

Thermogelation of methylcellulose: rheological considerations

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Abstract

Methylcellulose is a natural polymer which gels on heating. This gelation is thermoreversible and attributed to hydrophobic interactions. Its mechanism is not well understood but the presence of hydrophobic zones is needed to initiate the physical crosslinking. Dynamic mechanical experiments performed in a large frequency range are presented and allow discussions for improving our understanding of the gelation mechanism. Two temperature domains are studied on both sides of the gelation temperature range. In the low temperature domain the frequency spectra are typical of an entangled solution and the activation energy is determined. From the high temperature domain the gelation temperature may be determined and may be related to the experimental temperature at which the viscosity increases and turbidity occurs. The rheological results are interpreted as the signature of heterogeneities that become more and more important with temperature and are superimposed on the chain entanglements in semi-dilute solutions. The junctions in the inhomogeneities are most likely due to hydrophobic interactions between highly substituted units, as previously demonstrated by fluorescence spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

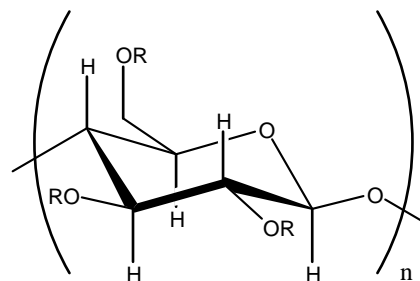
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1. Introduction

Hydrophilic polymers containing a few hydrophobic units can form temporary hydrophobic association networks in aqueous media at relatively low polymer concentrations [1]. The main microstructural characteristic of such polymeric systems is their ability to give rise to weak intra and intermolecular hydrophobic interactions in water solutions. Indeed, the hydrophobic groups distributed along the polymer chain associate to minimize their exposure to water [2]. In the concentration range of industrial interest (in the semi-dilute or moderately concentrated regime) these intermolecular interactions are predominant. They form a temporary associating network which serves to reinforce the entangled network, as studied theoretically by Leibler [3]. The most commonly used hydrophobically associating water soluble polymers are based on poly(ethylene oxide) (HEUR-type), polyacrylamides, polyacrylates or polysaccharides. The tendency for such polymeric systems to undergo association leads to various interesting and unusual linear and non-linear rheological behaviour, which make them candidates as rheology modifiers in many industrial applications [4,5]. Over the past few years, the associative and rheological

properties of hydrophobically modified polymers have given rise to widespread investigations, either theoretically [3,6], or numerically [7] and experimentally [8–11].

Natural derivatives such as hydrophobically modified celluloses, which belong to this class of associating polymers, suffer from a lack of fundamental physicochemical studies. The difficulty arises mainly from the absence of model polymer samples with a precise distribution of the substituents. Nevertheless a large number of investigations have been carried out on commercially available polymers to characterize their ability to form a gel on heating, and which melts again on cooling. Methylcellulose (MC) is the simplest cellulose derivative, and has been known for a long time. Its chemical structure is as follows:



where R is H or CH₃.

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The number of substituted hydroxyl groups per anhydroglucose unit is the degree of substitution (DS); it may vary from 0 to 3. Commercial methylcellulose (MC) is a heterogeneous polymer consisting of highly substituted zones called “hydrophobic zones” and less substituted ones called “hydrophilic zones” [12]. Most of the experimental work 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) [13–16]. The behaviour of this polymer does not change monotonically when the temperature varies: the viscosity of a semi-dilute solution decreases when temperature is increased up to a critical value, above which the viscosity increases. Then, the formation of a gel may be observed and this phenomenon is associated with turbidity, indicating phase separation [13]. All these phenomena are thermoreversible. All these effects are convoluted by kinetic factors, since some of the processes are quite slow. This makes comparisons with other work quite difficult.

Very few studies have been performed on the evolution of the methylcellulose solutions and their “thermodynamic” behaviour with temperature, in a large concentration range. Recently Nishinari [17] studied the gelation mechanism of aqueous solutions of methylcellulose of different molecular weights by small deformation oscillatory rheological measurements and differential scanning calorimetry. He demonstrated that gelation is promoted by the increase of molecular weight. His results are in good agreement (bearing in mind the caveats above) with data we have obtained [18]. Nevertheless there is still some controversy regarding the mechanism of gelation and especially on the nature of junctions involved during this gelation.

Savage [19] ascribed the ability to gel to the presence of zones coming from the original cellulosic structure but his work was refuted by Heyman [13] who studied highly substituted methylcelluloses. Rees [20] spoke about micellar interactions and Sarkar [14] postulated that gelation was due to hydrophobic or micellar interactions. Haque [21] implied the crystalline zones of cellulose within the gelation process while Kato concluded that the “cross-linking loci” of methylcellulose gels consist of crystalline sequences of trimethylglucose units [22], which was confirmed subsequently by Khomutov [23]. Moreover it is not known what role the chemical structure (distribution of the substituents along the macromolecular chain) plays on the solution behaviour. Finally the lack of knowledge of relations between molecular structure and macroscopic behaviour of these polymers prevents the improvement of these industrial products.

We have carried out experiments to improve the understanding of the structure—properties relationships, and the gelation behaviour. Calorimetric experiments were presented [24] and the nature of the interactions was demonstrated from spectroscopy fluorescence and the influence of parameters such as the nature of the salts added to the methylcellulose solutions...[25].

In this paper detailed rheological experiments on aqueous methylcellulose solutions during gelation are presented. These exploit the advantages of a novel instrument designed and built in Grenoble.

2. Experimental section

Methylcellulose was kindly provided by Dow Chemical under its trade name Methocel A4C. The sample is purified by dissolution in water, filtration through a Sartorius cellulose nitrate membrane (porosity 0.8 μm) and then by ultrafiltration until the filtrate approaches the conductivity of distilled water. The solution is then freeze-dried.

The aqueous solutions were prepared by dissolution of freeze-dried methylcellulose in water at 5°C for 24 h to ensure complete dissolution. The complete dissolution was checked using dynamic light scattering: only one population of monomeric species was observed [26]. The nominal polymer concentration of the solution was 39 g/l.

Its average degree of substitution (\overline{DS}) was determined from ^{13}C NMR spectroscopy at 353 K in DMSO- d_6 on a Bruker AC300 spectrometer at 75 MHz. The polymer concentration is around 30 g/l. \overline{DS} was found to be 1.7. The viscosity average molecular weight \overline{M}_v is determined from the intrinsic viscosity of the aqueous solution at 20°C using the Mark–Houwink relation [27]:

$$[\eta] = 0.28M^{0.63}$$

where \overline{M}_v was found to be 149,000 g/mol.

The intrinsic viscosity was determined using a Couette type rheometer (Contraves Low Shear 40). The rheological temperature sweep and creep experiments were performed using a stress-controlled rheometer (Carri Med CS50). The oscillatory shear experiments were carried out at a fixed frequency of 1 Hz.

Other rheological experiments were carried out on a unique piezorheometer built by Palierne at the Rheology laboratory in Grenoble. The principle is described by Cagnon and Durand [28–30]. The solution is placed between glass plates that are cemented to piezoelectric ceramics. The sample available surface is a 5 × 12 mm² rectangle and the thickness adjusted from 30 to 200 μm using adjustable spacers. The upper ceramics are driven by an ac voltage to induce an ac shear strain parallel to the plates. The lower ceramics, submitted to the transmitted shear stress, give an output voltage. The instrument is able to work in a wide frequency range (from 0.1 to 10⁴ Hz). The enclosure is watertight and according to the test temperature it may be saturated with water to avoid evaporation when temperature was increased. It is well described by Ribotta and Durand [31]. To be in equilibrium conditions, temperature was increased between 20 and 50°C in steps of 5°C and the temperature was kept constant for 1 h before measurements. Between 50 and 70°C the steps were of 2°C only and the temperature was kept constant for 2.5 h because of

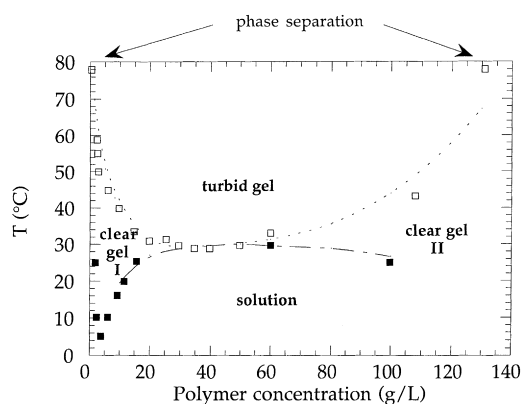


Fig. 1. Phase diagram of an aqueous methylcellulose A4C solution ($\overline{DS} = 1.7$) including the cloud point curve (\square) and the sol-gel line (\blacksquare) determined from oscillatory experiments.

kinetic factors. The height of the liquid sample was adjusted to 65 μm using a spacer as described previously.

The cloud point is determined visually using solutions which are heated in a thermostated bath to the required temperature [32]. As the process of separation can be very slow, tubes were left in the bath for about one 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.

From the cloud point determination and the rheological experiments the phase diagram was determined [33].

3. Results and discussion

The (inverse temperature type) phase diagram of the methylcellulose is presented in Fig. 1. Four domains are found [33]. Below the binodal curve two homogeneous gel phases I and II are observed, separated by a solution phase and there is a two-phase domain above and within the binodal curve. We have studied the influence of the temperature on the rheological properties of a methylcellulose solution, with a nominal concentration of 39 g/l.

A continuous temperature sweep was carried out (Fig. 2). The temperature was increased from 20 to 75°C at a rate of 0.5 °/min. The G' value initially decreases. At around 40°C this changes, a sharp increase is seen for temperatures larger than 45°C, where turbidity also appears. The turbidity is due to phase separation which, in turn, is concomitant with gelation [25]. The sharp increase in G' is related to the one phase–two phase transition. Gelation temperature may be, in a first approximation, defined as the temperature at which G' is equal to G'' and at this concentration it is close to 51°C. For lower polymer concentrations a second

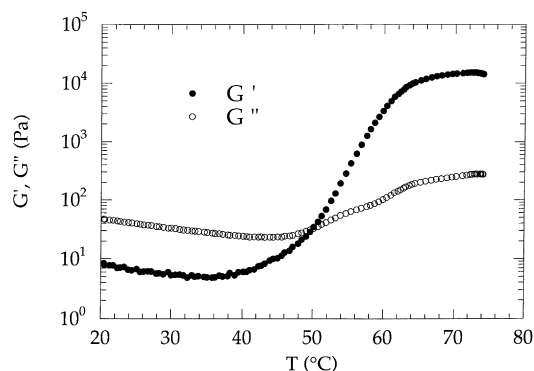


Fig. 2. Elastic moduli of A4C solutions during a temperature sweep (G' and G'' moduli at 1 Hz, $c = 39$ g/l).

wave (corresponding to a second transition) was observed, at lower temperatures, corresponding to the formation of the clear gel I (Fig. 1). The influence of kinetics was shown on such solutions [26] and during the temperature sweep the solution was not at equilibrium. This is one of the main reasons why the transition temperatures we have determined are not the same as the ones determined from the phase diagram, another one being the fact that we have chosen the temperature at which $G' = G''$, this criterion being an approximation for this complex system. For example, if we had used another criterion such that gelation corresponds to the first increase in G' [34], the temperature of relevance would be approximately 39°C.

To improve our understanding of the gelation mechanism, dynamic mechanical experiments were carried out as a function of temperature. The different rheograms are presented in Fig. 3 and they may be studied within three temperature domains. The first one below 40°C corresponds to the solution domain, a further domain, for intermediate temperatures between 40 and 60°C, for which kinetics does not allow us to draw firm conclusions, and the highest temperature which gives rise to two phase behaviour. This reinforces information for the different domains, observed in Fig. 1.

3.1. Low temperature domain (from 20 to 40°C)

In this domain the curves present only the terminal zone and the rheograms are typical of an entangled solution [35] because the overlapping concentration is measured to be around 4 g/l [18]. When the frequency is increased $G'(\omega)$ crosses over $G''(\omega)$ at a value G_X for a frequency ω_0 (Table 1). Taking the cross-over points as reference points it is possible to build a master curve (Fig. 4). In the low frequency terminal zone, G' increased as $\omega^{1.53}$ and G'' as $\omega^{0.9}$ compared with the respective theoretical values of ω^2 and ω^1 (Fig. 5). The observed discrepancy may be explained by the absence of very low frequency data. Taking the temperature of 313 K as the reference temperature (T_{ref})

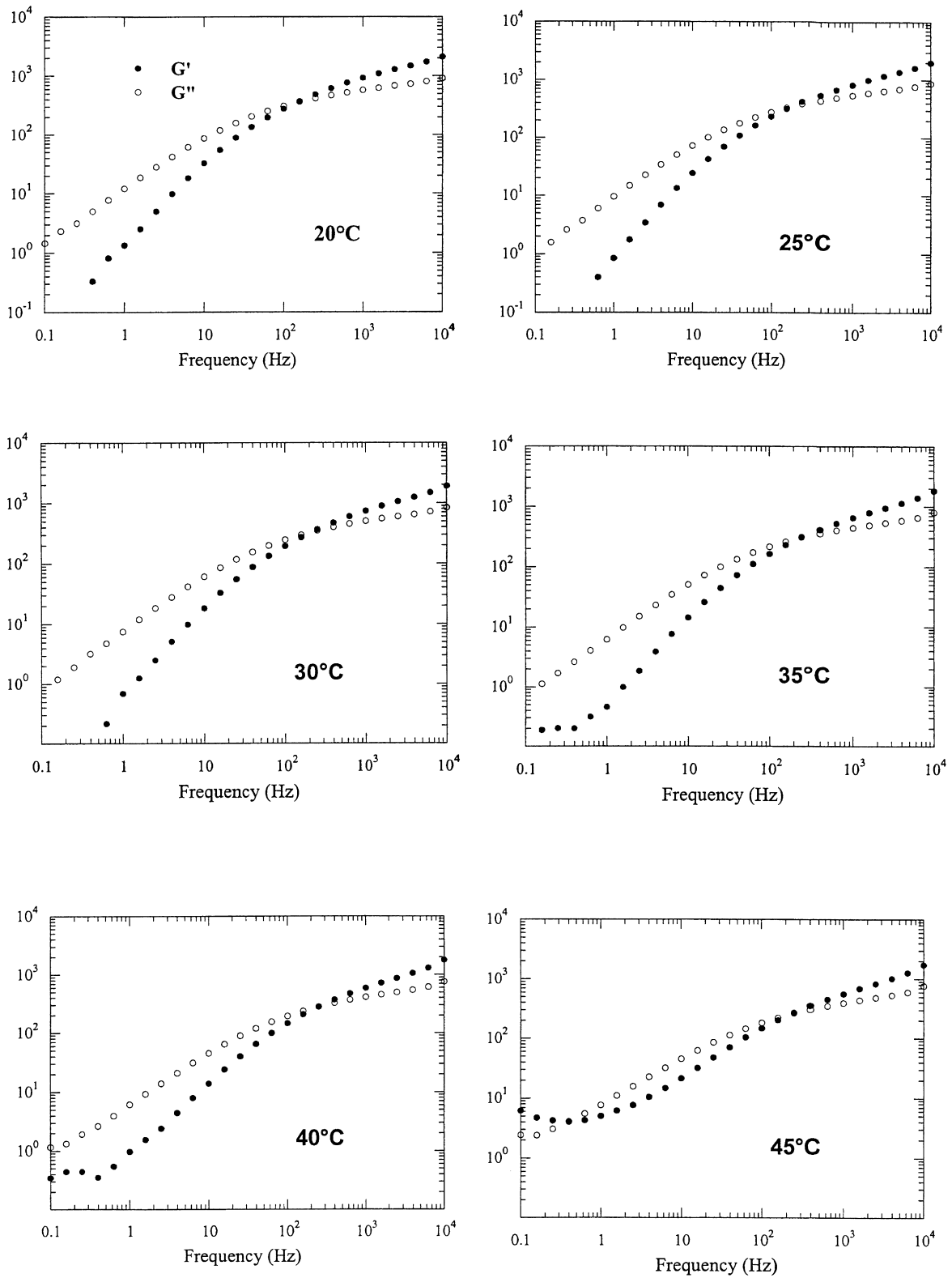


Fig. 3. Influence of temperature on the variation of elastic moduli as a function of the frequency.

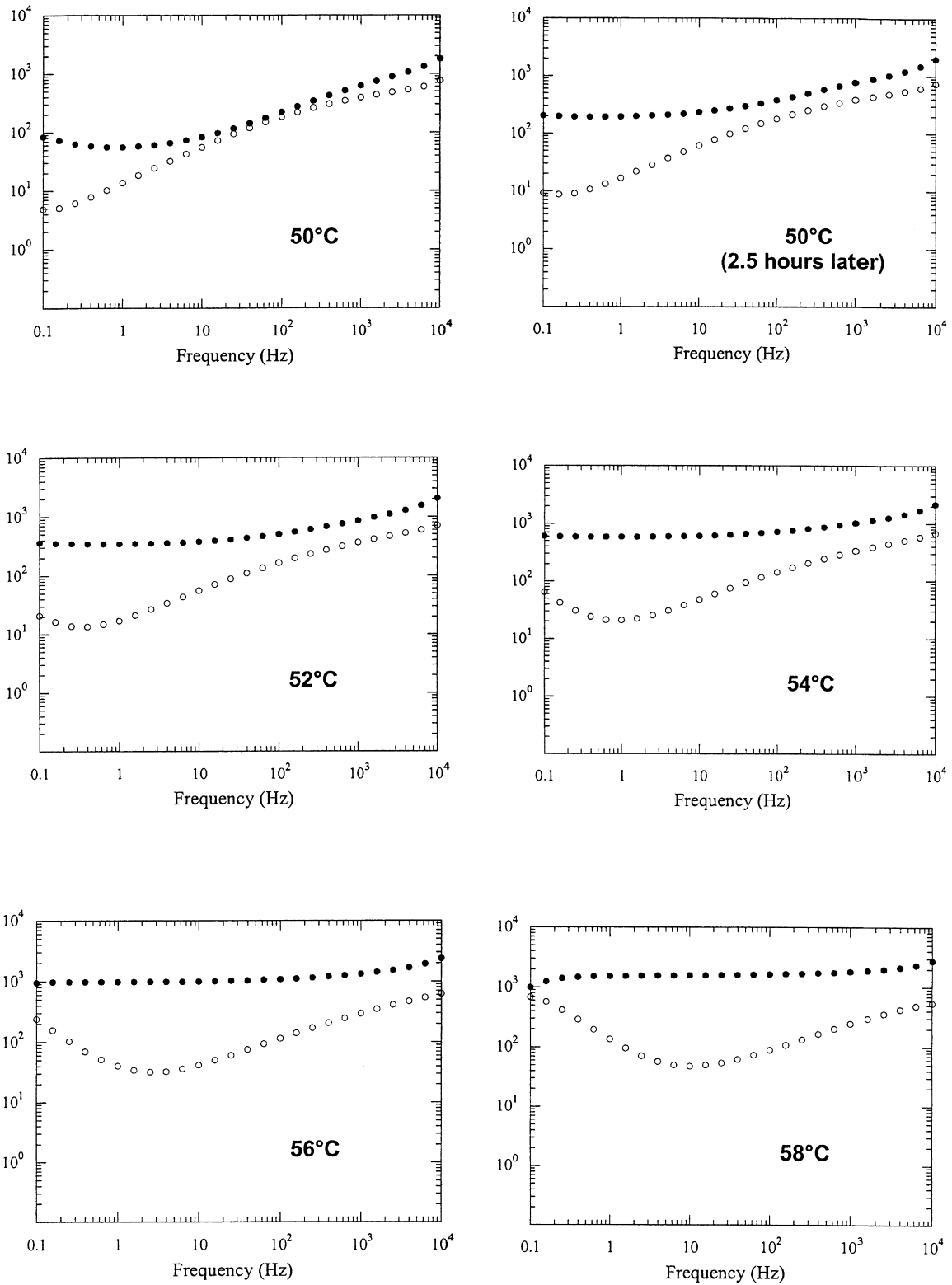


Fig. 3. (continued)

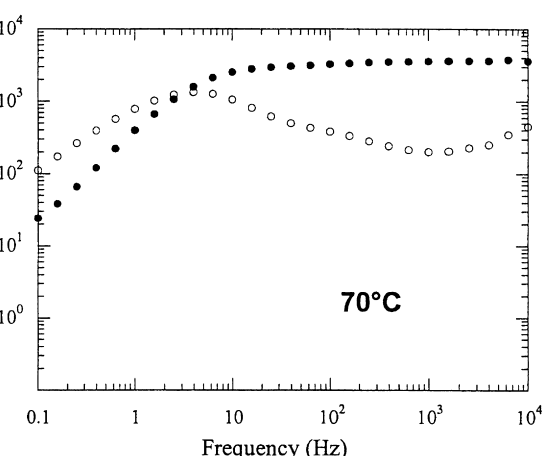
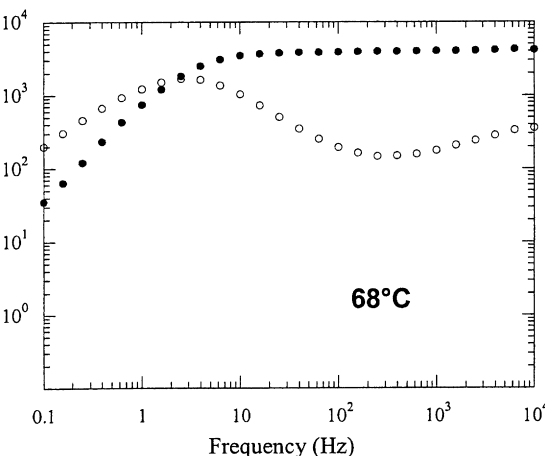
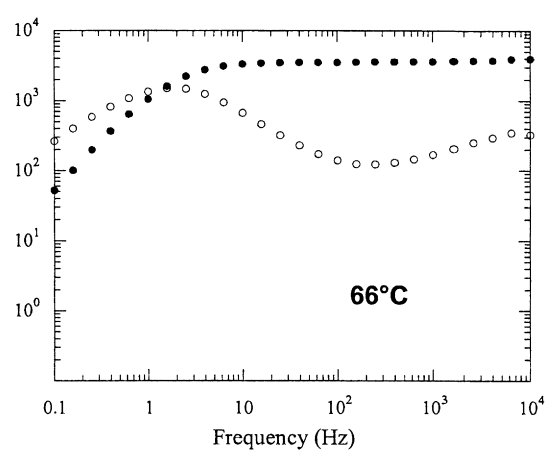
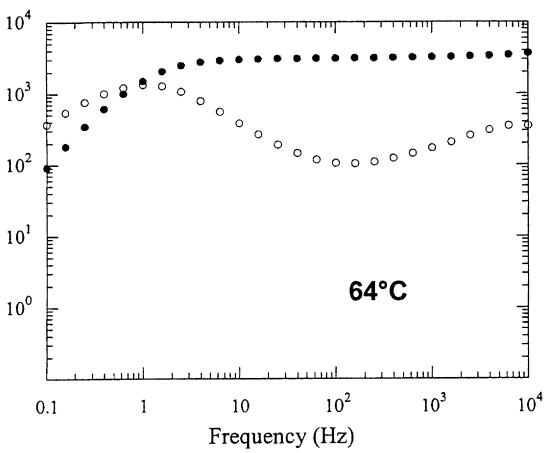
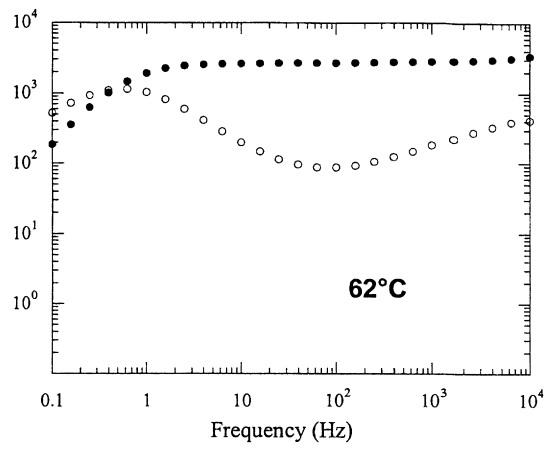
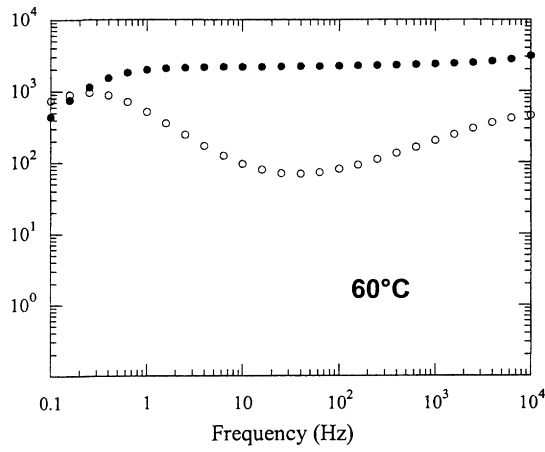


Fig. 3. (continued)

Table 1
Influence of the temperature on the cross-over values (frequency, ω_0 and modulus, G_x) of an aqueous A4C methylcellulose solution

Temperature (°C)	Cross-over frequency ω_0 (rad/s)	Cross-over modulus G_x (Pa)
20	895.94	340.84
25	1097.86	340.34
30	1306.22	328.81
35	1376.13	294.08
40	1462.43	272.02
60	1.154	895.3
62	2.467	1038.4
64	4.667	1202.3
66	7.942	1373.1
68	12.247	1516.8

the WLF law may be obtained as:

$$\log a_{v,T} = \frac{0.14(T - T_{ref})}{32.1 + (T - T_{ref})}$$

where $a_{v,T}$ is the shift factor on the frequency axis.

The linear viscoelastic responses allow the determination of a long characteristic time characterizing reptation-like chain motion, i.e. the disengagement time of the reptation model [36]. As a solution is studied, these results may be expressed as the variation of the complex viscosity, η^* . The dynamic viscosity, η' , is defined as G''/ω and the elastic part of the complex viscosity, η'' , as G'/ω . To determine the characteristic parameters of the evolution of our system as a function of the temperature from experimental mechanical spectra we have used the Cole–Cole empirical equation [37]:

$$\eta^*(\omega) = \frac{\eta_0}{1 + (i\omega/\omega_c)^p}$$

The use of this model implies that the viscoelastic properties come from the existence of a continuous spectrum of relaxation times. η_0 is the Newtonian viscosity, $1/\omega_c$ is the

characteristic time of the relaxation spectrum and p is related to the width of the relaxation time distribution. When p is equal to 1, this model corresponds to the simple Maxwell model with only one relaxation time. Fig. 6 represents the fit of experimental data with the Cole–Cole equation for a temperature of 25°C. The data for all the temperatures was given in Table 2. The solutions were characterized by a distribution of relaxation times and the Newtonian viscosity decreases with increasing temperature as for the solvent. The appearance of a second mode of relaxation was also observed when the polymer concentration was increased above 40 g/l [33]. Moreover this distribution extends towards higher frequencies with polymer concentration in contradiction to the predicted evolution of the reptation time in semi-dilute solutions. The mechanism of aggregation is, of course, more complex for such cellulose derivatives than for simple reptation models or even for hydrophobically modified synthetic polymers. The corresponding longest characteristic time, τ_c , directly calculated from ω_c was around 0.03 s. for all the temperatures (Table 2).

By applying the Arrhenius law to the temperature dependence of the Newtonian viscosity it is possible to determine an activation energy for flow of 31.8 kJ mol⁻¹, or 12.83kT at 298 K. This value is half that of HEUR [8] but of the same order of magnitude of that obtained for non-associative polymers. For a methylcellulose solution at a concentration of 25.67 g/l it was found equal to 14kT [25]. We assume therefore that the activation energy evaluated at lower temperatures describes the non-associative part of the macromolecular chain. Obtaining truly molecularly dispersed solutions of cellulose derivatives in water requires far more extreme solubilization conditions than are employed here, i.e. at very low temperatures such as 5°C. Nevertheless this “low temperature” behaviour reflects simpler behaviour than that seen above 30°C but, even here, almost certainly, the chains are partly associated. Nevertheless since the activation energy is close to that

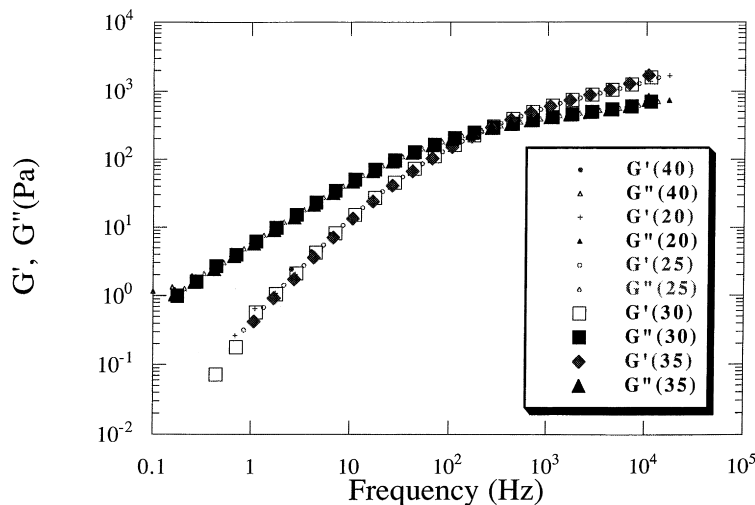


Fig. 4. Master curve within the low temperature domain for A4C methylcellulose solutions (25°C < T < 40°C).

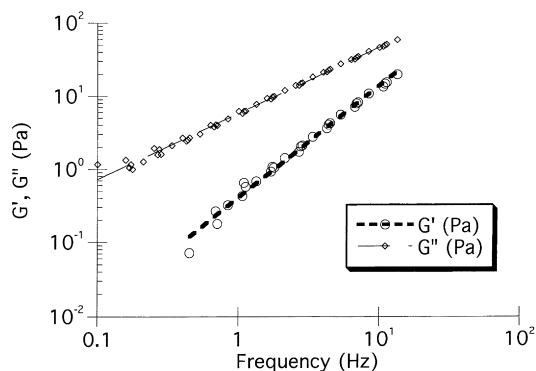


Fig. 5. Influence of the frequency on the G' and G'' values within the terminal zone in the low temperature domain.

for non-associative chains in other systems, this state can be regarded as a “baseline”.

In the intermediate temperature domain kinetic factors have great influence and the results were too difficult to be interpreted. At a temperature of 50°C two rheograms performed with a delay of 2.5 h between them were different. However a rubbery plateau appeared in the time and frequency sweeps as the signature of the gel formation, as the evolution of mechanical moduli in Fig. 2 suggests. Moreover the data presented in Fig. 3 at 45°C shows some hints of the more classic indications of critical gel behaviour; the variation of G' and G'' with frequency appear to follow a power-law dependence over the frequency region between approximately 1 and 100 Hz. Although the fact that two cross-over points are observed (near 1 and 100 Hz) certainly indicates more complex behaviour than is normally associated with “standard” critical gels, the evolution of the moduli as the sample forms a substantial gel in the temperature range 45–50°C, may be related to the formation of a critical gel. Indeed the initial signature of this is already seen in the low frequency data for G' at temperatures larger than 35°C. What this suggests is that under the prevailing kinetic conditions, the temperature range 35–50°C corresponds to an ever increasing tendency to gel.

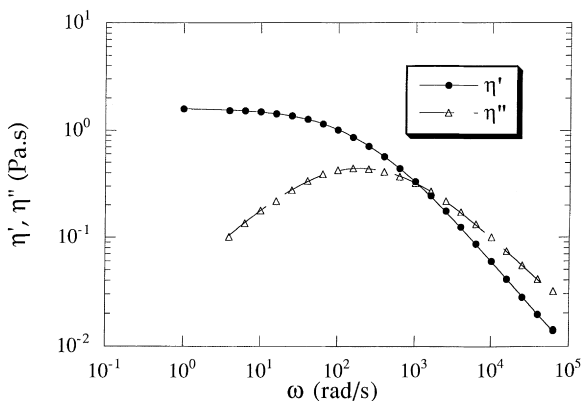


Fig. 6. Cole–Cole plot for the viscosity of methylcellulose A4C solution at 25°C (solvent: water, $c = 39$ g/l).

3.2. High temperature domain (higher than 60°C)

For temperatures higher than 60°C a constant value in the G' evolution with time was obtained within 2 h and it was expected to be at quasi-equilibrium.

A G' plateau region and a maximum in G'' appeared within the studied frequency domain. A cross-over between G' and G'' is also observed, determined by G_X and ω_0 . The values are given in Table 1. The comparison of, respectively, G_X and ω_0 values within the two temperature domains shows the modification of the behaviour of the polymer solution between the two regions. At low temperatures the relaxation time is between 100 and 1000 times smaller than the value at high temperature. In other words the characteristic time describing the chain in junction zones is larger at higher temperature. When the cross-over frequency is plotted as a function of temperature (Fig. 7) there is a clear discontinuity in the “melting–reforming” range indicating a change in the behaviour of the system. For a macroscopic gel the cross-over frequency must go to very low frequencies. Both branches of Fig. 7 diverge towards low frequencies in a temperature range close to 55°C. This temperature has to be compared with the temperature at which there is a very substantial viscosity increase and turbidity occurs ($T = 51^\circ\text{C}$, Fig. 2) [18] and for which calorimetry experiments give an indication of gelation (T close to 55°C) [24]. Using the same procedure as in the low temperature domain a master curve may be defined (Fig. 8). The variation of G' and G'' in the low frequency regime are described, respectively, by $\omega^{1.27}$ and $\omega^{0.8}$ indicating that we are only in the beginning of the terminal zone. The WLF law, in this domain, is as follows:

$$\log a_{v,T} = \frac{-1.94(T - T_{\text{ref}})}{22.8 + (T - T_{\text{ref}})}$$

taking 68°C (341.15 K) as the reference temperature.

The sol–gel transition seems, for a given concentration when the temperature is increased, to be described by a percolation process [38]. Let us compare our experimental data with the predictions of the theory of Leibler [3] for the viscoelastic properties of entangled associating polymers with many reversible association sites. The theory predicts the existence of two maxima in the loss modulus $G''(\omega)$ corresponding to two main measurable time scales: the low frequency maximum corresponds to the terminal relaxation (disengagement) time and the high frequency maximum to the average lifetime of an association. As the continuous association and dissociation processes effectively contribute to the friction coefficient of the chain, the reptation diffusion in the tube is slowed down and the terminal time can be much larger than the association lifetime. We cannot observe a second $G''(\omega)$ maximum during our experiments, but this is most likely because of the complexity of the system itself due to the distribution of substituents along the macromolecular chain giving rise to “blocks” of different nature, and the chain and block polydispersity.

Table 2
Cole–Cole parameters for the viscosity of A4C methylcellulose solutions within the low temperature domain

Temperature (°C)	Newtonian viscosity η_0 (Pa s)	ω_c (rad/s)	τ_c (sec)	p
20	2,063	149.1	0.042	0.82
25	1,612	198.9	0.031	0.82
30	1,244	256.1	0.0245	0.86
35	1,088	231.6	0.027	0.78
40	1,072	172.3	0.0365	0.71

That said the frequency range of this instrument (0.1 – 10^4 Hz) is different to that of most mechanical rheometers (10^{-4} – 10 Hz).

The variation of G'' over G' follows the Cole–Cole equation (Fig. 9):

$$G''(\omega) = [G'(\omega)G_\infty - G'(\omega)^2]^m$$

A good semi-circle is obtained for $m = 0.5$ and the data we have obtained is given in Table 3. The m value (around 0.49) obtained whatever the temperature implies that a single relaxation process controls the viscoelastic response of these media and its behaviour is derived from the Maxwell model. This behaviour is different from the one observed before gelation for which a distribution of relaxation times was obtained. The G_∞ value may be compared with the plateau storage modulus G_0 taken as the value of G' corresponding to the minimum in the $G''(\omega)$ function (Table 3). The values are very close. The small secondary maximum in the Cole–Cole plot reflects the high frequency data. For semi-dilute polymeric systems G'' does not tend towards zero at high frequencies, so strictly the behaviour is not truly Maxwell-like. Nevertheless it is very different from the low temperature data. As the appearance of a G' -plateau is a consequence of the existence of a network in the medium, the G_0 values can be used to estimate the average molecular weight of the polymer segments between two junction zones, M_e for purely entangled systems (Table 4):

$$G_0 = \frac{RTc}{M_e}$$

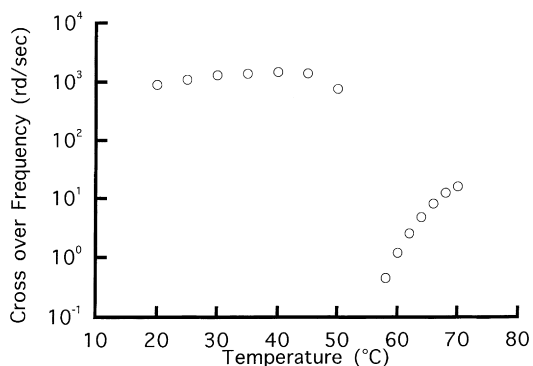


Fig. 7. Influence of the temperature on the cross-over frequency.

where R is the perfect gas constant, T the temperature and c the polymer concentration.

When the temperature was increased the number of junction zones increased in a good agreement with the increase of viscosity. Considering the average molecular weight of the methylcellulose (149,000 g/mol) this may be interpreted as between 3 and 5 crosslinks (or junctions) per chain, a quite reasonable value considered the approximations involved in treating an “enthalpic” network as if it were simply “entropic”.

The hydrophobic interactions cause the cellulosic chains to aggregate to mutually shield each others. This leads to an increase in aggregate molecular weight (which in turn shifts the relaxation spectrum to very much long times), but also induces heterogeneities throughout the “solution”. At higher temperatures the aggregates appear to come apart again to a limited extent. In thermodynamic terms, we have a system, which is partly of LCST type phase behaviour, but there are kinetic factors as well.

Although some viscoelastic data are in agreement with entangled systems we have performed creep experiments at 65°C to observe that a gel-like response is obtained in these conditions (Fig. 10). The creep compliance increases only a little during the time scale of the experiment, and when the stress is removed it decreases rapidly to a value around ten times smaller. The concentration employed was around half that used in frequency sweeps (Fig. 3), but in this concentration range the phase diagram shows little concentration dependence. The lower concentration employed tends to reduce “kinetic” effects. We are in a situation of a polymer network system [35] for which the single relaxation time observed at high temperature is the aggregate one.

As it was observed previously (existence of a distribution of relaxation times) these results were interpreted as the signature of inhomogeneities which are more and more important and become superimposed on the chain entanglements in semi-dilute solutions. These heterogeneities appeared when the polymer concentration and/or the temperature were increased. The heterogeneities are aggregates, a consequence of the hydrophobic interactions between highly substituted zones [33]. The heterogeneities tend to “smear” out the relaxation behaviour, so we may actually see only one G'' maximum. It may be considered that there are not two well-separated transitions in this system, and thus that the theory of Leibler is not applicable to this data. For instance, it is possible that the chains undergo hydrophobic association to form aggregated clusters that diffuse as an unit.

The physics of a collection of such clusters would be significantly different than the “sticky reptation” discussed in the work of Leibler et al. [3] If the lifetime of the association was long compared to the experimental time scale probed in the rheological experiments, only the relaxation due to the diffusion of the cluster themselves would be observed. This picture is similar to that proposed in the work of Semenov [6]. From the experimental observations

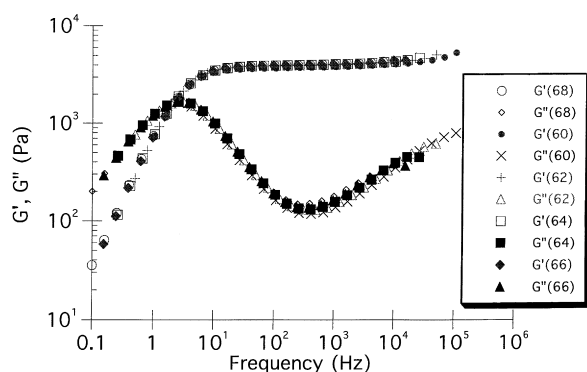


Fig. 8. Master curve within the high temperature domain for A4C methylcellulose solutions ($60^{\circ}\text{C} < T < 68^{\circ}\text{C}$).

such as the increase of the plateau modulus (indicating an increase of the number of junction zones) and the increase of the cross-over frequency with temperature we suggest that for temperatures higher than 60°C the number of junctions increase but the macromolecular chains remain for shorter times within these junction zones.

From the study of relationships between the structure of the macromolecular chain and the macroscopic properties (using samples prepared according to a process in which cellulose is dissolved in DMAC-LiCl [18]) we have demonstrated that the junctions in these inhomogeneities were due to hydrophobic interactions between highly substituted units. Indeed the role of the temperature [39] and the salts was studied and demonstrate the hydrophobic nature of the interactions. Moreover from fluorescence spectroscopy, in which pyrene is used as a probe because the vibrational structure of its fluorescence emission spectrum is very sensitive to the polarity of its environment [40], the presence of hydrophobic domains is clearly demonstrated. The nature of the interaction zones was demonstrated from calorimetric experiments by comparing the behaviour of heterogeneously prepared methylcelluloses (in which the distribution of substituents is not homogeneous and hence leads to a block-like copolymer) and methylcelluloses prepared in our laboratory using a homogeneous process and leading to

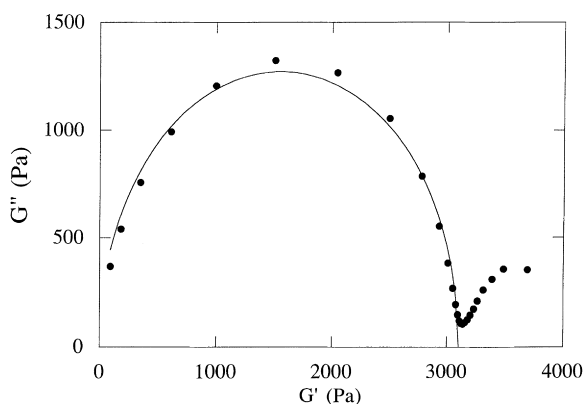


Fig. 9. Cole-Cole plot for the modulus of methylcellulose A4C solution at 64°C (solvent: water, $c = 39 \text{ g/l}$).

Table 3

Cole-Cole parameters for the modulus of A4C methylcellulose solutions within the high temperature domain

Temperature ($^{\circ}\text{C}$)	G_{∞} (Pa)	m	G_0 (Pa)
60	2180	0.488	2241
62	2679	0.486	2695
64	3097	0.487	3241
66	3523	0.487	3664
68	3924	0.486	4144

samples with statistical distribution of the substituents [24]. Low substituted units do not participate in junction zones but favour connections leading to a three dimensional network. Due to the hydrophobic nature of these interactions the number of these ones increase with temperature as observed in Table 4. Indeed the hydrophobic interactions are favoured by temperature [39]. The aggregates formed by interactions between highly substituted units can be connected but the small width of the sample in the rheometer does not allow us to observe the macroscopic physical gel we have observed from the creep experiments.

4. Conclusion

The ability to work on a large frequency scale has enlarged the domain of study of such autoassociative polymeric solutions. The rheological behaviour was compared with the phase diagram conclusions. The same transitions were observed and the reasons for which the transition temperatures were different were understood. Moreover quantitative data was obtained from these rheological experiments.

From the role of the temperature, which favoured the observed interactions, the presence of hydrophobic interactions between the macromolecular chains was confirmed as previously demonstrated from fluorescence spectroscopy experiments and the influence of salts on the rheological data [25].

Different temperature domains were defined and analyzed. In the low temperature domain (from 20 to 40°C for a solution with a polymer concentration of 39 g/l) the rheological behaviour is largely typical of an entangled solution and the linear viscoelastic responses allow the determination of a long characteristic time related

Table 4

Influence of the temperature on the molecular weight between entanglements or junctions of aqueous methylcellulose media

Temperature ($^{\circ}\text{C}$)	G_0 (Pa)	M_e (g/mol)
60	2241	48,200
62	2695	40,320
64	3241	33,730
66	3664	30,000
68	4144	26,700

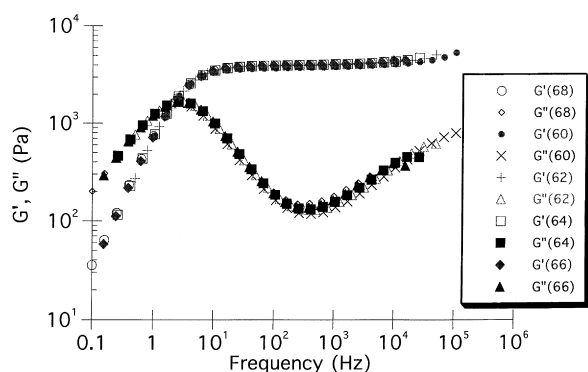


Fig. 10. Creep experiment on a methylcellulose solution stabilized 2 h at 65°C (solvent: water, $c = 15$ g/l).

with a reptation-like chain motion. In the high temperature domain (higher than 60°C for this concentration range) there is a change in the behaviour of the system: a gel is observed and it may be described reasonably well by the Maxwell model. Finally it is shown that the system itself is very spatially heterogeneous in the “gel” state.

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