

REVERSIBLE THERMOASSOCIATION OF WATER-SOLUBLE POLYMERS

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THERMOASSOCIATION RÉVERSIBLE DE POLYMÈRES HYDROSOLUBLES

Dans différents secteurs de l'industrie, les polymères hydrosolubles sont couramment utilisés comme agents épaississants pour contrôler la rhéologie des fluides aqueux. Cependant, leurs propriétés s'affaiblissent lorsque que la température augmente. Pour faire face à ce problème, le concept de polymères hydrosolubles et « thermoassociatifs » a été développé.

De tels systèmes amphiphiles de ce genre peuvent être obtenus en greffant sur une structure hydrophile des chaînes latérales qui ne sont plus hydrosolubles au-dessus d'une température critique inférieure de solution (Lower Critical Solution Temperature = LCST). Des solutions semi-diluées de ces copolymères présentent des propriétés d'épaississement réversibles lorsque la température augmente et atteint une valeur critique proche de la température LCST des chaînes latérales. Ce comportement peut être corrélé à l'agrégation des greffons au-dessus de leur température LCST en « microdomaines hydrophobes » conduisant à la formation d'un réseau tridimensionnel. À des températures plus élevées, la viscosité de la solution cisailée à vitesse constante atteint une valeur maximum. Ceci peut être interprété en termes de réorganisation du réseau physique sous cisaillement, passant d'une structure avec principalement « des associations intermoléculaires » à un système avec un nombre croissant « d'associations intramoléculaires ».

Compte tenu de la diversité des polymères solubles dans l'eau présentant une séparation de phases lors d'une élévation de la température (LCST), différents copolymères « thermoassociatifs » ont été réalisés [14] and [15] en utilisant soit un polyélectrolyte soit un polymère neutre. En vue de l'application de tels systèmes dans l'industrie pétrolière, on a développé des copolymères contenant de l'acide 2-acrylamido-2-méthyl-propane sulfonique (AMPS) et en utilisant de l'oxyde de polyéthylène (PEO) comme greffons à LCST. Une description générale de leur comportement rhéologique sera donnée ici. Leurs propriétés peuvent être contrôlées soit en variant les caractéristiques de la solution (concentration en polymère, salinité, etc.) soit en modifiant la structure chimique du copolymère (taux de greffons, poids moléculaire, etc.). Cette étude rhéologique a montré la potentialité des systèmes « thermoassociatifs », particulièrement pour l'industrie pétrolière [31]. Il est maintenant possible d'avoir des laitiers de ciment fluides à température ambiante et toujours visqueux à la température du fond de puits, selon les propriétés recherchées. La réversibilité du phénomène, conjointement avec les propriétés de rhéofluidification de la solution de polymères, constitue un plus pour la conception des laitiers de ciment et des fluides de forage.

Le phénomène thermoassociatif a également été étudié par diffusion de neutrons aux petits angles (SANS), en utilisant des copoly-

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mères composés d'un squelette de polyacrylate « deutéré » et des greffons d'oxyde de polyéthylène « protonés ». Les propriétés de diffusion de nos systèmes ont été étudiées en faisant varier la température, la salinité et la concentration en polymère de la solution. Un bon accord entre les caractéristiques microscopiques des solutions et leurs propriétés rhéologiques a été constaté.

REVERSIBLE THERMOASSOCIATION OF WATER-SOLUBLE POLYMERS

In various industrial fields, water soluble polymers are commonly used as thickening agents to control the rheology of aqueous fluids. Nevertheless, their properties are weakened as the temperature increases. In order to overcome this problem, the concept of "thermoassociative" water soluble polymers was developed.

Such new amphiphilic systems can be obtained by grafting on an hydrophilic backbone, side chains which become non water soluble above a Lower Critical Solution Temperature (LCST). Semidilute solutions of these copolymers present reversible thickening properties as the temperature increases and reaches a critical value, close to the side chains LCST. This behaviour can be related to the aggregation of the grafts above their LCST, into "hydrophobic microdomains", inducing the formation of a three dimensional network.

At higher temperature, the viscosity of the solution sheared at a constant rate reaches a maximum value. This can be interpreted in terms of the reorganisation of the physical network under shear, from a structure with mainly "intermolecular associations" to a system with an increasing number of "intramolecular associations".

Owing to the diversity of water soluble polymers exhibiting a phase separation on heating (LCST), different "thermoassociative" copolymers were realized [1] and [2], using either polyelectrolyte or neutral hydrophilic backbone. In the aim of applications of such systems in the oilfield industry, copolymers containing 2-acrylamido 2-methyl propane sulfonic acid (AMPS) were developed, using polyethylene oxide (PEO) as LCST grafts. A general description of their rheological behaviour will be given here. Their properties can be controlled either by varying the solution characteristic (polymer concentration, salinity, etc.) or by modifying the chemical structure of the copolymer (grafting ratio, molecular weight of the backbone, etc.). This rheological study showed the potentiality of the "thermoassociative" system, particularly towards the oilfield industry [3]. It is now possible to have thin cement slurries at ambient temperature and still viscous slurries at bottom hole temperature, as desired. The reversibility of the phenomenon joint to the shear thinning properties of the polymer solution are adding a plus for cement slurries and drilling fluids designs.

The thermoassociative phenomenon was also studied by Small Angle Neutrons Scattering (SANS), using copolymers composed by a deuterated polyacrylate backbone and protonated polyethylene oxide grafts. The scattering properties of our system were studied by varying the temperature, the salinity and the polymer concentration of the solution. A good agreement between the microscopic characteristics of the solutions and their rheological properties was found.

TERMOCOMBINACIÓN REVERSIBLE DE POLÍMEROS HIDROSOLUBLES

Los polímeros hidrosolubles se utilizan corrientemente como agentes de espesamiento para controlar la reología de los fluidos acuosos, en distintos sectores de la industria. No obstante, sus propiedades se debilitan a medida que aumenta la temperatura. Para hacer frente a este problema se ha desarrollado el concepto de polímeros "termocombinativos" solubles en el agua.

Nuevos sistemas anfífilos de este género se pueden obtener por injerto en una estructura hidrófila de las cadenas laterales que dejan de ser solubles por encima de una temperatura crítica inferior de solución (Lower Critical Solution Temperature = LCST). Las soluciones semidiluidas de estos copolímeros presentan propiedades de espesamiento reversibles a medida que aumenta la temperatura y alcanza un valor crítico cercano de la temperatura de LCST de las cadenas laterales. Este comportamiento se puede poner en relación con la agregación de elementos de injertos por encima de su temperatura LCST en microsectores hidrófobos que conducen a la formación de una reticulación tridimensional. Con temperaturas más elevadas, la viscosidad de la solución cizallada con valor constante alcanza un valor máximo. Esto se puede interpretar en términos de reorganización de la red física debido al esfuerzo de cizallamiento, que pasa de una estructura con "combinaciones intermoleculares" principalmente a un sistema con un número incremental de "combinaciones intramoleculares".

Habida cuenta de la diversidad de los polímeros solubles en el agua que presentan una separación de fases al proceder a un recalentamiento (LCST), se han realizados distintos copolímeros "termocombinados" [1] and [2], utilizando un polielectrolito, o sea una estructura hidrófila neutra. Con objeto de proceder a la aplicación de estos sistemas en la industria del petróleo, se han desarrollado copolímeros que contienen ácidos sulfónicos de propano 2-acrilamida 2-metil (AMPS) utilizando el óxido de polietileno (PEO) como elemento de injerto LCST. En el presente artículo figura una descripción general de su comportamiento reológico. Sus propiedades se pueden controlar, ya sea variando las características de la solución (concentración de polímero, salinidad, etc.) o por modificación de la estructura química del copolímero (relación de injertos, masa molecular, etc.). Este estudio reológico ha demostrado la potencialidad de los sistemas "termocombinativos", particularmente para la industria del petróleo [3]. En la actualidad existe la posibilidad de obtener escorias de cemento fluidas a la temperatura ambiente y escorias siempre viscosas a la temperatura de fondo de perforación, según aquello que se desea obtener. La reversibilidad del fenómeno, conjuntamente con las propiedades de fluidificación al cizallamiento de la solución de polímeros, constituye un complemento para el establecimiento del concepto de las escorias de cemento y de los fluidos de perforación.

El fenómeno termocombinativo se ha estudiado también por Difusión de Neutrones a Pequeña Reducción (SANS), utilizando copolímeros compuestos por un esqueleto de poliácido deuterado y de óxido de polietileno protonado como injerto. Las propiedades de difusión de nuestros sistemas se han estudiado por variación de la temperatura, la salinidad y la concentración de polímero de la solución. Se ha comprobado una correcta conformidad entre las características microscópicas de las soluciones y sus propiedades reológicas.

INTRODUCTION

Water soluble polymers are well-known for their thickening properties in aqueous solutions. In various industrial applications, highly expanded macromolecules (high molecular weight polymers or polyelectrolytes) are commonly used as they are good viscosifiers even at low polymer concentrations. However, these thickening agents can exhibit a loss of efficiency when they are submitted to "extreme" conditions: high mechanical deformation, increasing ionic strength, etc. So as to overcome these drawbacks, associative polymers have been developed for the last 15 years. The insertion of a small amount of hydrophobic sequences into hydrophilic macromolecules can lead to a water-soluble system which self-aggregates in water. This associative character gives rise to a thickening effect [1] and [3].

The viscosifying properties of water-soluble polymers are weakened as the temperature increases. This behaviour has to be carefully taken into account in many industrial applications such as in the oil industry where aqueous fluids face temperature variations of high magnitude.

Only few macromolecular systems which present a rather constant or increasing viscosity on heating have been studied: aqueous solutions of methyl and hydroxypropylmethyl cellulose of sufficiently high concentration [4], solutions of PEO/PPO/PEO block copolymers at concentrations of about 20% [5], systems constituted by ionic surfactants and non ionic cellulosic ethers such as ethylhydroxyethyl cellulose (EHEC) [6], hydrophobically modified polyacrylic acid in presence of non ionic surfactant [7].

For each of these systems, the viscosifying phenomenon on heating is observed in specific conditions of concentration and temperature and it can be related to the formation of associative aggregates between the main chains. In this context, our objective was to develop a general concept of "thermoassociative" water-soluble polymers which would present reversible thickening properties as the temperature raises. In the aim of applications in the oil industry, these new systems would ensure flexibility in chemical composition, which is necessary to have temperature resistant copolymers but also to solve compatibility problems in drilling fluids and cement slurries.

The concept and design of these new associative systems are depicted in this paper. After a general

description of their rheological behaviour, some parameters controlling the viscosifying effect are presented. A molecular interpretation of their specific rheological properties is proposed.

1 CONCEPT AND DESIGN

The basic concept proposed to obtain a "thermoassociative" system consists in inserting into a water-soluble macromolecule, some "block" units or side chains which present a loss of water solubility above a critical temperature (Lower Critical Solution Temperature or LCST). A typical phase diagram of LCST polymer in water is given in Figure 1. Such phase behaviour has been described for various polymers in water, as for example polyethylene oxide [8] and [9], polypropylene oxide [10], poly N-isopropylacrylamide [11], polyvinyl methylether [12] or hydroxyalkyl cellulose [13].

A possible structure of our "thermoassociative" macromolecule can be represented by the Figure 2. At temperature lower than the grafts LCST, the system is entirely water-soluble and behaves as usual macromolecular solutions. However, as the temperature increases and reaches the side chains LCST, one can easily imagine these units self-aggregating into hydrophobic microdomains. In the semi-dilute regime, hydrophobic clusters involving grafts covalently linked to different water-soluble backbones can be expected (Fig. 3).

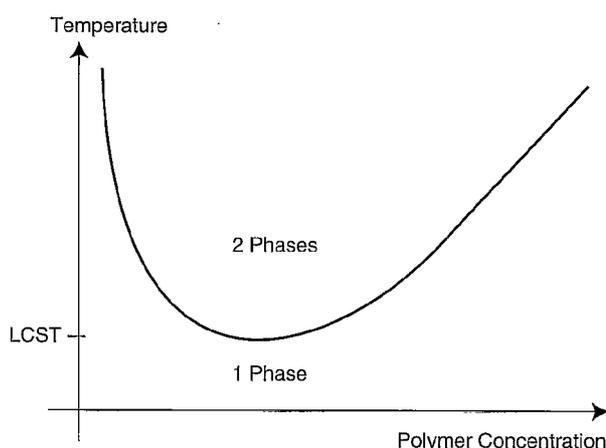


Figure 1

General phase diagram of a polymer/water system which presents a Lower Critical Solution Temperature (LCST).

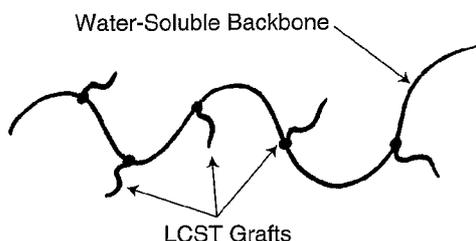


Figure 2
Possible chemical structure of a "thermoassociative" polymer.

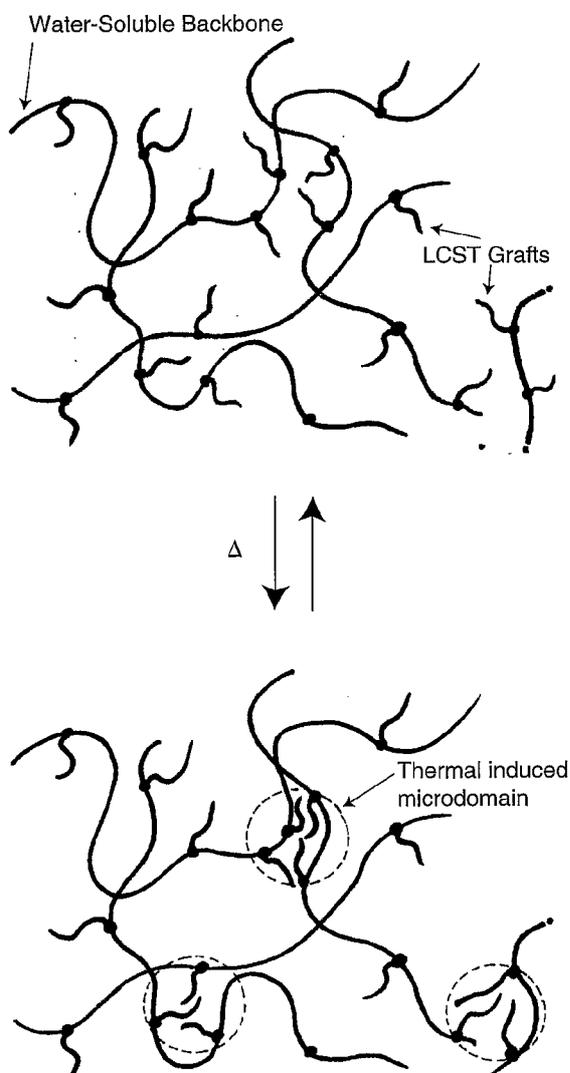


Figure 3
Concept of "thermoassociative" polymer.

Thus the thermodynamical properties of the LCST grafts should induce above a critical temperature the formation of physical cross-links between the main chains, giving rise to a viscosity increase on heating. Such phenomenon can be described as a microscopic phase separation of the LCST chains above their critical point, the global water solubility of the system being ensured by the hydrophilic backbone.

Owing to the diversity of water-soluble polymers exhibiting a phase separation on heating (LCST), various series of "thermoassociative" copolymers were realised using either polyelectrolyte or neutral hydrophilic macromolecules [14, 15, 16]. In the aim of applications in the oilfield industry, a large number of copolymers were synthesised using polyethylene oxide chains as LCST grafts. As a matter of fact, this low cost polyether presents a lower critical point in the temperature range (100-200°C) corresponding to potential applications for "thermoassociative" systems in cement and drilling fluids.

The phase behaviour of PEO in water is widely described in the literature [8, 9, 10]. The phase diagram of PEO/water systems is shown to be highly dependent on the molecular weight of the chains, as represented in figure 4 [9]. For short chain lengths, aqueous solutions of PEO are monophasic whatever the temperature and the polymer concentrations are. As the PEO molecular weight increases and becomes higher than 2000 g/mol, a closed solubility gap is observed. For even longer chain lengths, the UCST increases whereas the LCST can be lowered down to 100°C (Fig. 4).

So as to explain the specific behaviour of PEO chains in water, different theoretical approaches have been proposed. Kjellander [17] based his interpretation on the assumption that PEO chains fit well into the water lattice (adequate distances between the ether oxygens, hydrogen bonding interactions, etc.), inducing a well-organised structure at low temperature. In this context, various experimental works were carried out to better define the structural properties of PEO in water [1 - 22]. When the temperature is increased, the unfavourable entropic term in the free energy of mixing becomes predominant and the water structure around the PEO molecules is destroyed; this leads to a phase separation of the solution.

In a second approach, Goldstein [23] suggested that the intermolecular potential between PEO chains and water molecules has regions which are strongly attractive (hydrogen bonding: "bonded state") and domains which

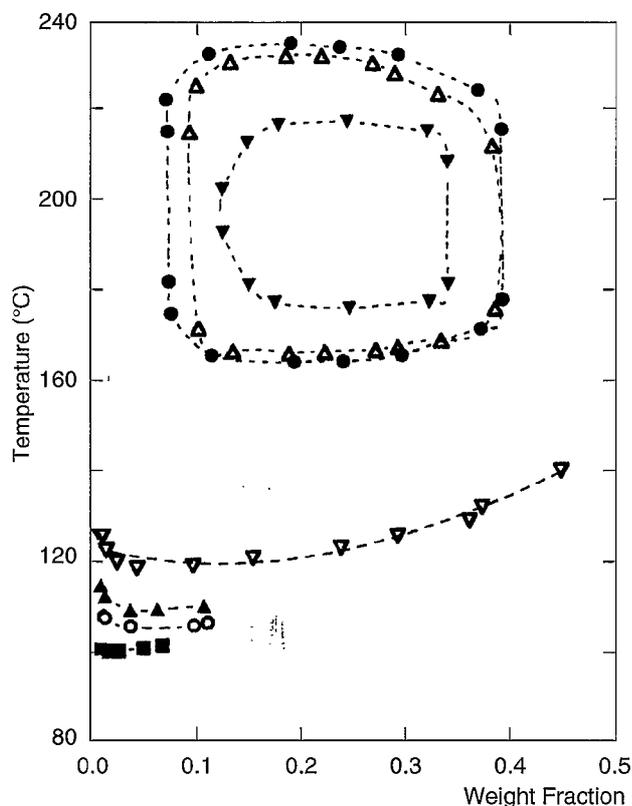


Figure 4

Temperature/weight fraction diagram for poly(ethylene oxide) samples in water [9]:

- , $M = 1\,020\,000$ g/mol; ○, $M = 21\,200$ g/mol;
- ▲, $M = 14\,400$ g/mol; ▽, $M = 8\,000$ g/mol;
- , $M = 2\,290$ g/mol; △, $M = 2\,270$ g/mol;
- ▼, $M = 2\,180$ g/mol.

are repulsive: “nonbonded state”. On the basis of the Flory-Huggins theory, the occurrence of the critical point is explained in terms of a decreasing proportion of the “bonded” state as the temperature raises.

Karlström [24] proposed a general model based also on the Flory-Huggins theory but considering the existence of two main conformations of PEO chains which have different energy and interact differently with other molecules. The thermodynamical properties of the polyether is then interpreted by the evolution of the PEO conformations with temperature.

The phase behaviour of PEO/water systems is also reported to be influenced by the salinity of the solution and these variations highly depend on the chemical nature and concentration of the added salt (Fig. 5) [8]. According to Florin’s analysis [25], this phenomenon

would be related to the influence of salt on the water structure around the PEO macromolecules. For most of the salt studied (Fig. 5), the presence of electrolyte induces a destruction of these “hydration shelves” near the ethylene oxide units with the result that the solution phase separates.

The thermodynamical properties of the LCST grafts such as PEO chains have to be carefully considered before elaborating any “thermoassociative” systems. The salinity of the medium, the molecular weight and the concentration of the LCST chains are part of the “key” parameters controlling the “thermoassociative” behaviour.

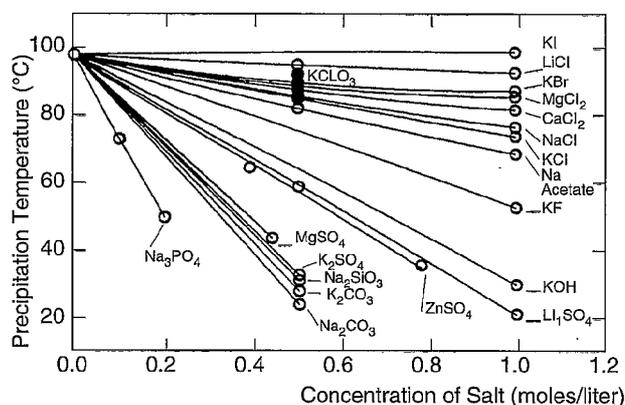


Figure 5

Lower critical solution temperature for 0.5% poly(ethylene oxide), $M_w = 4 \cdot 10^6$ g/mol, as function of salt concentration [8].

2 SYNTHESIS AND NOMENCLATURE

On the basis of a comb-like structure (Fig. 2), these new copolymers were synthesised by grafting monoaminated LCST chains on hydrophilic macromolecules containing a minimum amount of carboxylic functions (Fig. 6) [16] and [26]. This reaction requires the presence of a coupling agent (e.g. N-ethyl-N’-(3-dimethylaminopropyl) carbodiimide, dicyclohexyl carbodiimide) and can be realised either in water or in an aprotic organic solvent (NMP, etc.) [14, 15, 16] and [26]. So as to avoid any cross-linking reaction in presence of difunctional LCST chains, the polymer concentration of the solution is kept below its critical value C^* . The incorporation of LCST chains into the water-soluble backbone is studied by SEC of

the bulk composition. After completion of the reaction, the proportion of LCST units in the copolymer, characterised by the "grafting ratio τ ", is first estimated by SEC and then confirmed by ^1H NMR. As the reaction is performed in a good solvent of the LCST chains, we can assume that the PEO chains are randomly grafted along the backbone which is either polyacrylic acid or a macromolecule with statistically distributed carboxylic groups.

This grafting method is thus relevant to synthesising homologous series of "thermoassociative" copolymers with a controlled architecture. Various systems were obtained in this way, either by varying the chemical nature of the copolymer or by modifying its chemical characteristics cited above (Table 1). In this context, a sample named "AMPS-AA/PEO5 $\tau\%$ " corresponds to a copolymer of Acrylamido-2-methyl propane sulfonic acid (AMPS) and Acrylic Acid (AA), bearing polyethylene oxide side chains of molecular weight 5000 g/mol; τ is the number of LCST grafts per 100 monomer units of the backbone. The molecular weight of the AMPS-AA copolymer is estimated at

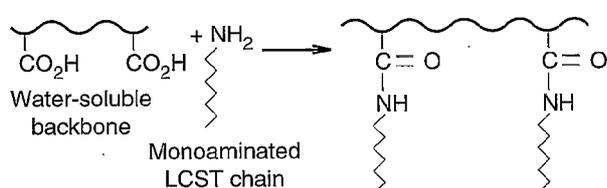


Figure 6
 Synthesis of grafted "thermoassociative" polymer.

TABLE 1
 Examples of "thermoassociative" polymer.

Copolymer	Water-soluble backbone	M_{backbone} g/mol	LCST grafts	M_{grafts} g/mol	Grafting ratio τ (molar %)
PAA50/PEO5 0.40%	PAA	50.000	PEO	5000	0.40
PAA150/PEO5 0.55%	PAA	150.000	PEO	5000	0.55
PAA500/PEO25 0.40%	PAA	500.000	PEO	25.000	0.40
AMPS-AA/PEO5 0.75%	AMPS-AA	700.000	PEO	5000	0.75
AMPS-AA/PEO10 0.50%	AMPS-AA	700.000	PEO	10.000	0.50
AMPS-AA/PEO25 0.50%	AMPS-AA	700.000	PEO	25.000	0.50
PAAD500/PEO25 0.30%	PAAD	500.000	PEO	25.000	0.30
CMC/PEO5 0.60%	CMC	1.000.000	PEO	5000	0.60
PAA150/PPO 21%	PAA	150.000	PEO	600	21

700 000 g/mol and its composition is the following one: AMPS 80%/AA 20% (molar %). As other example, the polymer "PAA500/PEO25 0.40%" is constituted by a polyacrylic acid backbone ($M \approx 500\,000$ g/mol) grafted at 0.40% (molar %) by polyethylene oxide chains of molecular weight 25.000 g/mol.

It is important here to notice that for copolymers grafted by PEO5 chains ($M \approx 5000$ g/mol), the grafting ratio is lower than 2% (molar %) whereas it is decreased down to 0.50% for PEO25 side chains ($M \approx 25.000$ g/mol). This grafting ratio, which is quite low compared to hydrophobically modified polyacrylic acids [3], has indeed to be sufficiently high to induce an aggregation process but not too high in order to prevent a macrophase separation of the system. A balance between the hydrophobicity of the LCST grafts over their critical point and the hydrophilic character of the backbone has to be found to observe the "thermoassociative" behaviour.

3 RHEOLOGICAL BEHAVIOUR

The viscosity measurements as function of the temperature were performed on two different rheometers, depending on the temperature range considered:

- From 20°C up to 80°C, a controlled stress viscometer Carri-Med CS 100 (RHEO) with a cone/plate geometry was used. The Carri-Med cone calibration given by the supplier was as follows: cone diameter = 2.0 cm, cone angle = 2° and truncation = 55 μm . Temperature was controlled by a high power Peltier system and the heating rate was fixed at 2° C/min.
- From 20°C to 200°C, rheological experiments were carried out on a controlled shear rate rheometer "FANN 50" with a Couette geometry. The pressure applied above the sample was fixed at 25 atmospheres and the heating rate at 2° C/min.

Specific viscosity measurements were performed on a Couette viscometer "Low-Shear Contraves 30" using the 1-1 bucket, at 35°C.

3.1 Influence of temperature

In order to evidence the "thermoassociative" phenomenon, two main conditions are required. Firstly, the system must be in its semi-dilute regime so as to make

“intermolecular” association possible whereas below the critical overlap concentration (C^*), only “intramolecular” aggregation may occur. Secondly, the temperature of the sample must reach the critical temperature of the grafts in order to induce interactions between the side chains.

In this context, a 3% w/w solution of the copolymer AMPS-AA/PEO25 0.55% was studied from 20°C to 200°C (Fig. 7). The shear rate applied is fixed at 104 s^{-1} . The viscosity variations can be described in three steps:

- From 20°C to 110°C, the viscosity decreases as usually observed for macromolecular solutions, according to an Arrhenius law.
- From 110°C to 170°C, an increase of viscosity is observed and the magnitude of the thickening effect is about 1.5 decade over 60°C. The onset temperature 110°C corresponds to the critical temperature of a 1.3% w/w solution of PEO25 chains, as described by their phase diagram. For the 3% w/w solution of AMPS-AA/PEO25 0.55%, the concentration of PEO25 grafts is also equal to 1.3% w/w as the weight percentage of the polyether in the copolymer

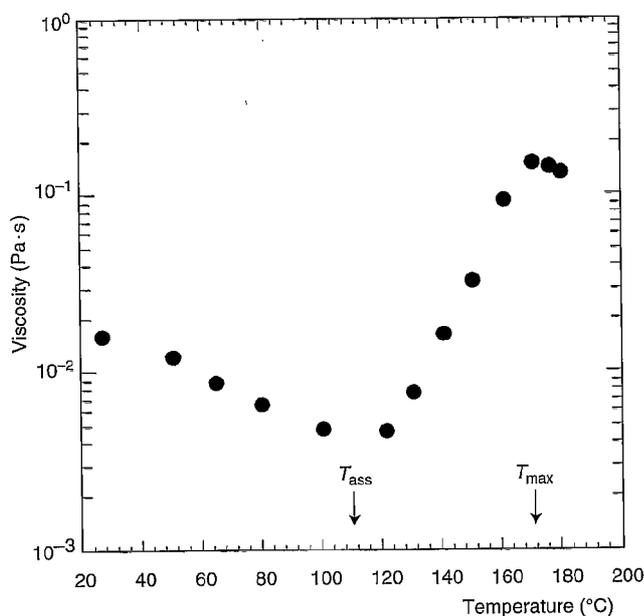


Figure 7

Variations of viscosity with temperature for a 3% w/w solution of AMPS-AA/PEO25 0.55%. The shear rate applied is fixed at 104 s^{-1} .

is estimated at 42% w/w. The viscosifying effect observed over 110°C can then be attributed to the aggregation of PEO25 grafts into intermolecular clusters above their critical point (Fig. 3).

- At 170°C, the viscosity reaches a maximum value before decreasing smoothly at higher temperature. An interpretation of this phenomenon, which reflects a loss of connectivity of the associative network, will be further proposed.

The rheological behaviour depicted here is reversible with temperature, which is consistent with the formation of a physical network on heating. It is typical of all “thermoassociative” polymer solutions and in complete agreement with the concept proposed.

3.2 Influence of salt concentration

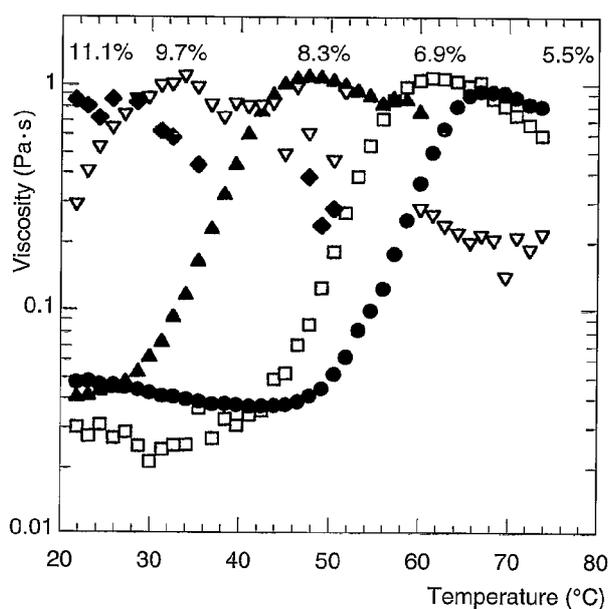
As the LCST of polymer/water systems is well known to be dependent on the salinity [8, 27, 28], variations of the thermoassociative behaviour in presence of electrolytes can be expected. In order to evidence this effect, the rheological properties of our systems were studied as function of potassium carbonate concentration. Among the salts depicted in Figure 5, K_2CO_3 was selected for its high solubility in water (112 g per 100 mL of water at 20°C) and its significant lowering effect on the PEO LCST. Figure 8 shows the evolution of viscosity with temperature for PAA500/PEO25 0.40% solutions ($C_p = 3\% \text{ w/w}$, $\dot{\gamma} = 50 \text{ s}^{-1}$), at different K_2CO_3 concentrations varying from 5.5% w/w to 11.1% w/w. The presence of electrolyte is also well known to favour intermolecular association of hydrophobically modified polyelectrolytes by weakening the electrostatic repulsions between the backbones [29]. However, this effect is negligible at the high ionic strengths studied.

Firstly, let us consider the solution containing 5.5% w/w of K_2CO_3 . From 20°C to 45°C, the viscosity decreases. A thickening effect is then observed from 45°C to 65°C, temperature corresponding to the viscosity maximum. The temperature 45°C at which the viscosifying properties occur is very close to the LCST (50°C) of a PEO25 solution in the same conditions of concentration ($[\text{PEO}] \approx 1.5\% \text{ w/w}$) and salinity ($[\text{K}_2\text{CO}_3] = 5.5\% \text{ w/w}$). These viscosity variations with temperature are consistent with the “thermoassociative” behaviour previously described.

As the salt concentration raises from 5.5% w/w to 11.1% w/w, the so-called “association temperature”

(T_{ASS}) decreases from 45°C down to a value lower than 20°C. At each salinity, a good agreement between T_{ASS} and the LCST of the PEO solution at the same concentration, is found (Fig. 8). Moreover, the magnitude of the viscosifying effect and the temperature range in which thickening properties occur, seem to be unaffected by the presence of salt: $\Delta\eta \approx 1.5$ decade over $\Delta T \approx 25^\circ\text{C}$. In other words, increasing the salt concentration induces, in this range of salinity, a shift of the viscosity variations down to a lower range of temperature.

This effect of salt concentration was observed for other series of copolymers [14, 15, 16] and confirms that the “thermoassociative” phenomenon is closely related to the thermodynamical properties of the PEO grafts.



$[\text{K}_2\text{CO}_3]$ (%)	T_{ASS} (°C)	LCST (°C)
5,5	45	50
6,9	35	32
8,3	≈ 20	22
9,7	< 20	< 20

Figure 8

Variations of viscosity with temperature for a 3% w/w solution of PAA500/PEO25 0.40%, at different K_2CO_3 concentrations: 5.5%, 6.9%, 8.3% and 11.1%. $\dot{\gamma} = 50 \text{ s}^{-1}$.

In the Table are compared the association temperature T_{ASS} and the LCST of PEO25 solution in the same conditions of concentration and salinity.

These results also point out that the thickening effect can be easily adjusted in a desired temperature range by varying the medium salinity.

3.3 Effect of the shear rate

The rheological behaviour of usual associative systems are well known to be sensitive to mechanical deformation [3, 29, 30]. As the thickening properties of “thermoassociative” copolymers are based on a similar mechanism of physical cross-linking, the viscosity enhancement observed on heating might also be dependent on the shear rate applied.

Figure 9a shows the viscosity of a PAA90/PEO5 0.55% solution ($C_p = 3\% \text{ w/w}$, $[\text{K}_2\text{CO}_3] = 8.3\% \text{ w/w}$) plotted versus the shear rate applied ranging from 8 s^{-1} up to 500 s^{-1} . These measurements were performed at different temperatures varying from 27°C to 181°C. The rheological behaviour of this system can be described in four temperature regimes:

- From 27°C to 61°C, the viscosity decreases and the solution is Newtonian. In this temperature range, the PEO5 grafts are water-soluble and the system behaves like usual macromolecular solution at quite low concentration.
- From 61°C to 103°C, a thickening effect is observed in the whole range of shear rate studied and the system remains Newtonian. The onset temperature 61°C corresponds to the LCST of a PEO5 solution in the same conditions of salinity and concentration ($\text{PEO5} = 0.8\% \text{ w/w}$, $[\text{K}_2\text{CO}_3] = 8.3\% \text{ w/w}$). The viscosity enhancement observed on heating is in agreement with the thermodynamical properties of the LCST grafts.
- From 103°C to 137°C, the viscosity keeps increasing with temperature but the Newtonian character is restricted to the low shear rates whereas a shear-thinning behaviour is observed at high shear values.
- From 137°C to 181°C, the viscosity decreases and the solution exhibits a shear-thinning character over the whole range of shear rate investigated.

It is clear from these results that the thermoassociative phenomenon is shear rate dependent. As the PEO5 grafts have reached their critical point, the Newtonian viscosity increases with temperature and the Newtonian plateau is limited to lower values of shear rate. The slope of the curve $\log \eta / \log \dot{\gamma}$ in the pseudo-plastic regime seems to tend towards -0.5 in the high temperature range.

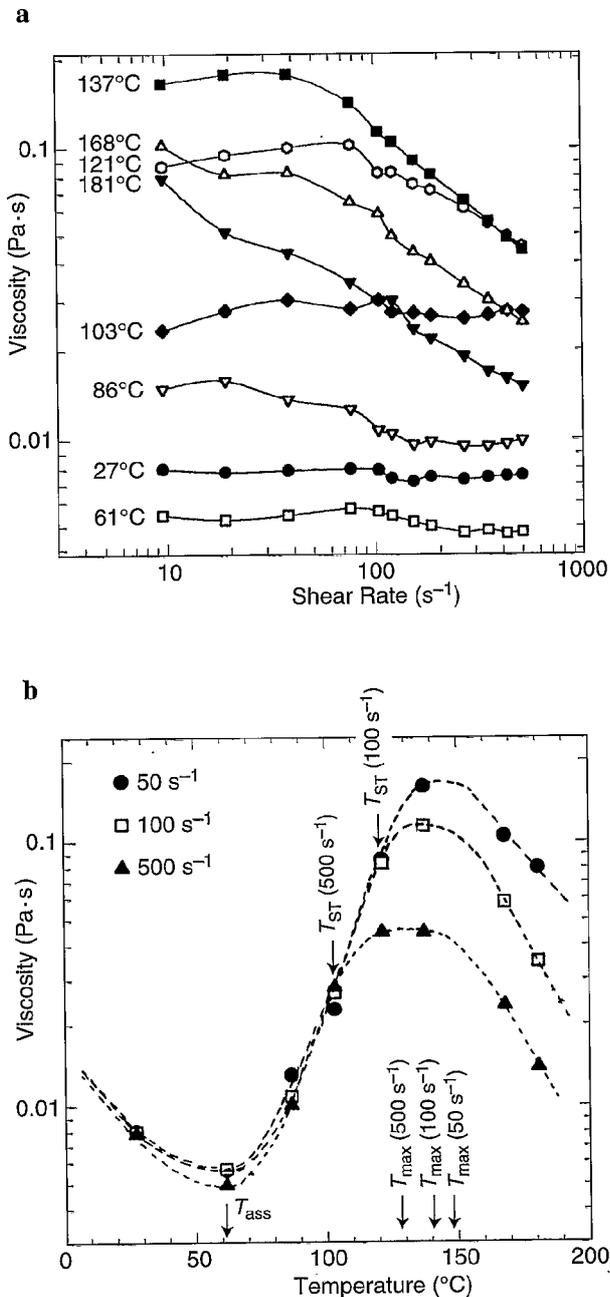


Figure 9

Rheological behaviour on heating of a 3% w/w solution of PAA90/PEO5 0.55% ($[K_2CO_3] = 8.3\%$ w/w).

a: Variations of viscosity with shear rate obtained at different temperatures: 27°C, 61°C, 86°C, 103°C, 121°C, 137°C, 168°C and 181°C.

b: Variations of viscosity with temperature, at three constant shear rates: 50 s⁻¹, 100 s⁻¹ and 500 s⁻¹.

In order to analyse this behaviour, let us consider the viscosity evolution with temperature at a constant shear such as 100 s⁻¹. From 27°C to 61°C, the viscosity decreases as the system is entirely water-soluble. From 61°C to 121°C, thickening properties occur in relation of PEO5 grafts interactions and the solution remains Newtonian. From 121°C to 137°C, the viscosity enhancement is yet observed but the system presents a shear-thinning character. Around 137°C, the viscosity reaches its maximum value before decreasing at higher temperature. These results show that for a given shear rate, two “critical” temperatures characterising the thermo-thickening behaviour can be defined:

- the “shear-thinning” temperature, T_{ST} , corresponding to the onset of the shear-thinning properties;
- the “maximum” temperature, T_{MAX} , at which the maximum of viscosity is observed.

Both of these temperatures are lowered as higher shear rates are applied, as opposed to the “association” temperature T_{ASS} which is independent of the mechanical deformation.

If the viscosity of the same solution is now plotted versus the temperature at three shear rate values: 50 s⁻¹, 100 s⁻¹ and 500 s⁻¹, the rheological behaviour depicted in Figure 9b is observed.

Thickening behaviour occurs above 60°C at the three shear rates studied, in agreement with the formation of PEO5 clusters as they reach their critical point. This thermoassociative system remains Newtonian from the “association” temperature up to a critical temperature T_{ST} over which it presents a shear-thinning character. T_{ST} is observed at 100°C for a shear rate of 500 s⁻¹ whereas it occurs at 120°C for 100 s⁻¹. From T_{ST} up to T_{MAX} , the viscosity is enhanced on heating before decreasing at higher temperature. T_{MAX} is lowered from 145°C down to 125°C as the shear increases from 50 s⁻¹ to 500 s⁻¹.

The occurrence of a shear dependent behaviour is responsible for the weakening of the thickening properties at high shear rates and also for the reduction of the temperature range between T_{ASS} and T_{MAX} . It is important to notice that the viscosity decrease above T_{MAX} is rather smooth and that the solution remains quite clear. Therefore interpreting the viscosity maximum as a macroscopic phase separation of the system is not realistic with these copolymers. Their behaviour is different from the one of cellulosic derivatives. Complementary experiments with a PEO5 grafted carboxymethyl cellulose evidenced above the association

temperature a sharp drop of viscosity down to a few mPa·s whereas the solution becomes cloudy. In that particular case, a macroscopic phase separation might occur, due to the weak water-solubility of the cellulosic backbone [16].

3.4 Discussion

In agreement with the “thermoassociative” concept proposed, we showed that a macromolecular system composed of a water-soluble backbone and LCST side chains can present thickening properties on heating. This viscosity enhancement is based on the formation of hydrophobic clusters which form physical cross-linking points between the main chains. This mechanism is similar to that of hydrophobically modified polymers but its originality lies in the fact that the association process can be stimulated by “external” parameters such as temperature or salinity.

The “thermoassociative” behaviour is correlated to the specific properties of each component of the copolymer. The characteristics of the water-soluble backbone, such as its molecular weight and its conformation in aqueous medium, set the critical polymer concentration Cp^c above which intermolecular association may occur. The side chains aggregation above the association temperature is closely related to the phase behaviour of this LCST polymer. At a given polymer concentration, a thermoassociative behaviour can be expected only if the critical temperature of the grafts is reached. The good agreement found between the thermodynamical properties of the side chains and the onset of the thickening properties demonstrates the ability to control the thermal behaviour of these systems. On the basis of the phase diagram of the LCST grafts and the rheological properties of the hydrophilic backbone, the thermoassociative behaviour can be easily adjusted in the required range of temperature and salinity. The thickening effect can be controlled either by varying the solution characteristics (salinity, polymer concentration, etc.) or by modifying the chemical structure of the copolymer (grafting ratio, molecular weight of the backbone, etc.). Thermoassociative systems can be used to control the rheology of aqueous fluids over a temperature range as large as 100°C. This shows the high potentiality of these systems, particularly towards the oilfield industry [31]. Above the maximum temperature T_{MAX} , the system is stable and the viscosifying properties remain efficient over some tens of degrees. The rheological study previously described

shows the evolution of this viscosity maximum with the key parameters of the system (salinity, shear rate, etc.). The occurrence of this maximum can then be easily controlled according to the desired thickening effect. The main point now is to interpret this upper limit of the viscosity enhancement.

Let us refer to the theoretical approaches elaborated to describe the rheological behaviour of physically cross-linked networks such as ionomers or water-soluble associative polymers. One of the most well known models, the “transient network theory”, was first elaborated by Green and Tobolsky [32] and then generalised by Tanaka and Edwards [33]. In this approach, the system considered corresponds to telechelic polymers: the macromolecules are linear and carry “sticky” functional groups at both ends. In the unentangled regime, these chains induce a transient physical network in which the cross-linking units are formed by aggregates of the “sticky” end groups. The junctions are sufficiently weak to break and recombine in thermal fluctuations, which induces a rapid interchange of the “sticky” end groups between the aggregates. The system can be characterised by two parameters:

- the number ν of “elastically active chains” which both ends are involved in two different clusters;
- the relaxation time τ_X of the physical network which represents the mean life time of a “sticky” end group inside an aggregate.

The viscosity of the system is proportional to the product of τ_X and ν .

In order to explain the shear-thinning character of physically cross-linked systems, Tanaka and Edwards considered the parameters τ_X and ν as functions of the mechanical deformation.

The rheological behaviour of “thermoassociative” polymers and especially the viscosity maximum can be described using a similar approach.

Our system is then characterised by:

- the number ν of “elastically active” chains which grafts are involved in distinct hydrophobic aggregates.
- its relaxation time τ_X which reflects the interactions between LCST grafts.

For a constant shear rate $\dot{\gamma}$, an experimental time τ_{exp} can be defined as inversely proportional to $\dot{\gamma}$. The following interpretation can be proposed (Fig. 10).

Below the association temperature, the parameters τ_X and ν are equal to zero as the system is entirely water-soluble.

As the temperature increases and becomes higher than T_{ASS} , τ_X and ν raise because of the formation of hydrophobic clusters. The relaxation time τ_X is expected to increase with temperature in parallel to the hydrophobicity of the LCST grafts. Two temperature ranges can be distinguished depending on the respective values of τ_X and τ_{exp} :

- As τ_X is lower than τ_{exp} , the destruction and rebuilt processes of the cross-linking points are so fast that the transient network is not affected by the mechanical shear. The system presents a Newtonian behaviour, which is observed at the onset of the thermoassociation phenomenon.
- The second temperature regime would then occur as the relaxation time τ_X becomes higher than the experimental time τ_{exp} . The grafts snap under shear from hydrophobic clusters faster than they can reengage. As a consequence, the number ν of "elastically active" chains reaches a maximum value at a critical temperature T_{ST} above which a shear-thinning behaviour is observed. The system viscosity which is deduced from the product of τ_X and ν presents a maximum value at a temperature T_{MAX} higher than T_{ST} (Fig. 10).

It is important to notice that the model of Tanaka and Edwards was developed for a system quite simple compared to our (unentangled state, two "sticky" groups per chain, polymers of uniform length). However, this theoretical approach is relevant to describe the rheological behaviour of our new polymers.

According to this interpretation, the number of "free" grafts which are disengaged from any aggregates would increase with the temperature above T_{ST} . However, the probability of having "free" grafts is very small as the hydrophobic interaction between LCST chains might be greater than the thermal motion kT . A more realistic description of our system above T_{ST} would then consider the reengagement of these "free" grafts into intramolecular clusters. In this context, the occurrence of the shear-thinning behaviour and the viscosity maximum can be interpreted in terms of the reorganisation of the physical network under shear, with an increasing number of intramolecular microdomains to the detriment of intermolecular associations.

Complementary experiments would be useful to characterise the evolution of our systems microstructure under shear (number and size of the cross-linking

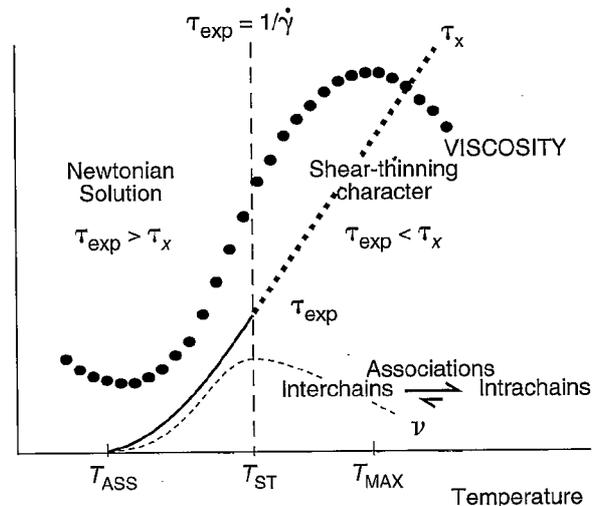


Figure 10

Schematic representation of the "thermoassociative" phenomenon, using the "Transient Network Theory" [33].

Variations with temperature of:

- the relaxation time τ_X of the system,
- the number ν of "elastically active chains",
- the viscosity of the solution.

units, composition of the aggregates). In a similar way, Yekta [34] studied the microstructure of HEUR polymer solution under shear by fluorescence measurements. The number of hydrophobic aggregates seems unaffected by the mechanical deformation, although a shear-thinning behaviour is observed. This was interpreted by an increasing proportion of "intramolecular" associations, to the detriment of "intermolecular" clusters.

CONCLUSIONS

As initially proposed, new macromolecular systems which viscosity in water remains rather constant or increases with temperature can be obtained by inserting LCST chains into hydrophilic polymer. The "thermoassociative" phenomenon is related to the sensitive properties of the LCST sequences but also to the rheological behaviour of the water-soluble backbone. Taking into account the diversity of hydrophilic polymers as well as LCST water-soluble macromolecules, the generality of the thermoassociative concept becomes obvious. Several families of thermoassociative

copolymers can be easily synthesised by grafting monoaminated LCST chains on a carboxylic acid functionalized polymer. This reaction process ensures a good control of the copolymer chemical structure (molecular weights of the backbone and the grafts, grafting ratio, etc.), which is a necessary condition to correlate the rheological properties observed with the characteristics of the macromolecules.

When heated, the viscosity of these systems starts to increase above a critical temperature, in agreement with the phase behaviour of the LCST grafts. At higher temperature, the viscosity of the solution under shear reaches a maximum value and then declines smoothly, while the system remains monophasic. This rheological phenomenon can be related to a topological transformation of the solution under shear with recombinations from "intermolecular" to "intramolecular" associations.

The viscosifying properties on heating of these new systems can be managed according to the desired effect either by modifying the chemical structure of the copolymer or by varying the solution characteristics (salinity, polymer concentration, etc.). This rheological study shows the potentiality of the thermoassociative systems which can be used to control the viscosity of aqueous fluids over a wide range of temperature. For example, applications of these new polymers in cement and drilling fluids can be expected as a constant viscosity of these aqueous systems is required from ambient up to 200°C. The reversibility of the thickening properties and the shear-thinning character of these polymer solutions enlarge their potential applications in the oil-field industry.

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