, and m_i , the injected

weight of sample, is a good indication of the ratio of polymer which is eluted. The smaller this ratio, the larger the weight fraction of aggregates. At low temperature this ratio is close to 1, indicating that all the polymer is eluted confirming the methylcellulose solution is a true solution. Two behaviours were obtained according to the DS values. For DS smaller than 1.5 this ratio does not vary significantly, while for DS larger than 1.5 this ratio is much decreased above 45°C . For temperatures higher than this value, interactions occur leading to the formation of aggregates.

Influence of the substituent distribution. The influence of the substitution distribution and of the DS values was studied further using the same rheological procedure as for the A4C sample (Figure 10). With the low DS samples (DS < 1.5) only one wave was observed, with a slight increase of G' with temperature. For the sample without trisubstituted units (S23), G' stays constant with temperature and G'' decreases following the viscosity of the solvent. The presence of hysteresis was also observed in relation with the presence of cooperative interchain interactions, except for the S23 sample. Furthermore, the temperature for which G' is equal to G'' is shifted towards higher temperatures. We had the same observation for a homogeneous methylcellulose sample with a similar degree of substitution than A4C sample (1.7). Moreover, it was revealed that a sol-gel transition may be observed even with methylcellulose samples prepared from an homogeneous process in discordance with many authors²⁹. But, for the sample with the highest DS value (2.2) a similar behaviour to that of A4C was observed with the presence of two waves on the evolution of G' in the studied temperature domain. With this degree of substitution, the proportion of trisubstituted units was relatively high and the presence of blocks of such units may be suspected. When temperature cycles of

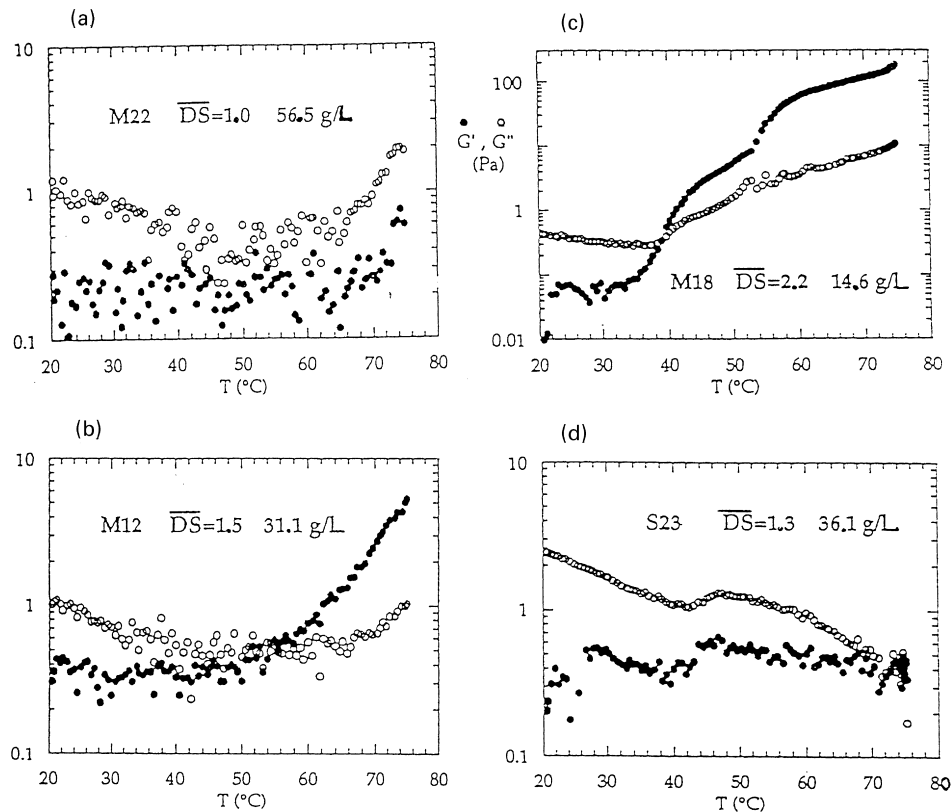


Figure 10 Rheological moduli of solutions of homogeneous methylcellulose in water as a function of temperature (G' and G'' moduli at 1 Hz): (a) M22, $DS = 1.0$, $c = 56.5$ g/l; (b) M12, $DS = 1.5$, $c = 31.1$ g/l; (c) M18, $DS = 2.2$, $c = 14.6$ g/l; (d) S23, $DS = 1.3$, $c = 36.1$ g/l

A4C ($DS = 1.7$) and M18 ($DS = 2.2$) were compared, hysteresis was still present, but the width of the cycle was much larger with A4C meaning stronger interactions.

The calorimetric behaviour was also compared (Figure 11). For homogeneously prepared methylcelluloses with a low degree of substitution ($DS = 1.5$, M12), a very wide peak was observed on heating, and the temperature of the maximum of this peak (on heating and cooling) was larger than that observed for an MC sample with higher DS ($DS = 2.2$, M18). For the M12 sample, a phase transition was also observed, but it was displaced very far from the heterogeneous A4C sample. This was one of the major discrepancies due to the structure. When the degree of substitution was 2.2 we found again the behaviour of A4C sample (Figure 8), but with a very sharp peak on heating and only one peak on cooling. The presence of one peak indicated an homogeneous repartition of substituent along the chain, but with commercial samples the presence of blocks of different natures of units was revealed by the presence of different peaks on cooling.

From fluorescence spectroscopy we observed a general behaviour similar to that of A4C. For M18 an increase of interactions was observed related with the decrease of the I_1/I_3 ratio at a temperature very close to the temperature for which a modification of behaviour occurs in calorimetry and rheology. But this technique allows to go further. Even on methylcellulose substituted only on 2- and 3-positions, a decrease of the intensity ratio was obtained, and it is the only technique which indicates the presence of loose interactions. Even when no visual gelation occurs, the hydrophobic domains are present due to interactions between di- and monosubstituted units.

When solutions of S23 or methylcellulose with low DS at high concentration (60 g/l) were left in an oven at 90°C for a

long period (up to weeks) phase separation was observed. This phenomenon is very common to polymers, the phase diagram depending upon the χ parameter.

Conclusion: mechanism of gelation proposed

From many years mechanisms of thermogelation of aqueous methylcellulose solutions were proposed. The major discussions concern the nature of the zones responsible of the gelation. Savage *et al.*³⁰ expressed the ability to gel from the presence of zones coming from the original cellulosic structure, but he was refuted by Heymann⁵ who has studied highly substituted methylcelluloses. Rees³¹ spoke about micellar interactions, and Sarkar⁶ postulated that gelation was due to hydrophobic or micellar interactions. Haque and Morris³² implied the crystalline zones of cellulose within the gelation process, while Kato *et al.* concluded that the 'crosslinking loci' of methylcellulose gels consist of crystalline sequences of trimethylglucose units³³, which was confirmed by Khomutov *et al.*³⁴.

From all our results we do not propose a new mechanism, but to go deeper into certain assertions. We have demonstrated from the influence of the temperature and salts, but also from the fluorescence and rheological experiments, that hydrophobic interactions were at the origin of the gelation of methylcelluloses. At low concentration and low temperature the methylcellulose is well dissolved in water and solutions without aggregates were obtained. When the temperature and concentration increase, whatever the methylcellulose samples, hydrophobic interactions due to the presence of methyl groups appear. According to the structure (repartition of substituents and presence or not of highly substituted units) the interactions lead to a viscosity increase and sometimes (in the case of the presence of highly substituted zones) to the formation of percolation

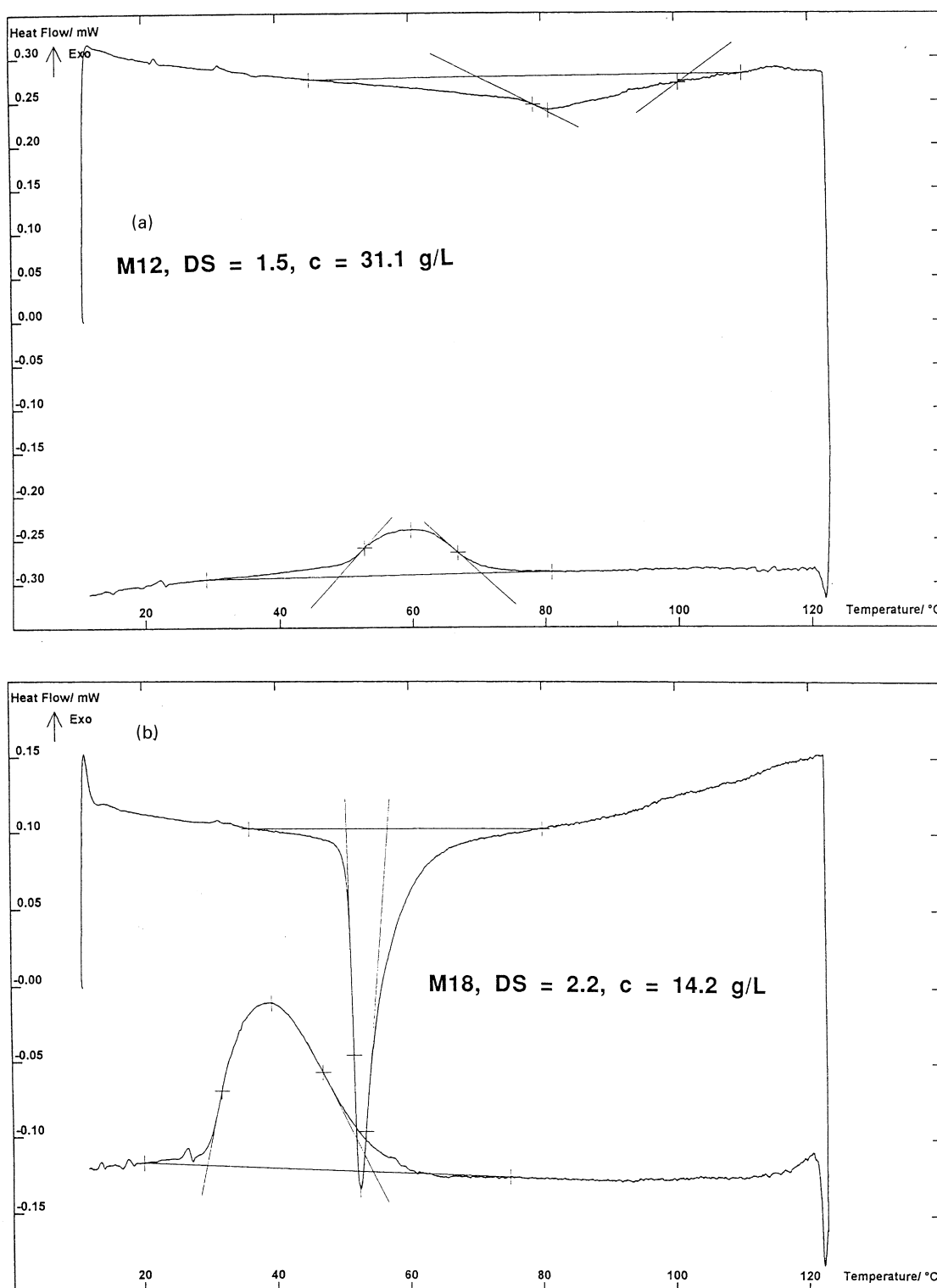


Figure 11 Calorimetric thermograms of solutions of homogeneous methylcellulose in water: (a) M12, DS = 1.5, $c = 31.1$ g/l; (b) M18, DS = 2.2, $c = 14.23$ g/l (temperature rate, $0.25^{\circ}\text{C}/\text{min}$)

aggregates leading to a clear gel. Low substituted units do not participate to junction zones, but favour their connection leading to a tridimensional network. At high concentration pseudo-crystalline zones form slowly within junction zones. The structure of these 'crystallites' is very close to trimethylcellulose crystals and confirms that the highly substituted units are involved in these junctions.

When the temperature is increased above the binodal curve the concentration fluctuations generated by the

phase separation lead to the formation of dense aggregates. The growth of these aggregates is limited by the concomitant gelation which decreases the mobility of the chains and hence forms rigid gels. The temperature at which the phase separation occurs (or the turbid gel is observed) depends on polymer concentration and chemical structure. Whatever the samples, the same steps occur, but physicochemical observations depend upon the substitution characteristics. Critical temperatures for the

changes in physical states are displaced towards higher values when the repartition of substituents is more uniform, or the degree of substitution is lower due to a smaller quantity of highly substituted zones. In any case, the presence of trisubstituted units is compulsory for observable gelation.

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