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Dispersion of calcite by poly(sodium acrylate) prepared by reversible addition–fragmentation chain transfer (RAFT) polymerization

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Abstract

Calcite is dispersed into nanoparticles with the use of polysodium acrylate, PAANa. The molecular weight distribution of PAANa greatly influences the characteristics of the dispersion. Near-monodisperse PAANa adsorbs irreversibly and totally onto the $CaCO_3$ surface, but for polydisperse PAANa, a mass segregation occurs, where only chains with a selected molecular weight are adsorbed. With polydisperse samples, small spherical $CaCO_3$ particles are generated in addition to calcite crystals. This bimodal dispersion is less viscous than the dispersion containing only calcite crystals.

Keywords: Poly(sodium acrylate); Calcite; Dispersant

1. Introduction

Calcite is a natural crystal of calcium carbonate which can be ground to form a free flowing powder. This powder can be further ground in the presence of water and a small amount of dispersant to form a colloidal calcite dispersion. Polysodium acrylate (PAANa) is most typically used for this application [1]. Each year, around 32 billions lbs of $CaCO_3$ are transformed into a colloidal dispersion which is then used in the paper industry. Ideally, one would want to be able to prepare a calcite dispersion with the highest possible solid content, and the lowest possible viscosity [2]. The viscosity of the resulting dispersion depends on a number of factors, which are often correlated to each other. Among those, one should cite the conditions used during the dispersion experiment (such as pH and CO_2 pressure), the molecular weight and molecular weight distribution of the PAANa and the granulometry of the resulting $CaCO_3$ particles.

The adsorption of PAANa on calcite is believed to be electrostatically driven [3]. Indeed, most dispersants are polyanionic water-soluble polymers, which contain pendant carboxylic groups. Neutral polymers have been shown to be very little efficient as dispersants [3]. The adsorption mechanism of PAA onto $CaCO_3$ surface first involves the adsorption of the shortest PAA chains, as these can diffuse first to the surface [4]. These chains are then displaced by medium length PAA chains through an entropically favorable process. At this stage, the calcium atoms which are at the surface (Ca^+, because coordinated by only one carbonate) are complexed, and the crystal is protected by a globally negative PAANa hairy layer. At low or moderate ion strength, the charges of the PAANa layer generate an electrostatic barrier which prevents the approach of other PAANa chains [5,6]. Therefore, in polydisperse PAA samples, only chains with a precise molecular weight are adsorbed: shorter and longer chains stay in solution, generating an increase in viscosity. At high ionic strength, electrostatic interactions are screened, and high molecular weight chains can exchange with adsorbed chains of lower molecular weight [7]. Consequently, unless working at high ionic strength, only chains of a given molecular weight participate to the dispersion process. This was demonstrated by Foissy et al. [4], who separated adsorbed from

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non-adsorbed chains in a calcite dispersion containing a polydisperse commercial PAANa.

For several years, we have investigated the controlled polymerization of acrylic acid by reversible addition–fragmentation chain transfer (RAFT) [8–10]. Acrylic acid (AA) polymerizes only via a radical mechanism, affording under typical conditions, very high molecular weight or even cross-linked materials. Low molecular PAANa are usually prepared by radical polymerization in the presence of a conventional chain transfer agent, leading to polydisperse polymers with ill-defined structures in terms of number of branches and end-groups. Near-monodisperse PAANa can be prepared by several techniques of controlled radical polymerization [11], among which we chose reversible addition–fragmentation chain transfer (RAFT) polymerization. In this work, we present our study on the adsorption of near-monodisperse, well-defined PAANa on calcite.

2. Experimental part

2.1. Materials

The polymers were prepared according to procedures outlined in Refs. [8,9]. Precise characterization of these polymers is described in Ref. [10]. Polymers 5 and 7 were kindly supplied by the company Coatex, but they are not commercially available. They were prepared by conventional radical chemistry in the presence of a chain transfer agent, and then fractionated in order to reduce the molecular weight distribution. $CaCO_3$ (>99%) was a precipitated calcium carbonate, purchased from Solvay (SOCAL P3, specific surface 13.8 m^2/g). The $CaCO_3$ calcite crystals were scalenohedral (cigar like shape) and their average size was determined by TEM and SEM (Fig. 5).

2.2. Molecular weight determination

Several methods were used to asses the molecular weight distribution. In a first method, molecular weights were determined on a GPC comprising a 515 Waters pump, one or two ultrahydrogel linear 7.8 mm×30 cm columns (mixed bed column with pore size ranging from 120 to 2000 Å) with a guard pre-column, and a 410 Waters refractometer. Elution was performed at 60 °C (0.5 ml/min) using an aqueous buffer ($NaHCO_3$ 0.05 M, $NaNO_3$ 0.1 M, triethanolamine 0.02 M, NaN_3 0.03%). Calibration was relative to PAA standards. GPC samples were prepared by neutralizing with sodium hydroxide, removing solvent in vacuum. The solid residue was dissolved in the GPC eluent before injection. In a second method, molecular weights were determined using an Agilent 1100 HPLC equipped with an autosampler, a column oven, one Shodex OH-Pak SB802 column, one Shodex OH-Pak SB806 column, a Wyatt Dawn EOS light-scattering detector and a Wyatt DSP refractometer. Elution was performed at 25 °C (0.6 ml/min) using an aqueous PBS buffer (300 mOsm, pH = 7.4).

2.3. Dispersions

Low solid dispersions: a suspension of calcium carbonate 25% wt/wt was prepared by introducing 250 g of calcium carbonate in 750 g of water under stirring. This dispersion A was stirred 7 days until obtaining a stable pH. A solution B of sodium polyacrylate was prepared by introducing 12.39 g of a poly(acrylic acid) ($M_w = 5880$ g/mol; solid content = 62.45%) neutralized by NaOH in 997.9 g of water under stirring. Using B as a stock solution, diluted solutions were obtained, with concentrations comprised between 0 g/l and C_B. The dispersions were carried out by mixing 25 g of the calcium carbonate dispersion A and 25 g of a diluted solution of sodium polyacrylates. These dispersions were stirred 24 h, then centrifuged in a Allegra 64R Centrifuge (from Beckman–Coulter) equipped with a F0650 rotor, at 10,000 rpm during 30 min. The supernatant was then separated from the precipitate and analyzed by total organic carbon (TOC) technique. Reference samples were prepared by the same method, but by replacing the 25 g of solution A by 25 g of water.

High solid dispersions: the mineral content for these experiments was 68% wt/wt in $CaCO_3$. In a typical experiment, a basic solution of PAA in water (25% wt/wt) was prepared. Then, in a dispersion apparatus comprising a dispersion bowl and a mechanical stirrer (Raynerie type with defloculation blade), the solution and the mineral were mixed together until the slurry became homogeneous (a few minutes). Viscosity was then recorded, and a new aliquot of PAA was added in order to build the curve viscosity vs. dispersant concentration.

2.4. Adsorption isotherms by total organic carbon (TOC)

The total organic carbon values were determined on a LAB-TOC apparatus (from pollution and process monitoring). Calibration was made between 0 and 100 ppm with a diluted solution of potassium hydrogen phtalate (HPP) prepared from a solution of 10,000 ppm of HPP in water (Purite Analyst 25, $\rho = 18.2$ MΩ. cm). The samples were passed through a solution of H_3PO_4 (85%) (68 g/l) and sodium persulfate (25 g/l) in water (to eliminate the inorganic carbon) using dioxygen as vector gas. The reactor temperature was fixed to 60 °C and the flow to 0.5 ml/min.

2.5. Granulometry

The measurements were effected on a COULTER LS 230 with LS Variable Speed Fluid Module Plus as circulating system. The light is provided by a laser diode at 750 nm. The values of refractive index for calcium carbonate given in the tables of the apparatus issued from literature are 1.59 for real part and 0.1 for imaginary part.

The real part is the part of light diffused and imaginary part is for absorbed light. The value of water is 1.332 (only real part. No absorbed light).

2.6. Zeta potential measurements

The measurements were achieved on a ZETASIZER-3 from MALVERN with a Series 7032 Multi-8 Correlator from Malvern Instruments. The solution of analysis was an aqueous solution of sodium hydroxide at pH = 12.21.

2.7. Electron microscopy

The scanning electronic microscopy (SEM) were achieved with a Hitachi S800 apparatus and the transmission electronic microscopy (TEM) were performed on a Phillips CM120 apparatus.

2.8. Measurement of the Brookfield viscosity

The viscosity was measured using a low shear viscometer from Brookfield Technology (RVT model) at 10 and 100 rpm at 20 °C.

3. Results and discussion

3.1. Polymers used for the dispersion

Several near-monodisperse PAANa (entry 1–4 and 6 in Table 1) were prepared by RAFT polymerization, using dibenzyl trithiocarbonate as chain transfer agent. Although prepared by RAFT polymerization, sample 6 is quite polydisperse. It has been shown that when higher molecular weights are targeted (as in the case for 6), transfer reactions to the solvent (dioxane) and to the polymer become significant, resulting in a loss of control during the polymerization. By contrast, low molecular weight PAANa generated by a RAFT process have a low PDI (Table 1). Samples 5 and 7, kindly provided by Coatex, were prepared by conventional radical chemistry, and were then fractionated by a series of dissolution-precipitation steps, using water and an organic solvent as selective solvent and non-solvent.

The low molecular weight RAFT polymers were found to be linear (only 1.9% branches are generated in the later stage of the polymerization [9]), contrarily to higher molecular weight samples. Sample 6 ($M_w = 31{,}000$ g/mol, PDI = 2.2) contained an average of six branches per chain (four short branches, two long ones) and sample 7 ($M_w = 8500$ g/mol, PDI = 2.6) contained 12 branches per chain (seven short ones and five long ones) [9]. Branches occur from reactions of transfer to polymer, which are significant in the radical polymerization of acrylic acid. Therefore, high molecular weight PAANa should not be regarded as linear products. Considered their level of branching, they are close to hyperbranched materials (branches on branches). On the other hand, for low molecular weight polymers produced by RAFT (polymers 1–4), we have been able to show that the transfer reaction can be avoided if one does not reach high conversion [9].

Using a combination of MALDI-TOF MS and NMR, we were able to show that low molecular weight polymers produced by RAFT polymerization are initiated by a benzyl group and mainly terminated by a proton [10] after neutralization by sodium hydroxide. For higher molecular weight samples, the nature of the end-group was not unravelled. However, the contribution of the end-groups to the adsorption process is expected to be negligible for higher molecular weight samples.

The polydispersity indices (PDI) of the polymers were measured by aqueous GPC, calibrated with PAANa. Such technique is notorious for generating analyte peaks that are broadened by a combination of axial dispersion and interactions of the polyelectrolyte with the packing of the columns, the eluent or with itself [12]. Thus, these PDI values should be taken as a relative measurement of the broadness of the distribution. Commercial PAANa standards, sold with a PDI of 1.4, were measured with a PDI of 1.7 with this technique. The PDI was also found to be dependent on the calibration method. When the GPC was calibrated with poly(ethylene oxide) standards, the PDI of

Table 1
Characteristics of the polymers used for this study

Polymer	M_n (g/mol)[a]	M_w (g/mol)[b]	PDI[b]	M_n (g/mol)[a]	M_w (g/mol)[a]	PDI[a]	Concentration (g/dl)
1	1500	2300	1.5	2400	2500	1.05	53.0
2	3200	4800	1.6	4400	4900	1.1	53.4
3	4000	6400	1.6	5700	6600	1.15	51.4
4	4800	8100	1.7	7300	8300	1.15	50.0
5[c]	2400	5800	2.4	3700	5900	1.6	34.8
6[d]	9200	26,000	2.8	14,000	31,000	2.2	50.8
7[c,d]	2800	8400	3.0	3300	8500	2.6	50.3

[a] Determined with the second GPC method (Section 2).
[b] Determined with the first GPC method (Section 2).
[c] Not obtained by RAFT polymerization.
[d] Branching present.

polymer 5 was found to be 1.3, and the PDI of sample 1 (Table 1) was found to be 1.1 which incidentally corresponded to the PDI as measured by MALDITOF spectrometry, as shown in a previous publication [9].

In the GPC chromatograms, most of the low molecular weight RAFT PAANa samples exhibited a tail toward high elution times (low molecular weights). With detectors, which are more sensitive to high molecular weights, such as light scattering and viscometric detector, the influence of this low molecular weight tail was found to be less pronounced, resulting in a drastic decrease of PDI. For example, the PDI of sample 1 (Table 1) was found to be 1.05 when using an online light scattering detector, and 1.15 when using a combination of online light scattering and viscometric detectors. In most cases, the low molecular weight tail extended to the solvent elution range. By adding ultra-low molecular weight columns, it was possible to achieve a better resolution, and have a clear separation between polymeric oligomers of molecular weight 200 g/mol and higher from species which are not polymeric (residual initiator, inhibitor, salt, dissolved air). However, in this case, it was also necessary to inject a larger amount of polymer because the peak was artificially broadened by the greater column length, resulting in a low signal over noise. When a larger quantity of analyte is introduced, the analyte peak becomes artificially broadened toward high molecular weight, likely because of the presence of electrostatic repulsion between polyelectrolyte chains which is a well-known effect in polyelectrolyte size exclusion chromatography [12]. Thus, it seems elusive to give an absolute measurement of PDI. But the ranking of the polymers from lowest to highest PDI was the same when using one analytical technique or another one, thus ensuring consistency. In Table 1, we have indicated two sets of PDI values: the pessimistic set (higher PDIs) corresponds to the values obtained for an aqueous GPC equipped with a refractometric detector (corresponding to previously published results [8–10]) and the optimistic one for an aqueous GPC equipped with a light-scattering detector (Section 2). Using both techniques, the weight-average molecular weights and peak average molecular weights of the polymers were virtually identical, whereas the number-average molecular weights were usually smaller for the RI detection (and PAANa calibration), because this detector is more sensitive to the presence of a low molecular weight tail. The PAANa were kept as aqueous solution of known concentration and ionic strength, in order to avoid the hydration of solid samples by environmental water. Their pHs were adjusted to 11.5 ± 0.5.

3.2. Viscosity of the dispersion

In a typical dispersion experiment, a slurry of mineral in water (typically 68% in weight) is mixed with a certain amount of PAANa and mechanically grinded. The stabilization of the resulting PAANa nanoparticles is due to electrostatic repulsion. Indeed, prior to dispersion, the zeta potential of $CaCO_3$ was measured at −14 mV and after dispersion, it was −43 ± 5 mV, independently of the characteristics of the PAANa.

Brookfield viscosity (measured at 10 rpm, Fig. 1 and at 100 rpm, Fig. 2) vs. the quantity of PAANa shows a typical bell curve: when not enough dispersant is present, the viscosity is high due to the presence of partially flocculated particles. The viscosity decreases with x until a minimum is reached, after which the viscosity increases because of the presence of water-soluble polymer in solution. When comparing the performance of RAFT polymers (1–4, PDI < 1.15) vs. a PAA made by a conventional radical process (7, PDI = 2.6), the amount at which the minimum viscosity is reached is lowered. This is a consequence of the narrower molecular weight distribution: in RAFT, most chains have the right molecular weight to contribute to the adsorption process. In an unexpected manner, the viscosity at saturation is slightly lower for the polymer with the highest PDI. Such behavior is not observed in the case of the dispersion of titanium dioxide by PAANa (Fig. 3) for which both the saturation amount and the viscosity at saturation decrease with the PDI of the polymer. Below, it will be seen that the irregular behavior of $CaCO_3$ has been attributed to the precipitation of PAANa chains by Ca^{2+} ions and the generation of a new crop of $CaCO_3$ particles during the dispersion process.

3.3. Adsorption isotherms of PAANa on $CaCO_3$

A typical adsorption isotherm, as shown in Fig. 4, represents the amount of adsorbed PAANa vs. the amount of free PAANa in solution. The first part of the curve (vertical part) corresponds to the complete adsorption of PAA onto calcium carbonate. In the case of a RAFT sample, which is

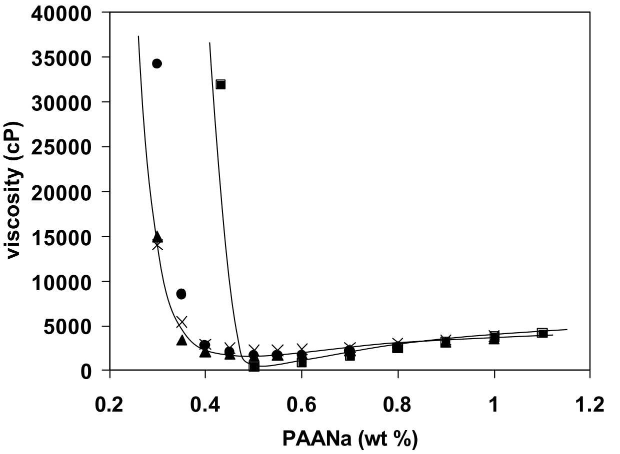

Fig. 1. Brookfield viscosity (at 10 rpm) vs. concentration of PAANa measured as the weight percentage of dry dispersant relative to the weight of dry $CaCO_3$. (■) polymer 7 (M_w = 8500 g/mol, PDI = 2.6), (×): polymer 2 (M_w = 4900 g/mol, PDI = 1.1), (●): polymer 3 (M_w = 6600 g/mol, PDI = 1.1), (▲): polymer 4 (M_w = 8300 g/mol, PDI = 1.15). The lines are only to guide the eyes.

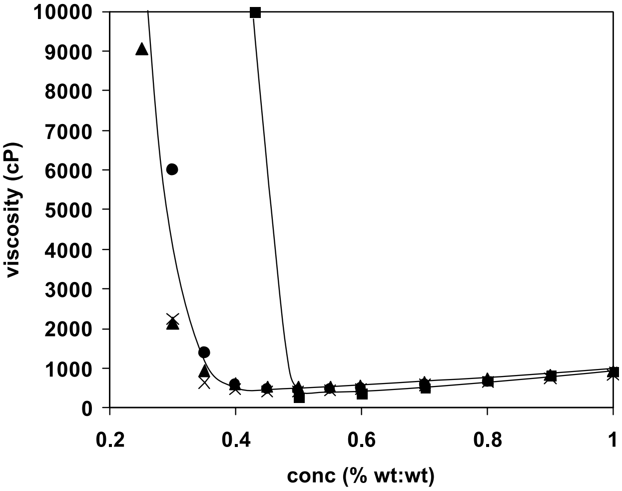

Fig. 2. Brookfield viscosity (at 100 rpm) vs. concentration of PAANa measured as the weight percentage of dry dispersant relative to the weight of dry $CaCO_3$. (■): polymer 7 ($M_w = 8500$ g/mol, PDI = 2.6), (×): polymer 2 ($M_w = 4900$ g/mol, PDI = 1.1), (●): polymer 3 ($M_w = 6600$ g/mol, PDI = 1.1), (▲): polymer 4 ($M_w = 8300$ g/mol, PDI = 1.15). The lines are only to guide the eyes.

near-monodisperse, adding more PAA past the saturation point does not result in any further adsorption: the second part of the isotherm is flat. However, with a polydisperse dispersant such as 7 (PDI = 2.6), additional adsorption is observed as shown by an upward curvature. This is due to the displacement of adsorbed low molecular weight chains by higher ones. These adsorption isotherms are typical of irreversible non-equilibrium adsorption regimes, and they do not correspond to Langmuir isotherms [13].

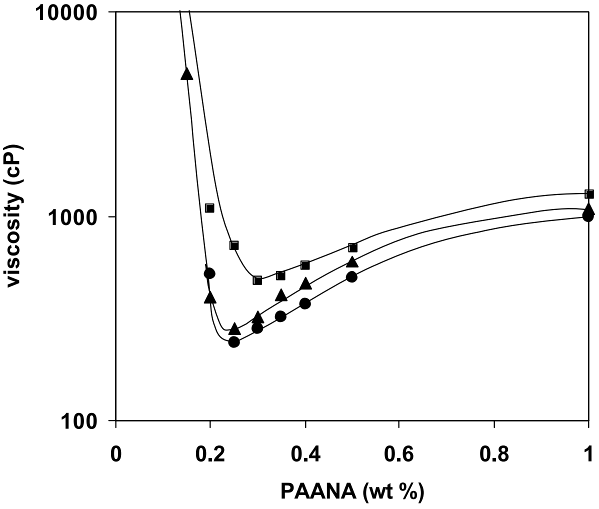

Fig. 3. Brookfield viscosity of a titanium dioxide dispersion 66 wt% in water (at 100 rpm) vs. concentration of PAANa measured as the weight percentage of dry dispersant relative to the weight of dry TiO_2. (■): polymer 7 ($M_w = 8500$ g/mol, PDI = 2.6), (▲): polymer 4 ($M_w = 8100$ g/mol, PDI = 1.15), (●): polymer 2 ($M_w = 4900$ g/mol, PDI = 1.1). The lines are only to guide the eyes.

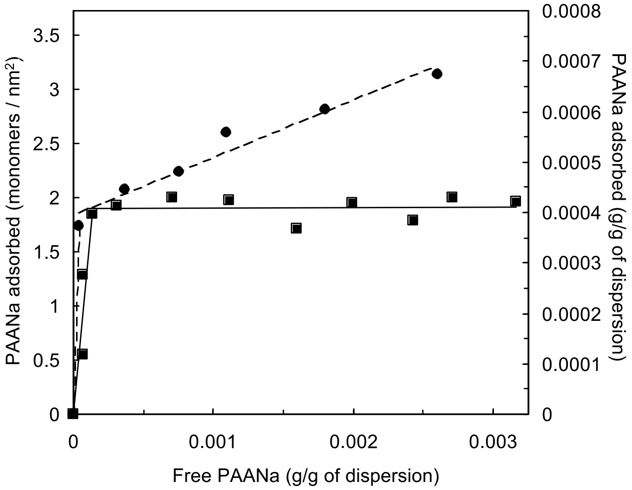

Fig. 4. Adsorption isotherms of PAANa on $CaCO_3$ (12.5 wt%), (■): polymer 2 ($M_w = 4900$ g/mol, PDI = 1.1), (●): polymer 5 ($M_w = 5900$ g/mol, PDI = 1.6).

Adsorption isotherms have been obtained for dispersions at 12.5 wt% $CaCO_3$ in water. At higher solids, the separation of the $CaCO_3$ particles from the supernatant proved to be difficult, leading to erroneous results. The saturation coverage by RAFT polymer is reached for 0.0004 ± 0.0001 g of PAANa per gram of dispersion, which corresponds to 0.32 ± 0.08% wt/wt of PAANa relative to the weight of $CaCO_3$. For the RAFT polymer, the saturation obtained by Brookfield viscosity measurements was found to occur at 0.40% wt/wt in the viscosity vs. concentration curve (Fig. 1). Because the concentration of $CaCO_3$ is different for both experiments, the saturation coverages are not necessarily identical [13]. For a polydisperse polymer, the saturation is not reached, even when 2.5% wt/wt are used (last point of the adsorption isotherm in Fig. 4). This seems to indicate that the minimum in the viscosity vs. dispersant concentration curve does not necessarily correspond to the point at which the surface is saturated. It is also interesting to note that it is possible to adsorb more of the polydisperse polymer than of the near-monodisperse one. Possibly, with a polydisperse dispersant, small chains can fill uncovered patches of the surface, resulting in an overall denser packing.

The specific surface of the calcite, as provided by the manufacturer, is 13.8 m^2/g. After dispersion, the average calcite crystal looks like two cones sharing a common circular base of radius 106 ± 22 nm, and of average height 741 ± 37 nm (Fig. 5, measured on 500 different crystals). The average surface of a crystal is 4.75×10^{-13} m^2, and its volume is 1.57×10^{-14} cm^3. Using a density of 2.71 for calcite, one finds a specific surface of $\sigma = 11.2$ m^2/g, which is in good agreement with the value quoted by the manufacturer. Using an average value of $\sigma = 11$ m^2/g and a saturation amount of 0.32% wt/wt, one finds that, on average, an acrylate stabilizes a surface of 54 Å^2. To our knowledge, crystallographical data for PAANa have not been published, but based on the density of bulk PAANa ($d \sim 600$ g/l), each acrylate occupies an elementary volume

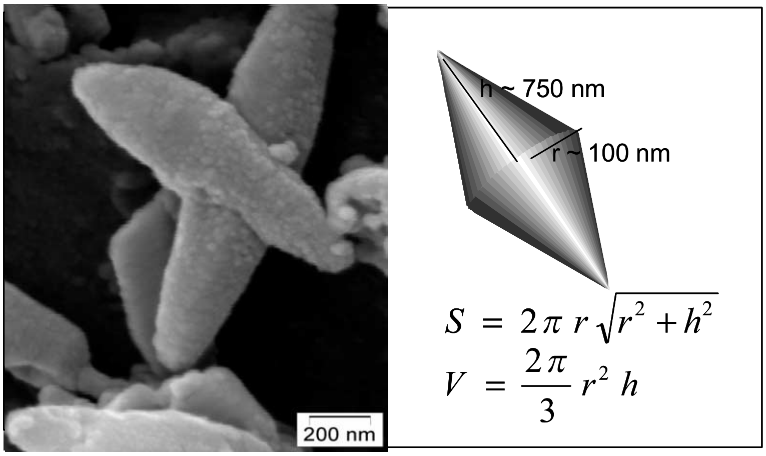

Fig. 5. Scanning electron microscopy picture (SEM) of calcite crystals dispersed with PAANa 2 (Table 1), and geometrical representation of an average crystal.

defined by $V = M_w/(dN_a)$, where M_w is the molecular weight of sodium acrylate, and N_a is the Avogadro's number. The surface covered by a series of flattened sodium acrylates will be close to $V^{2/3} = 41\ \text{Å}^2$. This very approximate calculation tends to indicate that the adsorbed PAANa has multiple attachment points to the surface, since its conformation is probably close to the one of a flattened PAANa. Depending on the persistence length of the polymer, the adsorption of a single chain of polyelectrolyte on a surface has been predicted by Odijk [14] to be coiled (low persistence length) or flat (high persistence length) [15], indicating that in our current conditions, we are probably under the second regime.

When one compares adsorption isotherms for polymers of different polydispersities (Fig. 4), one observes that for the less disperse polymer (2, PDI = 1.1), no chains adsorb after the saturation point, whereas for the polydisperse polymer (5, PDI = 1.6), an exchange between adsorbed and free chains of higher molecular weight occurs, as shown by a positive curvature of the isotherm past the saturation. Past this point, the surface is completely covered, but 'more' polymer (in weight) can be adsorbed, likely because of the displacement of small adsorbed chains by larger ones. This phenomenon was nicely predicted by De Laat et al. [16] and demonstrated by Geffroy et al. [4]. As stated in the introduction, the adsorption of PAANa on a surface is accompanied by a mass-segregation phenomenon. For the polydisperse polymer, the small chains are displaced by the larger ones, but very high molecular weight chains stay in solution because of the electrostatic barrier generated by the adsorbed layer.

The adsorption isotherm of polymers having molecular weight between 1500 and 9200 g/mol (polymers 1, 2 and 6) have striking similarities (Fig. 6). For all of them, a saturation point exists under which the adsorption of the polymer is complete and irreversible. This saturation point does not depend on molecular weight, and corresponds to a specific surface coverage of $54\ \text{Å}^2$ per acrylate. In agreement with the above observations, this again strongly suggests that the adsorbed polymer lays flat on the surface. If loops were present, one would expect that their size would increase with increasing molecular weight, resulting in an apparent increase of the amount of polymer used to saturate the surface.

When a low molecular weight polymer is used (1, $M_w = 2500$ g/mol, PDI = 1.05), the slope of the isotherm is slightly increasing past the saturation point, indicating that low molecular weight chains are displaced by higher ones. This indicates that despite its low measured polydispersity (PDI = 1.05), the polymer is not completely monodisperse, which is expected for the synthesis of a 16-mer, where the number of statistical events is not large enough to average out the heterogeneities generated for example by a non-instantaneous chain initiation or by chain termination events. For example, for a 16-mer obeying a perfect Poisson distribution, the fraction of chains which are smaller than 10 units or larger than 21 units represent no less than 26% (respectively 38%) in number (respectively in weight).

When a high molecular weight polymer is used (6, $M_w = 31{,}000$ g/mol), a *S*-curve is observed past the saturation point. This *S*-curve corresponds to the precipitation of high molecular weight chains in the presence of Ca^{2+} ions. Such an effect was already observed by Foissy et al. [17]. Just past the saturation point, the concentration of Ca^{2+} is high, and adding additional PAANa results in precipitation of the calcium salt of polyacrylic acid. When free PAANa chains are separated from dispersed calcite, the precipitated chains are also removed from the soluble fraction, resulting in an apparent increase of the amount of adsorbed (+precipitated) polymer. Further away from the saturation point, adding more PAANa does not result in precipitation, since the concentration of Ca^{2+} is smaller than the one of the acrylate. Thus, past the zone of precipitation in the adsorption isotherm, an essentially flat isotherm is observed, indicating that all no adsorbed chains are displaced, as expected for a near-monodisperse polymer.

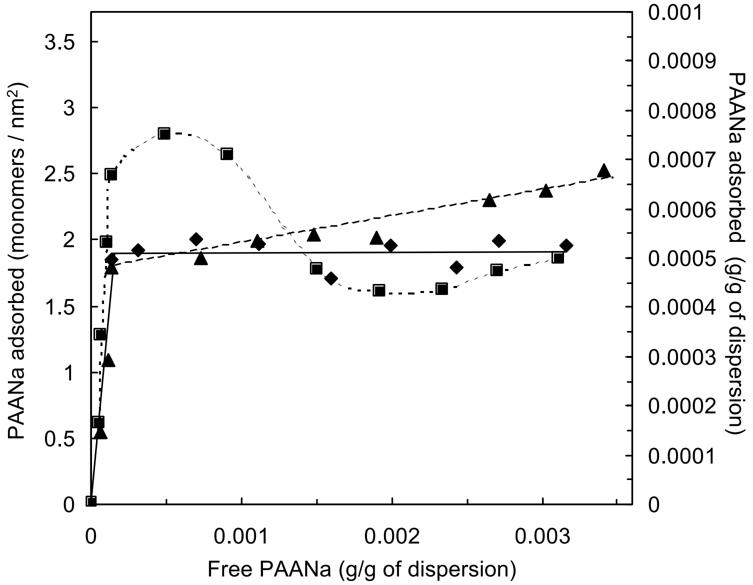

Fig. 6. Adsorption isotherm of PAA on CaCO$_3$ (12.5 wt%). (◆): polymer 2 ($M_w = 4900$ g/mol, PDI = 1.1), (■): polymer 6 ($M_w = 31{,}000$ g/mol, PDI = 2.2), (▲): polymer 1 ($M_w = 2500$ g/mol, PDI = 1.05).

3.4. Granulometry of the dispersion

In our experiments, a CaCO$_3$ slurry is transformed into nanoparticles via a mechanical grinding process performed in the presence of PAANa dispersant. Not surprisingly, during this experiment, fines are generated. These fines appear under the form of spherical particles (Fig. 7) having a number average diameter of 77 nm ($\sigma = 8$ nm). These particles do not correspond to calcite crystals, and are not present in the calcite samples prior dispersion.

At this stage, we were unable to quantify the exact amount of these fines, however, they appear to be in larger amount when the dispersion is carried out with polymer 7 (PDI = 2.6) rather than with polymer 2 (PDI = 1.1). Their amount also increases with the quantity of PAANa used for the dispersion. We putatively propose that these particles are formed upon precipitation of calcium polyacrylate, which may eventually act as nucleus for the formation of a new crop of CaCO$_3$ particles (Fig. 7). At neutral pH, CaCO$_3$ solubility is low ($<10^{-4}$ mol/l) but the equilibrium between the precipitate and the solute is rapid [18]. The precipitation of calcium polyacrylate will result in a diminution of the concentration of Ca^{2+} in solution, followed by a dissolution of calcite particles to maintain the concentration of ions at saturation. The dissolution of calcite particles to the benefit of growth of the spherical smaller particles can proceed until an equilibrium is reached, for example when all PAANa is used up, either under the form of a precipitate, or as a stabilizer at the mineral surface.

Above, it has been shown that precipitation is particularly notable with PAANa of higher molecular weight, explaining why these small spherical particles are virtually absent in samples prepared with near-monodisperse low molecular weight PAANa. This also may explain why the viscosity of a CaCO$_3$ dispersion is lower with a polydisperse dispersant (Fig. 1). Indeed, it is well known that at same solid content, the viscosity of a high-solid dispersion with a broad particle size distribution is less than the viscosity of a monodisperse dispersion [19]. This is due to the fact that small particles can fill the voids in between large particles, resulting in a more optimal packing. When a polydisperse PAANa is used, small spherical particles appear in addition to the calcite crystals, which can result in a decrease of viscosity. Interestingly, for the dispersion of titanium dioxide for which no precipitation occurs (since there are

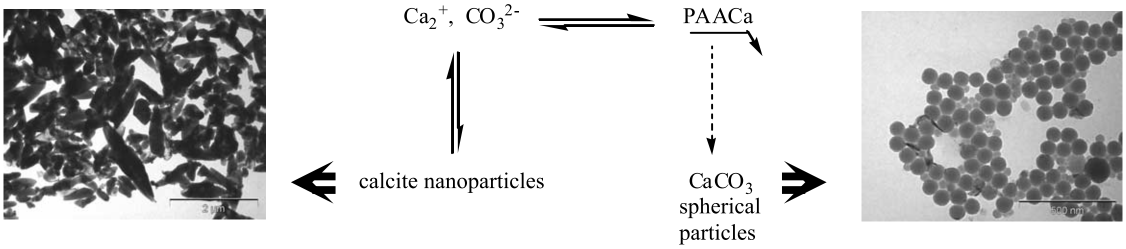

Fig. 7. TEM micrographs of calcium carbonate dispersion using polymer 5 for the dispersion. Both the clichés of the calcite crystals and the spherical particles are issued from the same microscopy grid.

no titanium ions in solution), the viscosity is larger with polydisperse PAANa, due to the presence of non-adsorbed chains in water (Fig. 3). By contrast, in the case of calcite dispersion, the viscosity is dictated by two competing phenomena: with polydisperse samples, high molecular weight PAANa are excluded from the surface resulting in an increase of the viscosity, but, upon precipitation, these high molecular weight chains serve as nuclei for a new set of particles producing a decrease of the viscosity. In our precise conditions, the second factor (surface reconstruction) seems to be predominant over the first one, but we expect that the balance between these two antagonistic factors should be highly dependent upon the precise conditions of the dispersion experiment, such as the temperature, the shear rate in the dispersion reactor, the CO_2 pressure and the pH. The influence of each of these factors is currently under scrutiny in our laboratory.

4. Conclusion

The dispersion of $CaCO_3$ by PAANa is a relatively complex process. Under our experimental conditions, the adsorbed chains are adsorbed in a flat conformation, and generate an electrostatic barrier against aggregation. When near-monodisperse PAANa is used, all chains are adsorbed at the interface until saturation is reached. For high molecular weight polymer, precipitation of calcium polyacrylate can occur if the concentration of dispersant is too low. When polydisperse PAANa is used, a mass segregation phenomenon occurs, and only chains of a given molecular weight ($M_w \sim 5000$ g/mol) adsorb, the other ones staying in solution. Unexpectedly, the presence of polymer in solution does not result into an increase of viscosity.

We have proposed that the formation of small spherical particles of $CaCO_3$ is responsible for the lower viscosity observed with polydisperse PAANa dispersants. It is possible that these particles are issued from the precipitation of calcium polyacrylate, which acts as a nucleus. This phenomenon is currently under scrutiny in our laboratory.

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