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ORIGINAL CONTRIBUTION

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Aqueous solution behavior of new thermoassociative polymers

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Abstract A new kind of water-soluble polymer was obtained by grafting side chains, characterized by a phase separation on heating (Lower Critical Solution Temperature LCST), on a hydrosoluble backbone. For semi-dilute solutions, the side chains associate as the temperature exceeds a critical temperature (T_{ass}), which is close to their LCST. Microdomains are formed which act like physical crosslinking units between the main chains, and an increase in the aqueous solution viscosity is observed. Systems based on 2-Acrylamido-2-methyl propane sulfonic acid (AMPS) backbone and polyethylene oxide (PEO) side chains were developed. Their rheological behavior in both dilute and semi-dilute states was studied by varying differents parameters such as polymer and salt concentrations, grafting ratio, etc. Fluorescence measurements indicate the formation of hydrophobic microdomains on heating, in agreement with the thickening properties of the solutions.

Key words Thermothickening – associative polymers – lower critical solution temperature – shear-thinning behavior – fluorescence

Introduction

Water-soluble polymers are commonly used to control the rheology of aqueous solutions, and their thickening properties are applied in many industrial fields where they are used in fracturing and drilling fluids, lubricants, suspending agents, etc. Nevertheless, their efficiency is reduced under extreme conditions. For example, degradation of high molecular weight polymers is sometimes observed under high shear rate and some polyelectrolytes lose part of their thickening properties in the presence of salts. So, in order to avoid such problems, associative polymers [1–3] have been developed in the last decade. Their viscosifying properties are due to the association of hydrophobic units carried by a water-soluble backbone. Also, the viscosifying effect of water-soluble polymers is lowered upon heating, which is a drawback of relatively high importance with respect to their industrial applications. Our aim was to develop a new type of associative polymer which, used as additives in aqueous solutions, would make the viscosity constant or increase as the temperature raises.

The concept and design of thermothickening polymers have been described in previous papers [4, 5] and can be summarized as follows: such systems are based upon a water-soluble macromolecular backbone containing some "block" regions or side chains. Aqueous solutions of these moieties present a phase separation above a Lower Critical Solution Temperature (LCST). The viscosity enhancement observed for the solutions of thermothickening polymers when the temperature exceeds this LCST, is due to the association of the grafts or blocks into hydrophobic microdomains which effectively cross-link adjacent polymer chains.

Temperature range over which thermothickening properties occur can be adjusted by varying "external" parameters such as salinity, polymer concentration, or the system characteristics like chemical structure and the molecular weight. Good agreement has been found between the rheological behavior observed as the temperature increases and the thermodynamical properties of the grafted chains.

Synthesis of 2-Acrylamido-2-methyl propanesulfonic acid (AMPS)/acrylic acid (AA) copolymers, their modification by grafting polyethylene oxide (PEO) and their resulting rheological properties with temperature are presented in this paper. The structure of the backbone has been defined by the desirable properties of AMPS in oilfield applications. It has good thermal and hydrolytic stability, high water solubility (1.5 g/ml at 25 °C) and tolerance to divalent cations. Thermoassociative properties of these systems were studied in semi-dilute solutions where the polymer concentration, the salinity, the chemical structure of the grafted polymers containing different amounts of LCST chains were all varied. The dependence of thermothickening properties on the applied shear rate was also observed. Complementary viscosity measurements were carried out on dilute solutions above the LCST of the side chains. Fluorescence experiments were performed to fully understand the microstructure changes involved in the viscosifying phenomenon on heating.

Experimental

Materials

- 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) and acrylic acid (AA) were purchased from Fluka Chemika and used without further purification.
- O-(2-Aminoethyl)-O′-methyl polyethylene oxide (PEO5) was obtained from Fluka Chemika. The molecular weight was given as $M = 5000$, but it was estimated to be 6800 by capillary viscometry measurements. The NH_2 content was studied by titration and was found to be close to 0.07 mmol/g, a low value which means that only 45% of the PEO5 chains were aminated.
- 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDC) was purchased from Aldrich.
- Ammonium persulphate ($(NH_4)_2S_2O_8$) was obtained from Prolabo and N,N,N′,N′-tetramethyl-ethylenediamine (TEMED) from Aldrich.
- The ammonium salt of 8-Anilinonaphthalene-1-sulfonic acid (ANS) was purchased from Fluka Biochemika. An aqueous ANS stock solution of $2.9 \cdot 10^{-4}$ M was used for further fluorescence studies.
- Water was purified with a Milli-Q system from Millipore.

Analytical methods

^1H NMR

AMPS/AA copolymer and its PEO5 modified derivatives were characterized by ^1HNMR on a Brucker WP 250 spectrometer (250 MHz).

Titration

Chemical composition of AMPS/AA copolymer was estimated by titration of the sulfonic and carboxylic functions using a "TT Processeur 2-Tacussel" titrator with a glass electrode.

Size Exclusion Chromatography (S.E.C.)

During the synthesis, the bulk composition was determined by size exclusion chromatography on a "Waters 6000A" apparatus equipped with four "Shodex" OH-pak (B803-B804-B805-B806) columns. The temperature was kept constant at 40 °C. Solvent was a $LiNO_3$ (0.5 M)/ $NaNO_3$ ($6.2 \cdot 10^{-3}$ M) solution. At the output of the columns, a differential refractometer R401 (Waters), coupled to a computer system, enables an estimate to be made of the "solute" concentration and molecular weight using a previous calibration done with standard PEO samples.

Viscosity measurements

Capillary viscometer

Intrinsic viscosity measurements were performed on an automatic Ubbelhode capillary viscometer "Viscologic Ti.1" from SEMATech. Each modified chain and AMPS/AA copolymer was characterized at 25 °C in NaCl 0.6% (w/w) (Table 1). Complementary studies on their behavior in the dilute regime were also performed at 35 °C in K_2CO_3 13.8% and 16.6% (w/w).

Rheological behavior upon heating

Viscosity measurements of a modified AMPS/AA copolymer were performed on a Carri–Med controlled stress rheometer (RHEO) with a cone/plate geometry. The Carri–Med cone calibration given by the supplier was as follows: cone diameter = 2.0 cm, cone angle = 2° and truncation = 55.0 mm.

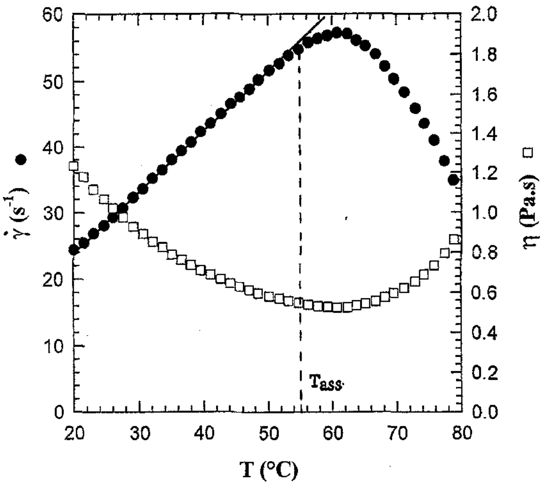


Fig. 1 Variation of shear rate ● and viscosity □ with temperature for a 10% (weight %) solution of an Acrylic acid (35%, molar %) /Isopropylacrylamide (65%) copolymer grafted by 0.4% of PEO5 chains. [K2CO3] = 6.9%, $\sigma = 30\,\mathrm{N \cdot m^{-2}}$

Temperature was controlled by a high power Peltier system that enables the viscosity to be studied between 20° and 75 °C with heating rate of 2 °C/min. The solution viscosity was measured at constant shear stress ($\sigma = 5\,\mathrm{N/m^2}$) in order to observe the onset of the thermothickening effect. The association temperature, T_{ass}, is easily determined from the shear rate variations on heating which show a characteristic change of slope, as depicted in Fig. 1. Complementary rheological experiments were carried out at constant shear rate ($100\,\mathrm{s^{-1}}$) to provide comparisons between different non-Newtonian solutions.

Low-Shear

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

Fluorescence

Fluorescence spectroscopic measurements were performed at 20 °C on an AMICO SPF 500 spectrometer with excitation at 377 nm, for wavelengths ranging from 450 nm to 600 nm to observe ANS fluorescence emission spectrum [6]. The slit widths were set at 5 nm (excitation) and at 0.5 nm (emission).

Synthesis and characterization

Synthesis of PEO5 modified AMPS/AA copolymers are divided into two parts:

1) AMPS/AA backbone was prepared, as follow, by free-radical polymerization in aqueous medium, using the couple $\{(NH_4)_2S_2O_8/\mathrm{TEMED}\}$ as redox initiator: (see Scheme 1 below).

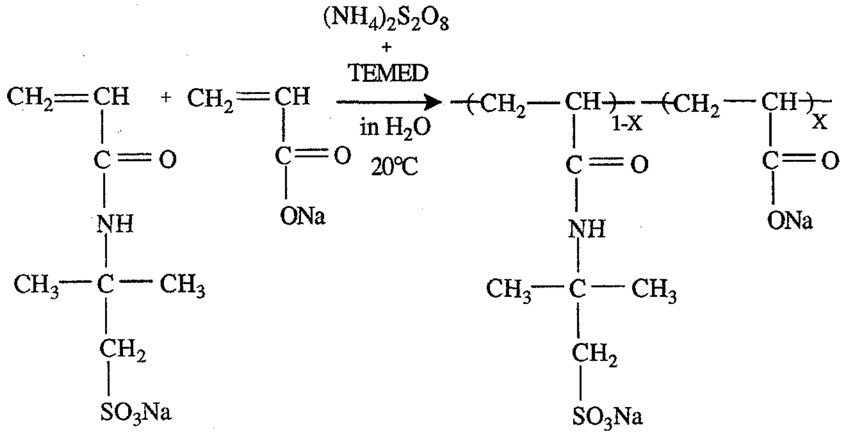
Polymerization was followed by S.E.C. Polydispersity of the AMPS/AA copolymer was found to be around 2. The copolymer obtained was purified by ultrafiltration, through a "pellicon" cassette system (Millipore), with membranes of 10 000 nominal molecular weight cut-off. The solution was then concentrated and freeze-dried. 30 g of AMPS/AA copolymer were obtained in this way. The yield, in weight, is estimated at about 95%.

The chemical composition of this copolymer was determined by ^{1}H NMR and agrees with the feed molar ratio of the two comonomers AMPS/AA:

AMPS: 80%
AA: 20% (expressed in molar percentages).

These proportions are consistent with titrating measurements of strong (AMPS) and weak (AA) acidic functions in the AMPS/AA copolymer.

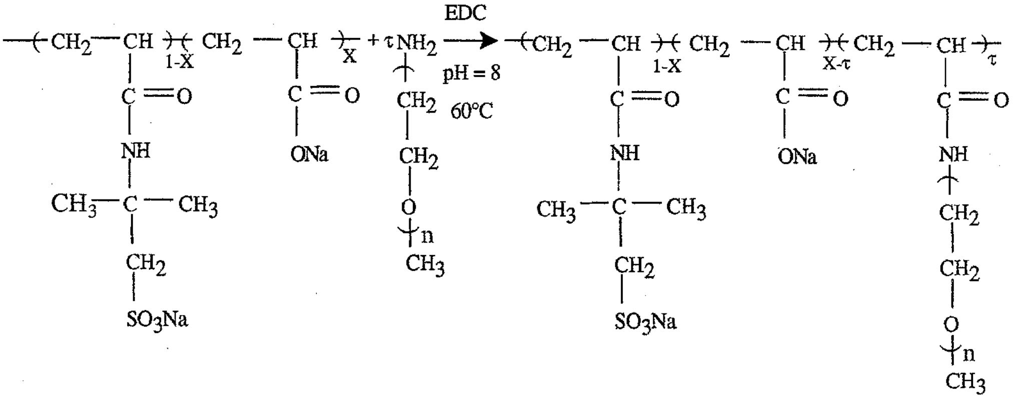
Scheme 1



Intrinsic viscosity was estimated in NaCl 0.6% (w/w) at 25 °C by capillary viscometry and an average molecular weight of 700 000 ($[\eta] = 230$ mL/g) was obtained using the Mark–Houwink coefficients relative to the poly AMPS homopolymer [7] ($K = 1.64 \cdot 10^{-3}$ mL/g and $a = 0.88$).

The distribution of AMPS and AA comonomers along the backbone is expected to be statistical as their reactivity ratios are both close to one [8]. Consequently, AA units are spread randomly along the chains and since their content is rather low (20% expressed in mole), most of the acrylic acid units must be separated by several AMPS entities.

2) PEO5 monoaminated chains were grafted on the AMPS/AA copolymer, in the presence of EDC as the coupling agent, in aqueous medium, as already done with aminated alkyl chains to obtain associative polymers [1, 9].



n ≈ 110.

Four different PEO5 modified AMPS/AA copolymers were synthesized by varying the molar grafting, τ. Their characteristics are reported in Table 1.

The grafted copolymers were obtained after precipitation in acetone of the reaction medium previously concentrated. That purification stage is necessary to eliminate the unreacted PEO5 chains.

As expected, the intrinsic viscosity of modified copolymers increases slightly with grafting ratio. The intrinsic viscosity of AMPS/AA-PEO5 1.20% chains is anomalously high compared to other copolymers because of interchains crosslinking during modification. This phenomenon is due to the presence of a small ratio of α-ω diaminated chains in the commercial PEO5. However, a higher grafting ratio of 1.35% can be obtained by diluting the reaction medium close to the critical overlap concentration, C^*, of the AMPS/AA solution.

The grafting yield is found to be about 35%, a value consistent with previous results obtained on similar PEO5 modification reactions [4], and it is in agreement with the low content of aminated chains in the commercial PEO5.

The backbone microstructure closely influences the PEO5 distribution along the chain. This is of great importance in understanding the rheological properties of modified AMPS/AA polymers, based upon the association of PEO5 side chains [4].

Since we expect the original copolymer to be a statistic copolymer, and considering that in the experimental conditions, aminated polyethylene oxide chains are free (no micelle-like clusters), then we can assume that the PEO grafts are statistically distributed along the macromolecular backbone.

The thermothickening behavior and its limits

For practical reasons, it is convenient to explore the thermal effects in a temperature range between room temperature and 70–80 °C, since in this area, the working temperature can be easily stabilized and any quick evaporation of the sample can be avoided. We saw [4] that the thermothickening effect can be easily controlled in this temperature range by varying the salinity of the solutions which influences the LCST of the PEO5 side chains. The chemical nature (potassium carbonate) and concentration of the salt were chosen because of their influence on PEO5 properties described in refs. [10, 11].

Influence of polymer concentration

Figure 2 shows the viscosity behavior upon of a AMPS/AA-PEO5 1.20% salt solution ($[K_2CO_3] = 13.8\%$ w/w)

Table 1 PEO5 modified AMPS/AA synthesis

Nomenclature	Modification* extent (τ, molar%)	Grafting yield%	Intrinsic viscosity (ml/g)NaCl 0.6%; 25 °C
AMPS/AA	0.00	0	230
AMPS/AA-PEO5 0.45%	0.45	30	200
AMPS/AA-PEO5 0.75%	0.75	45	230
AMPS/AA-PEO5 1.20%	1.20	40	310
AMPS/AA-PEO5 1.35%	1.35	35	270

*estimated by ^{1}H NMR

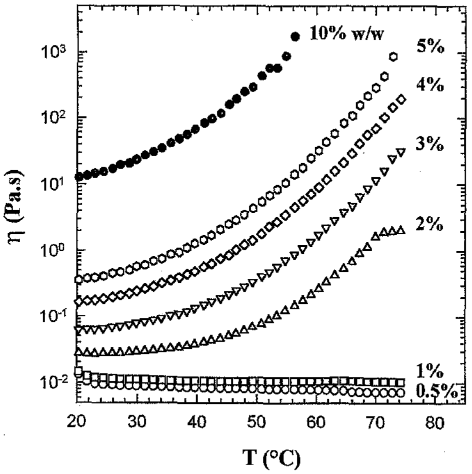


Fig. 2 Variation of viscosity with temperature for AMPS/AA-PEO5-1.20% samples at different polymer concentrations. *Cp* given in percentage by weight, [K2CO3] = 13.8%, $\sigma = 5\ \mathrm{N \cdot m^{-2}}$

on heating, for polymer concentrations varying between 0.5% and 10% (w/w).

– At low polymer concentrations ($C_p < 1\%$ w/w), the viscosity decreases from 20° to 75 °C, as expected for normal polymer solutions. This concentration range corresponds to the dilute state, in which PEO5 grafts attached to distinct AMPS/AA chains cannot induce intermolecular crosslinking above the LCST. On the contrary, PEO5 side chains associate into intramolecular microdomains which induce a viscosity decrease of the modified polymer solution compared to the behavior of the backbone. This phenomenon will be discussed in the next paragraph by studying the variations of chains expansion with the degree of modification.

– For a polymer concentration (C_p) of 1% (w/w), the viscosity drops to 45 °C and remains constant between 45° and 75 °C, due to PEO5 intermolecular associations which start to occur above the critical overlap concentration C^*. A solution at 1% (w/w) seems to be at the boundary between dilute and semi-dilute regimes.

– For higher concentrations ($C_p > 1\%$ w/w), the association temperature T_{ass}, above which thermothickening properties are observed, decreases as C_p is increased and is less than 20 °C at a polymer concentration of 2% (w/w). As previously described [4], this thickening effect is all the more important as polymer concentration is increased.

As described by De Gennes (12), the critical overlap concentration C^* is an important characteristic used to describe polymer solutions. It is also confirmed in our system in which the rheological behavior (Fig. 2) demonstrates that C^* controls the polymer concentration range over which thermothickening properties are observed.

Thermal limits of the thickening behavior: Influence of shear rate and salinity

Until now, our systems have been described by using constant shear stress measurements, in a temperature range corresponding to the onset of the viscosity enhancement. We reproduced the same kind of experiment by varying the shear rate ($\gamma = 10^{-2}$ to $10^2\ \mathrm{s^{-1}}$), at a given temperature. A typical result with a AMPS/AA-PEO5 1.35% solution ($C_p = 3\%$ and $[K_2CO_3] = 15.2\%$ w/w) is given in Fig. 3. During the first stage of association between PEO5 side chains ($T = 20\,°C$–$50\,°C$), Newtonian behavior persists over the shear rate range investigated, but a pseudoplastic character occurs at higher temperature (60 °C). It is clear that the thermothickening phenomenon is shear-rate dependent. At shear rates higher than $1\ \mathrm{s^{-1}}$, the viscosity of the AMPS/AA-PEO5 1.35% solution at 60 °C is less than that at 50 °C, and even smaller than the viscosity at 30 °C for a shear rate of $10\ \mathrm{s^{-1}}$. Similar shear-thinning behavior was observed with thermothickening polymers of various chemical structures.

These results, obtained at different temperatures, show the existence of a viscosity maximum on heating, which occurs at a particular temperature ($T_{\max}$), for a constant shear rate (in our example, for $1\ \mathrm{s^{-1}} < \gamma < 50\ \mathrm{s^{-1}}$, $50\,°C < T_{\max} < 60\,°C$). No other measurement was performed above 60 °C because of water evaporation, but in this example, a shear-thinning behavior would be expected to occur above 60 °C for shear rates less than $0.3\ \mathrm{s^{-1}}$, the

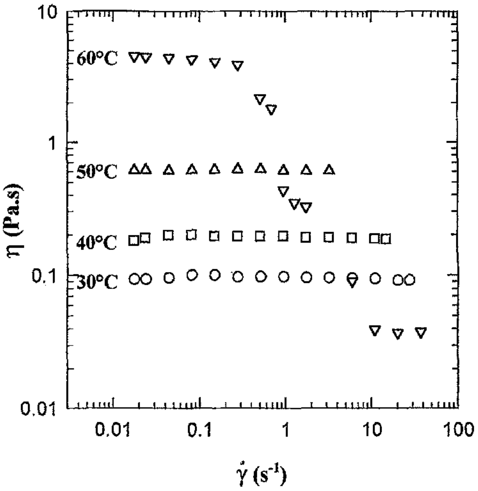


Fig. 3 Variation of viscosity with shear rate for an AMPS/AA-PEO5 1.35% sample at different temperatures. $Cp = 3\%$, [K2CO3] = 15.2%

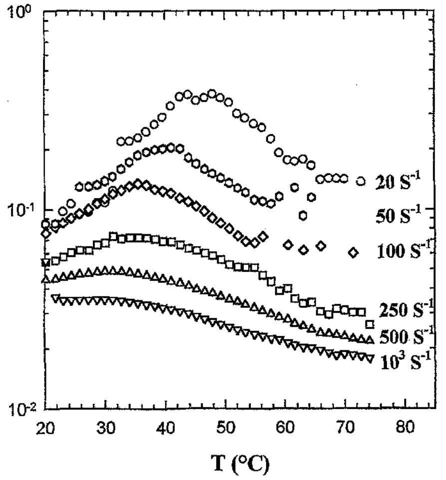


Fig. 4 Variation of viscosity with temperature for an AMPS/AA-PEO5 1.20% sample at different shear rates $\dot\gamma$ applied. $Cp = 2\%$, [K2CO3] = 16.6%

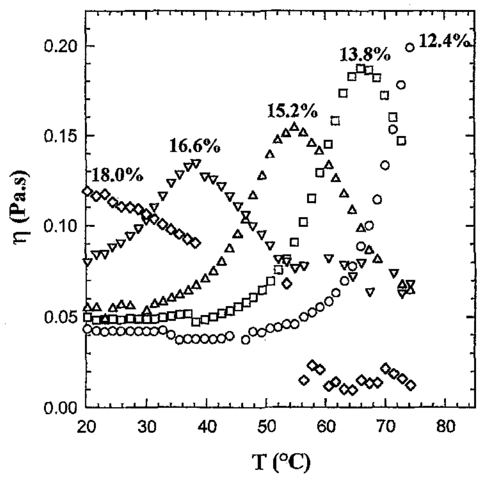


Fig. 5 Variation of viscosity with temperature for AMPS/AA-PEO5 1.20% samples at different salt concentrations, [K2CO3] given in percentage by weight. $Cp = 2\%$, $\dot\gamma = 100\ \mathrm{s}^{-1}$

Newtonian plateau being confined to a narrow range of shear rate as the temperature rises. The total increase of viscosity and the temperature T_{max} will be lowered by increasing the shear rate as shown in Fig. 4. There, high shear rates have been applied (20 to 1000 s^{-1}), and the viscosity maximum is reduced from 50° to 20 °C. Whatever the shear rate, the viscosity decrease above T_{max} is rather smooth and does not correspond to a macroscopic phase separation in the conditions of investigation.

Similar experiments, performed at constant shear rate (100 s^{-1}) and with increasing salt concentrations (Fig. 5), show a shift of T_{max} down to low temperature. In each cases the full range of viscosity enhancement appears to be rather constant ($T_{max} - T_{ass} \approx 45$ °C).

The thermothickening process is due to the hydrophobic interaction between PEO5 grafts associated into microdomains. Thus, the rheological behavior on heating can be correlated to variations of the number, the size and the cohesion (or PEO concentration) of these crosslinking units. With this assumption, it can be assumed that increasing the PEO concentration in the hydrophobic domains on heating, as suggested by the PEO phase diagram, accounts for the viscosity enhancement above T_{ass}. The decrease of viscosity observed above the critical temperature T_{max}, suggests a loss of connectivity in the physical network. This could be related to a progressive change in the composition of the microdomains to which part of the acrylic chains could be gradually taken along, due to the PEO association on heating. This evolution of the system would imply a size increase of the microdomains and thus a decrease of their number. The shear dependence of the viscosity maximum might be considered here, as the microstructure of our associative system near T_{max} could be highly influenced by shear. Measurements of the viscosity at zero shear rate have to be carried out above T_{max}, in order to better understand the origins of the maximum of viscosity.

Even if there is no sudden loss of thermothickening properties above T_{max}, the viscosity of the copolymer solution remains much higher than that of the backbone. Further experiments have to be performed in order to fully understand the correlation between the rheological properties and the characteristics of the PEO5 domains, i.e., their size, their numbers and their composition. The control of this is of prime importance with respect to potential applications, especially in the oilfield industry.

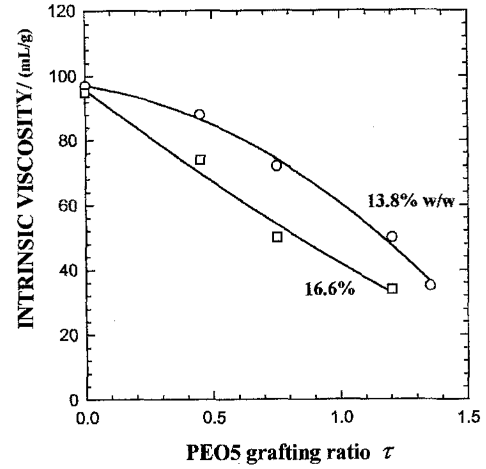


Fig. 6 Influence of PEO5 grafting ratio τ on the intrinsic viscosity of AMPS/AA-PEO5 τ% chains, at 35 °C and at two salt concentrations: [K2CO3] = 13.8%: ○ and 16.6%: □

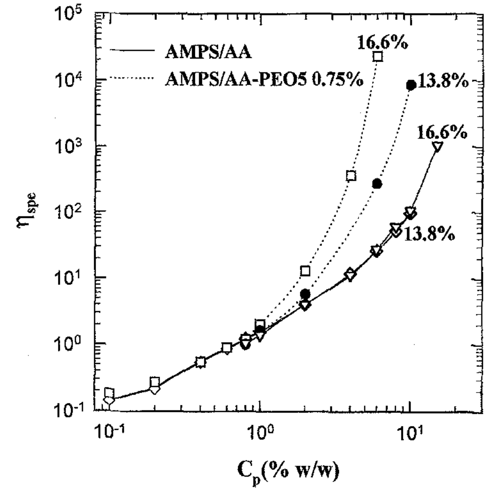


Fig. 7 Variation of specific viscosity (at low shear rate) with polymer concentration for AMPS/AA and AMPS/AA-PEO5 0.75% samples at two salt concentrations: [K2CO3] = 13.8% and 16.6% w/w

Rheological behavior in dilute regime

Rheological experiments on heating (Fig. 2) successfully showed the occurrence of PEO5 intermolecular associations for a polymer concentration C_p above 1% (w/w). The influence of PEO5 intramolecular associations on the modified chains behavior in the dilute regim was studied through intrinsic viscosity measurements.

In Fig. 6, the intrinsic viscosity of AMPS/AA-PEO5 τ% is plotted against the grafting ratio, τ, for salt concentrations of 13.8% and 16.6% (w/w). Experiments were performed at 35 °C, above the PEO5 LCST in both salinity conditions. As the ionic strength is high, the intrinsic viscosity of the original AMPS/AA copolymer ($\tau = 0$) does not depend on the K_2CO_3 concentration. As expected, the presence of PEO5 side chains induces a shrinkage of the copolymer due to intramolecular association between the grafts above their LCST. In the same way, the magnitude of this phenomenon is enhanced as the grafting ratio and salt concentration increases. For the highest grafting ratio (1.35%), the intrinsic viscosity was not measured at a salt concentration of 16.6% (w/w) because the turbidity of the copolymer solution meant that the PEO chain affinity for the aqueous medium is so poor that macroscopic phase separation occurred.

Transition from dilute to semi-dilute regimes

Comparison between PEO5 modified chains and their backbone

As described by Utracki et al. [13] for neutral polymers, a transition from dilute to semi-dilute states [12] can be demonstrated by plotting, on a double logarithmic scale, the specific viscosity (at low shear rate) against the polymer concentration, C_p. In both regimes, linear variations are observed, but the specific viscosity increase is steeper in semi-dilute solutions. The change of the slope, as C_p increased, enables us to estimate the critical overlap concentration C^*.

In this respect, specific viscosities of AMPS/AA and AMPS/AA-PEO5 0.75% salt solutions were studied and plotted against C_p, C_p ranging from 0.1% up to 10% (w/w) (Fig. 7). Measurements were performed at 35 °C with two salt concentrations (13.8% and 16.6% (w/w)), in experimental conditions where it is assumed that the LCST of PEO5 is lower than room temperature.

As expected, specific viscosity increases with polymer concentration (C_p) and two regions can be distinguished:

- At C_p lower than 1% (w/w), AMPS/AA-PEO5 0.75% has the same behavior as the backbone. Only intramolecular crosslinking units can be formed in the dilute regime, but the viscosity reduction induced by these associations are not detectable on the "Low-Shear" viscometer experiments.
- For C_p higher than 1% (w/w), the rheological behavior of the copolymer AMPS/AA is independent of salinity, because in the range of salt concentrations investigated, most of the charges are already screened.

Above $C_p = 1\%$ (w/w), PEO5 grafted AMPS/AA copolymer shows thickening properties of greater magnitude than its backbone. This is due to the PEO5 side chains association into intermolecular microdomains, the number and the effectiveness of the PEO5 crosslinking units increasing with salinity.

These results show that the critical overlap concentration C^* of AMPS/AA copolymer, at 35 °C in K_2CO_3 13.8% or 16.6% (w/w), seems to be close to 1% (w/w). This concentration also defines the lower limit of polymer concentration range at which thermothickening effects are observed.

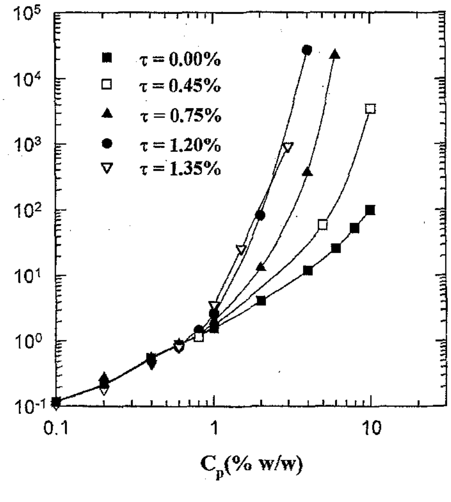
Modification extent effect

Transition between dilute and semi-dilute regimes has also been demonstrated for different degrees of modification, at 35 °C in K_2CO_3 16.6% (w/w) salt solutions, as shown in Fig. 8.

No thermothickening effect is observed for all modified polymer chains at concentrations less than 1% (w/w), corresponding to the dilute regime, whereas thickening properties are observed for the grafted chains, at C_p higher than 1% (w/w). Above a polymer concentration of 1% (w/w), the viscosity increase is all the more important when the PEO5 grafting ratio is high, a phenomenon described previously [4]. The slope of the curve $\log \eta = f(\log C_p)$ increases from about 3 for the unmodified chains, (a value commonly observed as polymer chains overlap [14]), up to 8 for a grafting ratio of 1.20%, because of the association of the PEO side chains.

Even for the most modified copolymer, the critical overlap concentration C^* does not seem to be affected by the PEO5 grafting, as viscosity enhancement is effective at C_p above 1% (w/w) for all degrees of modification. Thickening properties of AMPS/AA-PEO5 1.20% and 1.35% are quite similar at 35 °C, at a K_2CO_3 concentration of 16.6% (w/w), because under these conditions, the most modified chains are at their viscosity maximum: the thickening effect on heating is weakened before a viscosity decrease is observed, as described in a previous section. According to the specific viscosity measurements, the critical overlap concentration C^* is close to 1% (w/w) in these experimental conditions, for PEO5 grafting ratio ranging from 0 to 1.35% (molar %).

Fig. 8 Variation of specific viscosity (at low shear rate) with polymer concentration for AMPS/AA-PEO5 τ% samples, τ: 0 → 1.35%, expressed in molar percentage. [K2CO3] = 16.6% and T = 35 °C



Fluorescence

The correlation between the rheological results and the formation of hydrophobic microdomains can be demonstrated by several different techniques such as electron spin resonance spectroscopy studies [15], or more commonly, by fluorescence measurements. Fluorescence technique is particularly useful in identifying the occurrence of hydrophobic aggregates in aqueous solutions [16]. Pyrene is a commonly used probe to identify such type of aggregates. The dependence of polarity on the vibrational structure of pyrene emission was useful in studying the formation of interpolymeric associations in hydrophobically modified thickeners [9, 16, 17]. It was also used to estimate the critical surfactant micellar concentration [16]. The relative intensity I_1/I_3 of the first and third peaks of the pyrene fluorescence spectrum was used as a typical parameter to determine the polarity surrounding the pyrene probe.

Phase transition occurring in LCST polymers solution on heating was also investigated using fluorescence techniques [6, 18]. Although PEO is still a polar compound even above its LCST, attempts were made to demonstrate the formation of hydrophobic microdomains using this technique. In this respect, emission properties of pyrene in thermothickening solutions were tested at constant temperature by increasing the salt concentration. No significant variation of I_1/I_3, was found at the LCST.

However, an increase in the fluorescence emission intensity was observed at the onset of PEO5 association. The interpretation of such a variation is difficult to give because the pyrene spectrum is sensitive to both K_2CO_3 and PEO5 concentrations. K_2CO_3 is found to be a quencher, whereas fluorescence intensity is enhanced as the concentration of a PEO5 aqueous solution increases. Complementary experiments were performed to investigate the local PEO5 aggregation using an ammonium salt of 8-anilinonaphtalene-1-sulfonic acid (ANS) instead of pyrene.

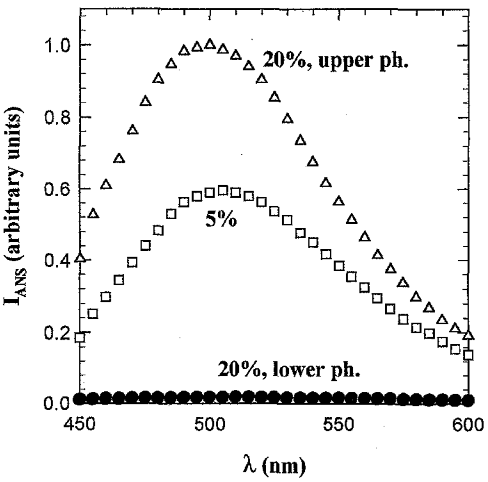
ANS is a fluorescence probe widely used in fields such as biomembrane research because its spectral properties are extremely sensitive to changes in the environment. ANS shows a dramatic drop in fluorescence quantum yield Φ_F when the solvent polarity increases. For example, when Φ_F equals to 0.65 in *n*-octanol, it is reported to be 0.003 in water [19]. Moreover, when this probe is transferred from polar to non-polar media, a large blue shift in the fluorescence emission maximum is observed [6, 19]: from 523 nm in water to 472 nm in *n*-octanol, this wavelength drop is also induced by an increase of the medium viscosity.

Several theories have been proposed to explain this strong solvent effect on ANS fluorescence, as described in [20]; one of them is related to a change of the excited state lifetime with environment polarity, a phenomenon giving rise to dynamic fluorescence experiments [21, 22].

The study of ANS spectral properties in aqueous medium is relevant in biology [23], using, for example, the strong increase of fluorescence emission when an ANS probe is in contact with proteins, compared to its state in water [19]. ANS has also been used to study micelle formation [24, 25] and to investigate the LCST transition of poly *N*-isopropylacrylamide when heated [6]. Initially, in a polar medium at low temperature, most of the ANS molecules move into the hydrophobic phase above the LCST. This transition is detected by a blue shift of the emission wavelength and an increase of the fluorescence quantum yield.

In the same way, the LCST of PEO5 chains was observed using ANS fluorescence properties. In Fig. 9, the fluorescence emission behavior of ANS in PEO5 salt solutions ([K_2CO_3] = 6.9% w/w) at two concentrations ([PEO5] = 5% and 20% w/w) is shown.

Fig. 9 ANS fluorescence emission spectrum for PEO5 solutions at 5%: □ and at 20% (● for the lower phase; △ for the upper phase). [K2CO3] = 6.9%, [ANS] = $2.9 \cdot 10^{-4}$ M, $T = 20\,°C$



– The sample at 5% PEO5 is monophasic, emission maximum being observed at 505 nm and maximum intensity I_{max} being equal to 0.60 expressed in arbitrary units.
– A phase separation occurs for the 20% PEO5 solution. Fluorescence spectra of both phases, plotted in Fig. 9, show that quantum yield of the lower phase is weak ($I_{max} = 0.02$) and negligible if compared to the upper phase one ($I_{max} = 1.00$) which exhibits an emission maximum at 495 nm. The behavior of ANS is in good agreement with the composition of both phases estimated by SEC. The upper phase that contains most of the PEO5 chains is more hydrophobic than the lower one, which is mostly a salt solution of K_2CO_3. According to its chemical affinity, the ANS probe is mainly located in the PEO5 phase that shows the most intense emission response and the shorter maximum wavelength. ANS sensitivity to changes in the environment is shown to be relevant to studying the formation of hydrophobic PEO5 microdomains in the thermoassociative solutions, above the association temperature T_{ass}.

In this respect, ANS fluorescence emission was recorded at 20 °C for AMPS/AA-PEO5 0.75% samples ($C_p = 2\% \Rightarrow [\text{PEO5}] = 0.4\%$ w/w), at various K_2CO_3 concentrations ranging from 0 to 20.7% (w/w). According to PEO5 phases diagrams obtained for solutions at 0.4%, the PEO5 LCST varies with the salinity as follows:

– At K_2CO_3 less than 13.5% (w/w), the PEO5 LCST is higher than 20 °C, thus the system remains entirely water soluble and no thickening property is observed near room temperature.
– For K_2CO_3 concentrations greater than 13.5% (w/w), the viscosifying power of the system is effective at or above 20 °C, due to PEO5 side chain association into hydrophobic microdomains, above their LCST.

Figure 10 illustrates the ANS fluorescence response in AMPS/AA-PEO5 0.75% solutions ($C_p = 2\%$ w/w) at several salt concentrations.

The behaviour of ANS in aqueous solution is consistent with the rheological properties of the five solutions where salt concentration ranges from 0% up to 20.7% (w/w). Fluorescence emission intensity at 0 and 6.9% (K_2CO_3 concentration) is weak and maximum wavelength appears respectively at 517 nm and 507 nm. The spectral characteristics are similar to the ANS behavior in aqueous medium. In parallel to the blue shift of emission maximum (500 nm at 11.1%, 495 nm at 16.6% and 492 nm at 20.7%), the increase of fluorescence quantum yield with increasing salt concentration is due to the change in the probe environment from a polar to a non-polar solution, resulting from the formation of PEO5 hydrophobic microdomains containing most of the ANS molecules. Variations of

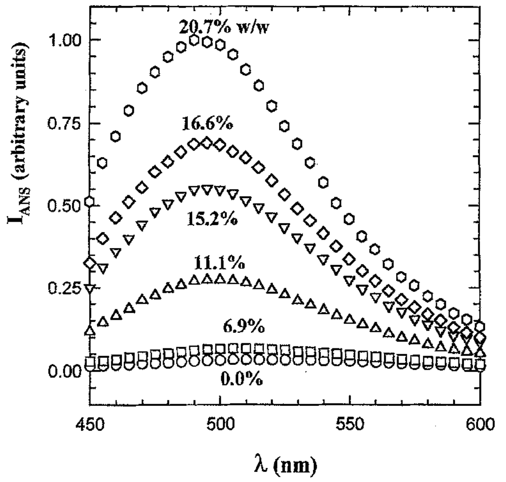


Fig. 10 ANS fluorescence emission spectrum for AMPS/AA-PEO5 0.75% samples at different salt concentrations, [K2CO3] expressed in percentage by weight. $C_p = 2\%$, $[ANS] = 2.9 \cdot 10^{-4}$ M, $T = 20\,°C$

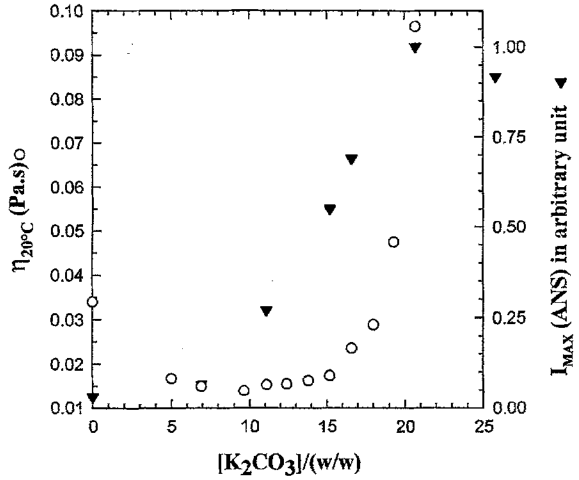


Fig. 11 Variation of viscosity ○ and intensity maximum ▼ of ANS fluorescence emission with salt concentration for AMPS/AA-PEO5 0.75% samples. $Cp = 3\%$, $[ANS] = 2.9 \cdot 10^{-4}$ M, $T = 20\,°C$

viscosity and emission maximum intensity with salinity are reported in Fig. 11 and show the agreement between fluorescence and rheological experiments. As expected, the maximum wavelength begins to shift at a lower salt concentration than the one when viscosity begins to increase. Such a lag is also described in hydrophobically modified polyelectrolytes solutions (9), suggesting that ANS probes are located near PEO5 side chains which begin to associate as the salinity is enhanced before any viscosifying effect is detected.

The viscosity decrease observed as the salt concentration raises from 0 to 10% (w/w), results from the charge screening of AMPS/AA backbone which shrinks in presence of K_2CO_3.

Conclusion

AMPS/AA-PEO5 τ% copolymers, obtained by grafting PEO5 monoaminated chains on the polyelectrolyte backbone, appear to be typical examples of thermoassociative polymers. As soon as the PEO5 chains are above their LCST, a thermothickening effect is observed for polymer concentrations larger than the critical overlap concentration and can be adjusted by varying "external" and "internal" parameters such as polymer and salt concentrations, and grafting ratio. When heated, the viscosity rises to a maximum and then declines smoothly, the solutions remaining as monophasic systems at even higher temperature.

Using ANS probe, the thickening properties can be clearly related to the formation of hydrophobic microdomains.

For dilute solutions, intramolecular associations of the PEO5 side chains are observed above their LCST and are also enhanced by increasing the grafting ratio.

Further work will focus on the mechanisms inducing thermothickening behaviour and on the evolution of the characteristics of the microdomains (number, size...) during heating, thus relating the microstructure of a thermothickening solution to its rheological properties. A better understanding of the thermoassociative phenomenon is of great importance because the thickening concept upon heating can be widened to a large range of water soluble polymers containing LCST units, this will be presented in a further publication.

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