

Viscometric behaviour of hydrophobically modified poly(sodium acrylate)

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SUMMARY

Hydrophobically associating poly(acrylic acid) was obtained by reaction of a small amount of octadecylamine on the carboxyl groups of the polymer. In pure water, this modified polymer exhibits a very high thickening power. By increasing the ionic strength of the aqueous solution a strong viscosity increase can be obtained instead of the decrease classically observed with polyelectrolytes. For instance, in 1% NaCl the modified poly(sodium acrylate) is of several orders of magnitude more viscous than the precursor polymer.

INTRODUCTION

Viscosification and gelation of aqueous solutions can be easily achieved with synthetic or natural water soluble polymers of high molecular weight. The presence of ionic groups along the polymer chain expands the coiled polymer by charge repulsion (polyelectrolyte effect) and thus increases its hydrodynamic volume and the viscosity of the solution. However, the polyelectrolyte effect can be largely reduced if salts are present, bringing down the viscosity of the solution (1,2).

On the other hand, it is well known that water soluble polymers bearing hydrophobic groups aggregate in aqueous solution through hydrophobic interactions (3-8). Recently, several studies (8-13) have been devoted to water soluble polymers bearing only a few content of highly hydrophobic groups. These hydrophobically associating polymers are quite soluble in pure water and give concentrated solutions of very high viscosity. Furthermore their viscosity can be substantially improved by addition of inorganic salts. This feature is particularly suitable when water soluble polymers are used in oil recovery, drilling fluids, cosmetics, paint and paper making industry. Most of these studies deal with nonionic polymers obtained by radical polymerization (9,11,13). Under these conditions, inasmuch as the solubility of the water soluble and hydrophobic monomer may be very different in the copolymerization solvent, it is very difficult to obtain random copolymers with a given molecular weight and various contents of hydrophobic groups.

In this work we present preliminary results relative to the viscometric behaviour of modified poly(sodium acrylate), PAA, in pure water and in aqueous NaCl solutions. Modification reaction was carried out by grafting the chain of PAA by a small amount of alkylamine. The hydrophobic group content never extends 10% (molar percentage of modified monomeric units). In this way, the polymerization degree of our hydrophobically

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associating polymers remains, for all the samples, equal to that of precursor PAA. Furthermore, an almost random distribution of alkyl groups along the polymer chain can be expected. When the grafted alkyl chain is long enough and the polymer concentration higher than a critical value the modified PAA aggregates. It results in a drastic increase in solution viscosity, especially in the presence of salts.

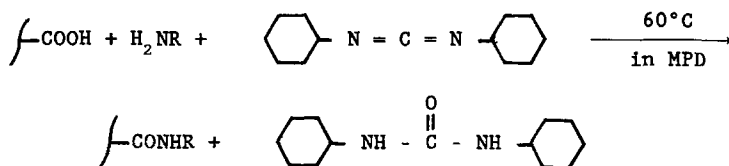
EXPERIMENTAL

Materials

Poly(acrylic acid) (PAA) in concentrated aqueous solution was purchased from Polyscience (25% solids in water) ; the average molecular weight given by the supplier was 150 000. In order to obtain pure PAA in the acid form, commercial solution was ultrafiltered at first with an aqueous HCl solution (10^{-2} mol l^{-1}), then with a large excess of pure water and finally freeze-dried. Technical grade octadecylamine was kindly supplied by Société Française Hoechst and used without further purification. Water was purified by a Milli-Q system (Millipore). All other reagents were of analytical grade.

Modification of poly(acrylic acid)

Modified PAA was obtained by the well known reaction of alkylamine on carboxyl group in an aprotic solvent, 1-methyl-2-pyrrolidone (MPD), in presence of dicyclohexylcarbodiimide (CDI) (14,15)



An example of modification reaction is the following : 5g (0.0694 mol) of PAA were dissolved (for 24 hours) in 150 ml MPD at 60°C. 0.565g of octadecylamine (0.0021 mol) and 0.474g of CDI (0.0023 mol) were separately dissolved in 10 ml MPD and introduced successively into the PAA solution under vigorous stirring. The temperature was maintained at 60°C for 24 hours. The system was then cooled to room temperature and the dicyclohexylurea crystals formed by CDI during the reaction were eliminated by filtration. The modified PAA was neutralized and precipitated by addition of concentrated NaOH aqueous solution (40%). The precipitate was washed by hot MPD (60°C) and methanol. The crude product was dissolved in water and precipitated in methanol (twice) and finally dried overnight at 50°C under reduced pressure (< 0.1 mmHg).

In order to obtain the degree of modification (or hydrophobic group content) of PAA, elementary analysis and ^1H NMR spectra were performed. Results of both methods indicate that the yield of modification reaction reaches 100%. Therefore, the above polymer contains $0.0021/0.0694 = 3\%$ hydrophobically modified repeating units.

According to this method three modified polymers were prepared and the following sample designation is adopted : e.g. PAA-3, which means that the molar content of octadecyl group is 3%. The other samples were : PAA-1

and PAA-10. A blank sample (PAA-0) was obtained by the same treatment but without addition of alkylamine in the reaction mixture.

Apparatus and conditions

Viscosity measurements were carried out with a "Low-Shear 30" apparatus (Contraves) and a controlled stress rheometer (Carri-Med). The temperature was 30°C, controlled to within 0.1°.

Firstly, concentrated stock solutions were prepared under magnetic stirring at least 24 hours before use. Final solutions of desired composition were obtained by dilution of the appropriate stock solution with water and, if necessary, addition of solid NaCl. The air bubbles in the highly viscous samples were readily eliminated by brief centrifugation.

RESULTS AND DISCUSSION

In order to cover adequately the viscosity range over more than four decades the ordinate in the following figures is represented by a logarithmic scale. Figure 1 presents the viscosity of modified and blank polymers as a function of polymer concentration, C_p , in pure water. A typical polyelectrolyte behaviour is found for PAA-0; the viscosity rapidly increases when the polymer concentration is low because of the charge repulsion, but for more concentrated solutions, when the repulsive electrostatic interactions are screened, the viscosity smoothly increases. This behaviour completely changes when the polymer bears octadecyl groups. Even for the polymer with the lower hydrophobic group content (PAA-1) the viscosity becomes higher than that of PAA-0 as soon as polymer concentration exceeds a critical value, C_p^c . This critical concentration decreases and the sharpness of the viscosity curve is all the more pronounced as the hydrophobic group content increases. Before the critical concentration, the viscosity of modified polymers is somewhat smaller than that of PAA-0. Such a behaviour is typical for associating polymers (16).

If association occurs through aggregation of the alkyl chains, the addition of inorganic salts must bring about important changes to the behaviour of our polymers. When a solution of non-modified poly(sodium acrylate) is used (2% PAA-0) the viscosity decreases continuously with addition of NaCl (figure 2). At the same concentration poly(sodium acrylate) bearing 1% of octadecyl groups (PAA-1) presents a somewhat lower viscosity in pure water but it remains almost unchanged with the quantity of NaCl added. More striking is the behaviour of the PAA-3 sample which has a clearly higher viscosity in pure water. Addition of NaCl brings up rapidly the solution viscosity. When 1% NaCl is added the viscosity of the system is two orders of magnitude higher than in pure water. Further addition of salt slowly brings down the solution viscosity. In any case the viscosity of PAA-3 remains several orders of magnitude higher than that of the precursor polymer (PAA-0) at least when the salt concentration does not exceed 3%. On the contrary, the most modified poly(sodium acrylate) PAA-10 although at the concentration used (2% in polymer) in pure water is completely gelled, the addition of traces of NaCl sharply brings down the viscosity and for salt concentrations higher than 0.1% phase separation occurs: a concentrated gel-like phase is in equilibrium with a very dilute supernatant.

In fact, it has been convincingly shown (4-7) that in dilute aqueous solution polysoaps (that means polymers bearing hydrophobic groups) form molecular micelles and undergo conformational changes which drastically

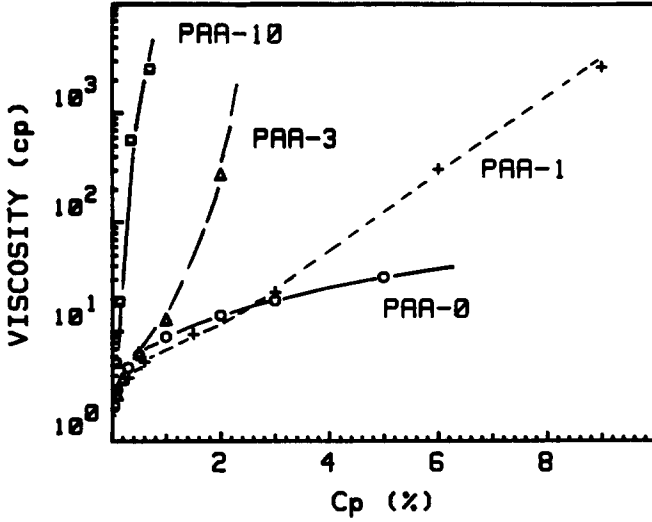


Figure 1

Solution viscosity of modified and precursor polymers in pure water as a function of polymer concentration, C_p . Shear rate, $\gamma = 1.28 \text{ s}^{-1}$.

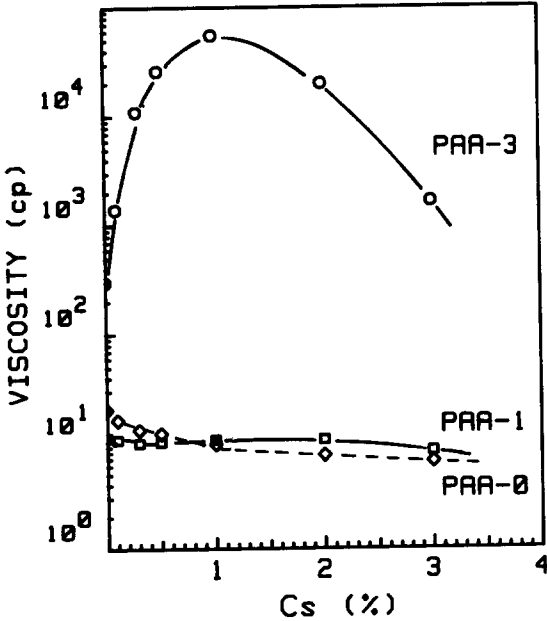


Figure 2

Solution viscosity versus NaCl concentration for three polymers : PAA-0, PAA-1 and PAA-3. Polymer concentration, $C_p = 2\%$. Shear rate, $\gamma_p = 0.06 \text{ s}^{-1}$.

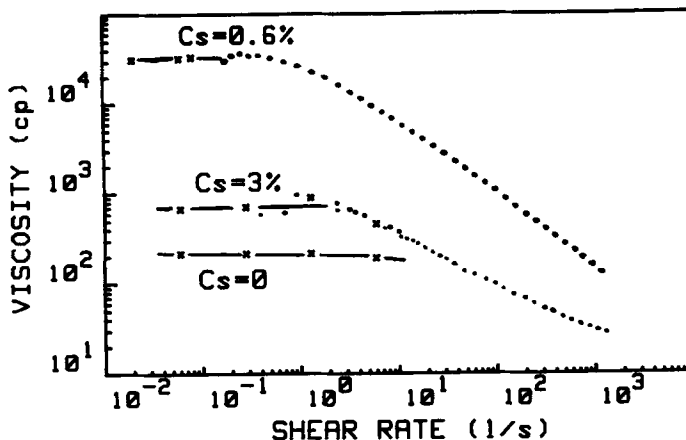


Figure 3

Dependence of viscosity on the shear rate for PAA-3 solutions at various salt concentrations : $C_s = 0\%$, 0.6% and 3% . Polymer concentration, $C_p = 2\%$. Experimental points were obtained with a Carri-Med rheometer, except (x) which were given by a Low-Shear-30 apparatus.

influence their specific viscosity (4). On the other hand, it is well known that the critical micelle concentration (cmc) as well as the average micelle size of ionic amphiphiles is strongly dependent on ionic strength (17). Taking into account the above considerations, one can interpret the results of figures 1 and 2 in terms of alkyl chain aggregation (micellization). When the polymer concentration is high enough (higher than the critical overlap concentration) and the alkyl chain concentration is greater than a critical aggregation concentration (equivalent to cmc of monomeric amphiphiles) the system aggregates and viscosity increases. Addition of a salt in the system brings about two opposite effects : screening of charge repulsion which tends to fall down the viscosity (2) ; and a drastic decrease of cmc (17) resulting a more effective interchain cross-linking. When viscosity enhancement due to interchain cross-linking prevails over polyelectrolyte effect, addition of NaCl results in an increase in final viscosity of the system (curve PAA-3 in figure 2). However, when interchain cross-linking in pure water is high enough (curve PAA-10 in figure 1), addition of a salt leads to a more compact network which rapidly collapses.

For polymer concentrations lower than the critical one, intrachain aggregation competes with interchain cross-linking and the viscosity of a modified polymer may be lower than that of PAA-0.

In order to make easier the comparison between several systems, the viscometric results presented in figures 1 and 2 were obtained at low shear rates, 1.28 s^{-1} and 0.06 s^{-1} respectively, and almost correspond to the newtonian viscosity of the systems (except for PAA-10 in figure 1). However, for solutions of associating polymers a great dependence of viscosity on shear rate is expected (12,16). This dependence is presented in figure 3 for PAA-3 in water and two salt solutions at polymer concentration of 2% . An almost shear rate independent (Newtonian) viscosity is observed when $\dot{\gamma}$ is low ($\leq 1 \text{ s}^{-1}$), but for higher $\dot{\gamma}$ values a typical shear thinning behaviour appears. Although shear rate dependence is more important for solutions of higher Newtonian viscosity, the relative position of the curves in figure 3 remains unchanged, at least in the range of shear rate studied.

In practice, a such rheological behaviour is suitable for many industrial formulations. Furthermore curves in figure 3 show that even the very viscous solutions (e.g. upper curve in figure 3) can be easily homogenized by a vigorous mechanical stirring ($\gamma > 1\ 000\ s^{-1}$).

CONCLUSIONS

The classical viscosity reduction of polyelectrolyte solutions in the presence of salts can be successfully prevented if the polyelectrolyte chain is grafted by a small amount of hydrophobic groups. In this case, hydrophobic groups aggregate all the more as ionic strength increases, leading to polymer chain cross-linking and thus to viscosity enhancement. This behaviour is actually observed for poly(acrylic acid) bearing octadecylamine moieties.

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