Preparation of highly concentrated inverse emulsions of acrylamide-based anionic copolymers as efficient water rheological modifiers

José González Rivera,[1] José Hernández Barajas,[2] Atilano Gutiérrez Carrillo,[3] Alberto F. Aguilera Alvarado[1]

[1]Chemical Engineering Department, University of Guanajuato, Noria Alta S/N, Guanajuato Gto, 36050, México
[2]Materials Engineering Department, ITESI, Carretera Irapuato–Silao Km. 12.5, Irapuato Gto, 36821, México
[3]Department of Chemistry, UAM-I, 55534, México D.F, 09340, México
Correspondence to: J. H. Barajas (E-mail: johernandezb@itesi.edu.mx)

ABSTRACT: Highly concentrated inverse anionic polymeric emulsions (with a solid content of up to 63 wt %) were prepared using a two-step methodology: (i) First, acrylamide, acrylic acid, and its ammonium salts crosslinked copolymers were obtained by inverse emulsion polymerization, (ii) The water/volatile oil mixture was then separated from the heterogeneous system by vacuum distillation. To maintain sufficient stability during the reaction and distillation processes, a ternary surfactant mixture was used. A surface response methodology was employed to obtain the optimal values of the factors involved in both process and product specifications, and to maximize the high performance of these inverse anionic polymer emulsions. This yielded a product containing up to 63.2 wt % solids capable of achieving Brookfield viscosities as high as 40.3 Pa·s, using an aliquote of these concentrated inverse polymer emulsions (1.8 wt % in deionized water). Rheological characterization (oscillatory and rotational measurements) was carried out to evaluate the behavior of the diluted inverse anionic polymer emulsion in water thickening. The methodology developed can be used to formulate a wide range of viscoelastic (G''/G') water-based products from anionic water soluble polymers. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43502.

INTRODUCTION

Synthetic water soluble polymers are used in a wide range of fields such as enhanced oil recovery,[1] water and wastewater treatments,[2] and controlled drug delivery.[3] Their commercial relevance is constantly growing due to emerging applications in the electrical and medical fields.[4] The successful use of acrylamide-based water-soluble polymers and their copolymers with anionic or cationic monomers is mainly due to their ability to modify the rheology of aqueous dispersion, their ionic behavior in solutions, and their thermal and pH responses.[5,6]

Several approaches to produce water soluble polymers have been used such as solutions, dispersions, inverse emulsions, and bulk-free radical polymerization.[4,5,7] If the appropriate methodology is selected, polymeric materials can be obtained with specific characteristics depending on their final applications. The production of acrylic polymers by inverse emulsion polymerization has several advantages such as easy handling and fast water redispersion for specific uses such as thickening agents.[8,9] In

addition, the inverse emulsion polymerization technique results in high molecular weight polymers that overcome the problems associated with the high viscosity levels reached during bulk, solution or dispersion polymerization approaches.[10] However, if the amount of active material in the final product is not sufficiently high, various drawbacks, such as the expensive transportation costs, may limit their market.[7]

The production of water-soluble polymers obtained by inverse emulsion is usually limited to maximum compositions of 30 wt % for anionic copolymers,[11] and 40 wt % for cationic copolymers.[12,13] A higher concentration of starting monomers in the reaction mixture can lead to clot formation causing a considerable loss of product and possibly hazardous conditions during the process which could in turn lead to undesirable runaway reactions due to its strong exothermic behavior.[11,14]

Concentrated acrylamide-based polymer inverse emulsions (where the solids percentage is >50%) containing an anionic or a cationic polymer, have been achieved with different approaches

such as semi-batch monomer feeding,[15] multiple reaction steps,[13] or the two-step reaction/separation approach.[16–22]

The present work deals with the two-step synthesis approach, where the low-concentrated products are first obtained by free radical polymerization. The polymer content is then increased through distillation. These products have enhanced features compared with their low concentration counterparts due to the lower cost of transportation and lower application dosages. In this case, both the inverse emulsion polymerization reaction and the separation/recovery of the water/organic phase by distillation need a mixture of very efficient stabilizers.

Several papers have described the use of traditional surfactants, such as sorbitan fatty esters, and polymeric dispersants such as low molecular weight stearyl methacrylate-co-methacrylic acid copolymers.[20] This system improves surface stability, reduces the interfacial tension, and water molecules to migrate through the interface film.[17,18,20]

The required number of traditional surfactants and polymer dispersants that provides sufficient stability to the emulsion in the reaction and in the distillation processes is high, generally ranging from 10 to 30 wt % (based on the weight of the oil used in the continuous phase). Although traditional surfactants, including sorbitan monooleate and sorbitan monostearate, are relatively inexpensive, the availability of copolymeric dispersants based on methacrylic acid-co-stearyl methacrylate in the market is limited. Additionally, the percentage of solid achieved in the final inverse emulsion using this combined surfactant system has been reported to be as high as 55 wt %.[18]

Diener et al.[23] describe another process to obtain highly concentrated inverse emulsions. This approach uses only a commercially available and expensive ester-based polymeric surfactant yielding in turn concentrated inverse emulsions with a very high solid content (60 wt %).

The concentration of inverse emulsions is not solely influenced by the use of special surface active agents. Because of its high interfacial energy, macro-emulsions are thermodynamically unstable. This instability promotes the complex diffusional processes involved in the concentration phase. Homogenization is therefore another important factor involved in the process of obtaining concentrated inverse emulsions.[24,25]

A uniform and small particle size distribution provides sufficient stability to produce a lump-free product and also the desirable properties for long-term storage and for a distribution time without phase separation or sedimentation.[25] Besides the factors related to the distillation process, other important aspects are related to the final specification of the products. The factors affecting both the product and the process characteristics such as solvents, solid concentration, bulk viscosity, among others, are seldom the subject of research in the literature.

This work presents the preparation of an anionic polymer material based on acrylamide and acrylic acid and its ammonium salts by a two-step methodology using a special ternary surfactant mixture. The prepared copolymers are crosslinked materials synthesized by an inverse emulsion polymerization procedure

and concentrated by a vacuum distillation. To maintain sufficient stability during the reaction and distillation stages, we explored the use of a ternary surfactant mixture, which includes traditional surfactants (sorbitan monooleate), methacrylic acid-co-alkyl methacrylate esters (synthesized and characterized in this work), and commercial polymeric dispersants, resulting in products with an active concentration material of between 58 and 63 wt %.

To reduce the energy consumption and the time invested in the concentration process, the effect of the homogenization time (using a high shear laboratory mixer) on the distillation process was studied. Other factors (pH, mixture of solvents, crosslinking agent concentration, sodium hypophosphite concentration, and distillation time) involved in both the final properties of the product and distillation time reduction were also investigated. Finally, since the concentrated inverse emulsion polymers are used as anionic thickeners, the rheological properties of aqueous diluted solutions obtained from the concentrated polymer inverse emulsions were also determined.

EXPERIMENTAL

All chemical reagents used and detailed methodologies involved in the preparation of highly concentrated acrylic-based copolymers by inverse emulsion polymerization are listed below. The overall methodology is shown in Figure 1.

Materials

Acrylamide [AM, $CH_2CHC(O)NH_2$, %], purchased from Fisher scientific; acrylic acid (AA, $CH_2CHCOOH$, 99.5%) and methacrylic acid [MA, $CH_3C(CH_2)COOH$, 99.5%], both supplied by Degussa, and alkyl methacrylate esters (AKM, $CH_3C(CH_2)COO(CH_2)_nCH_3$, with an aliphatic alkyl group mixture of $n = C_{15}$ to C_{17}, average molecular weight 324.6 g mol^{-1}, 99.8%), purchased from BASF, were used as monomers. N,N'-methylene-bis-acrylamide {MBA, $[CH_2CHC(O)NH_2]_2CH_2$} and sodium hypophosphite ($NaPO_2H_2$), both purchased from Fisher Scientific, were used as cross-linker and branching agents, respectively. The 2,2'-azobisisobutyronitrile {AIBN, $[(CH_3)_2C(CN)]_2N_2$,}, purchased from Akzo Nobel, was used as a thermal initiator. The redox initiators sodium bromate ($NaBrO_3$)/sodium metabisulfite ($Na_2S_2O_5$), both purchased from Fisher Scientific, were used at the low temperature activation level. The 2-mercaptoethanol [HS-$(CH_2)_2$-OH], purchased from Danamart Chemicals, was used as the chain transfer agent in the synthesis of dispersants by solution polymerization. The paraffinic solvents: Exxol D40 ($T_b = 162.2\,°C$), Isopar K ($T_b = 181.2\,°C$), and Isopar M ($T_b = 207.3\,°C$) were purchased from ExxonMobil Chemical. Cristec D110 was used as naphtenic solvent ($\rho_{25°C} = 0.857$ Kg/l, $\mu_{40°C} = 22.3$ cSt, paraffinic = 63.4%, naphthenic = 36.6%). Ammonium hydroxide (NH_4OH, 28.8%) and the ethylenediaminetetracetic acid (Versene 80) were used as the pH modifier and additive, respectively. Sorbitan monooleate (HBL = 4.3, Span 80), purchased from Fisher Scientific, and Hypermer 1083 (HLB = 4.3), purchased from Croda, were used as surfactants. All the materials mentioned above were used without further treatment.
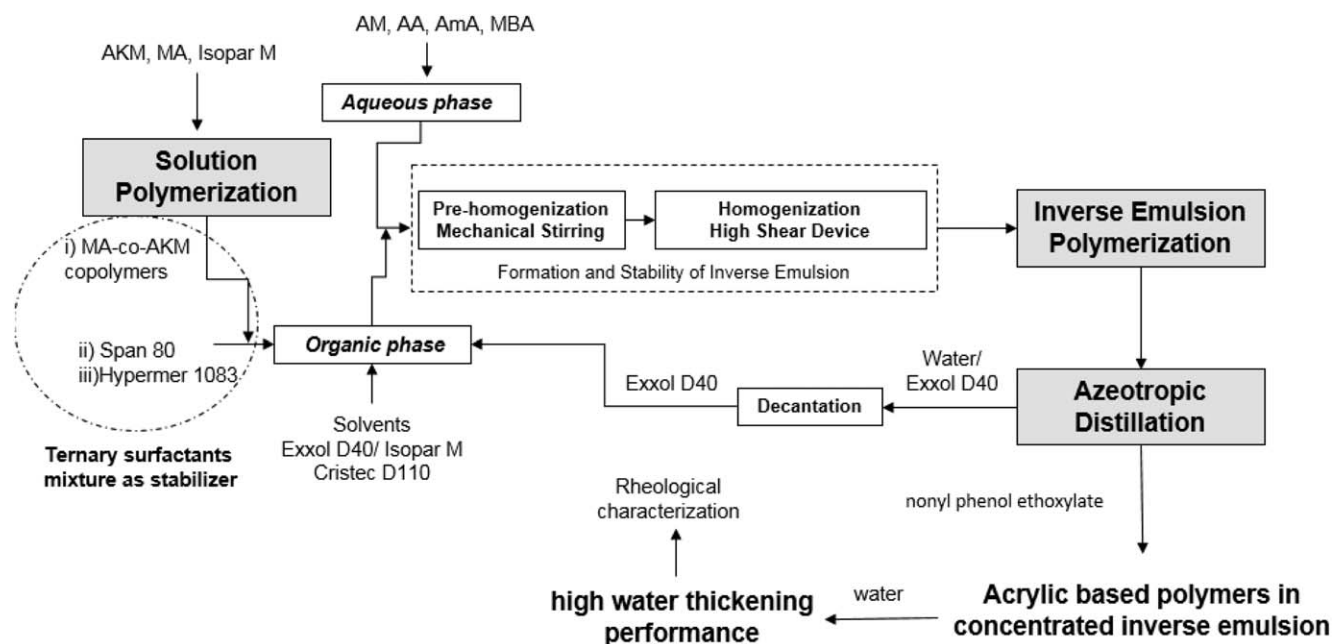
Figure 1. Synthesis of acrylic-based polymers in concentrated inverse emulsion using a ternary surfactant system.

Synthesis of Methacrylic Acid-co-Alkyl Methacrylate Copolymers by Solution Polymerization

Low molecular weight dispersants made up of a mixture of a hydrophobic (alkyl methacrylates) and hydrophilic (methacrylic acid) monomers were synthesized through free radical polymerization. The polymerization of the solution was carried out using a 300-mL five-necked glass reactor equipped with a mechanical stirrer, thermometer, and low pressure nitrogen line. A 200 g of reaction mixture were prepared using 25 wt % of monomers, Isopar M as a solvent, AIBN as a thermal initiator, and 2-mercaptoethanol as a chain transfer agent. Different molar ratios of hydrophobic/hydrophilic monomers (from 2:1 to 5:1) were investigated. The reaction mixture was loaded into the reactor, stirred at 300 rpm and purged with low pressure nitrogen for 20 min. The temperature of the reaction mixture was then increased to 55 °C and the polymerization reaction was initiated by the addition of 50% of the total amount of AIBN (1 wt % with respect to the monomer concentration) dissolved in acetone. The reaction temperature was maintained at 55 °C for 3 h by passing water from the thermostatically controlled water bath through the jacket of the reaction vessel. To complete the reaction, the rest of the AIBN was added and the temperature was raised to 90 °C and maintained for 2 h. The vessel was then quenched to stop the reaction. A sample of the polymers was precipitated in acetone, isopropanol or a mixture thereof (depending on the molar ratio used), washed several times and dried overnight at 40 °C in a vacuum oven, in order to complete their characterization.

Synthesis of Acrylamide/Acrylic Acid/Ammonium Acrylate Polymer Crosslinked with MBA by Inverse Emulsion Polymerization

Aqueous Phase. An aqueous monomer solution was prepared for an equivalent of 25 wt %, based on the total weight of the inverse emulsion (1.5 kg). The polymer composition consists of 35 mol % of acrylamide and 65 mol % of a mixture of acrylic acid and ammonium acrylate (AmA) (pH = 4.85 corresponding to an acid neutralization degree of 50%). A 1 g of Versene 80, increasing amounts of MBA (up to 1750 ppm of MBA, as a crosslinking agent) and of sodium hypophosphite (up to 500 ppm, as a branching agent) based on the weight percentage of the active material were added to the monomer solution. A 0.01% w/w of sodium bromate as redox initiator (oxidizing agent) was also added.

Organic Phase. The continuous phase was prepared using a mixture of aliphatic and naphthenic hydrocarbon solvents. Isopar K or Cristec D110 was used due to its high boiling point and Exxol D40 was selected as the azeotropic distillation agent on account of its chemical similarity to heavy solvents and its low boiling point (between 100 and 150 °C). The ratio of Isopar K/Exxol D40 was 45:55 wt %. The surfactant system was added to the solvents which was made up of 8.5% w/w of sorbitan monooleate, 10.5% w/w of the methacrylic acid-co-alkyl methacrylate copolymer in the aforementioned solution and 1.5% w/w of Hypermer 1083 (the w/w refers to the weight percentage of the organic phase).

Inverse Emulsion Polymerization. To prepare the inverse emulsion, the aqueous phase was added to the organic phase and the mixture was pre-emulsified by mechanical stirring at 400 rpm for 5 min. The dynamic viscosity of this preemulsion was 65 mPa s^{-1} (measured with a Brookfield RBT at 25 °C, Spindle 1, 30 rpm). The inverse unstable emulsion was then homogenized for 60 s at 6000 rpm in a high shear homogenizer (Silverson L4RT-A). The resulting inverse emulsion with a dynamic viscosity of 1321 mPa s^{-1} (measured with a Brookfield viscometer at 25 °C RBT, Spindle 3, 60 rpm) was transferred to a Buchi reactor BMD 300. The inverse emulsion was degassed with N$_2$ for 25 minutes and mixed at 400 rpm. AIBN was dissolved in acetone and added to the reactor. The polymerization began by the

Table I. Boundary Values for the Factors Explored in the Fractional Experimental Design with 5 Central Points

Parameter	Boundary values[a]		
	−1	0	1
x1	4.85	5.5	7
x2	Naphthenic	Mixture 50/50	Paraffinic
x3	750	1250	1750
x4	0	50	150
x5	90	120	180

[a] [x3] = ppm, [x4] = ppm, and [x5] = min.

addition of the redox initiator (sodium metabisulfite) dissolved in distilled water. After 3 min, the maximum reaction temperature (87 °C) was reached. The reaction mixture was stirred for 50 min without a temperature control. At this stage, the reaction was completed as the final temperature reaction decreased to 50 °C, even if more sodium metabisulfite catalyst were added.

Inverse Emulsion Concentration by Azeotropic Distillation
A total of 600 g of inverse emulsion prepared according to the conditions mentioned above was loaded into a 2000-mL long-neck flat-bottomed glass flask (especially designed for this purpose). The glass flask containing the inverse emulsion, a magnetic stirrer and a thermometer, was placed in a vacuum distillation system fitted with adapters, a condenser and a flask to collect the distillate, and a vacuum pump. A vacuum pressure of 25 mmHg was applied to the inverse emulsion which was then heated to temperatures ranging from 60 to 75 °C.

These conditions were maintained throughout the distillation, and the time it took to obtain a high solid percentage was recorded. The desired amount of time had elapsed when about 40–45% w/w of the original inverse emulsion placed in the 2000-mL flask had been removed. The collected distillate was an immiscible water/Exxol D40 mixture with easy separation/reuse properties. The solid percentage obtained after the azeotropic distillation was determined by gravimetry. For these purposes, a weight sample was precipitated in acetone, washed several times and dried overnight at 40 °C in a vacuum oven.

A high HLB surfactant such as nonyl phenol ethoxylate (with an HLB of at least 11) was added dropwise to the high-concentrated inverse emulsion after distillation. The latter allows the concentrated inverse emulsion to be water-dispersible by phase inversion under strong agitation.

Study of the Factors involved in the Product and Process Specification of the Concentrated Anionic Copolymers Synthesized by inverse Emulsion Polymerization
The study of the influence of five independent factors on inverse emulsion polymerization and the distillation of anionic copolymers was carried out by a surface response methodology. The fractional experimental design with five center points and with the following characteristics was chosen: x_1 = pH of the aqueous phase, x_2 = solvent (two different solvents were investigated: paraffinic solvent Isopar K and naphthenic solvent Cristec D110), x_3 = MBA concentration, x_4 = sodium hypophosphite

concentration, and x_5 = distillation time. Table I shows the boundary values for the factors involved in the product and process specification of the anionic copolymers synthesized by inverse emulsion. A typical run was carried out by the preparation of inverse emulsions using formulations according to the experiments in Table II and the methodology described above. The acrylamide/acrylic acid (35/65) molar ratio and homogenization time (30 s) were kept constant.

Two response variables were analyzed: (1) the thickening level of an aqueous dispersion of concentrated anionic inverse emulsion. The quantification of this response was followed by measuring the viscosity using an RBT Brookfield viscometer at 25 °C. Deionized water was thickened with 1.8 wt % of concentrated anionic polymer dispersed for 5 min at 10,000 rpm using a Silverson L4RTA homogenizer, and (2) the percentage of solids (weight content of anionic copolymer) of concentrated inverse emulsion was determined by gravimetric analysis.

This analysis correlates the two response variables as a function of five independent factors. The optimal values of the factors that maximize both response variables were also determined.

Characterization
Viscometry. Intrinsic viscosity measurements were performed for both the methacrylic acid-co-alkyl methacrylate copolymers

Table II. Full Experimental Values of the Factorial Fractional Experimental Design 5^{2-1} with 5 Central Points

Run	x_1	x_2	x_3	x_4	x_5	% solids (w/w)[a]	Viscosity (Pa s^{-1})[b]
1	−1	−1	−1	−1	1	59.6	19.2
2	1	−1	−1	−1	−1	36.5	17.3
3	−1	1	−1	−1	−1	46.6	18.5
4	1	1	−1	−1	1	63.1	19.7
5	−1	−1	1	−1	−1	35.1	23.1
6	1	−1	1	−1	1	58.8	27.4
7	−1	1	1	−1	1	63.2	40.3
8	1	1	1	−1	−1	45.8	28.5
9	−1	−1	−1	1	−1	35.9	10.2
10	1	−1	−1	1	1	59.6	18.5
11	−1	1	−1	1	1	62.9	13.2
12	1	1	−1	1	−1	44.9	11.1
13	−1	−1	1	1	1	58.8	20.8
14	1	−1	1	1	−1	34.5	17.5
15	−1	1	1	1	−1	45.9	18.2
16	1	1	1	1	1	63.3	21.1
17	−0.4	0	0	−0.3	−0.3	46.7	22.8
18	−0.4	0	0	−0.3	−0.3	45.9	22.9
19	−0.4	0	0	−0.3	−0.3	46.0	21.9
20	−0.4	0	0	−0.3	−0.3	46.9	22.6
21	−0.4	0	0	−0.3	−0.3	45.0	23.1

[a] Solid percentage determined by gravimetry after distillation.
[b] Viscosity of 1.8% (w/w) of concentrated inverse emulsion dispersed in water for 5 min at 10,000 rpm (Brookfield RBT Spindle 7, 20 rpm, 25 °C).

and the linear acrylamide/acrylic acid/ammonium acrylate copolymers. After the precipitation, washing and drying of the copolymers, the intrinsic viscosity was evaluated in 1M NaCl aqueous solution using an Ubbelohde viscometer at 25 °C.

FTIR Spectroscopy. FTIR spectroscopy was used to determine the composition of the copolymers synthesized. A total of 0.5 g of dried polymer dissolved in tetrahydrofuran was loaded into the sample holder of the instrument and dried until a thin film was obtained due to solvent evaporation. Spectra were recorded in the range of 4000–630 cm^{-1} using a Perkin Elmer 1600 spectrometer.

NMR Spectroscopy. NMR Spectra were recorded at 298 and 318°K on a Bruker AVANCE III 500 NMR spectrometer, 11.7 T, 500 MHz for 1H and 125 MHz for ^{13}C, using 5 mm BB-ID z-gradient probe. CDCl$_3$ and Pyridine-d5 were used as solvents and TMS as internal reference.

Rheology. Steady-state and oscillatory measurements of the rheological behavior of the concentrated anionic copolymers in inverse emulsion were taken using an Anton Paar Physica MCR 300 strain controlled rheometer at 25 °C. To perform these measurements, 18 g of concentrated inverse emulsion were dispersed in 982 mL of deionized water by mechanical stirring. The rheological flow of these thickened aqueous dispersions ("white pastes") was determined by varying the shear rate from 0.01 to 1000 s.$^{-1}$ Sweep flow was conducted using a cone-plate geometry of 50-mm diameter with a contact angle of 2° (CP50-2).

The storage G' and loss G'' moduli were analyzed through oscillatory tests using a frequency sweep with an interval of 0.01 to 100 Hz. The limit of the linear viscoelastic region was previously determined by oscillatory stress sweep between 0.1 and 300 Pa at a frequency of 1Hz.

RESULTS AND DISCUSSION

Synthesis of Alkyl Methacrylate-*co*-Methacrylic Acid Copolymer Using Solution Polymerization

Several amphiphilic polymers based on different molar ratios of alkyl methacrylate esters copolymerized with methacrylic acid were obtained by solution polymerization using a high concentration of 2-mercaptoethanol as the chain agent transfer (CTA) and AIBN as the thermal radical initiator.

Figure 2 shows the FTIR spectra for the synthesized copolymer. The peak signals at 1729 and 1698 cm^{-1} are attributed to the stretching of the carbonyl group (C=O) of alkyl methacrylates and methacrylic acid, respectively. Increments in the molar concentration of the hydrophobic monomer led to an increase in the signal at 1729 cm.$^{-1}$ The bands at 2924 and 2850 cm^{-1} correspond to the bending vibration (—C—H) of the —CH$_2$— and —CH$_3$ groups in the C$_{16}$ to C$_{18}$ aliphatic chain in the hydrophobic monomer. The methacrylates polymers also exhibit the typical bands caused by stretching vibration (C—O) at 1151, 1241, and 1271 cm.$^{-1}$ The sample PS5 shows similar spectra to that of PSC (a commercial sample). These two copolymers display similar structural (molar ratio) characteristics.

To obtain a small molecular size of polymeric dispersants, a high concentration of CTA was used. The intrinsic viscosity can be used as an indication of the size of the macromolecules.[26]
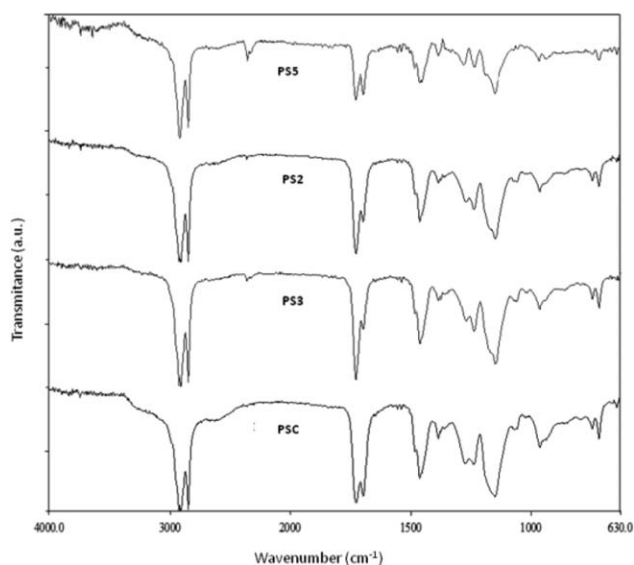

Figure 2. FTIR Spectra for the alkyl methacrylate-methacrylic acid copolymers with different molar ratios (AKM/MA): PS5 (2:1), PS2 (3:1), PS4 (4:1), and PSC (commercial sample).

The solution of PS1 to PS3 samples showed a high viscosity (PS1 > PS2 > PS3) with a gel-like appearance. This suggests that an increase in the molar concentration of the hydrophobic monomer was caused by an increase in the solution viscosity using the same CTA concentration (1 g L^{-1}). However, this fact can also be attributed to solubility according to Pantchev and Hunkeler.[27] The solubility of the copolymers synthesized in Isopar M changes when the molar ratio is modified at the same low CTA concentration. To obtain a hydrophobic copolymer with a molar ratio of 2:1 using Isopar M as solvent (AKM/MA, PS4 Figure 2), about 15 g L^{-1} of CTA were needed. When the initial monomer concentration was increased from 25 (sample PS4) to 50 (sample PS5) % w/w at the same molar ratio (2:1), the intrinsic viscosity of the solution was similar (0.11 and 0.09 dL g^{-1}, respectively). These copolymers showed an intrinsic viscosity similar to that of a commercial PSC sample ([η] = 0.17 dL g^{-1}) and materials ranging from 0.07 a 0.35 dL g^{-1}.[27]

The copolymer structure was verified by ^{13}C (1D and 2D ^{1}H-^{13}C HSQC, HMBC) NMR spectral data. Figure 3 shows the ^{13}C NMR spectra for copolymer PS5.

The NMR spectroscopy analysis not only enabled us to obtain the structural characterization of the copolymer but it also provided information on the behavior of the amphiphilic molecules in different chemical environments. It seems that the hydrogen of the acid in the methacrylic acid comonomer can act both as an intramolecular hydrogen bond and as ion exchange processes.

When the copolymer was analyzed using CDCl$_3$ at 298°K, the hydroxyl groups of the methacrylic acid comonomer tended to form hydrogen bonds restricting molecule mobility. This leads to a very efficient transversal relaxation of the backbone carbons making it difficult to determine the carbonyl, quaternary and methyl carbons of the copolymer. The spectra of both ^{1}H and ^{13}C did not show significant changes at different temperatures (298 and 318°K).
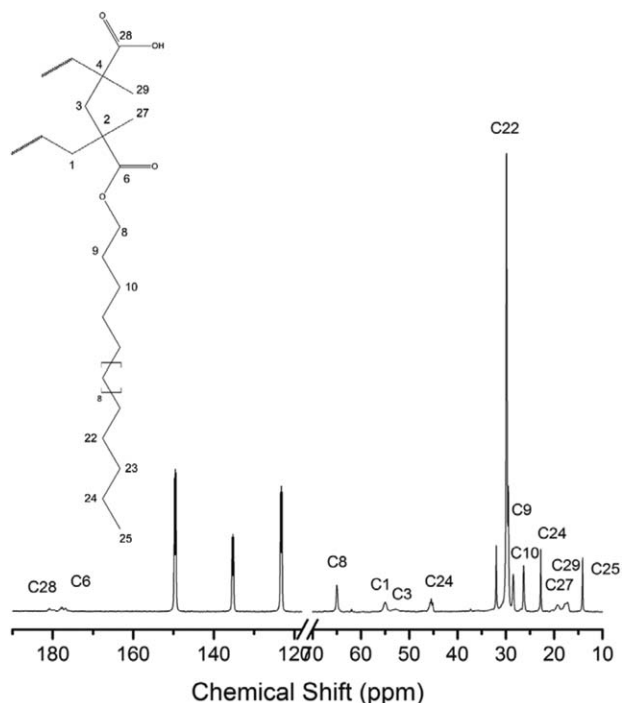
Figure 3. ^{13}C NMR spectrum of AKM/MA copolymer in Pyridine-d5.

The ion exchange behavior of the copolymer was observed when it was analyzed using Pyridine-d5 as solvent. A low field shift of the acid hydrogen from 13.0 ppm (CDCl₃, 298 and 318°K) to 14.8 ppm at 318°K (FWHH = 600 Hz) and 15.23 ppm at 298°K (FWHH = 400 Hz) was observed. Pyridine-d5 acts as a competing base in the ion exchange process. The observed chemical shifts and line shapes (FWHH), would seem to indicate the ion exchange process improves at higher temperatures. The pyridine-d5 demonstrated the ion exchange behavior of the copolymer.

According to the ^{13}C, ^{1}H-^{13}C HSQC and HMBC spectra, the chemical shifts of the carbons shown in Figure 3 can be attributed to the quaternary backbone carbons, C1(52.2 ppm), C2 (45.0 ppm), C3(53.0 ppm), and C4(45.6 ppm), the carbonyl carbon of the ester C6(176.9, 178 ppm) and acid C28(181.0 ppm) comonomers, the methyl carbons in the acid C29(17.5 ppm) and ester C27(19.5 ppm), the methyl carbon of the ester chain C25(14.4 ppm) and the carbon α-CH₂- bonded to the oxygen in the ester group C8(65.2 ppm).

The copolymer composition was determined through the ^{13}C NMR spectrum, once the nuclear Overhauser effect (NOE) was suppressed. The relaxation time was reduced when using Cr(A-cAc)₃ as a paramagnetic relaxation agent. The ^{13}C spectrum acquired under these conditions led to the quantitative integration of the signals belonging to the carbonyl carbon resonances of the ester and the acid. The ester:acid molar ratio was found to be 2:1. The copolymer composition determined by NMR spectroscopy was in agreement with the molar ratio of the feed values.

The polymeric dispersants synthesized in this work therefore featured structural characteristics and molecular sizes that pro-

vided surface stability during the polymerization and distillation processes in the acrylic acid-acrylamide inverse emulsion synthesis, as mentioned elsewhere.[17,18,20,27]

Synthesis of Acrylamide/Acrylic Acid/Ammonium Acrylate (AM/AA/AmA) Polymer Crosslinked with MBA by Inverse Emulsion Polymerization

Anionic copolymers were synthesized by a free radical inverse emulsion polymerization process at 25 wt % of active material. The anionic copolymers obtained were highly random materials composed of three different monomer units AM/AA/AmA and partially crosslinked with MBA (Scheme 1).

Sodium hypophosphite was also used as a branching promoter to increase the crosslinking degree. Because the heterogeneous polymerization is highly exothermic, the synthesis was activated by a system of biphasic initiators. The process was performed in a semiadiabatic approach. A temperature profile from 25 to 85 °C was obtained in three minutes. At the low temperature interval (from 25 to 50 °C), the water soluble redox pair initiators (NaBrO₃/Na₂S₂O₅) started to produce radicals and the reaction began, after which the highest temperature was reached (85 °C). The reaction progressed and finished with the consumption of the monomers due to both the free radicals generated by the redox initiators and the thermal decomposition of the AIBN. The temperature fell to 50 °C after 45 min of reaction time. Despite the strong thermal behavior of the system and high reaction rate in a short amount of time, the product obtained showed enough stability, and no clots were macroscopically detected in the reactor.

The molecular weight of the crosslinked copolymers cannot be determined because of their high insolubility in any solvent. However, in order to explore the molecular size of the anionic copolymer, several inverse emulsions were synthesized under the same reaction conditions, but without MBA. This approach
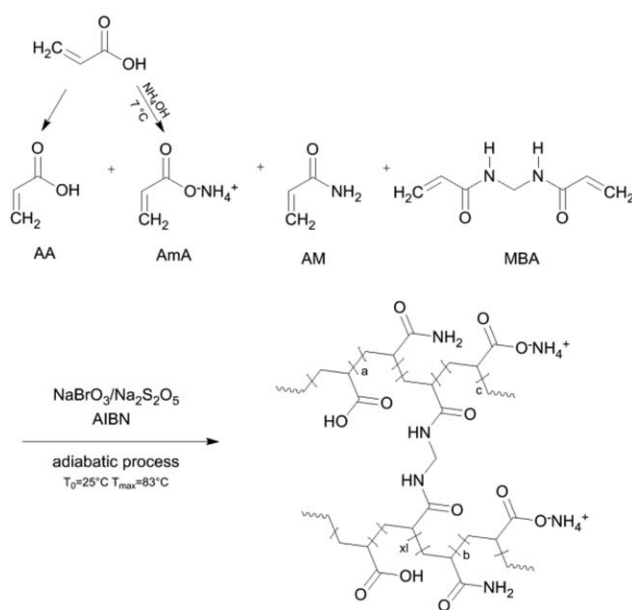
Scheme 1. Free radical polymerization of crosslinked AA/AmA/AM copolymers obtained by inverse emulsion.
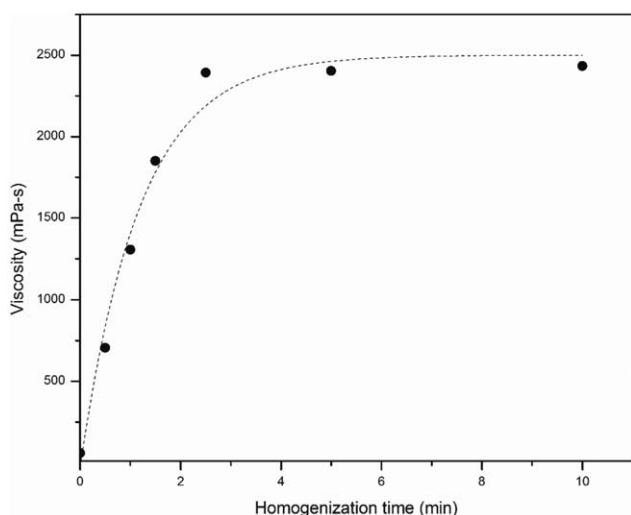
Figure 4. Viscosity of the inverse emulsion before polymerization as a function of the high shear homogenization time using a rotor stator homogenizer Silverson L4RT-A at 6000 rpm. (Viscosity measurements were performed using a Brookfield RBT viscometer at 25 °C).

leads to non-crosslinked materials and increases their solubility in solvents such as NaCl 1M. The intrinsic viscosity of the copolymers was thus determined at an interval ranging from 3.3 to 3.6 dL g^{-1}. These values were slightly smaller than the intrinsic viscosity (from 4 to 15 dL g^{-1}) reported for similar materials.[17]

Concentrated Inverse Emulsion by Vacuum Distillation

The concentration of inverse emulsions was successfully achieved using the surfactant system presented in this work. This can be described as a batch distillation operating at a vacuum pressure of 25 torr (the pressure was set by the vacuum device system used). To reach the boiling point of water and to promote separation, the temperature was increased from 60 to 90 °C. Temperature is an important factor during distillation since it can lead to changes in the interfacial tension between the two phases. The nature and viscosity of the interfacial film and the relative solubility of the emulsifying agent in the two phases can be also modified. The vapor pressures and viscosities of the liquid phases are also temperature-dependent.[24] Therefore, temperature changes usually cause considerable changes in the overall characteristics of emulsions.

Another factor to describe the distillation process under these simplifications is the time required to obtain concentrations of about 60 wt % of solids in the final product. Once the surfactant system (polymeric dispersant described above, sorbitan monooleate, and Hypermer 1083) and the final concentration of the solid percentage (60 wt %) in the concentrated inverse polymer emulsion were set, the distillation time still depended on the homogenization time required to form a "stable" inverse emulsion. It seems that the more stable inverse emulsion (better homogenized), the more difficult it is to distillate. Homogenization is a part of the emulsion formation and is carried out using special equipment such as high pressure mixers, shear rate homogenizers, or ultrasonic devices.[25]

The high shear stress applied to the inverse monomer emulsion by a rotor stator device provides enough stability to yield a product without phase separation or sedimentation during reaction, storage and market distribution time. However, a more stable emulsion could increase the resistance of mass transfer at the interface. The water and water/azeotropic agent mixture removal from the inverse emulsion can be qualitatively described as follows: (i) water must travel from the particles of the disperse aqueous phase surrounded by the complex surfactant system (since it has a strong influence on the stability and flexibility/breaking mechanism of the interface which also depends on the temperature), (ii) water breaks the interface (which involves high-energy requirements), (iii) water must still be transferred through the organic phase.

Regarding the synergy shown by the surfactant system, the vacuum pressure and the temperature, the hydrodynamics of the system are also complex in nature. In this work, we studied the effect of the homogenization time on the viscosity of the inverse emulsion and its effect on the distillation time. Further investigations on the absorption, mass transfer phenomena, and the hydrodynamics of the system are beyond the scope of this work.

Figure 4 shows the resulting viscosity of the inverse emulsion using 6000 rpm and different homogenization times using a rotor stator homogenizer. The viscosity values showed an exponential growth during the first two minutes with an increase from 0.058 to 2.4 Pa·s. The viscosity then remained unchanged around values of 2.4 Pa·s, even after 10 minutes of constant applied power.

Three different viscosities as a function of the homogenization time ($t_{h1} = 0$, $t_{h2} = 30$ and $t_{h3} = 60$ seconds, shown in Figure 5) were investigated in the inverse polymer emulsion distillation. The concentration profiles as a function of the distillation time for t_{h1}, t_{h2}, and t_{h3} are shown in Figure 5. According to these results, 280 min were required to achieve around 62 wt % of solids for t_{h3}. For these conditions, the concentration profile seemed to follow a linear trend. On the other hand, 140 minutes were needed to achieve a similar concentration in the
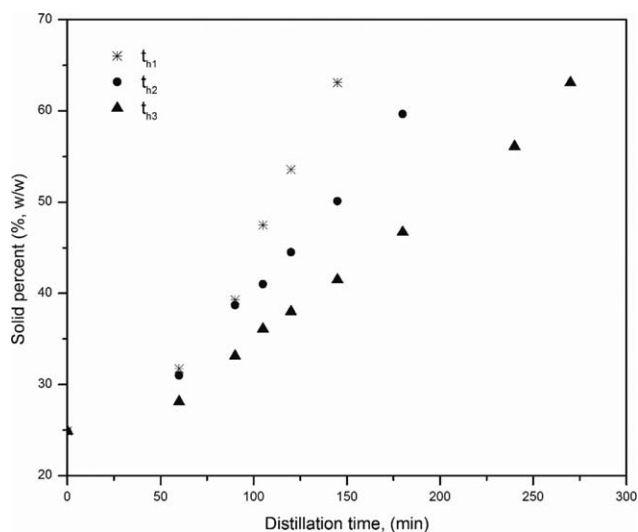

Figure 5. Batch distillation concentration profiles for different homogenization times of the anionic copolymers in inverse emulsion.

case of t_{h1}, whereas t_{h2} required 180 min to achieve around 60 wt % of solids.

A strong homogenization time effect on the total distillation time was found. The time reduction was 48 and 33% for t_{h1} and t_{h2} with respect to t_{h3}. These results suggest that increases in the homogenization time led to increases in both the inverse emulsion viscosity and stability. The distillation time was also longer, which increases the distillation cost. Batch distillation time is directly linked to energy consumption and process costs.[28] In addition, less stable inverse emulsions exhibited visible separation phases at short storage times: 2 weeks in the case of t_{h1}, while t_{h2} did not show sedimentation or phase separation over a period of 2 months. Thus, concentrated inverse emulsions can be obtained using 30 s of homogenization time in 180 min with the distillation conditions mentioned above. The concentrated products also exhibited desirable stability properties for storage and transportation times.

Effect of Factors involved in Product and Process Specifications

In the previous sections we discussed the factors associated with the concentration process of anionic copolymers obtained by inverse emulsion polymerization as a preliminary screening for the optimal product and process specifications. However, we have not yet considered the design of high performance anionic materials, which considers other factors related to the chemical properties of the copolymers such as the MBA concentration, pH, and the solvents used. A surface response methodology was therefore used to explore the main effects of these factors (pH, solvent, MBA concentration, sodium hypophosphite concentration, and distillation time) on the concentration process and the thickening of water (viscosity) using the concentrated inverse anionic polymer emulsion products.

Table II shows the results of the solid concentration percentage and viscosity for all the fractional factorial experimental design runs (5^{2-1}) with five central points. Concentrated inverse emulsions from 35.1 to 63.3 wt % were obtained. The water dispersion viscosity values ranged from 11.1 to 40.3 Pa·s.

According to the analysis of variance (ANOVA), for the first response variable (% solids, Table II entry 7), solvent and distillation time factors showed a positive effect (x_5 and x_1), while their binary interaction ($x_5 x_2$) had a negative effect. This negative solvent-time interaction effect is related to the physical properties of the solvents.

Regarding the viscosity (Table II entry 8), a more complex system was detected. In this case, a positive influence was determined by three individual factors (x_3, x_5, and x_2) while x_4 showed a negative effect. Surprisingly, the pH had no significant effect on the viscosity. The three binary interactions ($x_2 x_3$, $x_4 x_1$, and $x_3 x_5$) also showed a positive effect, and five binary interactions, corresponding to the pH and sodium hypophosphite concentration, affected the thickening level ($x_2 x_4$, $x_3 x_4$, $x_1 x_2$, $x_1 x_3$, and $x_1 x_5$). The branching agent, sodium hypophosphite, had a negative effect while the crosslinked agent (MBA) bears the most significant positive effect. The combination of both factors, led to an increase in viscosity. This is in agreement with
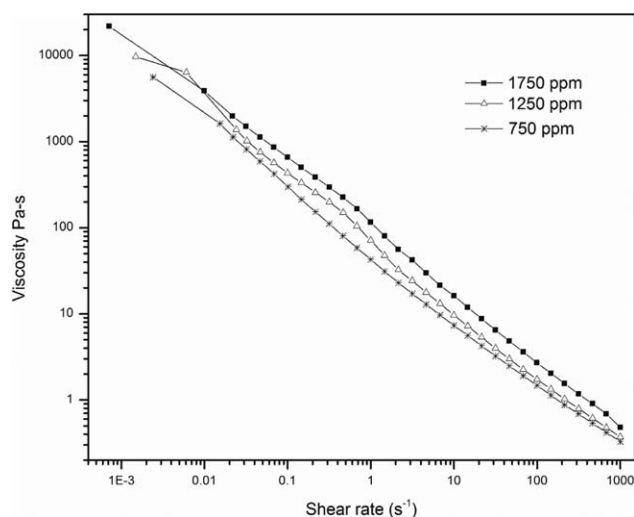

Figure 6. Shear viscosity profiles of crosslinked anionic copolymers using different MBA concentrations. [1.8% (w/w) of concentrated inverse emulsion dispersed in deionized water for 5 min at 10,000 rpm].

the fact that a crosslinked and branched polymer contributed to increased water thickening.

From the surface response analysis, the optimal levels to maximize the % of solids and viscosity were identified using the desirability function in the optimization method as: $x_1 = -1$, $x_2 = 1$, $x_3 = 1$, $x_4 = -1$ and $x_5 = 1$. According to Table I, the decoded values are: pH = 4.85, solvent = paraffinic solvent (Isopar K), MBA = 1750 ppm, sodium hypophosphite = 0 ppm and 180 min as distillation time. These values actually correspond to run 7 (see Table II) where anionic inverse emulsion achieved 63.2 wt % of solids and its thickening level was 40.3 Pa·s.

Rheological Characterization of Diluted Water Dispersion

The rheological behavior of anionic copolymers as thickeners is very important in, for example, paint applications[29] and textile pigment printing.[30–32] Furthermore, the viscosity dependence with the shear rate or stress, the thixotropy, and the viscoelastic behavior of polymeric materials are related to the microstructure[33] and in the case of acrylic thickeners, to the mechanism of thickening aqueous media.[34–36]

A family of anionic copolymers using the optimal values of the factors investigated was synthesized using the three levels of MBA mentioned in Table I. Shear viscosity profiles of water dispersion thickened by these three anionic copolymers are shown in Figure 6. The three thickener dispersions follow the same non-Newtonian behavior. They exhibit high viscosity at low deformation gradients. However, the viscosity decreased when the applied stress was increased. This is the typical profile of a thixotropic fluid.[37] When the MBA concentration was increased, the viscosity value was also higher. The anionic thickeners are thixotropic fluids because once they are dispersed in water, the thickening mechanics are associated with relatively weak physical binding forces, thus they are easily destroyed or modified after applying a force to the fluid. Because of their long branched morphology and their crosslinked chains, the structural changes induced by changes in gradient often take a considerable period of time to be seen.
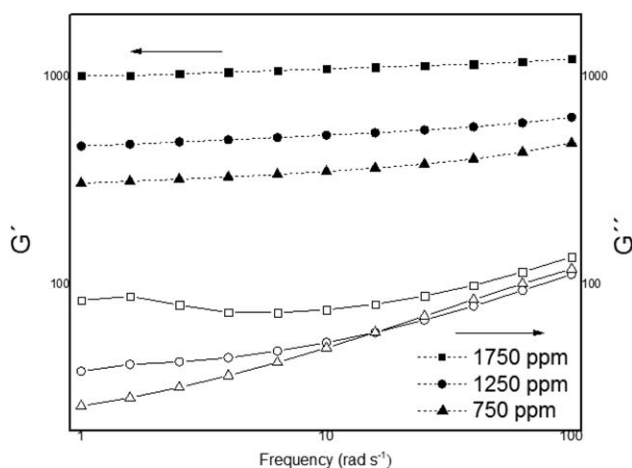
Figure 7. Viscoelastic moduli profiles of crosslinked anionic copolymers using different MBA concentrations. [1.8% (w/w) of concentrated inverse emulsion dispersed in deionized water for 5 min at 10,000 rpm].

The viscoelastic behavior determined by oscillatory tests was performed to obtain the storage G' and loss G'' moduli as a function of MBA concentration. Figure 7 shows G' and G'' profiles at 25 °C. All samples had a similar trend with respect to the frequency sweep (high elastic behavior, $G'>G''$). The values of G' were significantly higher at the high MBA concentration. This is a measure of the energy stored during deformation and is related to the solid-like portion of the system. Crossover zones represent the point at which the characteristic behavior of the gels shifted from elastic to viscous and were not determined in the frequency interval explored.

The viscoelastic properties of water dispersions depend on the crosslinked level of the anionic copolymers used to thicken them. Therefore, controlling the crosslinking level by the MBA concentration in the polymer inverse emulsion synthesis leads to the formulation of a wide range of viscoelastic (G''/G') water-based products for a broad range of practical applications, such as print pastes for the textile industry, personal care products, and cosmetics.

CONCLUSIONS

A reliable two-step methodology was developed to prepare anionic copolymers in inverse emulsion from a diluted to a high concentration of active material, and high water thickening performance with minimum dosage.

The use of a ternary mixture of surfactants, which consists of specially synthesized polymeric dispersants, traditional surfactants and polymeric emulsifiers during the organic phase of the synthesized inverse emulsions, provides sufficient stability throughout the polymerization and distillation processes, allowing for a high solid percentage without loss of product by clot formation.

We have shown that the factors involved in both process and product specifications result in energy and time reductions in the anionic copolymer concentration process. The products obtained by this approach also showed desirable stability properties for storage and transportation time periods. Thus, the developed methodology is highly attractive for scale-up projections for industrial production and applications.

REFERENCES

1. Kamal, M. S.; Sultan, A. S.; Al-Mubaiyedh, U. A.; Hussein, I. A. *Polym. Rev.* **2015**, *55*, 491.

2. Rabiee, A. *J. Vinyl Addit. Technol.* **2010**, *16*, 111.

3. Siyawamwaya, M.; Choonara, Y. E.; Bijukumar, D.; Kumar, P.; Du Toit, L. C.; Pillay, V. *Int. J. Polym. Mater. Polym. Biomater.* **2015**, *64*, 955.

4. Halake, K.; Birajdar, M.; Kim, B. S.; Bae, H.; Lee, C.; Kim, Y. J.; Kim, S.; Kim, H. J.; Ahn, S.; An, S. Y.; Lee, J. *J. Ind. Eng. Chem.* **2014**, *20*, 3913.

5. Dautzenberg, H.; Philipp, B. Polyelectrolytes: Formation, Characterization, and Application; Hanser Publishers, Munich (Germany), **1994**.

6. Dobrynin, A.; Rubinstein, M. *Prog. Polym. Sci.* **2005**, *30*, 1049.

7. Hawe, M. In Handbook of Industrial Water Soluble Polymers; Williams, P. A., Ed.; Blackwell Publishing, Oxford (UK), **2007**; p 32.

8. Hernández-Barajas, J.; Hunkeler, D. J. *Polymer* **1997**, *38*, 437.

9. Pabon, M.; Corpart, J. M.; Selb, J.; Candau, F. *J. Appl. Polym. Sci.* **2002**, *84*, 1418.

10. Hernández-Barajas, J.; Hunkeler, D. *Polymer* **1997**, *38*, 5623.

11. Hernández-Barajas, J.; Hunkeler, D. In Polymeric Materials Encyclopedia, Salamone, J. C., Ed.; Taylor & Francis, Boca Raton, **1996**, 3322.

12. Ochoa-Gómez, J. R.; Nieto-Mestre, J.; Escudero-Sanz, F. J.; Sasia, P. M.; Río, F.; Torrecilla-Soria, J.; Katime, I. A. *J. Appl. Polym. Sci.* **2009**, *114*, 3132.

13. Li, G. H.; Zhang, G. C.; Wang, L.; Ge, J. J. *J. Appl. Polym. Sci.* **2014**, *131*, 1.

14. Asua, J. M. *Prog. Polym. Sci.* **2014**, *39*, 1797.

15. Ochoa-Gómez, J. R.; Escudero-Sanz, F. J.; Sasia, P. M.; Río, F.; Nieto-Mestre, J.; Torrecilla, J.; Katime, I. A. *J. Appl. Polym. Sci.* **2009**, *114*, 2673.

16. Hübner, W.; Schroers, K. U.S. Patent 4,925,884 (**1990**).

17. Allen, A. S. U.S. Patent 4,554,018 (**1985**).

18. Flesher, P.; Farrar, D.; Benson, A. C. U.S. Patent 4,599,379 (**1986**).

19. Keller, W.; Müller, F. U.S. Patent 4,029,622 (**1977**).

20. Anderson, D. B.; Forder, J.; Johnson, I. M. *Brit. Pat.* *1482*,515, **1977**.

21. Hunter Wood, E.; Vallino, B. U.S. Patent 4,021,399 (**1977**).

22. Keggenhoff, B.; Rosenkranz, H. J. U.S. Patent 4,299,755 (**1981**).

23. Diener, B.; Gehler, V.; Küster, E.; Roulands, D.; Werhahn, D. U.S. Patent 6,861,469 B2 (**2005**).

24. Rosen, M. J. In Surfactants and Interfacial Phenomena, 3rd ed.; Wiley: New York, **2004**, p 303.

25. Atiemo-Obeng, V. A., Calabrese, R. V. In Handbook of Industrial Mixing Science and Practice; Paul, E. L., Ed.; Wiley: New Jersey, **2004**; p 479.

26. Peterson, J. M.; Fixman, M. *J. Chem. Phys.* **1963**, *39*, 2516.

27. Pantchev, I.; Hunkeler, D. J. *J. Appl. Polym. Sci.* **2004**, *92*, 3736.

28. Rodriguez Donis, I.; Gerbaud, V.; Joulia, X. *AIChE J.* **2002**, *48*, 1168.

29. Lu, C. F. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 412.

30. Fijan, R.; Basile, M.; Lapasin, R.; Šostar-Turk, S. *Carbohydr. Polym.* **2009**, *78*, 25.

31. Guion, T. H.; Hood, J. R. *Text. Res. J.* **1985**, *55*, 498.

32. Fijan, R.; Basile, M.; Šostar-Turk, S.; Žagar, E.; Žigon, M.; Lapasin, R. *Carbohydr. Polym.* **2009**, *76*, 8.

33. Kennedy, J. C.; Meadows, J.; Williams, P. A. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 911.

34. Jiménez-Regalado, E.; Cadenas-Pliego, G.; Pérez-Álvarez, M.; Hernández-Valdez, Y. *Macromol. Res.* **2004**, *12*, 451.

35. Samchenko, Y. M.; Ul'berg, Z. R.; Komarskii, S. A.; Kovzun, I. G.; Protsenko, I. T. *Colloid. J.* **2003**, *65*, 78.

36. Andrews, N. C.; McHugh, A. J.; Schieber, J. D. *J. Polym. Sci. B: Polym. Phys.* **1998**, *36*, 1401.

37. Kavanagh, G. M.; Ross-Murphy, S. B. *Prog. Polym. Sci.* **1998**, *23*, 533.