Semicontinuous Copolymerization of 80/20 wt % [2-(Acryloyloxy)ethyl]trimethyl Ammonium Chloride/Acrylamide in an Inverse Microemulsion at High Comonomer Concentrations

7 AUTHORS, INCLUDING:

José R. Ochoa-Gómez
Tecnalia
114 PUBLICATIONS **524** CITATIONS

SEE PROFILE

Issa Katime
Universidad del País Vasco / Euskal Herriko Un…
384 PUBLICATIONS **3,266** CITATIONS

SEE PROFILE

Semicontinuous Copolymerization of 80/20 wt % [2-(Acryloyloxy)ethyl]trimethyl Ammonium Chloride/Acrylamide in an Inverse Microemulsion at High Comonomer Concentrations

José R. Ochoa-Gómez,[1] Francisco J. Escudero-Sanz,[2]* Pedro M. Sasia,[3] Francisca Río,[2] Javier Nieto-Mestre,[2] Jesús Torrecilla,[2] Issa A. Katime[4]

[1]Department of Industrial Technology, Universidad Alfonso X el Sabio, Avenida de la Universidad 1, 28696 Villanueva de la Cañada, Spain
[2]Technological Center, Department of Sustainable Chemistry, Fundación LEIA Centro Technológico, Parque Tecnológico de Alava, Leonardo Da Vinci 11, 01510 Miñano, Spain
[3]Fundación Inversión Ahorro Responsable, Santa María 9, 48005 Bilbao, Spain
[4]Grupo de Nuevos Materiales y Espectroscopía Supramolecular, Department of Physical Chemistry, Universidad del País Vasco, Apartado 644, Bilbao, Spain

ABSTRACT: The semicontinuous inverse microemulsion copolymerization of 80/20 wt % [2-(acryloyloxy)ethyl]trimethylammonium chloride/acrylamide in an isoparaffin solvent at high comonomer concentrations (30–42 wt %) was studied with a mixture of nonionic surfactants (Crill 43 and Softanol 90) as the emulsifier and sodium metabisulfite as the initiator. The influence of the total comonomer concentration (TCC), emulsifier concentration (EC), hydrophilic–lipophilic balance (HLB), isopropyl alcohol (chain-transfer agent) concentration (IPC), and crosslinking agent concentration (CAC) on the weight-average molar mass (M_w), absolute viscosity (BV), and viscometric structuring index (VSI) of the obtained copolymers was analyzed. M_w and BV increased with TCC and HLB and decreased with EC. At the higher TCC, M_w decreased with IPC; meanwhile, at the lower TCC, M_w increased with IPC above 0.5 wt %. VSI increased with TCC, HLB, and IPC and decreased with EC. VSI increased dramatically with CAC, whereas BV showed a peak at the CAC of 10 ppm. In the absence of both chain-transfer and crosslinking agents, M_w increased linearly with VSI, and this suggests that linear copolymers of very high M_w values cannot be obtained by inverse microemulsion copolymerization, at least for high TCCs. The results are explained in terms of both the collapsed state of the copolymer chains inside the latex particles and changes in the interface structure and composition. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2673–2684, 2009

Key words: hydrophilic polymers; polyelectrolytes; surfactants; water-soluble polymers

INTRODUCTION

Acrylamide (AM)-based, water-soluble cationic copolymers are highly demanded industrial materials because of their applications as flocculants in wastewater treatment, antistatic agents for textile treatment, and solid retention agents in paper making, among others.[1] Most AM-based cationic flocculants of industrial interest consist of copolymers of

AM and [2-(acryloyloxy)ethyl]trimethylammonium chloride (ADQUAT) with different ADQUAT/AM ratios. Generally, high-molar-mass copolymers are desired for the aforementioned applications. However, the handling of these products in a solid form is not easy because of their hygroscopic character and because they are difficult to dissolve. On the other hand, their concentrated aqueous solutions are also difficult to handle because of their high viscosities. Additionally, cationic copolymers degrade continuously in aqueous solutions. To avoid these constraints, inverse emulsion copolymerization is broadly used.[2] This method involves the copolymerization of an aqueous comonomer solution dispersed in a continuous organic phase, which results in a copolymer inverse emulsion. However, although inverse emulsion latex particles are easy to handle and can be obtained with copolymer concentrations above 30 wt % with emulsifier concentrations (ECs) below 4 wt % (with respect to the total emulsion

weight), they lack thermodynamic stability, and this results in phase separation.

To overcome this problem, in the 1980s, a new polymerization method was used to obtain these products: inverse microemulsion polymerization.[3] Microemulsions are transparent, homogeneous mixtures of water or aqueous solutions of chemicals and oil stabilized by a fairly large amount of a surfactant or, in most cases, a surfactant mixture. Unlike emulsions, microemulsions are thermodynamically stable. The inverse microemulsion copolymerization of AM and ionic monomers allows the preparation of stable, clear or milky, low-viscosity microlatex particles of a high molar mass ($\sim 10^7$ g/mol). However, to achieve this goal, a higher concentration of the surfactant mixture must be used in comparison with inverse emulsions to stabilize the system. The EC used in an inverse emulsion is between 2 and 4 wt %, considerably lower than that used in an inverse microemulsion, which is generally greater than 10 wt %, although lower concentrations are employed if a heterophase water-in-oil polymerization process is used[4]; starting from an inverse emulsion of monomers, an inverse microemulsion is obtained after polymerization. Nevertheless, as far as we know, the lower ECs reported for inverse microemulsions of ADQUAT/AM copolymers with ADQUAT/AM ratios of 60/40[5,6] and 40/60[7,8] range from 7 to 9 wt %, being much higher than those used for inverse emulsions.

Lowering the EC as far as possible is a continuous necessity for both environmental and economic reasons. Up to now, attempts at decreasing the EC below the aforementioned levels have been unsuccessful, resulting in phase separation during or after polymerization. An alternative is to obtain latices with much higher copolymer concentrations than those currently reported in the literature, which are lower than 25 wt % for polyacrylamide inverse microemulsions[9–14] and AM-based anionic and cationic copolymer inverse microemulsions.[15–20] The only reported exceptions were ADQUAT/AM copolymers with ADQUAT/AM ratios of 60/40[5,6] and 40/60,[7,8] in which the total copolymer concentrations ranged from 28 to 34.5 wt %.

Polymerization kinetics are influenced by the comonomer concentration, and consequently, properties of polymers obtained at high concentrations can be different from the properties of those obtained at lower concentrations. Then, to design tailor-made products for the desired application with polymer concentrations as high as 42 wt %, a correlation between copolymerization variables and polymer properties is required. In this article, a semicontinuous inverse microemulsion copolymerization of 80/20 wt % ADQUAT/AM in an isoparaffin solvent, Isopar M, with high total comonomer concentrations (TCCs; 30–42 wt %) is studied with a mixture of nonionic surfactants (Crill 43 and Softanol 90) as the emulsifier and sodium metabisulfite (SMB) as the initiator. The influence of copolymerization parameters such as the TCC, EC, hydrophilic–lipophilic balance (HLB), isopropyl alcohol (chain-transfer agent) concentration (IPC), and crosslinking agent [N,N'-methylenbisacrylamide (MBA)] concentration (CAC) on the weight-average molar mass (M_w), viscosity, and viscometric structuring index (VSI) of the obtained copolymers is analyzed.

EXPERIMENTAL

Materials

A 50 wt % AM aqueous solution (SNF S.A., Andrézieux, France) and ADQUAT (80 wt % aqueous solution, Floerger, Andrézieux, France) were used as received. To obtain an aqueous phase of the desired concentration, the aforementioned solutions were diluted in demineralized water (conductivity < 10 μS/cm). The oil phase was Isopar M, an isoparaffin solvent with a distillation range of 223–254°C from Exxon Mobil Chemical (Leatherhead Surrey, United Kingdom). The emulsifier was a blend of two nonionic surfactants: Crill 43, a sorbitan sesquioleate (HLB = 3.7) supplied by Croda (East Yorkshire, United Kingdom), and Softanol 90, a C_{11}–C_{13} secondary ethoxylated fatty alcohol (HLB = 13.3) supplied by Ineos Oxide (Antwerp, Belgium). Nitrogen (purity > 99.99%) was supplied by Praxair España (Barcelona, Spain) S.L. SMB, MBA, and isopropyl alcohol (synthesis-grade; all from Panreac (Antwerp, Belgium)) were used as the initiator, crosslinking agent, and chain-transfer agent, respectively. Disodium salt of EDTA (synthesis-grade; Quimidroga S.A., Barcelona, Spain) was added to complex any metal cation that could inhibit copolymerization. All chemicals were used as received from the suppliers without further purification.

Copolymerization procedure

Comonomer inverse microemulsion formulations for copolymerization were selected from the microemulsion stability domain from pseudoternary phase diagrams obtained with the procedure described by Escudero Sanz et al.[5] and consisted of an aqueous phase (60.8 wt % with respect to the total microemulsion amount) composed of AM (9.8–14.1 wt % with respect to the total amount of the aqueous phase), ADQUAT (39.4–56.3 wt % with respect to the total amount of the aqueous phase), Na_2EDTA (0.1 wt % with respect to the total amount of the aqueous phase) and water (29.5–50.7 wt % with respect to the total amount of the aqueous phase);

an emulsifier (7.3–13 wt % with respect to the total microemulsion amount) at a specific HLB; and Isopar M (26.2–31.9 wt % with respect to the total microemulsion amount) as the oil phase. TCC ranged from 30 to 42 wt % with respect to the total microemulsion amount. The aqueous phase pH was adjusted to 4.0 with 10 wt % aqueous nitric acid. To study the influence of the chain-transfer and cross-linking agents, isopropyl alcohol and MBA were added to the aqueous phase in specific concentrations (based on the total comonomer amount) mentioned in the Results and Discussion section. The mass balance was kept by the removal of the same amount of water.

The HLB of the emulsifier mixture was calculated with the following equation:

$$HLB = HLB_{S1}W_{S1} + HLB_{S2}W_{S2} \qquad (1)$$

where W is the surfactant weight fraction based on the total amount of the emulsifier and subscripts S1 and S2 refer to surfactants 1 and 2, respectively.

Reactions were carried out in a 0.5-L, five-necked, jacketed reactor fitted with a thermometer and a mechanical stirrer (RZR 2021, Heidolph, Kelheim, Germany; 300 rpm). Semicontinuous free-radical copolymerizations were carried out by the continuous addition of an aqueous SMB solution (adjusted to pH 3.5 with 10 wt % aqueous nitric acid) to the comonomer inverse microemulsions, which were previously thermostated at 25°C and purged with nitrogen for 15 min with a constant flow (3 L/min at 25°C and 1 bar) for the removal of dissolved oxygen. A nitrogen purge was maintained during the entire reaction time. Copolymerizations were started by the addition of a 0.25 g/L SMB aqueous solution at a constant flow (77.8 mL/h/kg of total comonomers) with a Methrom Dosino 700 dosing unit (Methrom España, Toledo, Spain). The initial temperature was always 25°C. Because the copolymerizations were strongly exothermic, the temperature increased as soon the initiator was added. The reactions were considered to be finished when the temperature came back to its initial value (ca. 20–30 min after the initiator addition was started). The reactions were fast, and the peak temperature was reached within 10–15 min. The total volume of the initiator aqueous solution added was lower than 2% of the total amount of the inverse microemulsion measured before copolymerization. Therefore, the TCC difference in the latices before and after copolymerization was also lower than 2%. The values reported in this study are the final ones.

The inverse cationic copolymer microemulsions were stable: no phase separation was observed after centrifugation at 5000 rpm for 30 min. Their appearance varied from transparent and translucent at the lower copolymer concentrations to milky at the higher ones. A discussion of the mechanism of radical initiation by SMB is beyond the scope of this work, but it might be explained by the mechanism proposed by Mukherjee et al.[21] for monomers containing a methyl group attached to the vinyl group, a mechanism extended to the monomers used herein by Escudero et al.[5]

Conversion determination

The AM conversion was measured by high-performance liquid chromatography according to the method described by Vers.[22] A 2 g/L copolymer microemulsion solution in water was inverted by 15 min of stirring to allow both the copolymer and unreacted monomers to dissolve. Then, the solution was vigorously stirred with a high-speed mixer at 8000 rpm for 1 min. Then, the solution was allowed to stand for 10 min to allow occluded bubbles to rise. The final solution was prepared by the dilution of 5 g of this solution to 100 mL with demineralized water. One hundred microliters of the sample was filtered through a 25-μm pore filter and injected into a Waters E600 high-performance liquid chromatograph fitted with two columns in series (Novapack C18 followed by a Fast Fruit Juice column, both from Waters, placed inside an oven at 55°C) and a Waters (Saint-Quentin, France) UV E600 detector set at 200.4 nm. The flow rate of the mobile phase (ultrapure water adjusted to pH 3.5 with H_2SO_4) was 0.5 mL/min. The running time was 30 min.

In this article, we report the global conversion as the AM conversion. Because the reactivity ratios[23] for the AM and cationic monomer were 0.61 and 0.47, respectively, the comonomer blend became richer in AM as the conversion increased. Therefore, the global conversion values reported here are slightly lower than the real ones. In all cases, the AM conversion was greater than 97%.

Molar mass and radius of gyration (R_g) determinations

M_w and R_g values were determined by laser light scattering (LLS) with an AMTEC model 9863 photogoniodiffusometer (Nice, France) equipped with an Innova model I90C-4 argon laser (90C series; λ = 514 nm, 100 mW, Laser Coherent Auburn Group, Auburn, CA) and a sample cell thermostated to ±0.5°C by circulating water. Benzene was used as the reference. The refractive-index increment of the cationic copolymer dissolved in a 0.05M NaCl aqueous solution was determined with a Brice-Phoenix model BP-2000V differential refractometer (Phoenix Precision Instrument Co., Phoenix, AZ) equipped with a helium–neon laser. The measurement

procedure was as follows: the copolymer was precipitated from the microemulsion in acetonitrile (ACN) under vigorous stirring; solids were filtered off and washed with ACN. The washed solids were redispersed in ACN under stirring for 10 min. Then, the suspension was filtered, and the precipitate was subsequently subjected to Soxhlet extraction for 3 h with acetone as the solvent. Afterwards, the solids were removed and oven-dried at 60°C. The water content was determined by thermogravimetry (first with scanning from 30 to 150°C at 10°C/min and then at a constant temperature of 150°C for 10 min with a nitrogen flow rate of 200 mL/min) just before the samples were prepared for LLS measurements. With knowledge of the copolymer water content, a 0.5 g/L (with respect to the water-free copolymer) stock copolymer solution in 0.05M NaCl was prepared. After complete dissolution (2 days), the stock solution was diluted with an aqueous solution of 0.05M NaCl to obtain four samples with concentrations ranging from 0.10 to 0.5 mg/L. These solutions were centrifuged at 10,500 rpm for 4 h to remove dust and then transferred to precleaned glass vials. After the vials were sealed, M_w and R_g were determined by extrapolation of the LLS data at 25°C and 514 nm with the classical Zimm plot procedure and the I-ZPW static light scattering software. For each copolymer sample, three independent measurements were carried out, and the reported M_w value was the average value.

Viscosity measurements

The copolymer absolute viscosities (BVs) were obtained by the measurement of the viscosity of a 0.5 g/L aqueous solution of the copolymer in demineralized water (type I). Copolymer aqueous solutions were prepared by the inversion of copolymer inverse microemulsions in demineralized water (type I) for 30 min. Measurements were carried out with a Brookfield (Brockfield Viscometers Ltd., Harlow, UK) LVDVII+ with a ULA spindle at 3 rpm and 25°C. Standard viscosities (SVs) were measured in the same way and under the same conditions used for BV, except that a concentrated NaCl solution was added to the inverted copolymer microemulsions 30 min after inversion so that the final NaCl concentration was 0.005M. Then, stirring was continued for 10 min, and SV was subsequently measured. The ionic strength increase provided by NaCl produced a dramatic decrease in the viscosity.

Structuring degree determination

The BV/SV ratio is an index of the structuring degree of a copolymer,[24] and in this article, it is called the VSI. The higher the VSI is, the higher the copolymer structuring degree is. In this article, the term *structuring* encompasses branching and crosslinking.

RESULTS AND DISCUSSION

As previously stated, comonomer inverse microemulsion formulations were selected from the microemulsion stability domain obtained from pseudoternary phase diagrams according to the procedure described by Escudero Sanz et al.,[5] but we took into account that in addition to stability, the formulations of our interest must meet the following criteria:

1. A TCC as high as possible with 30 wt % as the minimum. Thus, the studied range was 30–42 wt %. Preliminary experiments showed that above 42 wt %, latices are too viscous (gel-like), and this would prevent their handling for industrial applications.
2. An EC as low as possible. The studied range was 7.3–13 wt %. Screening experiments showed that below 7.0 wt %, phase separation occurs during or after copolymerization.
3. An HLB as high as possible to facilitate the self-inversion of final latices when they are diluted in water; this is a necessary step for industrial applications. The studied range was 9–9.9. Earlier experiments showed that phase separation occurs during copolymerization above 9.9. Below an HLB of 9, self-inversion is not produced, and an additional inverting surfactant (HLB > 13) must be added to water during the inversion procedure.
4. A specific flow rate of initiator addition that is not too low as phase separation at high TCC occurs at the beginning of copolymerization[9] (because the heat generated during copolymerization is insufficient to enlarge the inverse microemulsion domain in the phase diagram to compensate for the shortening of the domain on account of the consumption of AM and ADQUAT comonomers, which behave as cosurfactants[10–12,17]) and not so high that the reaction could become out of control because of its highly exothermic character or that the copolymer molar masses could become too low, this being undesirable for certain industrial applications. Preliminary experiments showed that for purposes herein pursued, a suitable specific flow rate of initiator addition was 77.8 mL/h/kg of the total comonomers.

Accordingly, a set of reactions was carried out under experimental conditions listed in Table I, in which the properties of the obtained cationic copolymer are also reported. These reactions enable the analysis of

TABLE I
Experimental Conditions and Results

Run	TCC (wt %)	EC (wt %)	HLB	IPC (wt %)	CAC (ppm)	BV (cP)	SV (cP)	VSI	$M_w \times 10^{-6}$ (g/mol)	R_g (nm)
1	30.0	7.3	9.5	0	0	110.0	29.4	3.7	4.83	163
2	33.5	7.3	9.5	0	0	158.2	33.0	4.8	5.84	171
3	37.5	7.3	9.5	0	0	181.8	36.2	5.0	6.24	195
4	42.0	7.3	9.5	0	0	177.4	30.4	5.8	9.33	255
5	42.0	10	9.5	0	0	149.6	33.6	4.5	9.89	188
6	42.0	13	9.5	0	0	156.0	34.2	4.5	4.13	137
7	42.0	7.3	9	0	0	138	27.8	5.0	6.77	187
8	42.0	7.3	9.9	0	0	200.2	31.1	6.4	9.54	197
4-bis[a]	42.0	7.3	9.5	0	0	161.4	33.2	4.9	8.89	222
9	42.0	7.3	9.5	0.5	0	142.0	32.4	4.4	6.34	171
10	42.0	7.3	9.5	0.75	0	134.2	25.8	5.2	7.39	196
11	42.0	7.3	9.5	1.0	0	128.6	23.2	5.5	5.89	186
12	42.0	7.3	9.5	1.5	0	128.0	23.6	5.4	2.21	108
13	34.5	7.3	9.5	0	0	164.4	32.4	5.1	4.85	156
14	34.5	7.3	9.5	0.5	0	137.2	31.8	4.8	4.37	162
15	34.5	7.3	9.5	0.75	0	133.2	24.6	5.4	4.67	161
16	34.5	7.3	9.5	1.0	0	126.8	24.0	5.3	7.32	181
17	34.5	7.3	9.5	1.5	0	124.6	17.8[b]	7.0	7.62	211
18	42.0	7.3	9.5	0	10.0	>200[b]	16[b]	>12.5	—	—
19	42.0	7.3	9.5	0	30.0	182.4	7.2[b]	25.3	—	—
20	42.0	7.3	9.5	0	62.2	157.0	3.0[b]	52.3	—	—
21	42.0	7.3	9.5	0	122.8	169.0	2.4[b]	70.4	—	—

TCC and EC are based on the total inverse microemulsion amount; IPC and CAC are based on the total comonomer amount (the crosslinking agent was MBA). The initial temperature was 25°C, and the specific flow rate of initiator addition was 77.8 mL/h/kg of total comonomers.

[a] Run 4-bis was run 4 repeated. It was necessary for comparison because the ADQUAT monomer used from run 9 to run 16 came from another manufacturing batch, so its reactivity was different. This explains the difference in the results obtained for the two runs.

[b] These values are outside the recommended viscometer measurement range (20–200 cP). The viscosity accuracy was lower than 1 for the rest of the samples (±2%).

the influence of TCC, EC, HLB, IPC, and CAC on the following cationic copolymer properties: M_w, BV, and VSI.

All reactions were characterized by high copolymerization rates and were highly exothermic. Although they were performed in a thermostated bath, the temperature increased during copolymerization from 25°C at the onset up to 49 and 34°C with TCCs of 42 and 30 wt %, respectively. Then, the copolymerizations proceeded under nonisothermal conditions. Before copolymerization, lower TCC formulations were true inverse microemulsions as visually observed by the transparency of the dispersions as well as their stability after centrifugation at 5000 rpm for 30 min. No phase separation was observed. However, formulations at higher TCCs were not inverse microemulsions before copolymerization but were inverse emulsions, and they underwent phase separation in less than 1 h. Despite this, a stable, milky microemulsion was obtained after copolymerization. Hernández-Barajas and Hunkeler[9] explained such a phenomenon as characteristic of a heterophase water-in-oil polymerization process, by means of which, starting from an inverse emulsion of monomers, an inverse microemulsion is obtained

after polymerization under some experimental conditions.

Regardless of the formulation state before copolymerization, its evolution during copolymerization is similar to that of other AM-based inverse microemulsion copolymerizations reported in the literature: the reaction mass turns into a viscous and turbid macroemulsion in the early stages of copolymerization and later returns to a transparent (at low TCC) or milky (at high TCC) low-viscosity system with an inverse microemulsion structure. Candau et al.[3] described this transition as due to microstructural changes from a bicontinuous microstructure to an inverse globular one. The transformation of the comonomer microemulsion in a viscous, turbid macroemulsion in the early stages of copolymerization may be related to the comonomer consumption. In fact, if we take into account that both AM and ADQUAT behave as cosurfactants,[10,12,17] the depletion of the comonomer concentration results in a reduced microemulsion domain; therefore, the system evolves into a macroemulsion that will turn back to an inverse clear microemulsion only if another factor counteracts the loss of comonomer cosurfactant action. According to Hernández-Barajas
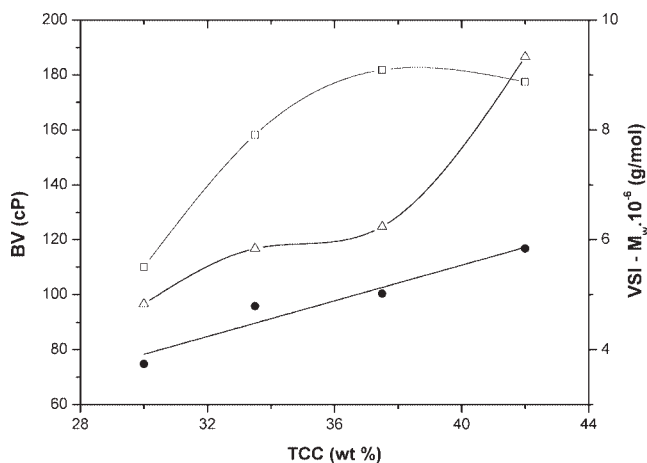
Figure 1 Variation of (□) BV, (●) VSI, and (△) M_w as a function of TCC (HLB = 9.5, EC = 7.3 wt %).

and Hunkeler,[9] this factor is the temperature rise produced during polymerization, which enlarges the inverse microemulsion domain in the phase diagram. However, this explanation cannot justify why the system remains a stable microemulsion just after copolymerization has been completed and the temperature returns to room temperature. At this point, with an almost zero comonomer concentration, the inverse microemulsion domain in the phase diagram would be shortened again, and this would lead to phase separation. As this does not happen, we must conclude that the cationic ADQUAT/AM copolymer has a strong cosurfactant character as well.

Influence of TCC

The influence of TCC on the copolymer properties at an HLB of 9.5 and with a 7.3 wt % EC can be analyzed with runs 1–4 in Table I. The results are plotted in Figure 1.

M_w increases greatly with TCC. The same results have been obtained for the AM polymerization in an inverse microemulsion at AM concentrations between 25 and 27.5 wt %[13]; for the 40/60 wt % ADQUAT/AM copolymerization in an inverse microemulsion at TCCs between 32 and 34.5 wt %,[7] and for the 22/70/8 mol % AM/sodium acrylate/ ADQUAT terpolymerization in an inverse emulsion at TCCs between 10 and 40 wt %.[25] The increase in M_w with increasing TCC cannot be due to changes in the comonomer/initiator ratio because the specific flow rate of initiator addition was kept constant in all the experiments. The M_w increase should be associated with the collapsed nature of the growing copolymer chains inside the inverse microemulsion droplets. The sizes of the latex particles were less than 150 nm. For a similar system, 40/60 wt % ADQUAT/AM copolymerization in an inverse microemulsion at TCCs up to 34.5 wt %[8] with the

same emulsifier, the average size of the latex particles was 88 nm. Hernández-Barajas and Hunkeler[9] obtained stable latices of polyacrylamide at a moderate monomer concentration (20 wt %) by a hybrid inverse emulsion/inverse microemulsion polymerization with a particle size lower than 150 nm. The copolymer R_g values range from 163 to 255 nm (Table I, runs 1–4). The particle sizes are smaller than R_g, and this indicates that the copolymer chains grow in a highly collapsed state, as stated previously. Under these conditions, two mechanisms of branching and crosslinking can act:

1. Radical transfer to copolymer chains results in branching and/or crosslinking.
2. One of the components of the emulsifier, Crill 43 (sorbitan sesquioleate), is an interfacially radically active emulsifier with several labile (extractable hydrogens) hydroxyl functionalities on the hydrophilic head and a double bond on the hydrophobic moiety. Consequently, Crill 43 can act as a terminating agent for the growing macromolecules through the extractable hydrogens on the hydrophilic head, producing an emulsifier radical. This transfer to the surfactant reaction lowers M_w. The emulsifier radical polymerizes, generating a macroradical with a terminal double bond.[26] These macroradicals contain terminal emulsifier groups with multiple reactive functional groups (extractable hydrogens of the hydroxyl groups and a double bond on the hydrophobic moiety), so they can participate in a long-chain-branching reaction cascade, which leads to high-molar-mass macromolecules.[26]

Both mechanisms result in an increase in the molar mass by increasing the branching and crosslinking of macromolecular chains. Therefore, if we take into account that, at a constant EC, the collapsed state of copolymer chains increases with TCC, M_w must also increase with TCC as experimentally observed. From 30 to 37.5 wt %, M_w varies almost linearly with TCC (correlation coefficient = 0.92). However, above this value, M_w increases exponentially with TCC, and this may be easily explained by the very high comonomer concentration resulting in a dramatic increase in the collapsing degree of growing chains, which favors the synthesis of highly branched and crosslinked copolymers, that is, highly structured copolymers. Consequently, the VSI parameter, which measures the copolymer structuring degree, must also increase with TCC, as can be observed in Figure 1.

The variation of BV agrees with this discussion. BV increases by 65.3% when TCC increases from 30 to 37.5 wt % because of the M_w increase. However,
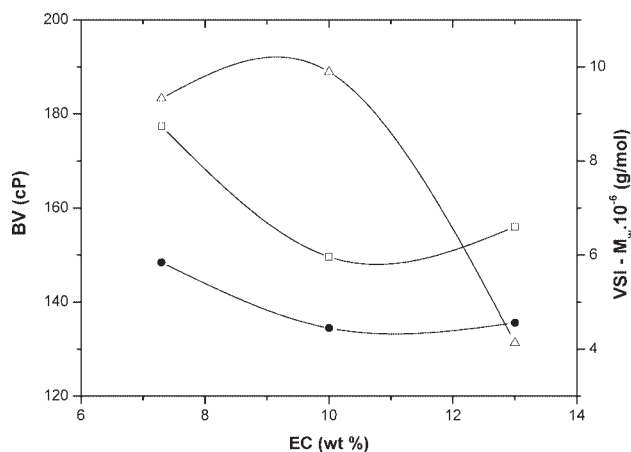
Figure 2 Variation of (□) BV, (●) VSI, and (△) M_w as a function of EC (HLB = 9.5, TCC = 42 wt %).

above 37.5 wt %, BV remains practically constant up to 42 wt %, and this can be explained by the rise of the structuring degree of copolymer chains, which results in a dramatic decrease in their swelling capacity in an aqueous solution. Consequently, macromolecular chains are less expanded, and the viscosity cannot further increase.

Influence of EC

The influence of EC on the copolymer properties with a 42.0 wt % TCC and an HLB of 9.5 can be analyzed from the results of runs 4–6 in Table I. The results are plotted in Figure 2.

As can be seen, M_w remains practically constant when EC increases from 7.3 to 10 wt %. Above a 10 wt % EC, M_w decreases sharply (when EC increases by 30%, M_w drops by 58.2%). The same behavior was reported by Río et al.[8] for 40/60 (by weight) ADQUAT/AM copolymerization in an inverse microemulsion at TCCs ranging from 32 to 34.5 wt % with the same emulsifier. Candau and Buchert[17] also reported a decrease in M_w with increasing EC for the polymerization of [2-(methacryloyloxy)ethyl] trimethylammonium chloride in an inverse microemulsion stabilized by Arlacel 83 (a sorbitan sesquioleate like Crill 43 herein used but marketed by ICI) and Tween 80 (a sorbitan monooleate with 20 ethylene oxide residues; HLB = 15). Vašková et al.[27] and Candau et al.[28] also found a decrease in M_w with increasing EC for the AM homopolymerization in an inverse microemulsion stabilized by bis(2-ethylhexyl)sulfosuccinate with both water- and oil-soluble initiators. An explanation for this behavior can be easily deduced if we consider that the number of micelles increases with EC. Consequently, there are more places for the initiator to dissolve and then to produce more radicals, which lead to lower M_w values than those obtained at lower ECs.

It is apparent from Figure 2 that EC has a strong influence on M_w but a slight one on BV. From a 13 wt % EC to a 7.3 wt % EC, M_w increases by 125.9%, whereas BV increases by only 13.7%. This may be due to the fact that macromolecules synthesized at the lower EC are in a much more collapsed state than those obtained at the higher EC, as can be deduced from differences in R_g, which increases by 86% from a 13 wt % EC to a 7.3 wt % EC. Macromolecular chains are shorter (lower M_w) for the reasons previously discussed, and because TCC is constant, the number of comonomer molecules per particle decreases as EC increases. Then, the probability of transfer to both the radically active surfactant and copolymer chains is lower, leading to a lower copolymer structuring degree. A less structured cationic copolymer is obtained at higher ECs (Fig. 2). A less structured copolymer has a higher swelling capacity in an aqueous solution. Then, the smooth viscosity decline observed as M_w decreases is a result of two counteracting factors: the decrease in M_w, which favors the viscosity decline, and the swelling capacity increment, which favors the viscosity rise.

Influence of HLB

The influence of HLB on copolymer properties at a 42.0 wt % TCC and a 7.3 wt % EC can be analyzed with runs 4, 7, and 8 in Table I. The results are plotted in Figure 3.

A dramatic M_w increase is produced when HLB is increased from 9 to 9.5. Above this value, M_w remains constant. These results are completely different from those reported by us[8] for a 40/60 (by weight) ADQUAT/AM copolymerization in an inverse microemulsion for an HLB range of 7.75–8.26 at a 32.2 wt % TCC and an 11 wt % EC with the same emulsifier, for which the opposite variation was observed. Apparently, these results are
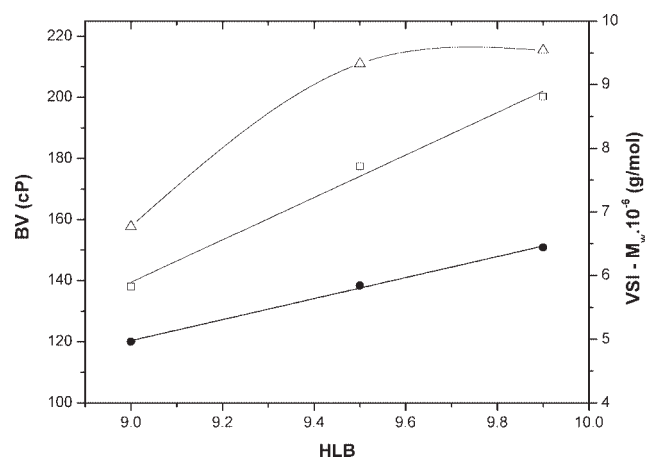

Figure 3 Variation of (□) BV, (●) VSI, and (△) M_w as a function of HLB (EC = 7.3 wt %, TCC = 42 wt %).

controversial but can be explained if we take into account that sorbitan sesquioleate (Crill 43) is a radically active emulsifier and that the HLB ranges in which the two copolymers were obtained were different (lower HLB and less hydrophilicity for 40/60 ADQUAT/AM copolymers and higher HLB and more hydrophilicity for 80/20 ADQUAT/AM copolymers) and, consequently, the interface compositions were different as well. As stated previously, sorbitan sesquioleate may participate in the copolymerization, favoring a cascade of long-chain-branching reactions leading to high-molar-mass structured macromolecules. Then, for 40/60 ADQUAT/AM copolymers obtained by inverse microemulsion copolymerization at low HLB numbers, the increase in M_w as HLB decreases is a result of the increasing concentration of sorbitan sesquioleate in the emulsifier (55 wt % at HLB = 8) as HLB decreases. For the 80/20 ADQUAT/AM copolymers herein obtained by inverse microemulsion copolymerization at high HLB numbers, the sorbitan sesquioleate concentration in the emulsifier is much lower (39% at HLB = 9.5) and decreases with increasing HLB values; therefore, a decrease in M_w with HLB is to be expected according to the aforementioned explanation. However, it is well known that, because of their cosurfactant nature, comonomers are partially located at the interface.[10,29] Then, as both comonomers are highly hydrophilic, their concentrations at the interface will be higher at high HLB numbers than at low ones. At the high HLB numbers used in the system reported here, this effect counteracts the depletion of the sorbitan sesquioleate concentration with HLB, favoring the probability of a reaction between growing macroradicals and the interfacially radically active emulsifier; that is, favoring the cascade of long-chain-branching reactions, which leads to high-molar-mass macromolecules. Thus, for ADQUAT/AM copolymers obtained at HLB > 9, M_w increases as HLB increases. According to this explanation, copolymer structuring must rise with HLB as it is experimentally shown that VSI increases with HLB.

M_w, BV, and VSI increase with HLB (Fig. 3). Even though VSI increases, BV also increases, and this indicates that structuring is due to branching and not to crosslinking. Crosslinking decreases the copolymer swelling capacity and then its BV in an aqueous solution; meanwhile, branching does not necessarily have the same effect.

Relationship between the molar mass and structuring degree

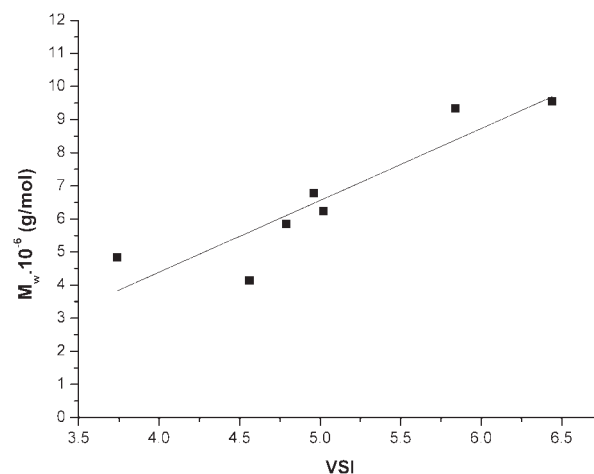The variation of M_w with VSI for runs 1–8 is plotted in Figure 4. Data from run 5 have not been included because they deviate strongly from the general pattern observed in Figure 4. In any case, it can be seen how seven dots out of eight result in a linear relationship between M_w and VSI. The higher VSI is, the higher M_w is. The correlation coefficient is 0.83, low for justifying a perfectly linear relationship between both parameters but high enough for accepting that it exists, mainly if we take into account that all runs were carried out under very different experimental conditions. This result is very interesting because it suggests that by the use of inverse microemulsion copolymerization as a synthetic technique, it is possible to obtain very high molar mass copolymers by increasing their structuring degree, that is, by branching and/or crosslinking.

Figure 4 Variation of M_w as a function of VSI for run 1.

Linear copolymers of very high molar masses cannot be obtained with inverse microemulsion copolymerization, at least with high comonomer concentrations. Results obtained by other researchers[26] for AM suggest that this also occurs if an inverse emulsion polymerization technique is used. This fact must be carefully considered when an AM-based copolymer is designed to be used in some application in which linear polymers with high molar masses are traditionally demanded, such as sludge dewatering. Then, a polymer with a higher M_w than others can lead to poorer dewatering results, which may be considered anomalous when really the anomaly can be attributed to the fact that the former is much more structured and less linear than the latter.

Another important question is whether the structuring is basically due to branching or crosslinking. From runs 1 to 8, VSI ranges from 3.7 to 6.5. From runs 4-bis to 17, in which a chain-transfer agent was added (see the next section), VSI ranges from 4.4 to 7.0. However, from runs 18 to 21, in which a well-known crosslinking agent (MBA) was added (see the section following the next one), VSI ranges from 12.5 to 70.5; these values are dramatically higher than those obtained from runs 1–17, the lower figure
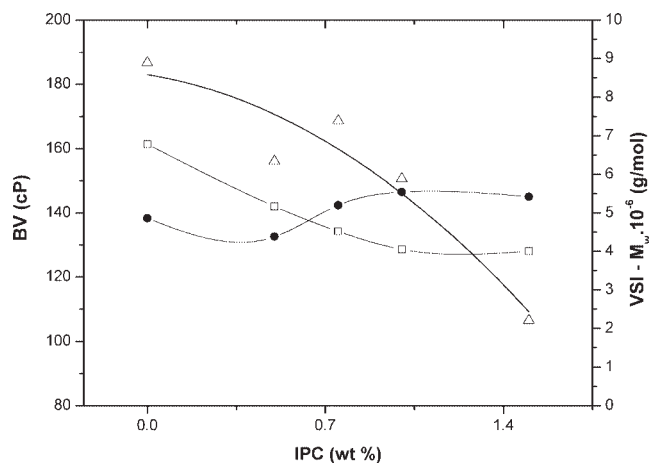
Figure 5 Variation of (□) BV, (●) VSI, and (△) M_w as a function of IPC (based on TCC; TCC = 42 wt %, HLB = 9.5, EC = 7.3 wt %).

(12.5) being almost double the maximum (7.0) reached in those runs. Consequently, it may be concluded that, in the absence of a crosslinking agent, the structuring of AM-based cationic copolymers obtained by inverse microemulsion copolymerization is mainly due to branching; meanwhile, in the presence of a crosslinking agent, it is basically due to crosslinking.

For some applications, synthetic conditions for controlling the copolymer structuring level may be necessary. Therefore, in the following sections, the influence of two structural modifiers, a chain-transfer agent (isopropyl alcohol) and a crosslinking agent (MBA), on AM-based cationic copolymer properties is reported.

Influence of IPC

The influence of IPC (based on the total comonomer content) on copolymer properties at a 7.3 wt % EC and with an HLB of 9.5 can be analyzed from runs 4-bis and 9–12 for a 42.0 wt % TCC and from runs 13–17 for 34.5 wt % in Table I. The results are plotted in Figures 5 and 6, respectively.

The BV variation with IPC follows the expected pattern for the two TCC concentrations studied (34.5 and 42%). BV decreases dramatically with IPC, indicating at first that molar masses are also decreasing. However, VSI and M_w behave differently for the two TCCs. At the higher TCC (42 wt %), VSI decreases slightly up to a 0.5 wt % IPC and then increases slightly with increasing IPC. At the lower TCC (34.5%), there is also a small decrease with IPC increasing up to 0.5%; then, VSI shows an increase with IPC above 0.5 wt %. This is not an expected result because VSI should decrease with IPC according to the discussion in the previous sections. This means that, above 0.5 wt %, isopropyl alcohol indu-

ces structuring in the copolymer mainly by branching according to the VSI values. Nevertheless, the VSI values indicate that the kind of structuring depends on the TCC. At the lower TCC value, the dramatic rise in M_w above 0.5 wt % is accompained by an increase in VSI but not in BV, which decreases. This means that M_w is probably growing by long-chain branching to such an extent that macromolecular swelling in an aqueous solution is reduced and hence BV decreases despite M_w increasing. On the contrary, at the higher comonomer concentration (42 wt %), both M_w and BV decrease continuously with IPC and VSI increases only slightly above a 0.5 wt % IPC. This means that copolymer chains are being structured by the introduction of short-chain branching, probably because, on account of the high comonomer concentration, once a branch starts to grow, the probability of transfer to the monomer is higher at this concentration than at the lower one; therefore, shorter branched chains are formed at high comonomer concentrations rather than at low comonomer concentrations.

Alcohols are often used as cosurfactants in microemulsion polymerization,[30] but because they can work as chain-transfer agents, they reduce the M_w. This explains the decrease in the molar mass as IPC is increased (Fig. 5) and the small decrease in M_w at low IPC values (Fig. 6). However, increasing IPC can induce some sorbitan sesquioleate, which is soluble in isopropyl alcohol, to be solubilized in the water phase, increasing the possibility for a sorbitol reaction with macroradicals, which results in copolymers with a double bond that can later react to form structured polymers of a high molar mass, such as that observed at the lower TCC studied (Fig. 6). However, when the high TCC concentration is used, because of the larger amount of the monomers present, the amount of solubilized sorbitol will be much
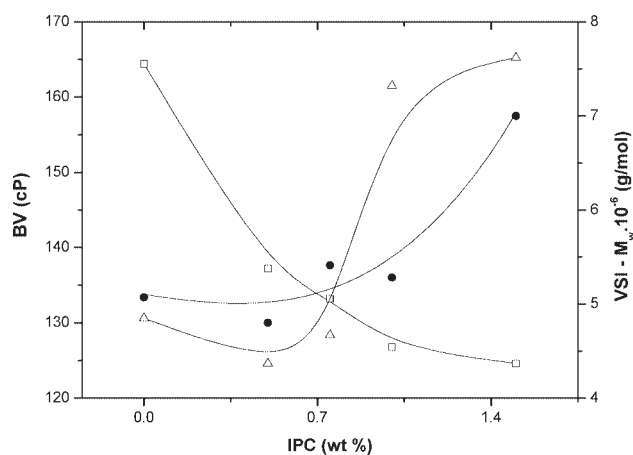

Figure 6 Variation of (□) BV, (●) VSI, and (△) M_w as a function of IPC (based on TCC; TCC = 34.5 wt %, HLB = 9.5, EC = 7.3 wt %).
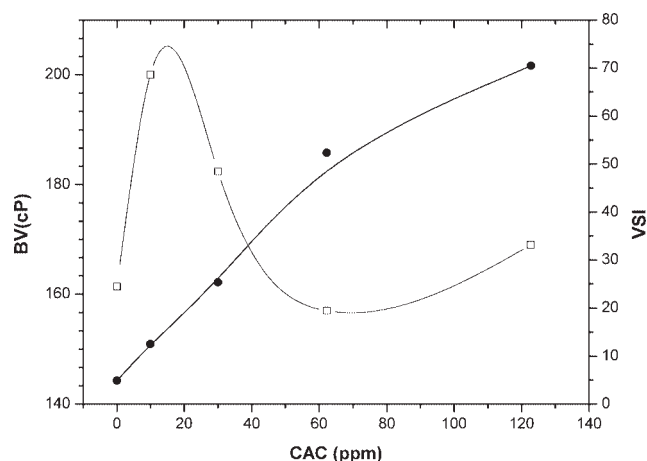
Figure 7 Variation of (□) BV and (●) VSI as a function of CAC (based on TCC; HLB = 9.5, EC = 7.3 wt %, TCC = 42 wt %).

less, and although some increase in the structuring degree can be observed, the net effect of the IPC will be to act as a chain-transfer agent, reducing M_w (Fig. 5).

Influence of CAC

The influence of CAC (based on the total comonomer content) on the copolymer properties at a 7.3 wt % EC and with an HLB of 9.5 can be analyzed from runs 4-bis and 18–21 for a 42.0 wt % TCC. The results are plotted in Figure 7.

As expected, VSI increases with CAC, and in the range studied, there is practically a linear relationship (correlation coefficient = 0.95) between them. The BV behavior is more complex. BV increases sharply with CAC up to 10 ppm. However, above 10 ppm, BV decreases dramatically up to 60 ppm, and then it remains practically constant because a 100% increase in CAC only modifies BV by 7.6%. It is apparent that below 10 ppm MBA causes an increase in M_w by crosslinking and branching, resulting in a higher BV because its structuring degree is not so high (VSI = 12.5) as to prevent swelling of macromolecular chains in an aqueous solution. However, above 10 ppm, the number of crosslinks introduced by MBA increases in such a way that the swelling capacity of the copolymer chains in an aqueous solution is seriously affected, and this leads to a decline in BV.

Although not studied here, it can easily be deduced from the results reported in the last two sections that by the addition of isopropyl alcohol and MBA to the comonomer inverse microemulsion, it is possible to obtain, after copolymerization, structured AM-based cationic copolymers with a wide spectrum of molar masses and structuring degrees, which may be very useful for designing tailor-made products for specific applications in which specific combinations of M_w and VSI values are needed.

CONCLUSIONS

The semicontinuous inverse microemulsion copolymerization of 80/20 wt % ADQUAT/AM in an isoparaffin solvent, Isopar M, at high TCCs (30–42 wt %) has been studied with a mixture of nonionic surfactants (Crill 43 and Softanol 90) as the emulsifier and SMB as the initiator. The influence of several copolymerization parameters on the copolymer properties has been analyzed, and this has led to the following conclusions.

First, TCC has a great influence on M_w. M_w increases strongly with TCC, and this is associated with the fact that latex particle sizes are smaller than copolymer R_g values, and consequently, copolymer chains grow in a highly collapsed state. This results in branching and crosslinking by two mechanisms: transfer to copolymer chains and transfer to one of the components of the emulsifier, Crill 43 (sorbitan sesquioleate), an interfacially radically active emulsifier with several labile (extractable hydrogens) hydroxyl functionalities on the hydrophilic head and a double bond on the hydrophobic moiety, which can participate in a long-chain-branching reaction cascade. Both mechanisms favor the synthesis of highly structured copolymers, as confirmed by VSI, which also increases with TCC. BV increases linearly with TCC from 30 to 37.5 wt %. Above this concentration, BV remains practically constant up to 42 wt %, and this can be explained by the structuring degree rise of the copolymer chains, which results in a dramatic decrease in their swelling capacity in an aqueous solution.

Second, EC has no influence on M_w from 7.3 to 10 wt %. Above 10 wt %, M_w decreases sharply with EC because the size of the latex particles decreases as EC increases. Consequently, the higher the EC is, the higher the surface area (area/volume ratio) is of the micelles; therefore, there is a larger area available for initiator diffusion from the oil phase to water pools inside the micelles, which, in turn, results in a larger number of effective radicals generated, leading to lower M_w values in comparison with the ones obtained at lower ECs. EC has a slight influence on BV. BV increases very slightly with M_w. From a 13 wt % EC to a 7.3 wt % EC, M_w increases by 125.9%, whereas BV increases by only 13.7%. This behavior may be related to two counteracting factors: on the one hand, the decrease in M_w for reasons given previously, which favors the viscosity decline, and on the other hand, the swelling capacity increment, which favors the increase in the viscosity.

The swelling capacity increment is a result of the low number of comonomer molecules per particle as EC increases, leading to a decrease in the probability of transfer to the radically active surfactant and other growing copolymer chains and, consequently, to a decrease in the structuring degree as shown by the lower VSI values obtained at higher ECs. A less structured copolymer has a higher swelling capacity.

Third, M_w increases dramatically from an HLB of 9 to an HLB of 9.5. Above 9.5, it remains constant. This result could be due to the cosurfactant nature of the comonomers, which makes them partially located at the interface. As both comonomers are highly hydrophilic, their concentrations at the interface will be higher at high HLB numbers than at low ones, favoring the probability of a reaction between the growing macroradicals and the interfacially radically active emulsifier sorbitan sesquioleate; that is, they favor the cascade of long-chain-branching reactions, which lead to high-molar-mass and more structured (VSI increases with HLB as well) macromolecules. BV increases continuously with M_w, even though VSI reaches its peak value at an HLB of 9.9, probably because at these high HLB numbers, copolymer structuring can be mainly attributed to branching and not to crosslinking. Crosslinking decreases the copolymer swelling capacity and then its BV in an aqueous solution; meanwhile, branching does not necessarily have the same effect.

Fourth, a linear relationship between the molar mass and structuring degree has been found for copolymerizations carried out in the absence of both chain-transfer and crosslinking agents. This result suggests that by the use of inverse microemulsion copolymerization as the synthesis technique, it is possible to obtain very high molar mass copolymers by increases in their structuring degree, that is, by branching and/or crosslinking. Linear copolymers of a very high molar mass cannot be obtained by inverse microemulsion copolymerization, at least for high comonomer concentrations. Results obtained by other researchers[26] for AM suggest that this also occurs if an inverse emulsion polymerization technique is used.

Fifth, VSI values suggest that the structuring of AM-based cationic copolymers obtained by inverse microemulsion copolymerization is mainly due to branching in the absence of a crosslinking agent but is due to crosslinking in the presence of a crosslinking agent such as MBA.

Sixth, as expected, below 0.5 wt % (with respect to the total comonomer amount), the addition of isopropyl alcohol as a chain-transfer agent results in shorter and less structured molecular chains. However, above 0.5 wt %, isopropyl alcohol favors the formation of branched copolymers with a higher VSI at lower comonomer concentrations than at higher ones. The results are assumed to be related to the ability of isopropyl alcohol to solubilize some sorbitan sesquioleate in the aqueous phase.

Seventh, the addition of MBA as a crosslinking agent dramatically increases the copolymer structuring degree as measured by VSI. In the studied range, there is a linear relationship (correlation coefficient = 0.95) between VSI and CAC. BV values indicate that, below 10 ppm MBA, the crosslinking degree is not so high as to prevent the swelling of macromolecular chains in an aqueous solution. However, above 10 ppm, the crosslinking degree increases in such a way that the swelling capacity of copolymer chains in an aqueous solution is negatively affected, leading to a decline in BV.

The obtained results indicate that by the proper selection of the reaction variables, it is possible to synthesize stable inverse microemulsions of cationic copolymers based on 80 : 20 (by weight) ADQUAT/AM with a copolymer content as high as 42 wt %. Additionally, reaction variables can be adjusted in such a way that cationic copolymers with a wide spectrum of different properties, such as the molar mass, BV in an aqueous solution, and structuring degree, can be obtained. Then, it is possible to tailor their properties as a function of the desired application.

Taking into account the structural characteristics of the cationic copolymers herein reported, we envisage that they may be useful as flocculants.

References

1. Thomas, W. M.; Wang, D. W. In Encyclopedia of Polymer Science and Engineering; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1986; Vol. 1, p 169.
2. Kulicke, W. M.; Kniewske, R.; Klein, J. Prog Polym Sci 1982, 8, 373.
3. Candau, F.; Anquetil, J. Y. In Micelles, Microemulsions and Monolayers: Science and Technology; Shah, D. O., Ed.; Marcel Dekker: New York, 1998; p 193.
4. Hernández-Barajas, J.; Hunkeler, D. Polymer 1997, 38, 5623.
5. Escudero Sanz, F. J.; Ochoa Gómez, J. R.; Sasia, P. M.; Díaz de Apodaca, E.; Río, P. J Appl Polym Sci 2007, 103, 2826.
6. Ochoa Gómez, J. R.; Escudero Sanz, F. J.; Sasia, P. M.; Santos García, A.; Díaz de Apodaca, E.; Río, P. J Appl Polym Sci 2007, 103, 186.
7. Sasia, P.; Ochoa, G., Jr.; Río, F.; Escudero, F. J.; Díaz de Apodaca, E.; Nieto, J.; Torrecilla, J.; Katime, I. e-Polymers 2006, No. 038.
8. Río, F.; Ochoa, G., Jr.; Sasia, P.; Escudero, F. J.; Díaz de Apodaca, E.; Nieto, J.; Katime, I. e-Polymers 2007, No. 059.
9. Hernández-Barajas, J.; Hunkeler, D. Polymer 1997, 38, 5623.
10. Holtzscherer, C.; Candau, F. Colloids Surf 1988, 29, 411.
11. Candau, F.; Leong, Y. S.; Pouyet, G.; Candau, S. J. J Colloid Interface Sci 1984, 101, 167.
12. Candau, F.; Zekhinini, Z.; Durand, J. P. J Colloid Interface Sci 1986, 114, 398.

13. Rentería, M.; Muñoz, M.; Ochoa, J. R.; Cesteros, L. C.; Katime, I. J Polym Sci Part A: Polym Chem 2005, 43, 2595.
14. Barton, J.; Stillhammerova, M. Angew Makromol Chem 1996, 237, 113.
15. Candau, F.; Zekhinini, Z.; Durand, J. Prog Colloid Polym Sci 1987, 73, 33.
16. Colpart, J. M.; Candau, F. Colloid Polym Sci 1993, 271, 1055.
17. Candau, F.; Buchert, P. Colloids Surf 1990, 48, 107.
18. Buchert, P.; Candau, F. J Colloid Interface Sci 1990, 136, 136.
19. Sáenz de Buruaga, A.; de la Cal, J. C.; Asua, J. M. Polymer 2000, 41, 1269.
20. Neyret, S.; Candau, F.; Selb, J. Acta Polym 1996, 47, 323.
21. Mukherjee, R.; Ghosh, P.; Chadha, S. C.; Palit, S. R. Makromol Chem 1964, 80, 208.
22. Vers, L. M. J Chromatogr Sci 1999, 37, 486.
23. Huang, S.-Y.; Lipp, D. W.; Farinato, R. S. Encyclopedia of Polymer Science and Technology; Wiley: New York, 2002; p 41.
24. Chen, H. L.; Farinato, R.; Hawkins, P. (to Cytec Tech Corp.). World Intellectual Property Organization Pat. WO 97/18167 (1997).
25. Peng, X.; Peng, X. J Appl Polym Sci 2006, 101, 1381.
26. Hunkeler, D.; Hamielec, A. E.; Baade, W. Polymer 1989, 30, 127.
27. Vašková, V.; Juraničová, V.; Bartoň, J. Makromol Chem 1990, 191, 717.
28. Candau, F.; Sing-Leong, Y.; Fitch, R. M. J Polym Sci Polym Chem Ed 1985, 23, 193.
29. Holtzscherer, C.; Durand, J. P.; Candau, F. Colloid Polym Sci 1987, 265, 1067.
30. Antonietti, M. Macromol Chem Phys 1995, 196, 441.