

Influence of Quaternary Ammonium Salt Addition on the Surface Activity of Polyacrylic Dispersants

I. Pantchev, D. J. Hunkeler*

Laboratory of Polyelectrolytes and Biomacromolecules, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

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ABSTRACT: A variety of poly(alkyl methacrylate-co-acrylic acid) (PS) copolymers were synthesized under conditions resembling those used in industrial processes. The interfacial tension dependence on the composition, the concentration of the polymers, and the presence of water-soluble quaternary ammonium salt (octadecyltrimethylammonium chloride) were investigated. The studies reveal that the presence of a quaternary ammonium salt decreases the interfacial tension to a high degree and

improves the dispersing properties of the synthesized copolymers. Some examples of using PS copolymer with 15 mol % acrylic acid content as a dispersant in inverse suspension copolymerization process of acrylamide and acrylic acid are presented. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3736–3743, 2004

Key words: dispersions; radical polymerization; stabilization; water-soluble polymers

INTRODUCTION

Suspension polymerization is an established method, with the first disclosure some 80 years ago.¹ It is particularly suited to the preparation of large polymer beads, typically in the range of 5–1000 μm . The use of inverse suspension polymerization for producing water-soluble polymers is a relatively recent development.¹ Because they are unstable systems, the preparation of suspensions requires the use of emulsifiers, traditionally small-molecule surfactants. There has also been an interest in the stabilization of liquid-liquid dispersions with polymeric stabilizers.^{2–5} The polymeric stabilizers employed for inverse suspension copolymerization include nonionic and ionic surfactants. It is more interesting when the polymeric stabilizers are based on amphiphilic charged macromolecules. In some papers different hydrophobically modified acrylamide graft and random copolymers have been synthesized and used for emulsion and suspension stabilization.^{2–7} The stabilizing properties of such polymers are influenced by various factors including molecular weight, copolymer composition, and structure. On the other hand, only a few amphiphilic charged surfactants are commercially available.^{8–10} In the majority of published works and commercial recipes, the stabilizers used for the mentioned application

are low-molecular-weight ionic surfactants that provide electrostatic stabilization.

In this paper surface-active amphiphilic charged copolymers of acrylic acid and a mixture of linear alkylmethacrylates with different composition were prepared. The reaction conditions were maintained similar to those typically followed in industrial syntheses of a similar type of copolymers. This article focuses on the dependence of the interfacial tension versus the concentration and the composition of the polymers. The effect of a quaternary ammonium salt dissolved in the aqueous phase on the interfacial tension values for the polymers was examined. The amphiphilic charged macromolecules obtained were tested as dispersants in some examples of inverse suspension copolymerization of acrylamide and acrylic acid.

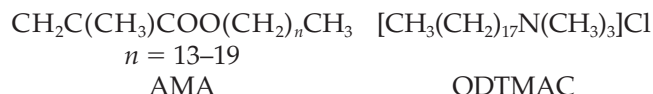
EXPERIMENTAL

Materials

Industrial grade linear alkylmethacrylates (AMA) with a length of the alkyl group between C_{14} and C_{20} were kindly supplied by Ciba Specialty Chemicals (Water Treatments, Inc., Suffolk, VA). Acrylamide (AAM) (Mitsui Chemicals, Tokyo, Japan), acrylic acid (AA) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), Isopar M (Esso Schweiz GmbH, Zurich, Switzerland), octadecyltrimethylammonium chloride (ODT-MAC) (Fluka, Buchs, Switzerland), and the initiators potassium persulfate (Fluka) and 2,2'-azobis(2,4-dimethylvaleronitrile) (Wako Chemicals GmbH, Neuss, Germany) were used as received.

Correspondence to: I. Pantchev (ivan.pantchev@epfl.ch).

*Present address: Aqua + Tech Specialties S. A., 4 Chemin du Chalet-du-Bac 4, La Plaine, 1283 Geneva CP 28, Switzerland.



Synthesis of the dispersant

The amphiphilic charged copolymers were synthesized by radical solution polymerization of 25 wt % monomer solution with various ratios of acrylic acid and alkylmethacrylate mixture¹¹ in aliphatic hydrocarbon Isopar M. The polymerization was performed in a 0.3-L glass reactor equipped with mechanical stirrer, heating jacket, reflux condenser, and nitrogen line. The reaction mixture was purged with nitrogen and the polymerization was initiated by the addition of 0.034 g of 2,2'-azobis(2,4-dimethylvaleronitrile) at 60°C. After several hours the temperature was increased to 90°C for an additional 2 h to complete the polymerization. The obtained copolymers were precipitated in acetone, washed, and dried at 40°C in a vacuum oven.

Inverse suspension copolymerization of acrylamide and sodium acrylate—typical procedure

Step 1. Preparation of the aqueous phase

In a 2-L beaker, 65 g of acrylamide and 30 g of acrylic acid were dissolved in 135 g demineralized water. EDTA–disodium salt (0.026 g) was added as a sequestering agent and the pH was adjusted to 6.0 by the addition of sodium hydroxide solution.

Step 2. Preparation of the oil phase

A total of 0.9 g of alkylmethacrylate–acrylic acid copolymer (PS15) was dissolved in 307 g of Isopar M by stirring with a mechanical stirrer.

Step 3. Suspension polymerization

The aqueous phase was added rapidly to the organic phase and the mixture was pre-emulsified for 5 min and subsequently emulsified by a laboratory homogenizer, type Silverson L4RT (Silverson Machines, Ltd., England). The suspension obtained was poured into a 0.8-L stainless-steel reactor equipped with heating/cooling coil and digital thermocontrolling system and connected to a nitrogen line. After purging with nitrogen for 45 min, the polymerization was initiated at 40°C by the addition of 0.025 g of potassium persulfate dissolved in 1 g demineralized water. After 3 h, the temperature was increased up to 50°C for an additional 2 h to complete the polymerization.

Conversion measurements for the dispersant

The conversion measurements were performed gravimetrically. At the end of the reaction, 0.5 g of the polymer solution was precipitated in a vial containing 30 mL of acetone. The vial was put in a shaker for at least 1 h; after that the acetone was decanted and the polymer was dried at 50°C for 12 h in a vacuum oven. The dry polymer was weighted to calculate the total conversion.

Conversion measurements for acrylamide and sodium acrylate

The measurements for residual monomers were performed using an HPLC system consisting of a Hitachi L7110 isocratic pump (Hitachi Instruments, Tokyo, Japan), a Hitachi L4000H variable wavelength UV detector operating at 197 nm, and a column Lichrosorb RP-18, 5 μm , 250 mm. The mobile phase used was acetonitrile–water (5:95 vol %) at pH 2.5.

Particle size estimation

The particle size was estimated using a standard inverted light microscope, Axiovert 100 (Carl Zeiss GmbH, Jena, Germany).

Interfacial tension measurements

The polymers were dissolved and transferred to a 1-L volumetric flask to give the appropriate concentration in Isopar M. The solutions were serially diluted. A similar procedure was followed for preparing water solutions of the quaternary ammonium salt. The interfacial tension measurements were performed by using a tensiometer (Sigma 7⁰³, KSV Instruments Ltd., Finland) at 20°C.

Infrared spectra measurements

The IR spectra were recorded by an ATI Mattson Genesis Series FT-IR (Henri Sarasin AG, Basel, Switzerland) equipped with a single reflection diamond attenuated total reflection system, P/N 10,500 (Graseby Specac, Aartselaar, Belgium).

Size exclusion chromatography (SEC)

The SEC measurements were performed in tetrahydrofuran (THF) with SEC Viscotec TDA Model 300 apparatus, triple detection—LS, RI, IV—equipped with PSS columns: 100, 1000, and 10,000 Å. Polystyrene calibrations were applied.

TABLE I
Poly(alkyl methacrylate-*co*-acrylic Acid) Polymers

Polymer code	Content of AA mol %	\bar{M}_n	\bar{M}_w	Conversion (%)
PS5	5	137,200	54,600	80
PS15	15	88,600	40,900	82
PS30	30	74,400	37,700	87
PS40	40	54,700	49,000	90

RESULTS AND DISCUSSION

Various amphiphilic random copolymers, differing in composition, were synthesized. The percentage of the hydrophilic component varied from 5 to 70 mol % by total monomer weight. The composition and the molecular weight characteristics of some examples are specified in Table I. Depending on the composition of the started reaction mixture, the Fourier transform infrared (FT-IR) spectra of the obtained copolymers show a regular increase of the peak at 1710 cm^{-1} corresponding to the CO group in the acrylic acid units and a decrease of the peak corresponding to the CO group in the methacrylate units at 1727 cm^{-1} when the hydrophilic component in the reaction mixture is increased (Fig. 1). The solubility of the obtained polymers also changes with the change in composition (Table II).

It has been proposed that the use of polymeric stabilizers might lead to improved stability and better performance of the latex. Since the stabilizer is adsorbed at the *w/o* interface (inverse dispersions), it will reduce the surface tension, which in itself would lead to smaller droplets. However, the low-molecular-weight ionic stabilizers⁸ decrease the surface tension via electrostatic stabilization only. Therefore, the use of the charged amphiphilic copolymers with higher molecular weights (more than several thousand g/mol) will form an interfacial layer around the droplets, which reduces the rate of coalescence, additionally by an important steric stabilization mechanism. The combination of both effects (electrostatic and steric) is known as electrosteric stabilization.⁸ As the molecular weight of the polymer chains increases, larger loops and thicker films will form around the droplets, increasing the steric stabilization. On the other hand, as reported by some authors,^{7,12} our observations also showed that very high molecular weight of the copolymers causes decreased stability of the dispersion. The probable reason is that longer hydrophobic loops spread in the oil phase can cause particle coalescence due to bridging flocculation, especially in smaller droplet size of the primary suspension. On the other hand, in our case when we prepared the dispersing agents we did not observe the limitation with respect to lower molecular weight,¹² because of the higher reactivity of the acrylic acid

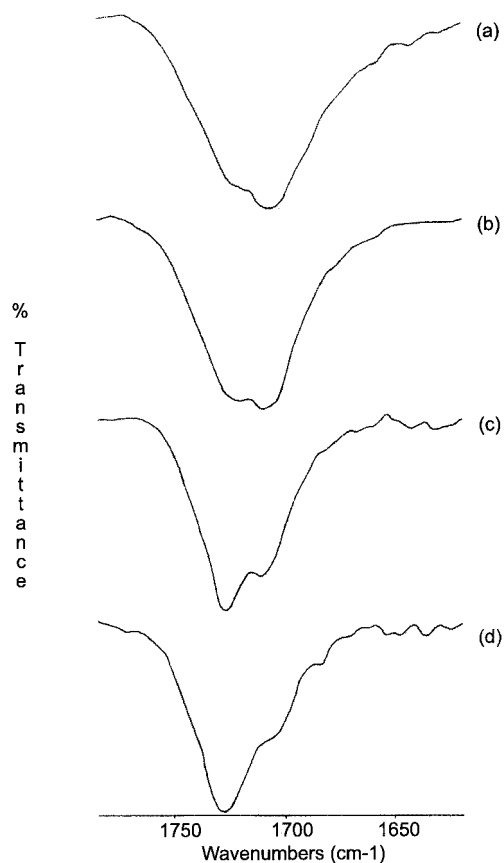


Figure 1 FT-IR spectrum of poly(alkyl methacrylate-*co*-acrylic acid) as a function of AA content of the total molar monomer content: (a) 70 mol % (PS70); (b) 60 mol % (PS60); (c) 40 mol % (PS40); (d) 30 mol % (PS30).

versus the alkylmethacrylate mixture during the preparation of the dispersants.

Our observations show that the dispersing properties can be improved by using in the preparation of the amphiphilic charged macromolecules a mixture of linear alkylmethacrylates with hydrophobic moieties of

TABLE II
Solubility of Poly(alkyl methacrylate-*co*-acrylic Acid) Polymers in Tetrahydrofuran (THF), Chloroform (CHCl_3), Acetone, and Isopar M

Polymer code	Initial composition [AMA]/[AA] (mol %)	Solubility in			
		THF	CHCl_3	Acetone	Isopar M
PS7	93/7	+	+	-	+
PS15	85/15	+	+	-	+
PS18	72/18	+	+	-	+
PS30	70/30	+	+	-	+
PS40	60/40	+	+	+-	+
PS60	40/60	+	+-	+-	+-
PS70	30/70	+-	-	+-	-

Note. +, Soluble; -, insoluble; +-, poorly soluble.

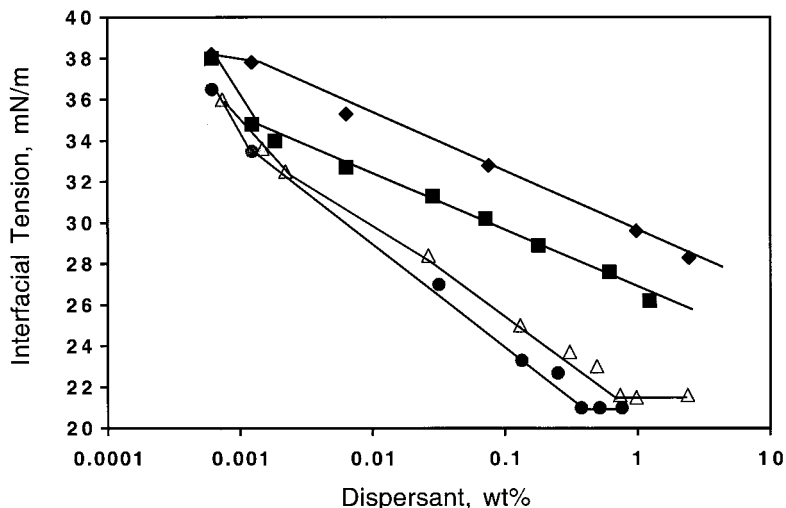


Figure 2 Interfacial tension of poly(alkyl methacrylate-*co*-acrylic acid) solutions as a function of the polymer concentration (wt % based on total concentration): \blacklozenge , 5 mol % AA (PS5); \blacksquare , 15 mol % AA (PS15); \blacktriangle , 30 mol % AA (PS30); \bullet , 40 mol % AA (PS40).

different length.¹¹ Specifically in our studies, we synthesized charged amphiphilic copolymers under the same reaction conditions, but different monomer composition. Figure 2 shows the decrease in the interfacial tension between the oil and water phases versus the change in concentration and the composition of the copolymers. The curves presented are for copolymers with, respectively, 5, 15, 30, and 40 mol % acrylic acid content by total molar monomer content in the stabilizer. Dispersants with a higher percentage of the hydrophilic component are not suitable for stabilization of inverse dispersions.⁶ The interfacial tension regularly decreases with increasing acrylic acid content and the concentration of the copolymer. Because of lower surface activity, the critical micelle concentration (CMC) for the polymers with 5 and 15 mol % acrylic acid cannot be reached within the studied con-

centrations. The kinetic curves presented in Figures 3 and 4 show that the relaxation time to obtain the highest decrease in interfacial tension is between 15 and 20 min. Since the limiting factor is the release by diffusion of the carboxyl groups of the acrylic acid units in the interface, the relaxation time slightly increases with increasing acrylic acid content. The kinetic curves for the interfacial tension γ , (Figs. 3 and 4) exhibit typical power law behavior ($\gamma = K \cdot x^{-n}$) where the n values are quite different due to the different surface-active properties of the presented copolymers. The n values decrease with decreasing acrylic acid content in the dispersant, although neither the correlation coefficients nor the limited data are sufficient to make significant conclusions.

The theoretical findings in the film drainage model for emulsion stability suggest¹³ that the increase of the

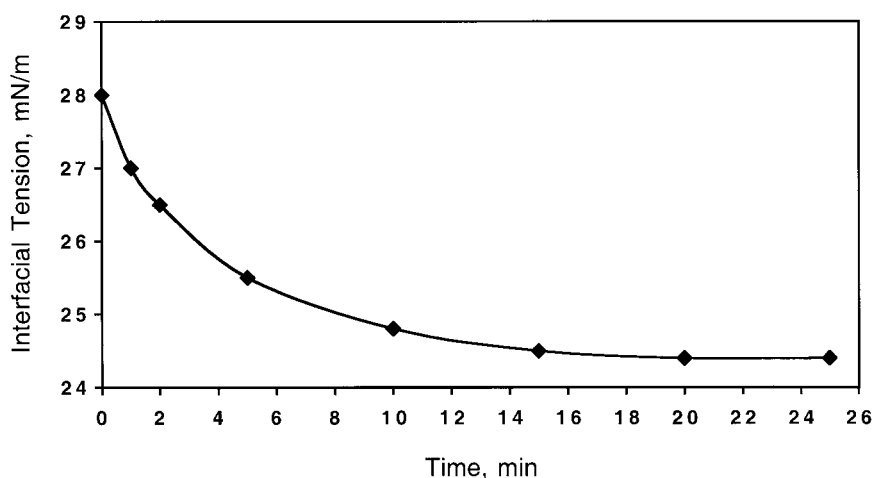


Figure 3 Kinetic curve of the interfacial tension for poly(alkyl methacrylate-*co*-acrylic acid)-PS40, 3 g/L ($\gamma = 27,001 \cdot x^{-0.034}$).

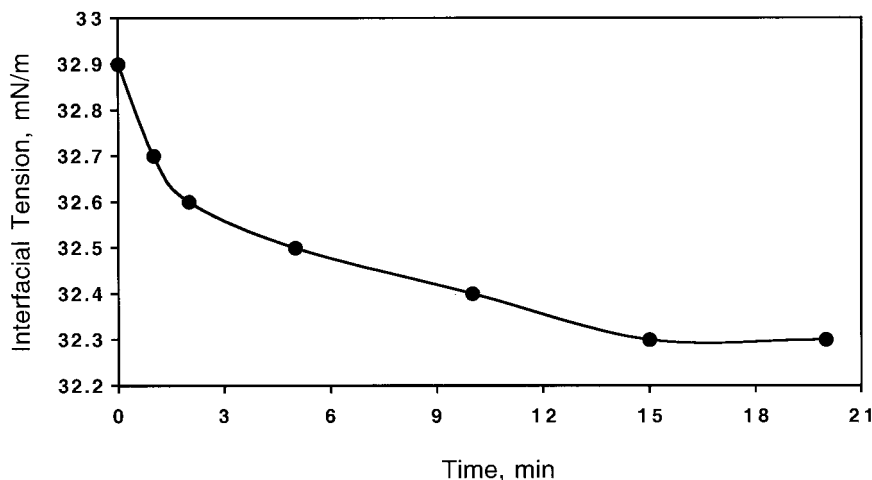


Figure 4 Kinetic curve of the interfacial tension for poly(alkyl methacrylate-*co*-acrylic acid)-PS5, 3 g/L ($\gamma = 32,703 \cdot x^{-0.004}$).

interfacial viscosity results in decreased interface mobility, increased dilational modulus, and, hence, longer drainage time. This promotes the dispersion stability. The dilational modulus of the interfacial polymer layer may be increased in number of ways. As an example, for some systems, it is possible to crosslink the adsorbed polymer molecules to form an interfacial gel layer.¹⁴ However, the concentration of the crosslinker must be kept at a sufficiently low level to prevent interparticle bridging by cross-linking polymers occurring.

In the case of inverse suspensions, water-soluble alkyl quaternary ammonium salts, with solubility opposite to the solubility of the charged amphiphilic stabilizer, can be added to increase their stability.⁹ The authors suppose that the reason is a complex formation between the stabilizer and the salt, although no information has been published on how this complex formation influences the interfacial tension due to dif-

ferent concentrations of the salts. We have studied the dependence of the interfacial tension on salt concentration (Fig. 5). Octadecyltrimethylammonium chloride is used as a quaternary ammonium salt, given in mol % by total molar AA content in the presented copolymer. The dependence of the interfacial tension upon the salt concentration is in agreement with our general observation that the additional presence of a low-molecular-weight electrolyte, with charge opposite to the charge of the stabilizer in the dispersed phase, is essential for preparing stable suspensions during the polymerization process. The water-soluble salt employed also has surface-active properties (Fig. 5, filled squares), although is not suitable alone for the formation of inverse dispersions. The effect of dissolved quaternary ammonium salt in the aqueous phase on the interfacial tension values for the polymeric charged stabilizer could be attributed to the opposite charged interactions between the ionic

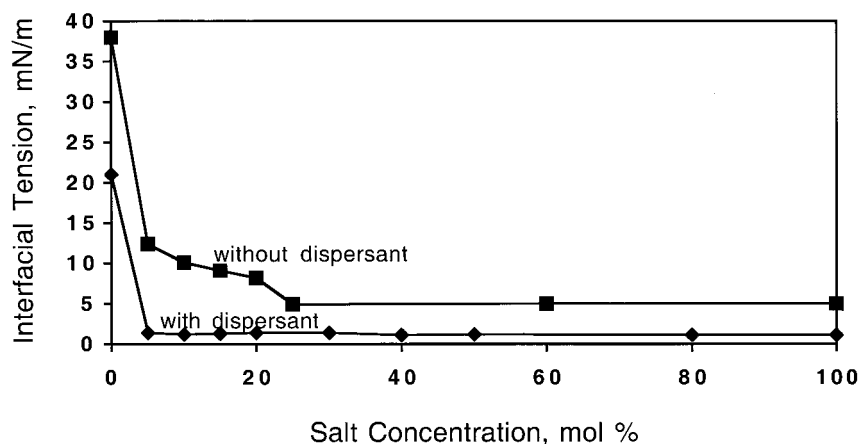


Figure 5 Interfacial tension as a function of the quaternary ammonium salt concentration (octadecyltrimethylammonium chloride in mol % by total molar AA content in the stabilizer): ■, oil-water-salt system, and ♦, oil-polymer (PS40, 6 g/L)-water-salt system.

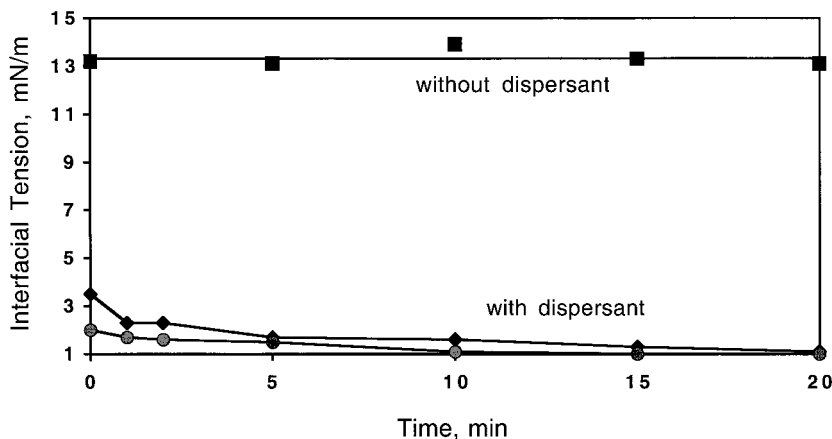


Figure 6 Kinetic curves of the interfacial tension for constant salt concentration—0.08 g/L: ■, oil–water–salt system; ◆, oil–polymer (PS40, 3 g/L)–water–salt system; ●, oil–polymer (PS40, 6 g/L)–water–salt system.

groups of the polymeric stabilizer and quaternary ammonium groups of the water-soluble ionic salt. We observed (Fig. 5, filled diamonds) a maximum decrease in the interfacial tension even at relatively low concentrations of the salt (up to 5 mol % by the total molar content of AA in the stabilizer), different from the empirically estimated values of similar salts used in much higher concentrations.⁹ The extent of the decrease in the interfacial tension is much higher than that of the oil–polymer–water system for the same polymer (Fig. 2). The plateau value of the interfacial tension at higher polymer concentration [Figs. 5 (filled diamonds) and 6 (filled diamonds and filled circles)] (in the area of CMC) of about 5 mN/m and less, with the presence of quaternary ammonium salt, compares well with standard surfactants such as sorbitan sesquioleate and suggests a dense alkyl layer at the water/oil interface. Therefore, a stabilization of inverse emulsions can be expected by such a combination of the synthesized copolymers and alkyl quaternary ammonium salt. The graphs (Fig. 5) show also that the

interfacial tension for the oil–polymer–water–salt system drops to a greater degree than when using a salt only. The probable reason, as mentioned above, is the attraction of opposite charges of the salt and the polymeric dispersant, leading to a faster and higher release of the dispersant’s molecules at the interface. More support for this explanation lies in the behavior (Fig. 5, filled squares) of the oil–water–salt system, which shows a similar trend comparing to the oil–polymer–water system (Fig. 2). The complex formation in the interface is supposed to be a reason for decreasing the interface mobility and increasing the dilational modulus of the interfacial polymer layer.

The behavior of the kinetic curves when salt is present is completely different compared to that in the absence of a salt (Fig. 6). To study the influence of the quaternary ammonium salt addition on the changes of interfacial activity of the copolymers, we chose a copolymer comprising 40 mol % acrylic acid units by total molar monomer content for which it is possible to reach the CMC with the studied concentrations. The

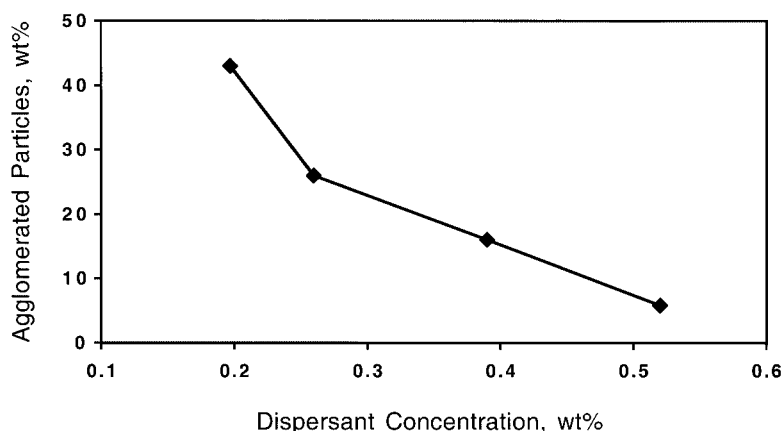


Figure 7 Agglomerated particles from inverse suspension copolymerization of AAM and AA (wt % by total copolymer weight) as a function of the poly(alkyl methacrylate-co-acrylic acid) (PS15) concentration.

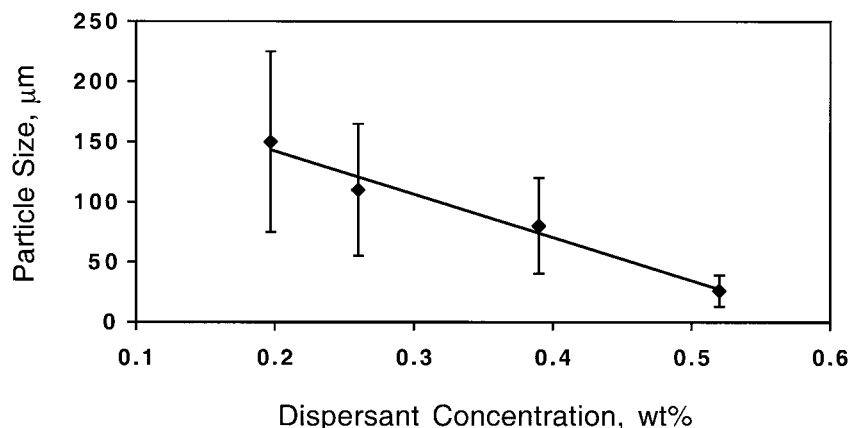


Figure 8 Particle size and the extremes of the average particle size of beads obtained by AAM-AA inverse suspension copolymerization as a function of the dispersant (PS15) concentration (wt % by total suspension weight).

first polymer concentration examined (Fig. 6, filled diamonds) is chosen near the CMC, where it is supposed that we have a saturated solution of the dispersant but no micelles. The second concentration is in the CMC area (Fig. 6, filled circles), where we have micelle formation. In these two cases we have a similar trend, but different slope of the kinetic curves. Since the relaxation time is diffusion dependent, we can observe that this time for the polymer concentration near the CMC is slightly longer than for polymer concentration in the CMC area. As shown in Figure 6 (filled squares), the interfacial tension for the oil-water-salt system does not vary by time. Since the dispersant molecules are dissolved in the oil phase, the following equation for the diffusion (D) of these molecules may be applied:¹⁵

$$D = kT/3\pi\eta d$$

where d is the diameter of the dispersant molecule. The equation shows that, under isothermal conditions and with constant bulk viscosity (η), the diffusion depends on the diameter of the dispersant molecule. The larger this diameter, the longer is the relaxation time because of decreased diffusion rate (Figs. 3, 4, and 6). If we accept these considerations, when we have a smaller molecule as in the case of the low-molecular-weight quaternary ammonium salt, the relaxation time for this molecule is shorter (Fig. 6, filled squares). When both a dispersant and a quaternary ammonium salt are present in the two phases (Fig. 6, filled diamonds and filled circles), the diffusion rate increases, supported additionally by the attraction between the opposite charged molecules resulting in a lower interfacial tension, compared with the case where a salt is not present (Fig. 2).

The obtained amphiphilic copolymers show good properties as dispersants in inverse suspension copolymerization process. Figures 7 and 8 present some

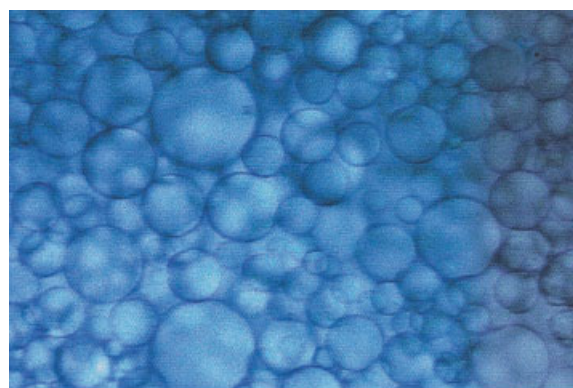
examples of a copolymer with 15 mol % of acrylic acid content used as a dispersant in different concentrations. Among the different factors the quality of the final suspension depends highly on the percentage and the composition of the dispersant used. The figures show the change in average particle size and the percentage of the buildup of agglomerated particles with the change in concentration of the dispersant. The particle size regularly decreases with increasing the amount of the dispersant used. We observed a similar trend in aggregate formation (Fig. 7).

For the presented copolymeric dispersing agent's composition, the threshold of the stability of the suspension versus the dispersant concentration is 0.2 wt % by total suspension weight. Below 0.2 wt % of the stabilizer the suspension failed and formed a large chunk of polymer. When a small amount of quaternary ammonium salt was added, the suspension was still stable until the end of the copolymerization even with 0.15 wt % of dispersant and the agglomerated particles were twice less than in case of 0.2 wt % of dispersant used alone, because of the aforementioned reasons.

Table III presents typical conversion values for acrylamide and acrylic acid-sodium acrylate polymerized under the aforementioned conditions. The microscopic observations of the suspension show that all the

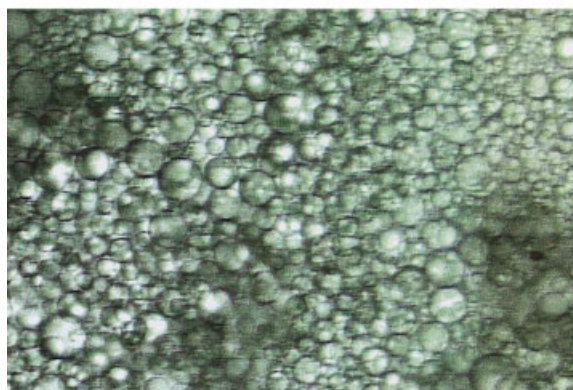
TABLE III
Conversion of Acrylamide (AAM) and Sodium Acrylate (ANa)

Time (min)	Conversion of AAM (%)	Conversion of ANa (%)	Total conversion (%)
60	60.41	50.06	57.41
120	70.40	58.26	66.88
180	82.55	71.26	74.53
300	92.82	84.46	90.40



100 μm

(a)



200 μm

(b)

Figure 9 Photomicrographs of particles obtained by inverse suspension copolymerization of AAM and AA at pH 6.0, [dispersant] = 0.2 wt %: (a) particles in the suspension, original magnification 200 \times ; (b) agglomerated particles, original magnification 100 \times .

particles are spherical. The agglomerated particles also are spherical, a few hundred micrometers in size (Fig. 9). The photomicrographs were taken at the threshold (0.2 wt % dispersant concentration) of the suspension stability without the addition of an ionic salt. These conditions are the reason for the highest degree of agglomeration when the suspension is still stable to the end of polymerization. At lower dispersant concentration, complete destabilization of the dispersion occurred, followed by total agglomeration of

the particles. When the composition of the copolymer is changed, the dispersing properties are also changed. For example, when we used a dispersant with 5 mol % of acrylic acid content only, without salt addition, with a concentration of the copolymer 0.5 wt % by total suspension weight, the agglomerated particles were 80 wt % by total monomer weight, compared with 15 mol % acrylic acid content when we had (for the same dispersant's concentration) only 5.8 wt % agglomerated particles.

CONCLUSION

The interfacial tension decreases with increasing hydrophilic component in the acrylic-based oil-soluble amphiphilic charged macromolecules. This decrease is higher when a water-soluble quaternary ammonium salt is added, even in relatively low concentrations. In the latter case the relaxation time for these copolymers decreases as well. The aforementioned combination of the synthesized copolymers and a quaternary ammonium salt is suitable as a dispersing system for inverse suspension copolymerization of water-soluble monomers.

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References

1. Dowding, P. J.; Vincent, B. *Colloids Surfaces A Physicochem Eng Aspects* 2000, 161, 259.
2. Perrin, P.; Lafuma, F. *J Colloid Interface Sci* 1998, 197, 317.
3. Perrin, P.; Monfreux, N.; Audebert, R. *Prog Colloid Polym Sci* 1997, 105, 228.
4. Perrin, P.; Monfreux, N.; Dufour, A. L.; Lafuma, F. *Colloid Polym Sci* 1998, 276, 945.
5. Perrin, P. *Langmuir* 1998, 14, 5977.
6. Perrin, P.; Monfreux, N.; Thierry, F.; Lafuma, F.; Lequeux, F. *Proc ACS Div Polym Mater Sci Eng* 1999, 81, 492.
7. Kato, S.; Sato, K.; Maeda, D.; Nomura, M. *Colloids Surfaces A Physicochem Eng Aspects* 1999, 153, 127.
8. Perrin, P.; Millet, F.; Charleux, B. In *Physical Chemistry of Polyelectrolytes, Surfactant Science Series*, 2001; p 99.
9. Flesher, P.; Allen, A. S. U.S. Patent 4,506,062, 1985.
10. Stanley, Jr., X.; Frederick, W.; Lamphere, J. C.; Chonde, Y. U.S. Patent 4,833,198 (1989).
11. Pantchev, I.; Hunkeler, D. J; U.S. Patent application, 2003.
12. Antonietti, M.; Weißenberger, M. *Macromol Rapid Commun* 1997, 18, 295.
13. Wasan, D. T. *Chem Eng Educ* 1992, 26, 104.
14. Casassa, E. Z.; Sarquis, A. M.; Van Dyke, C. H.; *J Chem Educ* 1986, 63, 57.
15. Kim, Y. H.; Wasan, D. T. *Ind Eng Chem Res* 1996, 35, 1141.