Synthesis of Cross–Linked, Partially Neutralized Poly(Acrylic Acid) by Suspension Polymerization in Supercritical Carbon Dioxide

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Synthesis of Cross-Linked, Partially Neutralized Poly(Acrylic Acid) by Suspension Polymerization in Supercritical Carbon Dioxide

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ABSTRACT: A novel process for producing superabsorbent polymer of cross-linked, partially neutralized poly(acrylic acid) via suspension polymerization in supercritical carbon dioxide was developed. The process utilized siloxane-based surfactants as suspension stabilizers to produce particles with acceptable size range for commercial applications. The behavior of the suspension mixture and its relation to the final product morphology is discussed. The product performance in terms of water absorbency is presented.

INTRODUCTION

Superabsorbent polymers (SAPs) are usually made of partially neutralized, slightly cross-linked poly(acrylic acid), PAA. Aqueous solution polymerization is commonly used for SAP production where the resulting polymer is pulverized and dried to give particles in the 200−800 μm range.[1] A less commonly used technique for SAP production is the inverse suspension polymerization in organic medium where particles of the desired range are directly produced. Both processes have some inherent disadvantages in terms of processing (heat transfer limitations, and energy extensive milling and drying), product quality (residual monomer, organic contaminants), and safety issues (volatile and flammable organics in the case of the suspension process).

Carbon dioxide has been recognized as a potential alternative for many aspects of polymer processing and synthesis.[2−5] In addition to its benign nature, CO_2 provides the advantage of easy separation from the product.[6] These advantages can overcome other economical and operating obstacles and result in commercialization, as is the case with the DuPont process to produce certain grades of Teflon in CO_2.[7] Therefore, producing SAP particles with the desired size range using CO_2 seems promising.

Unlike traditional suspension media, most common monomers, including AA, are quite soluble in CO_2 at typical temperatures and pressures employed in CO_2 processing ($P >$ 200 bar and $T > 30$ °C).[8,9] This has limited the use of CO_2 as a suspension medium for polymerization.[2] Most reported studies on heterogeneous polymerization in CO_2 involved emulsion, precipitation, or dispersion processes.[9−14] As discussed next, the polymer particles produced in these studies were smaller than 100 μm in size; not suitable for SAP applications.

All reported syntheses of PAA in CO_2 have been via precipitation polymerization. Several patents have been issued on the production of water-soluble and water-insoluble PAA in CO_2.[15−18] More recent studies on the subject have also been published. The first such report was that by Romack et al.[19] In this study, uncross-linked PAA (MW ≈ 150k) was produced at 62 °C and pressures from 125 to 345 bar. PAA was obtained as a white powder with submicrometer particle size. This precipitation polymerization process was further developed by

Liu et al., who devised a continuous process for the production of PAA.[20−24] Liu et al. demonstrated that cross-linked PAA could be produced by feeding a cross-linker to the reactor along with AA, and also demonstrated that a partially neutralized PAA could be produced by postpolymerization neutralization. The polymerization was carried out at 207 bar and temperatures between 50 and 90 °C. Again, the product was obtained as a white powder having a MW between 5k and 200k and a particle size from 0.1 to 100 μm, depending on the conditions. Finally, Xu et al. investigated the precipitation polymerization of AA in CO_2 in the presence of a cosolvent (acetic acid and ethanol).[25] The polymer obtained in this study was in the form of a white powder with submicrometer particles. In addition, CO_2 has been used for processing and modification of PAA.[26−29]

In this work, SAP particles were synthesized by inverse suspension polymerization of partially neutralized AA in CO_2. Various siloxane copolymer surfactants were evaluated as suspension stabilizers. The main focus of the study was to obtain particles within the desired size range (200−800 μm). The effect of operating conditions on the size and morphology of the particles is explored.

EXPERIMENTAL SECTION

Materials. Glacial acrylic acid (AA) with 200 ppm MEHQ inhibitor was provided by Evonik (Greensboro, NC). Sodium hydroxide aqueous solution (50.5 wt %) and deionized water (2.0 $\mu\Omega$) were purchased from Fisher Scientific. The initiator, sodium persulfate (98+%), and cross-linker, N,N′-methylene-bisacrylamide (99%), were purchased from Aldrich Chemical. Carbon dioxide (SFC grade; 99.998%) was purchased from National Specialty Gases. Siloxane block copolymer surfactants (Gelest, Inc.) were used as suspension stabilizers. Composition and properties of the surfactant are listed in Table 1, as well as the hydrophilicity of the surfactants, expressed in terms of the

hydrophilic/lipophilic balance (HLB).[30] All chemicals were used as received.

Table 1. Siloxane Block Copolymers Used As Suspension Stabilizers in This Work

product code[a]	surfactant component[b]	HLB[c]	density (g/mL)	M_n (kDa)	water solubility[d]
DBE-224	PDMS-b-(25−30% PEO)	5	1.02	10	N
DBE-621	PDMS-b-(50−55% PEO)	11	1.03	3	M
DBE-712	PDMS-b-(75% PEO)	15	1.01	0.6	S
DBE-814	PDMS-b-(80% PEO)	16	1.03	1	S
DBE-821	PDMS-b-(80−85% PEO)	16	1.07	3.6	S

[a]All products were manufactured by Gelest, Inc. Data taken from manufacturer Web site (www.gelest.com). [b]PDMS: polydimethylsiloxane; PEO: poly(ethylene oxide), composition given on weight basis. [c]Hydrophilic/lipophilic balance; calculated as defined in literature, ref 30, p 440. [d]N: not soluble, M: moderate solubility, S: soluble.

Monomer Solution. The monomer solution was prepared in an ice bath to absorb the heat released during mixing. First, the desired quantity of NaOH was mixed with H_2O. After the solution cooled down to about room temperature, AA was added. The neutralization of AA with NaOH produces sodium acrylate (NaAA). Once NaAA was completely dissolved, the cross-linker was added. Finally, the initiator was added and the solution was allowed to mix for 1 h. The degree of neutralization was varied by controlling the amount of AA added, as shown in Table 2. The composition used in the

Table 2. Compositions of Typical Monomer Solutions Used in Polymerization

solution no.	1	2
component	composition (wt%)	
water	52.6	61.8
NaAA	37.6	36.9
AA	9.6	0.9
MBA	0.1	0.5
sodium persulfate	0.1	0.5
total mass (g)	208	206
degree of neutralization (%)	75	97

majority of the experiments is that of solution 1 in Table 2, which gives a neutralization degree of 75%. The total monomer solution mass was about 207 g for all experiments.

Apparatus. Figure 1 shows a schematic drawing of the experimental setup used to perform the batch inverse suspension polymerization in $scCO_2$. The reactor was an 800 mL, high-pressure autoclave with a magnetically driven agitator. Three three-blade downward-pumping propellers were arranged on the agitator shaft. The agitator was setup to rotate at a fixed speed of 1200 rpm. All parts of the reactor contacting the reaction mixture were made of stainless steel. A heating/cooling fluid was circulated through a jacket on the reactor to control the reaction temperature.

Polymerization. The monomer solution and suspension stabilizer were charged into the reactor, which was then sealed and the jacket temperature was set to 25 °C. Carbon dioxide was added until the reactor pressure was 110 ± 4 bar, then the
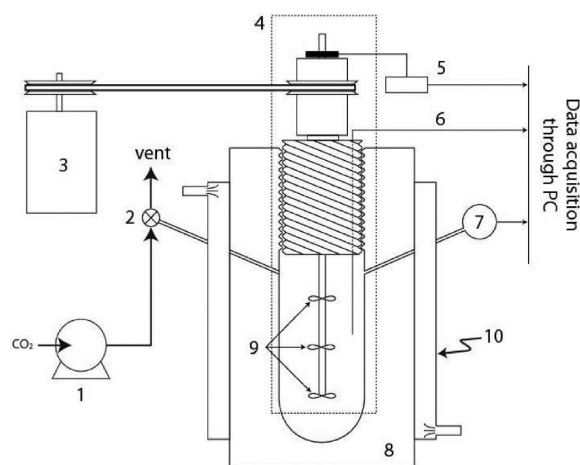

Figure 1. Experimental system used for the polymerization runs. 1. syringe pump, 2. 2-way valve, 3. electrically driven motor, 4. MagneDrive Assembly, 5. tachometer, 6. thermocouple, 7. pressure transducer, 8. High pressure vessel, 9. removable propellers, 10. water jacket.

agitator was started. The CO_2-to-monomer solution volume ratio was about 2.8 inside the reactor. After 10 min, the jacket temperature was set to 75 °C. The temperature, pressure, and agitation speed inside the reactor were recorded as a function of time. An example of the collected temperature and pressure data is shown in Figure 2. As the polymerization progressed, a sharp increase in the reactor temperature was observed. Once the peak was observed, the reaction was allowed to run for about 1 h, which was enough for the reactor temperature to return to its set point. The agitator then was turned off, the jacket temperature was set to 25 °C, and the reactor was allowed to cool. Finally, the CO_2 was released slowly before opening the reactor and collecting the polymer.

In most cases, the polymer obtained consisted of small white particles plus large pieces adhering to the walls and the agitator surfaces. Particle product is taken as any polymer that passes through No. 10 mesh. The total yield was calculated from the total mass of the particles (m_1) and large pieces (m_2), i.e.,

$$\text{total yield} = \frac{m_1 + m_2}{m_o} \times 100\% \tag{1}$$

where m_o is the total mass of the monomer solution plus surfactant. The total yield was typically higher than 95% (some of the polymer was inside the agitator and could not be collected). The yield reported in this document, however, is that of the particles, which was calculated as follows:

$$\text{particle yield} = \frac{m_1}{m_o} \times 100\% \tag{2}$$

Characterization. The collected particles were imaged using an optical microscope (Nikon SMZ-10) at a magnification of 3× or less. Scanning electron microscopy (Hitachi S3200) and energy-dispersive X-ray spectroscopy (EDS) were used to analyze the morphology and surface composition of the particles. EDS (Oxford Isis EDS) analysis was performed at an electron energy of 20 keV, corresponding to 2−5 μm penetration depth. Two spots of 1×1 μm^2 area were analyzed for each sample and the average value is reported. Water absorbency of the particles was analyzed using centrifuge retention capacity (CRC) and absorption under load (AUL)
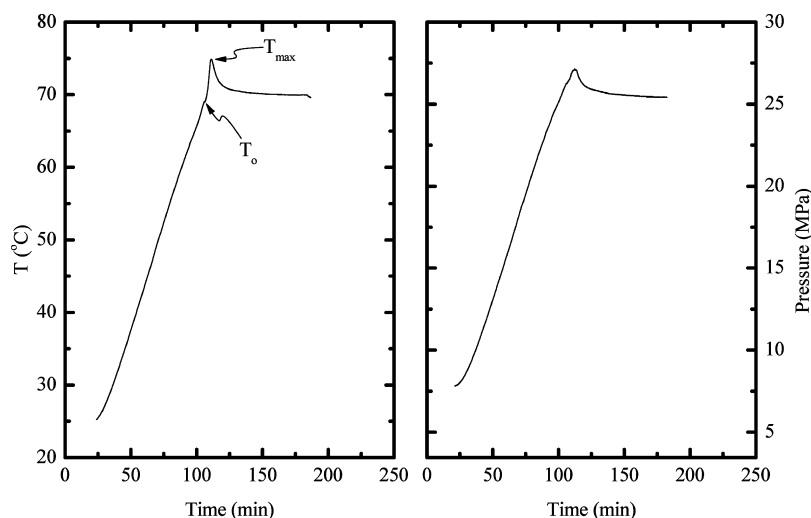
Figure 2. Example of data acquired during a typical polymerization reaction of partially neutralized AA in $scCO_2$. Conditions: solution 1 in Table 2, 6 mL DBE-621, 64% particle yield, 97% total yield.

standard tests. The procedures for these tests are described in standard references.[1]

RESULTS AND DISCUSSION

Our previous studies on precipitation polymerization of AA in CO_2 suggested that coalescence of primary polymer particles led to the formation of larger PAA particles the size of which is affected by the reaction temperature and polymer molecular weight.[24] It was proposed that the coalescence process is favored by higher temperatures and lower molecular weights, resulting in larger particles. However, particle size was limited to less than 100 μm as the molecular weight of the polymer at that point becomes too large for particle coalescence. In order to produce larger PAA particles in CO_2 with acceptable size range for SAP applications, suspension polymerization must be employed.[8]

To overcome the problem imposed by AA solubility in CO_2, use is made of a neutralization step in which AA is reacted with a base, e.g., NaOH, to produce an acrylate salt, e.g., sodium acrylate (NaAA). Neutralization is commonly applied in SAP production processes (solution and suspension) to improve water absorption and retention properties.[1] If CO_2 is to be used as a suspension medium, then neutralization becomes especially important since the acrylate salt is not soluble in either CO_2 or AA.[31] Water is needed to dissolve the monomers, initiator, and cross-linker. The resulting aqueous solution then can be suspended in CO_2 to carry out the polymerization. Typically, only 60−75% of AA is neutralized,[1] therefore the remaining AA can partition into CO_2. Studies on the phase behavior of AA/water/CO_2 system are not available. On the basis of reported data for other carboxylic acids[32] and AA-CO_2 phase behavior,[21] significant partitioning of AA in CO_2 is expected which, as will be shown later, affects the final product.

Polymerization Progress. Figure 2 shows the temperature and pressure profiles during a typical polymerization experiment. Initially, the reactor content was heated and its temperature increased. During this interval, some polymerization is expected to occur. Our previous studies on precipitation polymerization of AA in CO_2 suggested a polymerization rate of the form $[AA][1]^{1/2}$ based on a surface and interior polymerization model.[22] However, since the initiator is not soluble in CO_2, little reaction is expected to occur outside the polymerization medium (aqueous droplets) at this stage.

The polymerization rate in the aqueous droplet can be assumed to resemble that of solution polymerization at the same conditions (temperature and neutralization degree).[8] On the basis of this assumption, the polymerization dependence on acrylic acid and initiator concentrations was expressed as follows:[33,34]

$$R_p = k_p[AA]^{3/2}\left(\frac{fk_d[I]}{k_t}\right)^{1/2} \tag{3}$$

where k_p, k_d, and k_t are the propagation, initiator decomposition, and initiator termination rate constants, respectively, and f is the efficiency factor for the initiator. The propagation and initiator decomposition rates were found to decrease with increasing the degree of neutralization.[34] It was reported that within 3 h, only 40% of the initiator decomposes at 65% neutralization and 70 °C; the decomposition rate is even slower at higher neutralizations and lower temperatures. From the above discussion, we can hypothesize that, during the initial heating period, polymerization will take place at slower rates, resulting in a low molecular weight polymer. The resulting polymer in this stage will affect the viscosity and the suspension, but the final particle size is not expected to be established yet. Indeed, the reactor was found to contain syrup-like dispersion in one experiment where the reaction was stopped just when the sharp increase in temperature was observed. This is typically observed in suspension polymerization during the initial stage of the process (20−60% conversion).[35]

After the initial period of heating, a sharp increase in both temperature and pressure, attributed to a rapid increase in the exothermic polymerization reaction rate, was observed. The temperature at which the rapid increase was observed T_o was between 60 and 70 °C. This point corresponds to the well-known gel effect where the polymer chains become entangled and the termination rate is significantly reduced leading to autoacceleration in polymerization.[36] Within a few minutes of the onset of autoacceleration, the temperature reached a maximum (T_{max}) which ranged between 75 and 95 °C. No studies on PAA polymerization in similar experimental settings

have been found to evaluate the conversion during this period. However, based on methyl methacrylate (MMA) polymerization studies, the major part of conversion occurs within the autoacceleration period and almost complete conversion is reached few minutes after T_{max}.[36] For all of the runs performed in this study (more than 70 with different conditions and surfactants), the total yield was 97 ± 3%, which indicates that polymerization was consistently successful. The particle size is expected to be established in the vicinity of T_{max}.

Temperature control during the autoacceleration period is difficult, as seen from the temperature profile, and can affect the final particle yield. One method to reduce this temperature overshoot is by controlling the degree of cross-linking. Cross-linking has been found to exacerbate the temperature peak in MMA polymerization.[36] A strong effect of cross-linker concentration on the temperature peak was also observed in this work, as can be seen in Figure 3. Controlling cross-linking
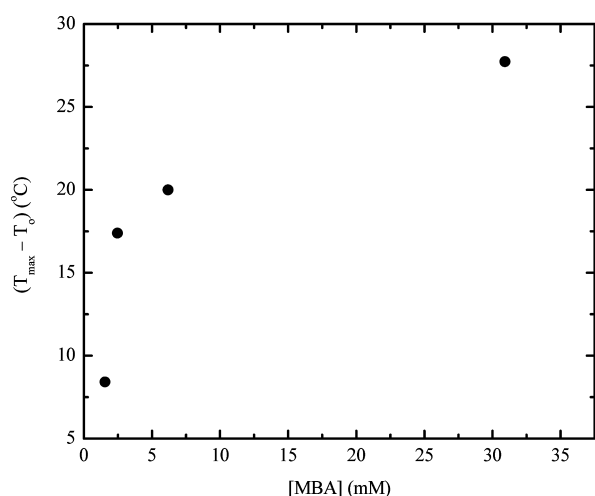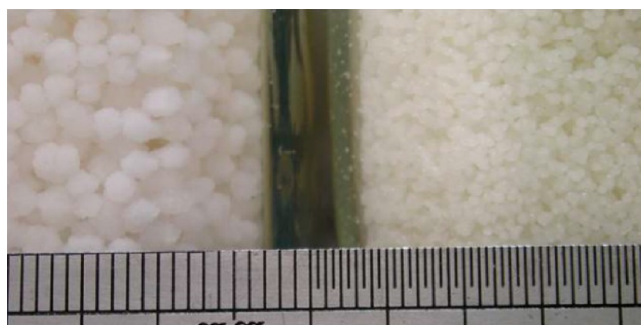

Figure 4. Examples of produced SAP particles after 10 min (left) and the same sample after two hours (right) of opening the reactor. Production conditions: solution 1 in Table 2, 8 mL of DBE-621 surfactant.

Figure 3. Effect of cross-linker concentration on the temperature overshoot in the autoacceleration period. Polymerization conditions: solution 1 (except for the cross-linker), and 8 mL of DBE-621.

is a common practice in commercial production of SAP, where the water absorbency and retention can be improved by limiting the cross-linking density during polymerization and performing postpolymerization surface cross-linking.[1]

Particle Size and Surface Composition. The produced polymer particles were collected after the reactor was depressurized. It was observed that the particles were initially foamed by CO_2. Figure 4 shows the produced particles of one sample at different times after the reactor was depressurized. The particle volume was reduced to less than a quarter of its initial volume within a couple of hours. While not investigated in this study, it is expected that foaming will have a positive effect in reducing the amount of low molecular weight polymer, usually termed extractables,[37] by dissolving or facilitating the diffusion of such materials. This can be advantageous in improving the quality of the SAP product but further studies are needed to investigate the effect of pressure and depressurization rate.

An important aspect of the suspension process is the proper choice of a suspension stabilizer. A stabilizer is usually needed to prevent the droplets from coalescing and to control particle size and morphology.[38] For heterogeneous polymerization in CO_2, various organic surfactants have been used as stabilizers. These surfactants are made of copolymers of hydrophilic, e.g.,

alkene oxide, and CO_2-philic compounds.[6,10,12,14,39] Since CO_2 is not a good solvent for most commercially available surfactants, fluorinated and siloxane-based are commonly employed as the CO_2-philic part.[40,41] However, in most of the reported studies the produced particles were smaller than those usually produced by suspension polymerization (>10 μm)[8] and those suitable for common SAP applications.[1]

In this work, initial studies on polymerizations carried out without using a stabilizer produced no particles. Various stabilizers where considered and the ones shown in Table 1 were found to give the best performance. Optical images of particles produced with the different surfactants are shown in Figure 6. The performance of the different stabilizers was somewhat similar. The particles produced in all cases were consistently larger than 200 μm. The as-produced samples in Figure 6 contain about 1 g water per gram polymer. However, due to the high water absorbency of this material (in excess of 50 g water per g polymer),[1] the particle volumes are not expected to change upon drying at such low water content. This is indeed shown by comparing samples 2 and 6 (before and after drying) in Figure 6.

Most of the polymerization runs in this work utilized 8 mL of the DBE-621 surfactant. While the various stabilizers showed comparable performance, DBE-621 was a reasonable choice for further investigations as it has an HLB value suitable for water-in-oil emulsification.[30] A range of suspension stabilizer levels from 2 to 8 mL, corresponding to 10−40 ppm, was tested. No significant change in particle yield or size was observed at the different stabilizer levels. It is possible that the concentration range tested was too small to cause noticeable change in the product. The 8 mL limit was utilized to provide sufficient stabilization.

To compare the particle yield, it is noted that the process was characterized in terms of the total yield in eq 1, indicating the overall extent of polymerization, and the particle yield in eq 2, indicating the effectiveness of suspension stabilization. While the total yield was consistently high, the particle yield showed much higher variations. On average, the recorded particle yield was 57 ± 20%. The large variation in particle production can be greatly reduced by careful control of operational conditions. Examples of such conditions include the need to apply antifouling agent for the reactor interior walls and the effect of initial reactor purging. Some of these factors have been studied in this work and others require further investigation; but such discussion is beyond the scope of this report.
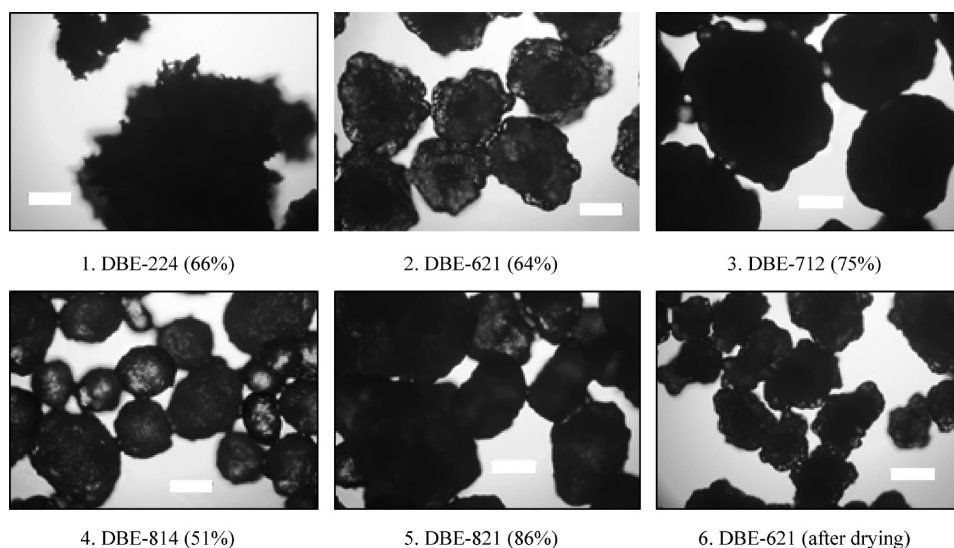
Figure 6. Optical images of SAP particles produced using different surfactants. All images are for as-produced samples (wet), except sample 6 which was dried under vacuum and 80 °C for 2 days. Percentage particle yield for the first five samples is indicated. The scale bar is 200 μm. Production conditions: solution 1 in Table 2, 4 mL of surfactant.

In terms of morphology, it was observed that surfactants with high hydrophilicity (longer hydrophilic chain) produced smoother particles with oilier surface. As the stabilizer hydrophilicity increased, the stabilizer is expected to be more efficient in covering the droplet surface and preventing the AA (which is soluble in CO_2) from leaving the droplets. This is essential as AA is soluble in CO_2 at all reactor conditions throughout the polymerization process.[21] Any AA dissolved in the CO_2 phase could diffuse back into the aqueous droplets during the process and polymerize on the surface. The surfactant molecules might then be trapped in the polymer particles. As a result, the particle surfaces become less smooth and oily. This observation was further confirmed by studying the effect of AA on particle morphology.

As mentioned before, neutralization of AA produces NaAA, which is immiscible in CO_2. Therefore, it is expected that increasing the degree of neutralization will minimize the amount of AA dissolved in CO_2 during the process. The results discussed so far were done using 75% neutralized solution (solution 1 in Table 2). On a different set of experiments, a solution with 97% degree of neutralization (solution 2 in Table 2) was used. The concentrations of initiator and cross-linker were increased as the rate of polymerization at such high degree of neutralization is significantly reduced.[34]

Figure 7 shows optical images of the particles produced at different degrees of neutralization. The 97% neutralized particles had a smoother surface than those at 75%. These
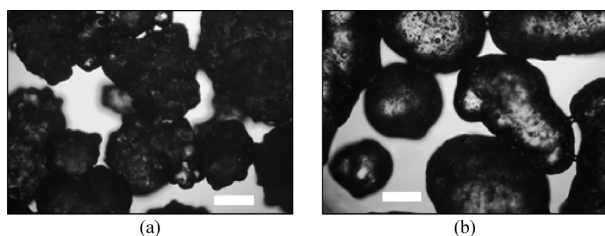
particles looked oily to the naked eye, while the surface of the 75% neutralized particles appeared clean. This is in agreement with the conclusion regarding the effect of AA miscibility in CO_2 on the morphology.

Particle surface composition was analyzed using EDS and compared using the silicon to carbon peaks ratio for each sample. A high Si/C ratio indicates higher surface concentration of the siloxane-based surfactant. Figure 8 shows an
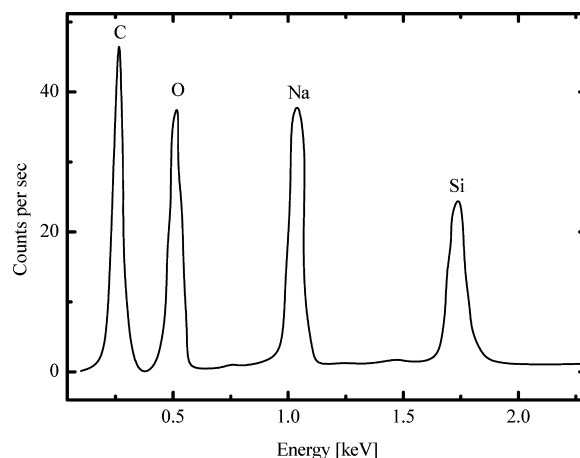

Figure 8. An example of the EDS spectrum obtained from the analysis of polymer particles.

example of the EDS spectrum. Figure 9 shows optical and SEM images taken for samples showing different degrees of agglomeration with the corresponding Si/C ratio. As conversion progress during suspension polymerization, the growing polymer chains in the aqueous droplets form microdomains that aggregate to produce primary particles. These primary particles agglomerate and fuse to form the final particle.[35] The stabilizer role is to control the breakage and coalescence of the droplets during the different growth stages.[42] The images show that more defined agglomerates are formed as the surface concentration of DBE-621 increased. This confirms

Figure 7. The SAP particles produced using 75% (a) and 97% (b) neutralized solutions. The scale bar is 200 μm. Production conditions: 8 mL of DBE-621 surfactant.
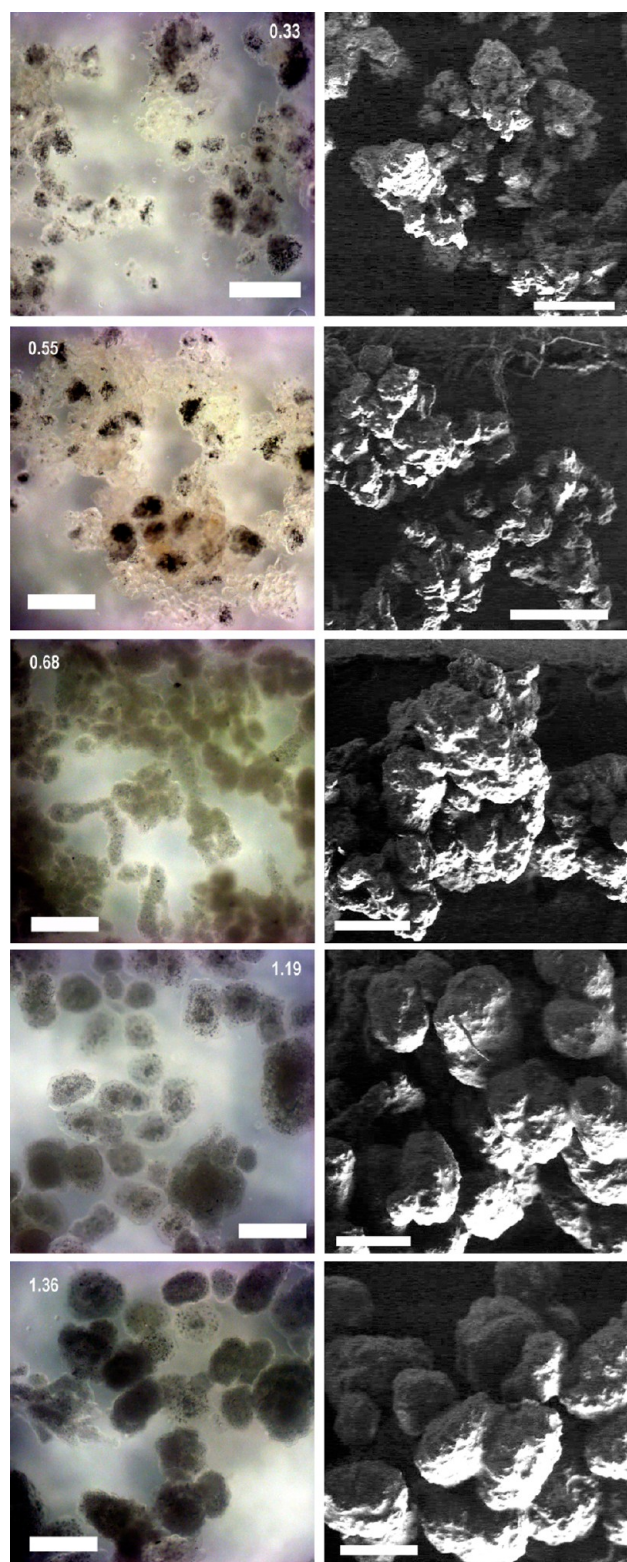
Figure 9. Five different polymer samples imaged using optical microscope and SEM. The corresponding Si/C ratio from EDS analysis is indicated on the optical images. For optical imaging the samples were dispersed in silicon oil using an ultrasonic bath. The scale bar is 1000 μm in the optical and 500 μm in SEM images. Production conditions: solution 1 in Table 2, 8 mL of DBE-621 surfactant.

the role of AA distribution between the aqueous and CO_2 phases in the suspension stability.

Water Absorbency. The performance of the particles produced in this work in terms of water absorbency was measured using two standard tests: centrifuged retention capacity (CRC) and absorption under load (AUL). Both of these tests report the mass of water absorbed per mass of polymer and correspond to different physical properties of application conditions. CRC represents the free-swelling uptake of SAP when surface water is removed by centrifuge.[37] Briefly, this test is done by soaking a known amount of the SAP sample in NaCl solution for a given time, centrifuging the sample, and measuring the mass uptake. In AUL, the amount of water uptake by an SAP sample subjected to a certain pressure is measured. AUL values are usually designated with the applied pressure, which is chosen to represent typical loads encountered in hygiene products applications.

The results for water absorbency analysis are shown in Table 3. The results are compared to corresponding values taken from

Table 3. Water Absorbency Analysis of SAP Particles Prepared Using DBE-621 Stabilizer[a]

property	this work	example of commercial values
CRC, g/g	20.8 ± 3.6	~31[43]
2.07 kPa AUL, g/g	24.2 ± 1.7	~23[17]
6.20 kPa AUL, g/g	15.3 ± 3.5	~18[44]

[a]Each value represents an average of 10 samples.

commercial sources. The data shows that AUL values are comparable to those of the commercial products, while CRC is considerably lower. The CRC test results indicate that it is easier to lose more surface water from the SAP sample produced in this work. This might indicate that the surfactant has an effect on water retention since it is concentrated on the surface of the particle. The overall absorption, as expressed by the AUL results, was not affected. Since the overall absorption is a bulk property, the bulk property of the SAP produced in this work seems to be comparable to that of the commercial product.

However, before exact comparison with commercial products can be made, other possible factors that affect product quality need to be investigated. Such factors include particle morphology and the surface property of the sample (surface cross-linking, as previously discussed).[45]

■ CONCLUSIONS

Particles of cross-linked poly(acrylic acid) were produced by inverse suspension polymerization of partially neutralized acrylic acid in CO_2. The produced polymer has promising characteristics in terms of particle size and water absorbency. Different siloxane-based surfactants were successfully used as suspension stabilizers, producing particles in the desired size range of with particle yield of 57% ± 20%. The fact that acrylic acid is soluble in CO_2 seems to have strong effect on the particle morphology. Reducing the amount of acrylic acid dissolved in CO_2 produced particles with smoother surfaces. It was suggested that the CO_2-dissolved acrylic acid polymerizes on the particle surface during the process reducing the efficiency of the suspension stabilizer. The water absorbency tests suggest that the presence of surfactant on the particle surface reduces its free-swelling absorption capacity but does not affect its bulk absorption.

Further studies are still needed to address some issues, such as the effect of foaming in reducing the extractable content of

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the final product, the exact composition profile of the SAP particles, and general optimization of the polymerization conditions (temperature, pressure, ratio between the CO_2-to-aqueous phases).

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Notes

The authors declare no competing financial interest.

■ DEDICATION

To the memory of Dr. George W. Roberts, who passed away before this manuscript was finalized.

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