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A calorimetric study of methylcellulose gelation

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Abstract

Thermograms of methylcellulose solutions have been obtained using samples with different distributions of methyl substituents. It is concluded that hydrophobic interactions between zones of highly substituted units are at the origin of the gelation. A minimal value of the degree of substitution (equal to 1.2) is demonstrated to be necessary for the gelation to be observed either from enthalpy calculations or by calorimetric experiments.

Keywords: methylcellulose; gelation; calorimetry

1. Introduction

Thermoreversible gelation of aqueous solutions of macromolecules has been attributed to the formation of a three-dimensional crosslinked network structure (Morawetz, 1975). Since this sol–gel transformation is reversible within a given temperature range, it does not involve the making or breaking of any covalent bonds, and the physical crosslinks in the gel network structure are due to non-covalent interactions. Some of the classical examples of natural polymers exhibiting the sol–gel transformation phenomenon based on hydrogen bonding are gelatin (protein) and carrageenan (anionic polysaccharide). In these cases the polymers exist as helical interacting segments in the gel state and go into solution as random coils on heating. Upon cooling, a continuous network is reached due to partial reformation of the helix (Harrington and Von Hippel, 1961; Anderson et al., 1969). Several synthetic polymers are also known to gel in either aqueous or organic medium. In many cases gels exhibit syneresis as the polymer network contracts on standing, liberating the pure solvent.

In contrast to these polymers, aqueous solutions of methylcellulose are known to gel when the temperature increases (Heymann, 1935). Gelation of methylcellulose (or hydroxypropylmethylcellulose) solution is primarily caused by the hydrophobic interaction between molecules containing methoxyl substitution (Borchard, 1983; Hirrien, 1996). Owing to unfavourable contact with water, hydrophobic blocks associate, leading to crosslinking. The viscosity increases progressively leading to the formation of a three-dimensional network. These gels are completely reversible.

There exists a certain degree of controversy regarding the mechanism of gelation. The major discussions concern the nature of the zones involved in the gelation. Savage et al. (1963) suggested that the ability to gel was a consequence of the presence of zones containing the original cellulosic structure. This is not consistent with the observations of Heymann (1935) who studied highly substituted methylcelluloses. Rees (1972) speaks about micellar interactions and Sarkar (1979) postulates that gelation is due to hydrophobic or micellar interactions. Khomutov et al. (1993) proposed that gelation is due to crystallization and Haque and Morris (1993) suggest crystalline zones within the gelation process, while Kato et al. (1978) concluded that the ''crosslinking loci'' of methylcellulose gels consist of crystalline sequences of trimethylglucose units. Solubility of the methylcellulose, on the other hand, is highly dependent on the uniformity of the substitution (Savage et al., 1963). Uniformly substituted methylcelluloses prepared homogeneously are water soluble at a much lower degree of substitution than the ones made from alkali cellulose under conditions leading to heterogeneous substitution (Hirrien, 1996).

As the gelation temperature increases with the decrease in methyl substitution, Vacher (1940) concluded that the lack of residues where all three sides were substituted was the cause of gelation. A lower gelation temperature can also be interpreted as resulting from increased hydrophobic

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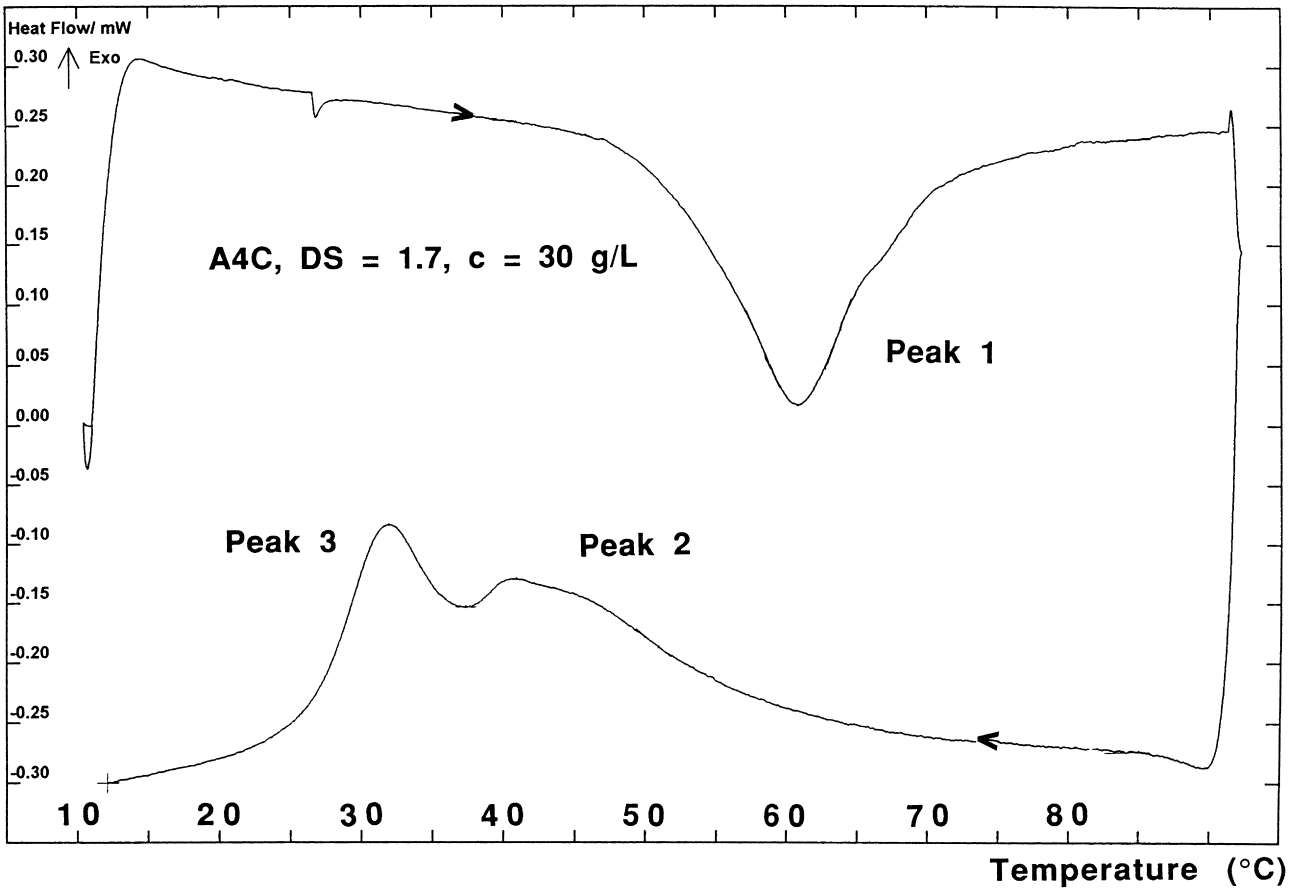
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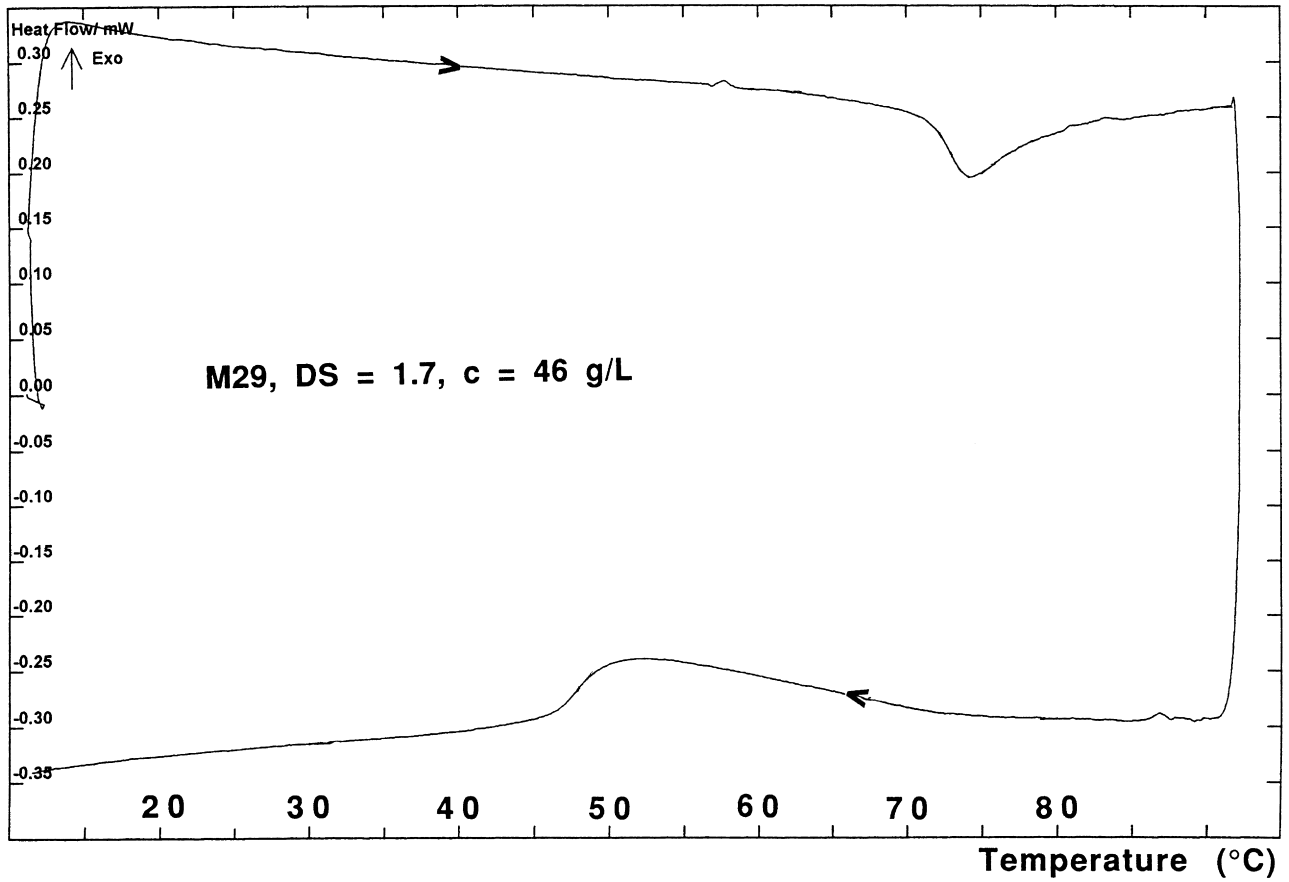
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
A4C, DS = 1.7, c = 30 g/L
Peak 1
Peak 3
Peak 2
10
20
30
40
50
60
70
80
Temperature (°C)


Heat Flow/ mW
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0.20
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0.10
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-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
M29, DS = 1.7, c = 46 g/L
20
30
40
50
60
70
80
Temperature (°C)

Table 1
Distribution of methyl substitution for the samples studied

Sample	A4C	M22	M12	M29	M18
DS[a]	1.7	1.2	1.5	1.7	2.2
% Non S	10	9	5	4	9
% MonoS	29	68	51	45	12
% DiS	39	19	29	32	36
% TriS	22	4	15	19	43

[a]Determination by ^{13}C n.m.r. in DMSO-d_6 (353 K)
DS is the average degree of substitution per glucose residue.

interaction with increasing methyl substitution. Rees (1972) therefore accurately described these gels as ''micellar gels'' analogous to the non-ionic surfactants, which also exhibit cloud points on heating.

The thermogelation of methylcellulose (MC) has promoted their use in a myriad of applications. Better characterization of the gelation properties of methylcelluloses is therefore important in order to control their properties better for different end-use applications.

The evolution of viscosity and turbidity of MC solutions with temperature over a small range of polymer concentrations (10–25 g L^{-1}) was studied (Heymann, 1935; Sarkar, 1979). But few calorimetric data are presented except by Sarkar and Walker (1995), Haque and Morris (1993).

In this paper, calorimetric investigation of the thermogelation of methylcelluloses and information on the mechanism involved are presented.

2. Experimental

Methocel A4C was a gift from Dow Chemical. It is a cellulose derivative prepared using a heterogeneous process. The consequence is a heterogeneous repartition of methyl substituents along the macromolecular chain and hence the presence of blocks of highly or lowly substituted units, respectively. Its average degree of substitution (DS) is 1.7 and the distribution of substituted units is given in Table 1.

Methylcelluloses were also prepared on the laboratory scale using a homogeneous original process based on a method for methylation previously proposed (Hakomori, 1964). The cellulose is dissolved in DMAc/LiCl 6 wt% through a process consisting of a swelling sequence followed by solvent exchange (Hirrien et al., 1996). A dimsyl sodium solution and then iodomethane were added to recover methylcellulose samples after dialysis and freeze-drying. According to the ratio between the different reagents and the duration of the synthesis the degree of substitution will be different. The structural characteristics given in Table 1 show that the repartition of methyl substituents is more statistical (Hirrien, 1996). The determination of the degree of substitution was performed from ^{13}C n.m.r. experiments carried out on a Bruker AC300 spectrometer at 353 K using DMSO-d_6 as solvent. The peak signals were attributed based on the assignments by Parfondy and Perlin (1977) and studies of Takahashi et al. (1986). The relative DS values at individual hydroxyl groups were estimated from the ratio between peak areas.

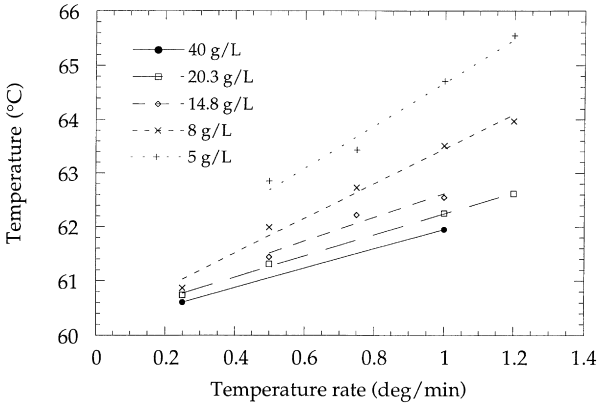


Fig. 2. Dependence of the maximum temperature of peak 1 on heating as a function of the heating rate (A4C, 10–90°C).

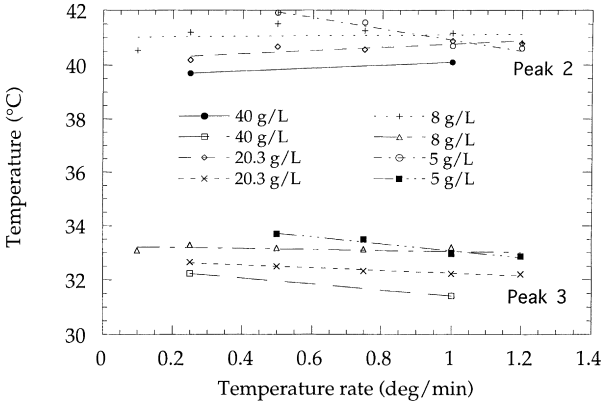


Fig. 3. Dependence of the maximum temperature of peaks 2 and 3 on the cooling rate (A4C, 90–10°C).

The solutions are prepared by dissolution of the polymer isolated in its freeze-dried form in water at 5°C for 24 h to ensure complete solubilization.

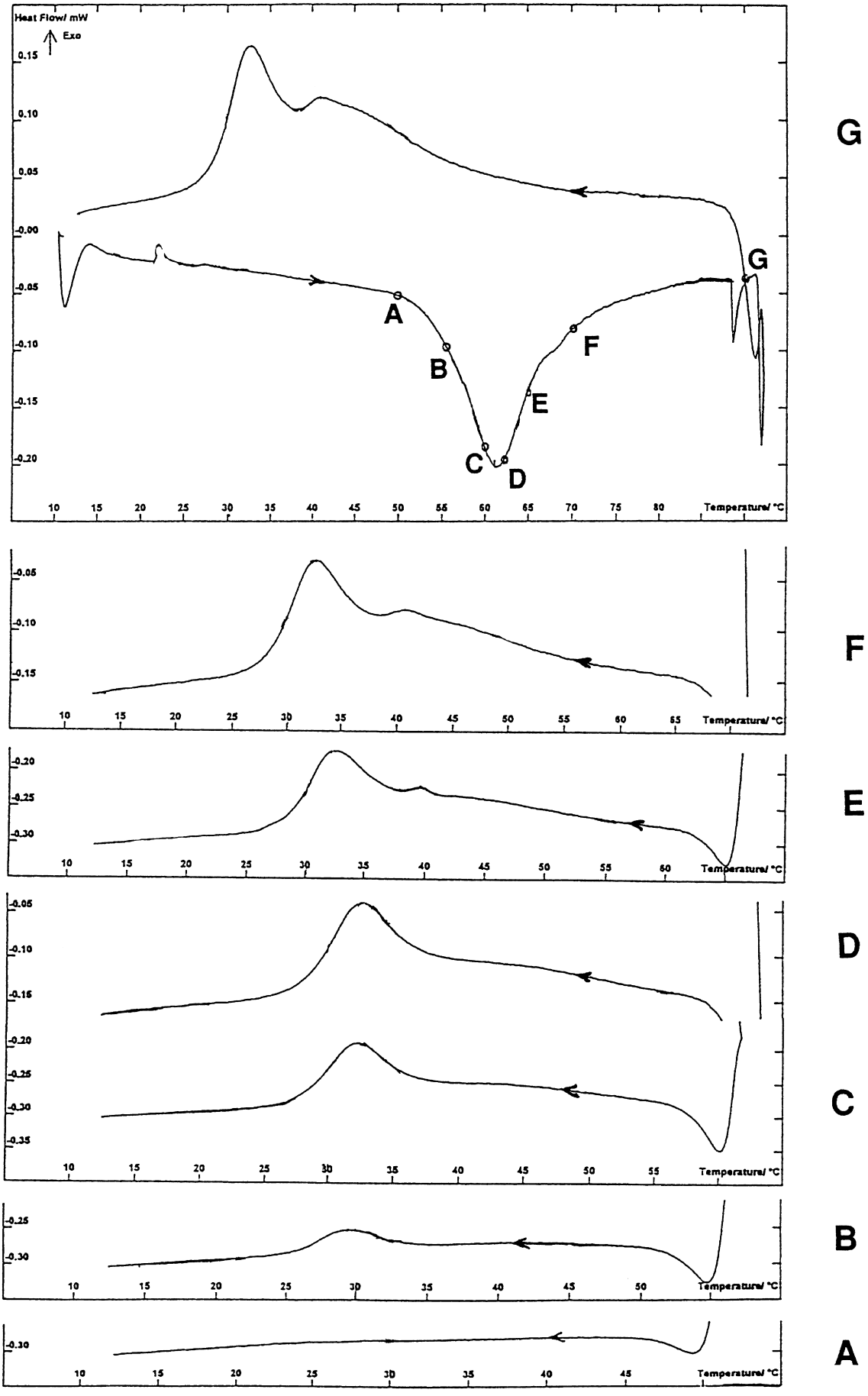
The calorimetric experiments are carried out using a Micro DSC III calorimeter from Setaram (France) equipped with batch cells in which 0.8 mL of solution with water as a reference was used. The same weight of liquids is introduced in the two cells to minimize the differences in heat capacity between these cells. The initial temperature was 10°C and the solution was equilibrated at this temperature for 5400 s.

3. Results and discussions

3.1. Study of A4C sample

From rheological measurements, it has been demonstrated in this laboratory (Vigouret et al., 1996) that this

Fig. 1. Thermogram of aqueous solution of A4C (DS = 1.7, c = 30 g L^{-1}) and M29 (DS = 1.7, c = 46 g L^{-1}) (heating and cooling rate 0.5 deg min^{-1}).


Heat Flow/ mW
Exo
Temperature/ °C
A
B
C
D
E
F
G
G
F
E
D
C
B
A

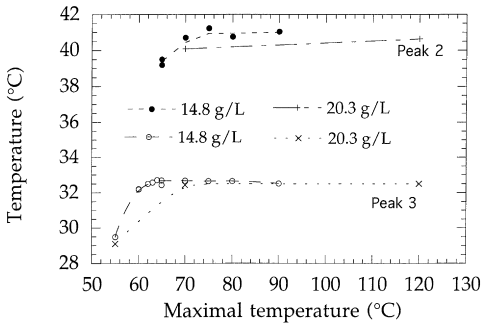


Fig. 5. Dependence of the maximum temperature of peaks 2 and 3 on cooling on the maximum temperature attained upon heating (A4C, 0.5 deg min^{-1}).

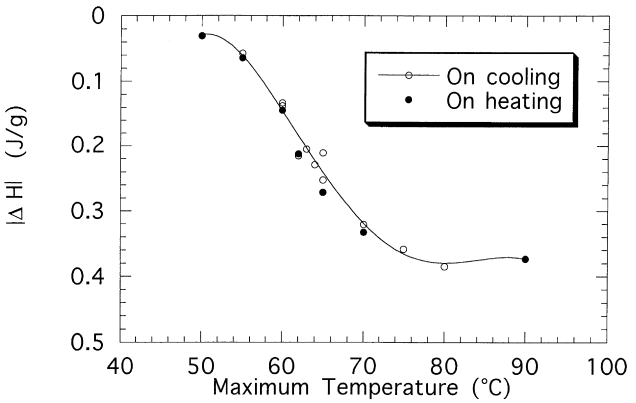


Fig. 6. Dependence of the enthalpy of transition (per gram of dry matter) on the maximum temperature attained upon heating (A4C, 0.5 deg min^{-1}). The ● points are for the cumulative numerical integrals of the heating curve, the ○ points are the sum of enthalpies of peaks 2 and 3 on cooling.

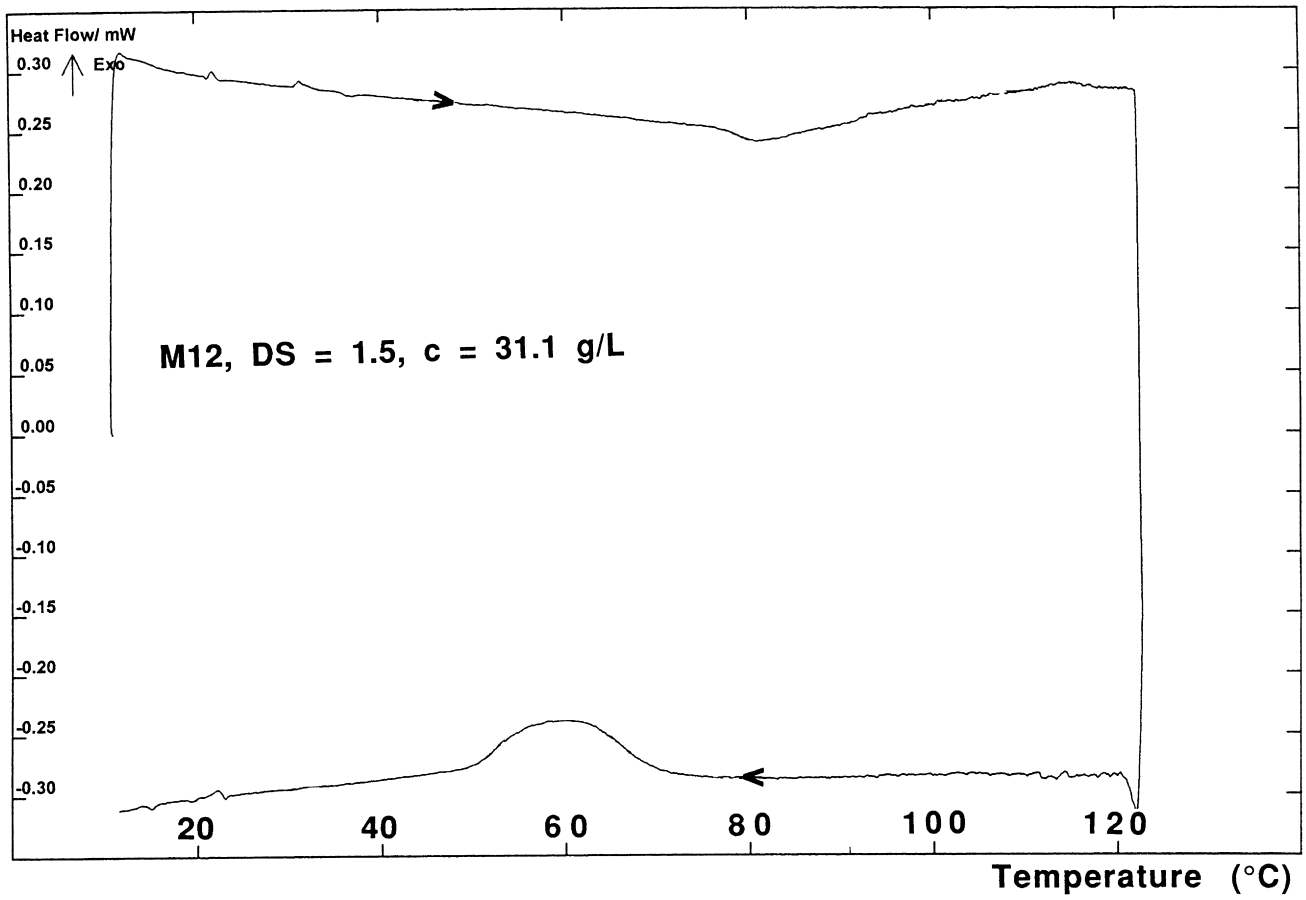
methylcellulose forms a gel, on heating, in two stages. First, a clear gel is formed at temperatures between 35 and 50°C depending on the polymer concentration; then a phase separation associated with turbidity occurs over 60°C associated with a large increase in viscosity. On cooling, a hysteresis is observed also in two stages. The microcalorimetric experiments are performed under similar conditions to elucidate further the mechanism of gelation.

In Fig. 1 the thermogram of the A4C sample is shown. The solution is heated from 10 to 90°C and then immediately cooled down at the same rate. During heating an endothermic peak is obtained (called peak 1) which is a maximum at 60°C. During cooling two exothermic peaks are distinguished, one at 40°C (called peak 2) and another one at 30°C (called peak 3). This difference in the behaviour during heating and cooling was previously observed by Haque and Morris (1993). The dependence of the position of these peaks on the heating and coling rates and the polymer concentration are shown in Figs. 2 and 3. In all cases three peaks are observed (one during heating and two during cooling). The endothermic peak is related to the physical change of the methylcellulose solution and attributed to the formation of the turbid gel. Its temperature is consistent with the rheological experiments (Hirrien et al., 1998). Its position depends upon the heating rate. The lower it is, the lower the temperature of the maximum of the peak. This variation is larger when the polymer concentration is small. Moreover, the higher the polymer concentration, the lower the temperature of the maximum. In solutions with high polymer concentration, more interactions are formed and observed at lowest temperatures. The kinetic effect is important as also shown from rheological measurements (Vigouret et al., 1996). The effects of the rate of temperature change and polymer concentration are smaller for exothermic peaks observed during cooling (peaks 2 and 3). Everything occurs as if starting from the gel the different interactions dissociate quickly compared with the cooling rate. The temperatures corresponding to these two peaks agree with the two stages observed by rheology on cooling.

To determine the nature of the interactions related to each cooling peak, we were interested in the influence of the maximum temperature attained on heating on the appearance of the different peaks (Fig. 4). Peak 3 appears first and it is necessary to heat up to 52°C (for a polymer concentration of 14.75 g L^{-1}) to observe peak 3 on cooling. Peak 2 only clearly appears when the maximum heating temperature is above 65°C, even if it may be suspected within peak 3 when the maximum heating temperature is 60°C. These two peaks correspond to interactions of different types. Peak 3 is characteristic of stronger interactions as they dissociate at lower temperature. They are attributed to interactions between zones of trisubstituted units as Kato et al. (1978) have previously suggested.

We have observed that the position of the maximum temperatures of these peaks depend on the maximum heating temperature for low maximum heating temperature Fig. 5. That means there is a definite temperature above which these interactions may be observed as demonstrated from hysteresis on rheological temperature cycles (Hirrien, 1996). Concerning the dissociation enthalpy, its absolute value increases with the maximum heating temperature (Fig. 6). This means that interactions are more numerous and/or stronger. This is related to the observation of an increase in the G' modulus on the rubbery plateau (Desbrieres et al., 1998). This enthalpy changes when the position of the peaks is stable. Hence, the interactions are more and more numerous when the temperature increases, especially those between zones of lower substitution degree (DS < 3). When the cumulative numerical integrals of the heating curve (from Fig. 4) are plotted on Fig. 6, they superimpose closely on the ΔH values for the corresponding cooling curves. This may be interpreted as ''peak 1'' consists of

Fig. 4. Dependence of the cooling curves on the maximum temperature attained during heating (A4C, $c = 14.8$ g L^{-1}, 0.5 deg min^{-1}). The points on the heating curve are related to the maximum temperature attained during heating for individual cooling curves: A (50°C), B (55°C), C (60°C), D (62°C), E (65°C), F (70°C), G (90°C).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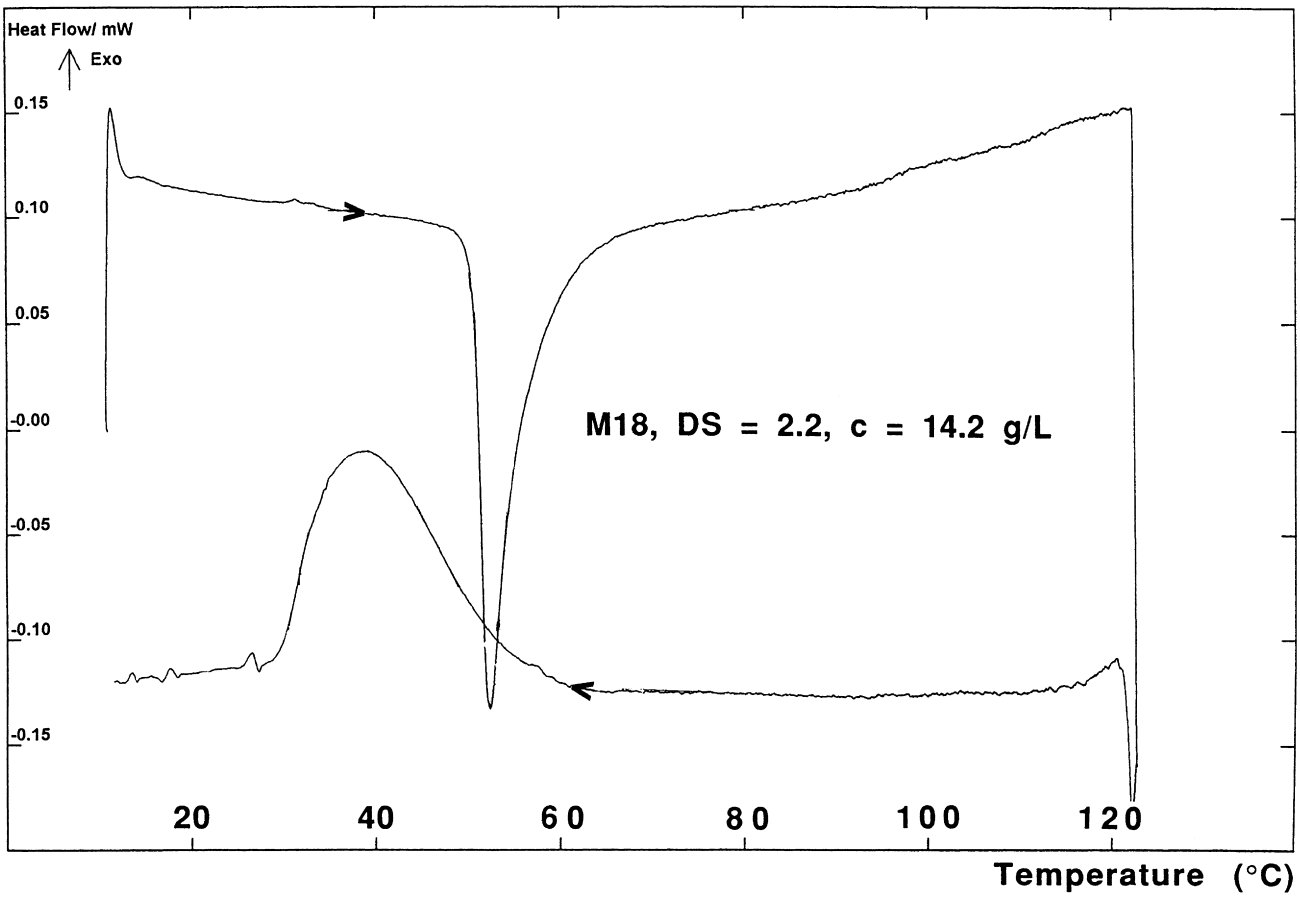
Exo
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
M12, DS = 1.5, c = 31.1 g/L
20
40
60
80
100
120
Temperature (°C)


Heat Flow/ mW
Exo
0.15
0.10
0.05
-0.00
-0.05
-0.10
-0.15
M18, DS = 2.2, c = 14.2 g/L
20
40
60
80
100
120
Temperature (°C)

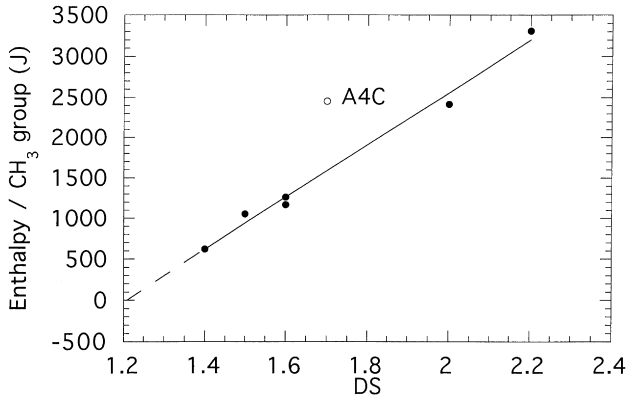


Fig. 8. Influence of the degree of substitution (DS) of methylcellulose on the interaction enthalpy per methyl group.

two endotherms corresponding to reversal of the processes giving rise to peaks 2 and 3 (as is indicated by the shoulder on the high-temperature side of the main endotherm (Fig. 1 or Fig. 4, G). Morever, it confirms the thermoreversibility of the gelation phenomenom as shown by the same values at 20°C of G' and G'' before and after the thermal treatment (Vigouret et al., 1996).

3.2. Comparison with homogeneous methylcellulose samples

For a better understanding of the gelation process, the A4C behaviour was compared with that of methylcellulose prepared using a homogeneous process. For samples with average degree of substitution smaller than 1.3 (as M22) no peak is observed even if the maximum heating temperature is 120°C. These results are in agreement with the results of steric exclusion chromatography (SEC) and dynamic viscoelasticity experiments; the phase separation was never observed within the temperature domain studied.

For homogeneously prepared methylcelluloses with moderate degree of substitution (as M12, DS = 1.5) a very wide peak is observed on heating and the temperature of the maximum of this peak (on heating and cooling) is higher than that observed for sample M18 (DS = 2.2) by nearly 20°C owing to its lower hydrophobic character (Fig. 7). For this sample a phase transition is observed but it is displaced very far from that of heterogeneous samples. It is one of the major differences between the two classes of sample. When a homogeneous sample is prepared with the same degree of substitution as A4C (sample M29 with DS equal to 1.7) the calorimetric behaviour is quite different from the A4C and close to the M12 with a temperature displacement of 15°C (Fig. 1). This is directly related to the heterogeneity of the substitution. When the degree of substitution is 2.2 (as M18), we find the same type of rheological behaviour as seen for the A4C sample but, from calorimetric experiments, a very sharp peak on heating and only one peak on cooling are obtained. The presence of this single peak indicates a more homogeneous repartition of substituents along the chain, but with commercial samples the presence of blocks of different natures of units is revealed by the different peaks on cooling.

From the enthalpy of dissociation of such interactions, it is possible to calculate the energy of interaction involved per methyl group. When this energy is plotted against the average degree of substitution a straight line is obtained for the homogeneous samples (Fig. 8). The fact that this value is not constant is evidence that the phenomenom is cooperative, the interaction energy increasing with the number of methyl groups on the macromolecular chain. But this interaction energy is zero for a DS equal to 1.2, which is close to the DS value for which no transition is observed, and this DS value is very comparable to the one found by Sarkar and Walker (1995). For a completely substituted polymer (DS = 3) this energy is 5783 J per methyl group, i.e. 2.3 kT at 298 K. This value may be compared with the one indicated for methylene groups (1.3 kT) (Jencks, 1969). This energy, which was calculated from the free energy of the transfer of a linear hydrocarbon chain from water to a non-polar solvent, provides at least a rough estimate of the free energy to be expected for a hydrophobic interaction of the considered entity. The A4C sample has its representative point outside the curve, indicating that the presence of zones of highly substituted units enhances the interactions and allows the transitions at lower temperatures when compared with homogeneous samples with the same DS (1.7). To reach an interaction enthalpy equivalent to that of the A4C sample, it is necessary for a homogeneous sample to have an average DS of about 2.1, which is confirmed from rheological and fluorescence experiments (Hirrien, 1996).

4. Conclusion

From calorimetric experiments carried out on solutions prepared from methylcellulose samples of different origins we have obtained information on the gelation mechanism of such derivatives.

The endothermic peak (observed on heating) is related to the physical change in the methylcellulose solutions and attributed to the gel formation. For the heterogeneous sample (A4C) two exothermic peaks (observed during cooling) are observed at about 40 and 30°C, respectively. The second peak is characteristic of strong interactions and attributed to interactions between zones of trisubstituted units; the first peak is attributed to connections between regions of lower substitution.

When the methylcellulose samples prepared from heterogeneous and homogeneous conditions are compared, it is

Fig. 7. Thermograms of aqueous M12 (DS = 1.5, $c = 31.1$ g L^{-1}) and M18 (DS = 2.2, $c = 14.2$ g L^{-1}) solutions in water (temperature cycle 10–120–10°C, 0.25 deg min).

demonstrated that a minimal value of the degree of substitution of 1.3 is required to observe the phase separation within the temperature domain studied (up to 120°C) in agreement with the prediction made from Fig. 8. For DS larger than this minimal value, the homogeneous samples present a transition but its temperature is displaced towards the highest values compared with heterogeneous samples with the same degree of substitution. This confirms that the presence of zones of highly substituted units enhances the hydrophobic interactions responsible for the gelation of methylcellulose.

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