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Influence of the structure and composition on surface tension of aqueous solution of graft copolymers of polyacrylamide backbone and polyalkyleneoxide branches

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Summary

Polyacrylamide homopolymers and graft copolymers of poly(acrylamide-g-ethylene oxide) and poly(acrylamide-g-propylene oxide) were synthesized, characterized by SEC, FTIR and ^{13}C-NMR and the behavior of their aqueous solutions was evaluated by surface tension measurements. By using the macromonomer technique, it is more difficult to incorporate poly(propylene oxide) branches than poly(ethylene oxide) branches. Graft copolymers of polyacrylamide and poly(propylene oxide) showed higher reduction of surface tension than poly(acrylamide-g-ethylene oxide) since they present a structure made up of hydrophilic and hydrophobic segments. Poly(acrylamide-g-propylene oxide) exhibits surfactant behavior, and the surface tension of its aqueous solution depends on the poly(propylene oxide) graft chain length and amount.

Introduction

Polyacrylamide is a biodegradable water-soluble polymer and is frequently used as a viscosity modifier[1]. Its physical properties change as a function of molecular weight and the intrinsic viscosity of the aqueous solution[2]. Polyacrylamide has several applications, e.g., in the oil recovery and cosmetic industries[1,3]. The preparation of linear polymer can be achieved by reaction of acrylamide dissolved in water under nitrogen with hydrogen peroxide[3].

When more than one monomer are added to the reaction and both are incorporated in the same chain, a copolymer is obtained. Copolymers comprising chemically dissimilar sequences act as a surfactant and, sometimes, present better performance than low molecular weight surfactants, which are already commercially used[4-5].

The influence of surfactant on properties can be evaluated by carrying out contact angle, adhesion, and surface/interfacial tension measurements. Surfactant adsorption at the liquid-air interface can be calculated by the surface

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tension as a function of solution concentration. There are four main methods to measure interfacial tension: ring, plate, contact angle and drop. Each method is based on a different concept. The ring method, which is based on force measurements, is used due to its accuracy and simplicity[5-6].

Works about poly(acrylamide-g-ethylene oxide), its systhesis and rheological properties, have been published[2,7-9].

The present work was directed towards preparing graft copolymers which act as thickening agents and are able to reduce the surface tension of water. The influence of structure and composition on the surface tension of aqueous solution of polyacrylamide, poly(acrylamide-g-ethylene oxide) and poly(acrylamide-g-propylene oxide) was evaluated.

Experimental

Synthesis

Polyacrylamide was synthesized in water and water/methanol using hydrogen peroxide as initiator (1.3% based on acrylamide) at 40°C (2 hours).

Graft copolymers were synthesized by reacting acrylamide and poly(ethylene oxide) methacylate, and acrylamide and poly(propylene oxide) methacylate, for 3 and 24 hours, respectively, in water/methanol (60/40) and using hydrogen peroxide as initiator, at 70°C.

Polymer solutions were poured into a large excess of methanol and the white precipitates were filtered and vacuum dried. The polymers were purified by reprecipitation from water into methanol, filtered and vacuum dried.

Characterization

Molecular weights were obtained from intrinsic viscosity measurements of polyacrylamide aqueous solutions using a Low Shear 40 - Contraves Rheometer (at 30°C) and the Mark-Houwink-Sakurada relationship.

IR spectra were recorded on Perkin Elmer-1720X FTIR spectrometer and ^{13}C NMR spectra were recorded on Varian VXR-300 apparatus.

Surface tension

Surface tension measurements of aqueous polymer solutions were performed on a Krüss K-10 digital tensiometer using the Du Nouy ring, at 30°C. Aqueous solutions of polymers were prepared over a range of 1-0.0003 wt%.

Results and discussion

Table 1 shows the results of intrinsic viscosity, $[\eta]$, and viscosity-average molecular weight, $\overline{M}_v$, of polyacrylamide as a function of reaction solvent. $\overline{M}_v$ was obtained through the Mark-Houwink-Sakurada relationship using $k=6.5 \times 10^{-5}$ [ml/g] and $a=0.82$[10]. It can be observed that by increasing the methanol content, the molecular weight decreases (chain transfer effect); the water/methanol (60/40) system, in which $\overline{M}_v \approx 33{,}000$ was obtained, was chosen as the solvent for copolymer synthesis.

It was observed that copolymer conversion is related to the molecular weight and hydrophilicity of the comonomer. The homopolymerization of pure acrylamide reaches satisfactory conversion in 2 hours; the copolymerizations of acrylamide and hydrophilic poly(ethylene oxide) methacrylate ($\overline{M}_n$=1000) were 3 hours; and, when copolymerizing acrylamide and hydrophobic poly(propylene oxide) methacylate ($\overline{M}_n$= 400 or 1000), 24 hour reactions were necessary.

Table 1: Intrinsic viscosity, [η], and viscosity average-molecular weight, $\overline{M}_v$, of polyacrylamide as a function of solvent composition.

Polymer	Solvent water/methanol	[η][(a)] (dl/g)	$\overline{M}_v$[(b)]
PA1	100/0	1.32	179,000
PA2	90/10	0.96	122,000
PA3	80/20	0.45	48,400
PA4	70/30	0.43	45,500
PA5	60/40	0.33	32,800
PA6	40/60	0.08	6,140

(a) Low Shear 40-Contraves Rheometer, at 30°C.
(b) By the Mark-Houwink-Sakurada relationship.

The IR spectra of polyacrylamide, poly(acrylamide-g-ethylene oxide) and poly(acrylamide-g-propylene oxide) exhibit the expected characteristic absorptions. The IR spectrum of poly(acrylamide-g-ethylene oxide) exhibits de characteristic absorptions of polyacrylamide and poly(ethylene oxide) as shown in Figure 1. Absorptions can be observed at (A) 3480-3350 cm^{-1} (stretching bands of OH and NH groups overlapped), (B) 2960 cm^{-1} (stretching bands of CH_3 group), (C) 1710-1640 cm^{-1} (ester carbonyl absorption and stretching band of NH group overlapped), (D) 1425 cm^{-1} (stretching band of CN group), and (E) 1150 cm^{-1} (asymetrical stretching band C-C(O)-O).

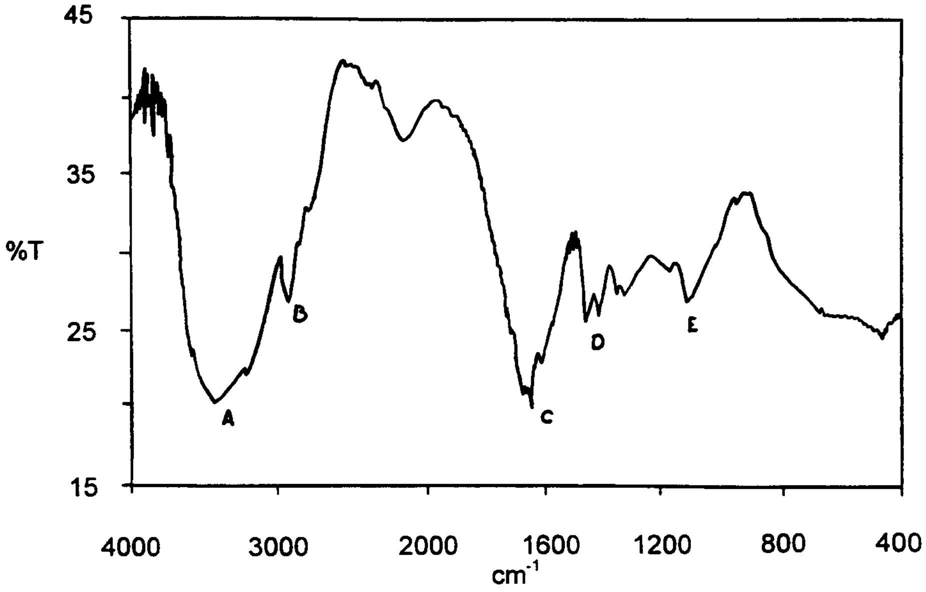

Figure 1: Infrared spectrum of poly(acrylamide-g-ethylene oxide)

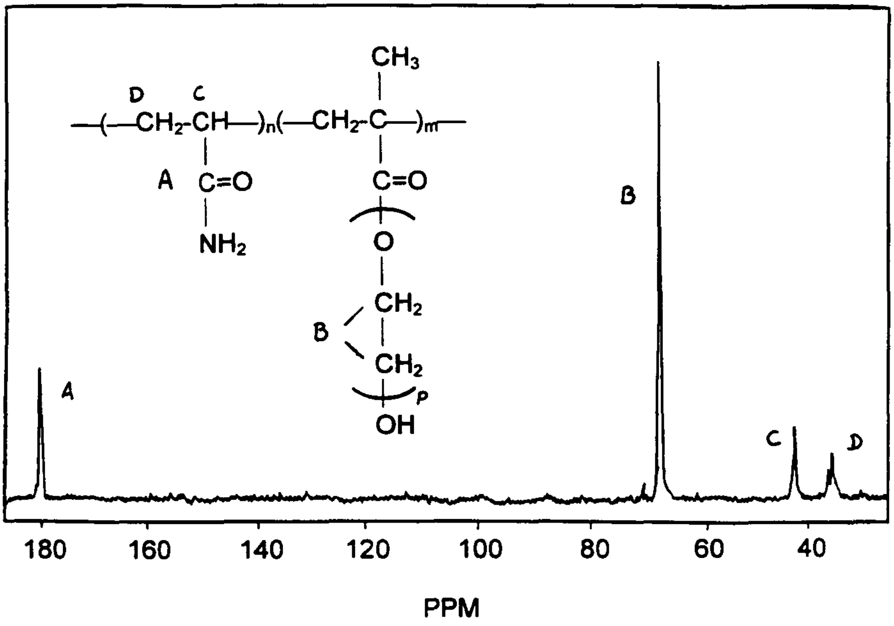

Figure 2: ^{13}C NMR spectrum of poly(acrylamide-g-ethylene oxide).

Figure 2 shows the ^{13}C NMR spectrum of poly(acrylamide-g-ethylene oxide). The quantitative analysis of graft copolymer composition can be calculated from ^{13}C-NMR spectrum peak intensities, by using the peak related to the carbonyl of the main chain (~180 ppm) and the one related to the ether CH_2 of the graft chain (~67 ppm).

Table 2 shows the surface tension results for different molecular weight polyacrylamides. It can be observed that the surface tension does not depend on homopolymer molecular weight.

Table 2: Surface tension of polyacrylamides of different molecular weights.

Polycrylamide	$\overline{M}_v$[a]	Surface tension[b] (dyn/cm)
PA1	179,000	69.1
PA2	122,000	69,1
PA3	48,400	69,3
PA4	45,500	69,2
PA5	32,800	69,2
PA6	6,140	69,0

[a] By the Mark-Houwink-Sakurada relationship.

[b] 0.1 wt% aqueous polymer solutions.

Characterization data of graft copolymers are summarized in Table 3.

Table 3: Composition and surface tension of graft copolymers

Polymer aqueous solution	Graft chain	Graft chain content(a) (%)	Surface tension(b) (dyn/cm)
-----(water)	-	-	73.0
Polyacrylamide	-	-	**69.0**
COP 1	PEO 1000	18.0	65.6
COP 2	PEO 1000	57.0	66.9
COP 3	PEO 1000	77.0	66.8
Poly(ethylene oxide)	-	-	**60.1**
COP 4	PPO 400	4.7	60.2
COP 5	PPO 1000	5.7	60.9
COP 6	PPO 1000	6.1	51.0
Poly(propylene oxide)		water insoluble	

(a) By ^{13}C NMR. Solvent: water. T=40°C.

(b) 0.1 wt% aqueous polymer solutions.

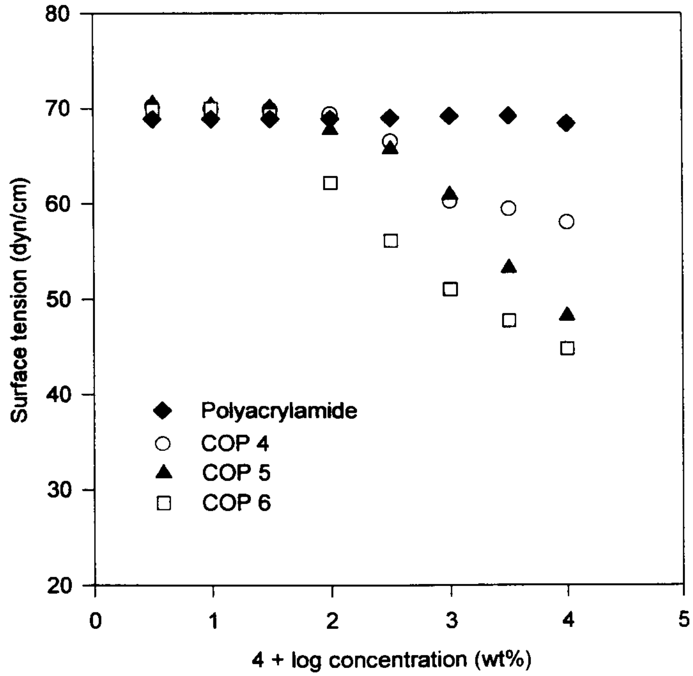

Figure 3: Surface tension versus concentration plots for aqueous solutions of polyacrylamide and poly(acrylamide-g-propylene oxide)s.

It was observed that is more difficulty to incorporate poly(propylene oxide) (PPO) grafts than poly(ethylene oxide) (PEO). This is likely due to the low solubility of PPO in the solvent, and to the copolymers micelle formation, which provides a suitable environment to the PPO-macromonomer in the micelle core.

Polyacrylamide and poly(ethylene oxide) are water soluble. The surface tension of water is about 73 dyn/cm. Polyacrylamide did not reduce markedly the surface tension of the aqueous solutions, poly(ethylene oxide) gave lower values, and poly(propylene oxide) is not water soluble. The poly(acrylamide-g-ethylene oxide) copolymers showed a behavior between the pure homopolymers, and graft chain content dependence on the surface tension was not observed over the composition range studied (18-77 % of graft chain).

The poly(acrylamide-g-propylene oxide) copolymers gave lower surface tensions than those obtained with copolymers containing ethylene oxide, because they are made up of hydrophilic (polyacrylamide) and hydrophobic (poly(propylene oxide)) sequences. By comparing the results for COP 4 and COP 5, it is suggested that shorter graft chain placed along the main chain forms structures which enhance surfactant behavior at 0.1wt%. Copolymers made up the same length poly(propylene oxide) graft chain exhibit markedly decreasing surface tension when the graft chain content is slightly increased, as shown on Table 3 and Figure 3. The results in Figure 3, for poly(acrylamide-g-ethylene oxide), show that, at higher concentrations, the surface tension decreases as function of graft chain content, independent of graft chain length.

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