Reversible thermothickening of aqueous polymer solutions

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A thermally induced associative polymer was developed by grafting lower critical solution temperature side chains onto a water-soluble backbone. Based upon the thermodynamic properties of the pendent chains, acting as reversible crosslinkers with varying temperature, such a system was prepared from a poly(ethylene oxide)-modified poly(acrylic acid) (PAA-*g*-PEO). In aqueous solution this polymer provides an enhancement of the viscosity on heating, the extent of which can be controlled by polymer concentration, grafting ratio and salt concentration.

(Keywords: thermothickening; associative polymer; water-soluble polymer)

INTRODUCTION

Water-soluble polymers (synthetic or natural) are widely used for their thickening and gelling powers in aqueous media. Until now the general trend, governed by economic considerations, was to achieve these specific properties at low polymer concentrations by using very high molecular weight polymers or at least expanded macromolecules (rod-like polymers), which present a very good thickening ability owing to their high hydrodynamic volume/molecular weight ratio.

Unfortunately, conventional water-soluble polymers often suffer from a loss of efficiency in many industrial applications which can involve drastic conditions, e.g.

1. mechanical degradation of high molecular weight polymers under high shear,
2. biodegradation of natural polymers,
3. reduction of the thickening properties of polyelectrolytes in the presence of salts,
4. a decrease in the viscosity of polymer solutions with increasing temperature and
5. chemical degradation or conformational changes under certain pH conditions.

Some of these drawbacks can be avoided by using associating polymers[1-4], which have shown a strong development in the past 10 years. Although the polymers of this family are effectively water soluble, a small amount of hydrophobic 'block' inserted into the hydrophilic backbone gives rise to self-aggregation in solution (micelle-like). As for polymer systems which provide stabilization or an increase in viscosity under heating, only a few have been described[5-8], in spite of their practical interest (for instance, fluids for the petroleum industry, water-based lubricants, etc.).

In this context, our aim was to develop a whole family of thermothickening polymers which can be used as a single system in aqueous medium for industrial applications. In the present paper we discuss the concepts and design of the thermothickening systems and present preliminary results obtained with a first generation of these new self-associating polymers.

CONCEPTS AND DESIGN

Let us consider a copolymer based on a water-soluble backbone but containing some 'block' regions or side chains which, if considered alone, are soluble in water at room temperature but precipitate on heating. In other words, these sequences or grafts exhibit a lower critical solution temperature (*LCST*). A typical structure corresponding to this description is pictured in *Figure 1a.* The polymer is fairly soluble at room temperature, but on heating to the critical temperature of the thermosensitive grafts it starts to self-aggregate.

Microdomains involving several grafts can be expected in semidilute solution (*Figure 1b*). However, a macroscopic precipitation is prevented by the water-soluble backbone. The microdomains play the role of crosslinks between the chains so that when they are formed an increase in viscosity will occur. In order to check this behaviour a poly(acrylic acid) backbone (PAA) was grafted with poly(ethylene oxide) chains (PEO).

The phase diagrams of the PEO–water system for different molecular weights, determined by Saeki *et al.*[9], are reproduced in *Figure 2.* At rather short chain lengths ($M < 2000$), PEO and water are completely miscible even at high temperature, but for slightly longer chains the system shows a closed solubility gap with lower and upper critical solution temperatures (*LCST* and *UCST*). By increasing the chain length, the *LCST* can be reduced progressively to 100°C for the highest molecular weights.

Introduction of a salt into an aqueous solution of PEO changes the phase separation temperature. This alteration varies considerably in magnitude depending on the kind of electrolyte introduced and its concentration[10,11] (*Figures 3* and *4*). This is the consequence of a destructuring effect of the salt on the hydratation shell of PEO.

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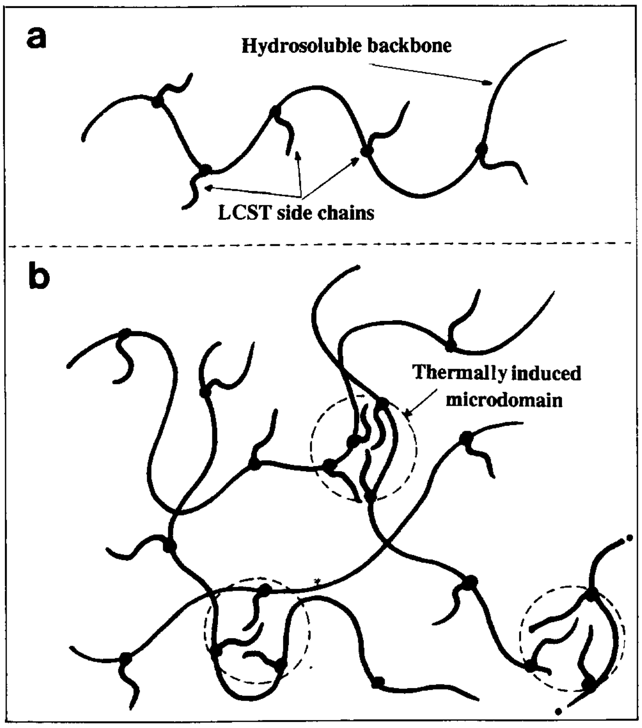


Figure 1 Thermothickening concept of PAA-*g*-PEO aqueous solutions: (a) copolymer structure; (b) association mechanism ($T > LCST$)

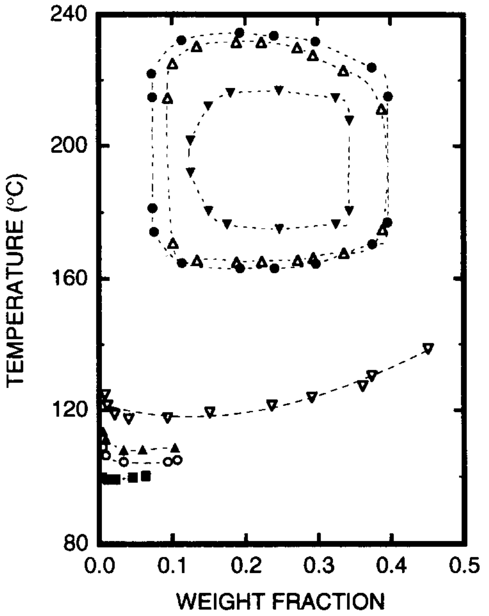


Figure 2 Temperature–weight fraction diagram for poly(ethylene oxide) samples in water: (■) $M = 1\,020\,000$; (○) $M = 21\,200$; (▲) $M = 14\,400$; (▽) $M = 8000$; (●) $M = 2290$; (△) $M = 2270$; (▼) $M = 2180$ (reproduced from ref. 9 by permission of Butterworth-Heinemann)

A good knowledge of the phase separation of PEO in water is essential if one is to produce a thermothickening PEO-based copolymer, and the aforementioned parameters such as concentration, molecular weight of PEO and the salt effect have been taken into account in our system.

EXPERIMENTAL

Materials

Poly(acrylic acid) (PAA) in concentrated aqueous solution (12.5% solid in water) was purchased from Polysciences. The weight-average molecular weight given by the supplier was $M_w = 500\,000$ (PAA500). In order to obtain pure PAA in acidic form, the commercial solution was diluted 10 times with HCl ($5 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$) and ultrafiltered with a large excess of pure water through a Pellicon cassette system (Millipore) with ultrafiltration membranes of a 10 000 nominal molecular weight cut-off. The PAA solution was then concentrated and freeze dried.

O-(2-aminoethyl)-*O*′-methylpoly(ethylene oxide) (PEO5) was obtained from Fluka. The molecular weight was given as $M = 5000$ and the NH_2 content higher than $1.7 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$. PEO5 was used without further purification.

Water was purified with a Milli-Q system from Millipore and all other reagents were of analytical grade.

N-methyl-2-pyrrolidone (NMP; 99% purity) and *N,N*′-dicyclohexylcarbodiimide (DCCI; 99% purity) were purchased respectively from Prolabo and Janssen.

Analytical methods

^{1}H n.m.r. Sample characterization was performed on precursors and modified samples by ^{1}H n.m.r. using a Bruker WP250 spectrometer (250 MHz).

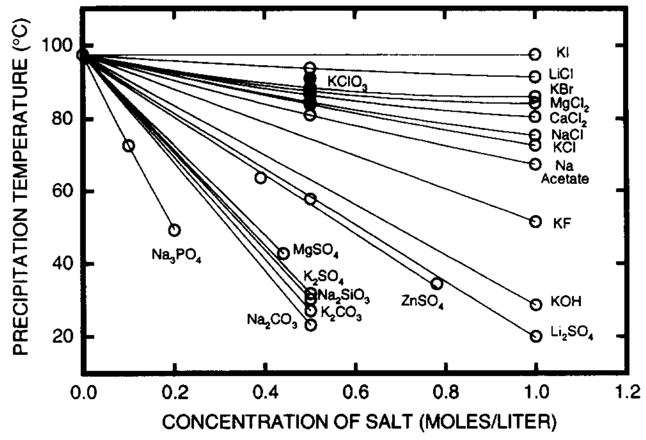


Figure 3 Upper temperature limits of solubility for 0.5% solutions of poly(ethylene oxide) ($M_w = 4 \times 10^6$) as a function of salt concentration (reproduced from ref. 10 by permission of John Wiley and Sons)

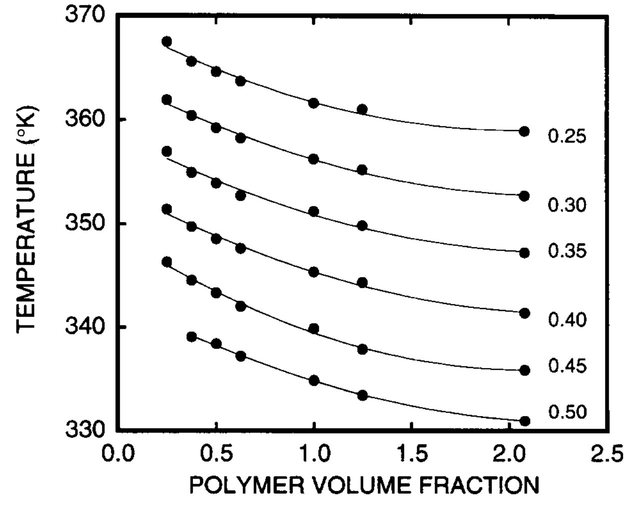


Figure 4 Dependence of cloud point on polymer volume fraction for various concentrations of ammonium sulfate (reproduced from ref. 11 by permission of John Wiley and Sons)

Viscosity measurements. Viscosity analyses of the modified PAA and the pure PAA were carried out on a Carri-Med controlled stress rheometer (RHEO) with a cone/plate geometry. The Carri-Med cone calibration given by the supplier was: cone diameter = 2.0 cm, cone angle = 2°-0-0 and truncation = 55.0 μm.

The temperature of the measuring unit was controlled by a high power Peltier system which provides very fast temperature control and a very short response time to sudden changes. Typically, the rheological behaviour of the samples was studied between 20°C and 75°C with a heating or cooling rate of 2°C min^{-1}. Viscosities (η in Pa s) were recorded at constant shear stress ($\sigma = 10\,\mathrm{N\,m^{-2}}$) during heating and at constant shear rate ($\dot{\gamma} = 10\,\mathrm{s^{-1}}$ and/or $100\,\mathrm{s^{-1}}$) during cooling. These three parameters are connected by the relation

$$\sigma = \dot{\gamma}\eta$$

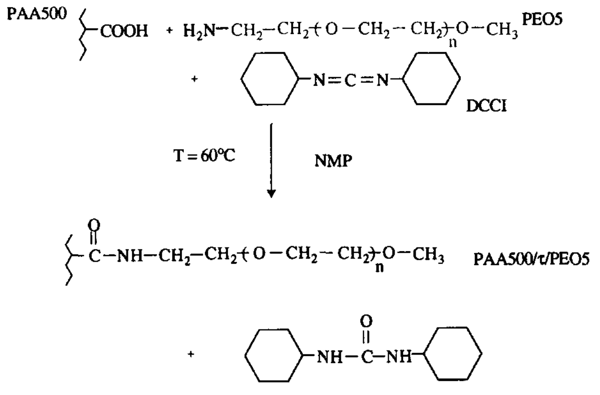
with $\eta = f(\dot{\gamma})$ for non-Newtonian fluids.

Analytical solutions were prepared by mixing at room temperature the whole components over 24 h with magnetic stirring. The mixtures were studied without further dilution. Concentrations are given in per cent by weight.

RESULTS AND DISCUSSION

Synthesis and characterization

PEO-modified poly(acrylic acid) (PAA500/PEO5) was prepared according to the classical reaction of amines with carboxylic acids[12,13] in the presence of a coupling agent (DCCI) and in an aprotic solvent (NMP) (*Scheme 1*).



Scheme 1

Typically, the reaction was carried out in the following way (reaction 1). A 250 ml three-necked flask was equipped with a thermometer, reflux condenser, addition funnel and magnetic stirrer. PAA500 (2 g, 2.8×10^{-2} mol) was dissolved over 24 h in NMP (65 ml) at 60°C. PEO5 (0.7 g, 1.4×10^{-4} mol) and DCCI (0.033 g, 1.6×10^{-4} mol) were separately dissolved in NMP (respectively 25 ml and 10 ml). Dissolution was instantaneous for DCCI at room temperature and for PEO5 at 60°C. After 24 h, the PEO5 solution was mixed with PAA500 under vigorous stirring and the mixture was fed dropwise (over 15 min) with DCCI solution.

The temperature was maintained at 60°C for 24 h. After cooling the mixture to room temperature the dicyclohexylurea precipitate, formed by DCCI during the reaction, was eliminated by filtration and the PEO-modified PAA was neutralized and precipitated with an excess of concentrated aqueous NaOH solution (7 g in 20 ml of water). The modified polymer was then washed with hot NMP (50 ml) and three times with methanol (50 ml) before drying under vacuum at 25°C. The product was then redissolved in a minimum of water (20 ml) and reprecipitated slowly in methanol (400 ml). The methanol was renewed and finally the polymer was filtered and dried under vacuum overnight at room temperature.

Three PAA500/PEO5 samples were synthesized by this reaction with various extents of modification (*Table 1*) and the total elimination of residual PEO5 chains was checked by size exclusion chromatography (samples 1 and 3).

For each reaction the modification extent, determined by 1H n.m.r. (*Figure 5*, sample 1), was always lower than that calculated from the molar feed ratio [PEO5]/[PAA500]. The grafting yield of ~35%, obtained for reactions 1 and 3, is surprisingly low compared to that reported for the modification of PAA with alkylamines (C_8–C_{18})[12,13], which is generally higher than 95%. Two reasons can be proposed:

1. a steric effect from the PEO chain which is composed of approximately 340 segments against 8 to 18 for alkylamine chains; and
2. a low concentration of amine groups (and carboxylic activated groups (i.e. in DCCI)), which is indirectly related to the high length of the chain to be grafted.

It is important to keep in mind that to achieve the thermothickening properties the modification extent must be sufficiently high to give a self-associative mechanism but not so high that the system precipitates.

Table 1 Details of the synthesis of PEO-modified PAAs

	Reaction/sample		
	1	2	3
[PAA500](mol l^{-1})	0.278	0.42	0.174
[PEO5](mol l^{-1})	1.4×10^{-3}	3.14×10^{-3}	3.48×10^{-3}
[DCCI](mol l^{-1})	1.6×10^{-3}	10×10^{-3}	5×10^{-3}
Molar ratio [DCCI]/[PEO5](%)	115	330	145
Molar ratio [PEO5]/[PAA500](%)	0.5	0.74	2
Modification extent[a] τ(%)	0.17	0.33	0.74
Grafting yield (%)	34	45	37
Nomenclature	PAA500/0.17/PEO5	PAA500/0.33/PEO5	PAA500/0.74/PEO5

[a] Molar ratio determined by ^{1}H n.m.r.

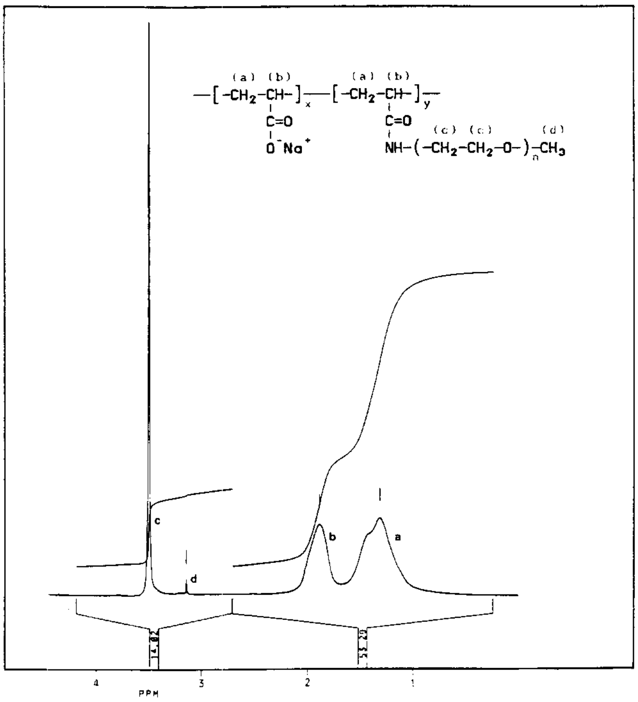


Figure 5 ^{1}H n.m.r. spectrum (250 MHz) of PAA500/0.17/PEO5 in D_2O

For example, with a moderate modification extent of 0.74% (sample 3), expressed as a molar ratio, the weight fraction of PEO in the modified polymer (in acidic form) is quite high (34%). For reaction 2, where we have increased both the PAA concentration and the molar ratio [DCCI]/[PEO5] (1.1–1.5 to 3.3), some interchain crosslinking was suspected during the modification. The grafting yield is in this case a little higher, reaching 45%, and dissolution of PAA500/0.33/PEO5 in water provides solutions of slightly higher viscosity compared with the two other PEO-modified PAAs. Although such behaviour has already been reported by Gramain and Frere[14,15] with PEO-grafted poly(acryloyl chloride) and interpreted as stereocomplex formation enhanced by PEO grafts, we are more inclined here to favour the presence of bifunctional PEO which could lead to chemical cross-linking. Consequently, the best way to achieve, according to this reaction, PEO-modified PAA with a controlled modification extent and without interchain reticulation is to operate at a lower PAA concentration, as described for reaction 1 and reproduced with reaction 3.

For the three syntheses, realized in homogeneous solutions, where both PEO5, precursor and modified polymers were entirely soluble, a random distribution of the graft PEO along the PAA backbone can be expected, as observed in similar conditions for the grafting of alkylamines[3].

THERMOTHICKENING BEHAVIOUR

Effect of modified polymer concentration

In order to obtain a thermothickening behaviour from the PEO-modified PAA, two basic conditions are required. Firstly a mechanism of interchain association, driven by graft PEO, can be expected only in the semi-dilute regime, above the critical overlap concentration of the polymer ($C_p > C^*$). For $C_p < C^*$, only intramolecular association may occur. Secondly, if we want to obtain graft PEO interactions in the temperature range 20–75°C, the *LCST* of the poly(ethylene oxide) chains has to be lowered by using an electrolytic cofactor (see *Figures 2* and *3*). Electrolytes are also well known to act favourably on the mechanism of intermolecular association of hydrophobically modified polyelectrolytes by lowering the electrostatic repulsions between the charged backbones[3]. Among the various salts studied by Saeki *et al.*[9] (*Figure 3*) we selected potassium carbonate, which is characterized by both a significant lowering effect upon the *LCST* of PEO and a very high solubility in water (112 g per 100 ml of water at 20°C).

The viscosimetric behaviour of PAA500/0.33/PEO5 salt solutions ($[K_2CO_3] = 13.8\%$ by weight) on heating is given for various polymer concentrations in *Figure 6*. For an adequate representation of the viscosity variations, the reduced viscosity (ratio of the polymer solution viscosities recorded at T°C and 20°C) was plotted against temperature on a semilogarithmic scale.

At low polymer concentration ($C^* < C_p = 1\%$), the initial part of the curve ($20°C \leqslant T < 40°C$) exhibits the typical behaviour of polymer solutions, i.e. a viscosity decrease on heating, which is mainly attributable to the viscosity drop of the solvent medium represented by H_2O in *Figure 6*. As the temperature is raised by 35–40°C the viscosity remains practically constant, and finally the viscosity increases slightly until 75°C, bringing to the fore an intermolecular association mechanism.

For higher concentrations ($C_p = 2\%$) the viscosity decrease previously observed occurs in a shorter range (20–30°C) and finally disappears for $C_p > 3\%$, while the viscosity increase becomes sharper with increasing polymer concentration, giving rise to a gel-like system at 60°C for $C_p = 5\%$.

Although the thermothickening process is purely reversible at low modified polymer concentrations ($C_p = 1\%$, 2%), a hysteresis effect is observed for higher concentrations during the heating/cooling cycle ($C_p = 5\%$; *Figure 6*). This behaviour can be attributed to the kinetics of association/dissociation of the PEO side chains, the observation of which is dependent on the heating (cooling) rate. Whatever the system considered, the initial

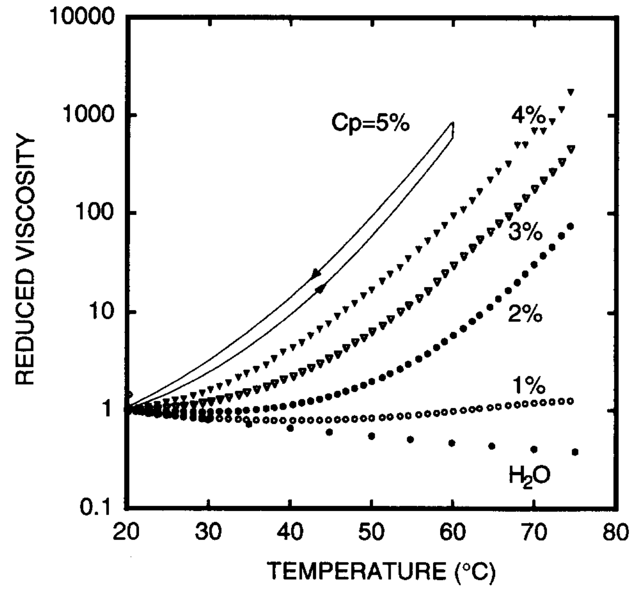


Figure 6 Variation of the reduced viscosity with temperature for PAA500/0.33/PEO5 at different polymer concentrations ($[K_2CO_3] = 13.8\%$, $\sigma = 10\,\mathrm{N\,m^{-2}}$)

viscosity (at 20°C) is always recovered after a complete cycle.

This first experiment agrees fairly well with the induced temperature association mechanism originally postulated and enables us to define better the general features. As depicted, an increase in the PEO-modified PAA concentration provides a viscosity enhancement of the solution which can be of several orders of magnitude in the temperature range investigated, by increasing the number and the effectiveness of the PEO crosslinking units.

The thermothickening behaviour of this modified polymer in salt solution is directly related to the thermodynamic properties of PEO in the same conditions. At a given concentration (above C^*), the intermolecular association mechanism, induced by PEO side-chain aggregation, does occur when the temperature is higher than a critical value T_c. In the same way, at a given temperature the interchain association may occur above a critical polymer concentration (C_p^c), or more exactly above a critical PEO side-chain concentration (C_{PEO}^c). This feature is consistent with the *LCST* phase diagram of PEO in aqueous medium reported in *Figure 4*.

The critical temperature corresponding to the beginning of the viscosity enhancement can be more easily monitored by plotting the reduced shear rate $\dot{\gamma}(T)/\dot{\gamma}(20°C)$ *versus* temperature (*Figure 7*). The virtually linear dependence of shear rate with temperature observed in the absence of aggregation, in pure water for instance, disappears beyond T_c for the modified polymer solutions, giving rise to a maximum followed by a decreasing function of $\dot{\gamma}$ *versus* T. In the case of PAA500/0.33/PEO5 critical temperatures around 30–35°C and 20–25°C can be estimated respectively for $C_p = 1\%$ and 2%. For polymer concentrations higher than 3% the chain aggregation is already effective at room temperature.

Effect of the modification extent

The reduced viscosities $\eta(T)/\eta(20°C)$ of the precursor and the PEO-modified polyacrylates, differing by their ratios of grafting ($\tau = 0.17\%$, 0.33% and 0.74%), are plotted *versus* temperature on a semilogarithmic scale in *Figure 8*. The viscosity measurements were carried out in the same conditions for all the samples ($C_p = 4\%$, $[K_2CO_3] = 11\%$, $\sigma = 10\,N\,m^{-2}$). For the polyacrylate precursor, a typical viscosimetric behaviour is observed with a monotonous decrease of the viscosity with temperature. The introduction of a small amount of PEO side chains ($\tau = 0.17\%$) induces a deviation from the reference curve, above $T_c \approx 45°C$, giving rise to an increase in viscosity on heating. This thermothickening behaviour becomes more pronounced with increasing modification extent leading, for $\tau = 0.74\%$, to a viscosity enhancement higher than four orders of magnitude in the temperature range 20–75°C.

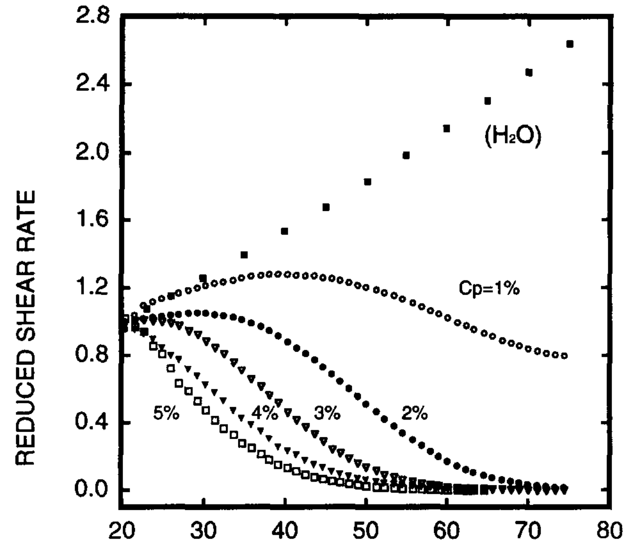


Figure 7 Variation of the reduced shear rate with temperature for PAA500/0.33/PEO5 at different polymer concentrations ($[K_2CO_3] = 13.8\%$, $\sigma = 10\,N\,m^{-2}$)

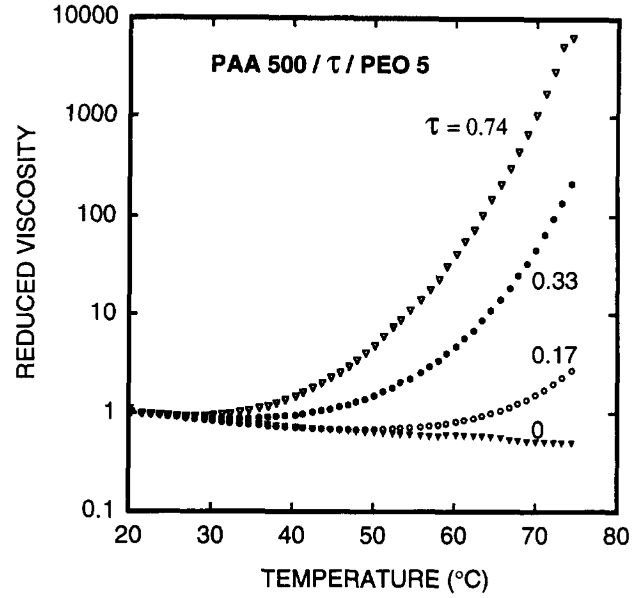


Figure 8 Variation of the reduced viscosity with temperature for different PEO-modified PAA samples ($C_p = 4\%$, $[K_2CO_3] = 11\%$, $\sigma = 10\,N\,m^{-2}$)

In a similar way to previously described, increasing the PEO modification extent of the water-soluble backbone favours, at constant C_p, the formation of PEO side-chain microdomains by decreasing the incipient association temperature and consequently increasing the physical crosslinking efficiency at a given temperature. By using the variations of the reduced shear rates on heating for the three modified samples, the critical temperatures at which the curves first diverge from linearity were found to be $T_c = 45°C$, 33°C and 26°C for $\tau = 0.17\%$, 0.33% and 0.74%, respectively.

Effect of shear rate

Figure 9 displays the evolution of viscosity with shear rate for a PEO-modified PAA ($\tau = 0.17\%$) at constant polymer concentration ($C_p = 4\%$) in a salt solution ($[K_2CO_3] = 15\%$). In this experiment, where the interchain association is already effective at room temperature, we observe an enhancement of the pseudoplastic character of the polymer on heating. This rheological behaviour, which is typical for associating polymers[3], is related to the dynamic properties of the PEO segregated phases such as the number of PEO side chains per PAA chain involved in the microdomains and the time of residence of PEO in these microdomains. Taking into account this pseudoplastic behaviour of associating polymers it is important to have in mind that, when the analysis is carried out at constant shear stress, the shear

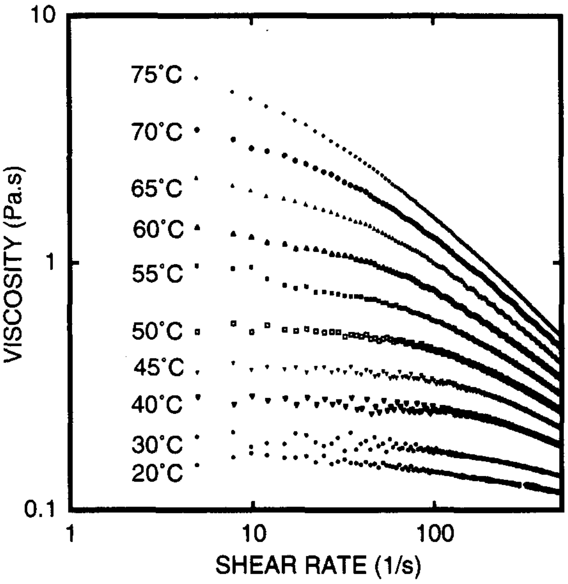


Figure 9 Influence of shear rate on the rheological behaviour of PAA500/0.17/PEO5 aqueous solutions ($C_p=4\%$, $[K_2CO_3]=15\%$)

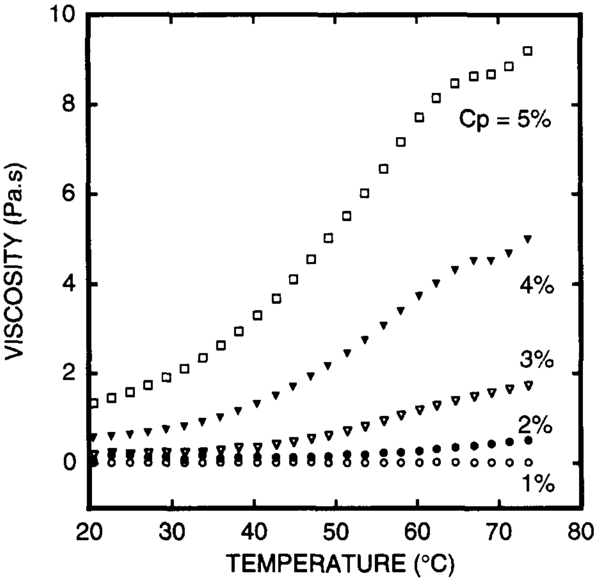


Figure 10 Thermothickening behaviour ($\eta=f(T)$) of PAA500/0.33/PEO5 aqueous solutions observed at constant shear rate ($\dot{\gamma}=100\,s^{-1}$, $[K_2CO_3]=13.8\%$)

rate dependence of the viscosity leads to an amplification of the thermothickening phenomenon. For example, systems which present a very high aggregation on heating can lead to zero shear rate and infinite viscosity at constant shear stress. When the experiments are carried out at a constant shear rate $\dot{\gamma}=100\,s^{-1}$ (*Figure 10*) the viscosity enhancement is weaker compared to that obtained at a constant shear stress $\sigma=10\,N\,m^{-2}$ (*Figure 6*), because of the severe competition between the thermodynamic phenomenon of PEO segregation and the high shear dissociation of the 'hydrophobic' clusters. At high polymer concentrations ($C_p=4\%$ and 5%) and elevated temperature (75°C), where the physical cross-linking is the more effective, application of a high shear rate leads to an incipient breakdown of the partially gelled structure in the temperature range 75–60°C (*Figure 10*).

Effect of salt concentration

The dependence of the thermothickening behaviour of PAA500/0.17/PEO5 on salt concentration is shown in *Figure 11*. At these high ionic strengths, the electrostatic repulsions between polyelectrolyte backbones practically do not depend on the charge of the salt, and we can consider the PEO aggregation mechanism to be independent of the polyelectrolyte effect. As a matter of fact, similar viscosities are obtained at 20°C for all the systems (modified PAA/salt) except at a salt concentration $C_s=15\%$, for which interchain association is effective at room temperature. As expected, an increase in C_s, which enhances the breakdown of the hydration shell of the PEO side chains, improves the thermothickening mechanism. The critical temperatures (T_c), calculated as previously described, are respectively 58°C, 45°C, 35°C, 23°C and lower than 20°C for K_2CO_3 concentrations of 9.6%, 11.1%, 12.1%, 13.8% and 15%. The curve corresponding to $C_s=3.8\%$ is used as a reference, no thermoassociative phenomenon being expected in these conditions.

Discussion

As initially postulated, a thermothickening system can be obtained by grafting onto a water-soluble backbone thermosensitive side chains characterized by a lower critical solution temperature. The general features of thermoassociative polymers is basically similar to that of hydrophobically modified polymers which can aggregate through interchain hydrophobic associations. Nevertheless, the main difference, which provides the originality for our system, lies in the fact that the hydrophobicity of the junction zones and consequently the driving force of the associative mechanism can be controlled through external factors such as temperature and/or salt concentration.

From the viscosimetric studies carried out on PEO-modified polyacrylates in salt solutions, it appears that the basic mechanism of association is directly correlated with the rheological and thermodynamic properties of each component. The molecular weight and the conformation of the polyelectrolyte backbone, a function of

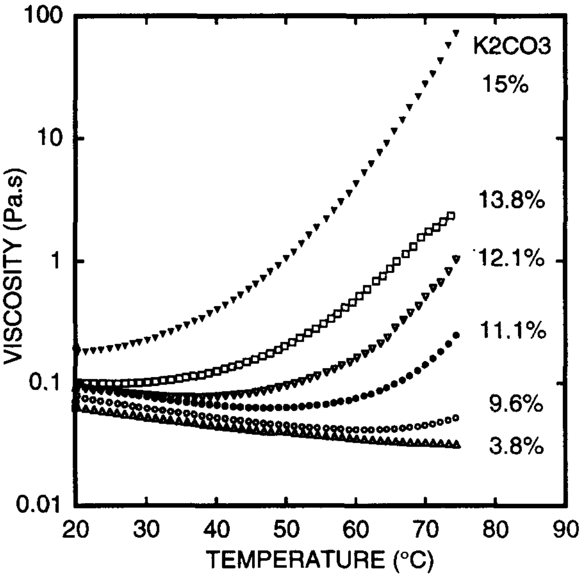


Figure 11 Effect of added salt concentration on the thermothickening behaviour of PAA500/0.17/PEO5 aqueous solutions ($C_p=4\%$, $\sigma=10\,N\,m^{-2}$)

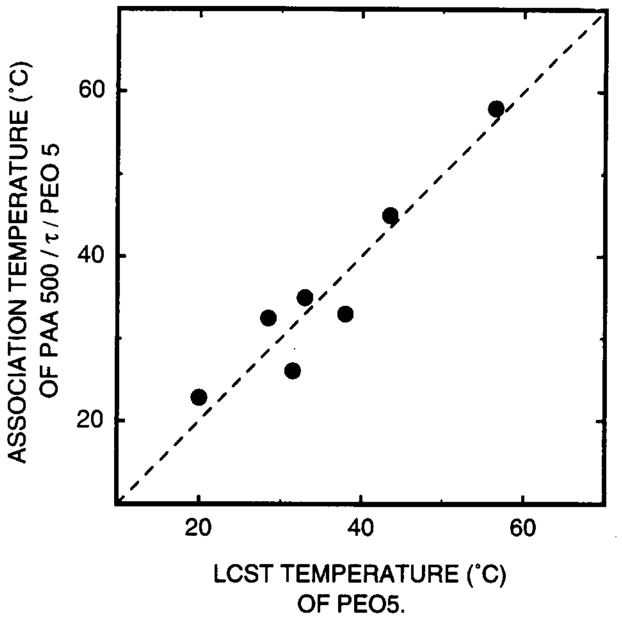


Figure 12 Comparison between the *LCST* of PEO5 and the incipient association temperature of PEO-modified PAA, measured at the same PEO and K_2CO_3 concentrations

the ionic strength, set the critical overlap concentration (C^*) above which an interchain association mechanism can be expected. The latter, driven by PEO side-chain segregation, can arise if at a given concentration of PEO the conditions for phase separation of PEO can be reached. An increase in temperature and/or salt concentration beyond these critical conditions enhances the hydrophobic driving force responsible for the PEO phase segregation, and consequently increases the crosslinking efficiency of the physical network.

A good agreement between the *LCST* phase diagram of PEO5 and the microdomain phase segregation of the modified polymers can be shown by plotting, *versus* the cloud point temperature of free PEO5, the incipient association temperature of the PEO grafts, measured at the same PEO and salt concentrations (*Figure 12*). Although we cannot neglect the possible influence of the PAA backbone on the T_c values, and there exists a certain inaccuracy concerning their determination, these results confirm the mechanism proposed. As the PEO grafts constitute only a minor part of the copolymers, the system does not demix when the *LCST* of PEO is reached but PEO side chains gather into hydrophobic microdomains which act as reversible crosslinks between the main chains. The good accordance between the *LCST* and T_c, exemplified by poly(acrylic acid)/poly(ethylene oxide) graft copolymers, demonstrates the ability to manage the thermal behaviour of polymer solutions. On the basis of the phase diagram of the *LCST* side chains and the rheological properties of the water-soluble backbone, it is possible indeed to adjust the thermothickening behaviour of modified polymer solutions in the required ranges of temperature and salt concentration.

The PAA-*g*-PEO system depicted here illustrates the potentiality of the thermothickening systems based upon copolymers containing moieties with an *LCST* behaviour. If we only consider aqueous media, various other *LCST* polymers have been reported, e.g. hydroxyalkylcellulose[16,17], poly(vinyl alcohol–vinyl acetate) copolymers[18], poly(propylene oxide)[19], poly(methacrylic acid)[20], poly(vinyl methyl ether)[21] and poly(L-proline)[22].

Taking into account the diversity of water-soluble backbones, one can see that the thermothickening concept may be extended to a very wide number of systems differing by:

1. the nature of the hydrophilic domains;
2. the nature of the *LCST* regions; and
3. the architecture of the system, i.e. block or graft copolymer.

A broader view on the generality of this concept will be given in a subsequent paper.

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REFERENCES

1 Valint, P. L. and Bock, J. *Macromolecules* 1988, **21**, 175
2 McCormick, C. L., Nonaka, T. and Johnson, C. B. *Polymer* 1988, **29**, 731
3 Wang, T. K., Iliopoulos, I. and Audebert, R. 'Water Soluble Polymers: Synthesis, Solution Properties and Applications' (Eds S. W. Shalaby, C. L. McCormick and G. B. Butler), ACS Symposium Series no. 467, American Chemical Society, Washington, DC, 1991, p. 218
4 Evani, S. and Rose, G. D. *Proc. Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.* 1987, **57**, 477
5 Schmolka, I. R. *J. Am. Oil Chem. Soc.* 1977, **54**, 110
6 Suto, S., Nishibori, W., Kudo, K. and Karasawa, M. *J. Appl. Polym. Sci.* 1989, **37**, 737
7 Carlsson, A., Karlström, G. and Lindman, B. *Colloids Surf.* 1990, **47**, 147
8 Evani, S. *US Pat. 4432881* 1984
9 Saeki, S., Kuwahara, N., Nakata, M. and Kaneko, M. *Polymer* 1976, **17**, 685
10 Bailey, F. E. and Callard, R. W. *J. Appl. Polym. Sci.* 1959, **1**, 56
11 Boucher, E. A. and Hines, P. M. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 2241
12 Wang, T. K., Iliopoulos, I. and Audebert, R. *Polym. Bull.* 1988, **20**, 577
13 Wang, T. K., Iliopoulos, I. and Audebert, R. *ACS Polym. Prepr.* 1989, **30**, 377
14 Gramain, P. and Frere, Y. *Polym. Commun.* 1986, **27**, 16
15 Gramain, P. and Frere, Y. *Makromol. Chem.* 1987, **188**, 593
16 Jullander, I. *Ind. Eng. Chem.* 1957, **49**, 364
17 Klug, E. D. *Food Technol.* 1970, **24**, 51
18 Nord, F. F., Bier, M. and Timasheff, S. N. *J. Am. Chem. Soc.* 1951, **19**, 289
19 Malcolm, C. N. and Rowlinson, J. S. *Trans. Faraday Soc.* 1957, **53**, 921
20 Eliassaf, J. and Silberberg, A. *Polymer* 1962, **3**, 555
21 Horne, R. A., Almeida, J. P., Day, A. F. and Yu, N. T. *J. Colloid Interface Sci.* 1971, **35**, 77
22 Mattice, W. L. and Mandelkern, L. *Macromolecules* 1971, **4**, 271