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Investigation of four different Laponite® clays as stabilizers in Pickering emulsion polymerization

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Abstract

Clay-armored polymer particles were prepared by emulsion polymerization in the presence of Laponite platelets that adsorb at the surface of latex particles and act as stabilizers during the course of the polymerization. While Laponite® RDS clay platelets are most often used, the choice of the type of clay still remains an open issue that is addressed in the present paper. Four different grades of Laponite were investigated as stabilizers in the emulsion polymerization of styrene. First, the adsorption isotherms of the clays, on preformed polystyrene particles, were determined by ICP-AES analysis of the residual clay in the aqueous phase. Adsorption of clay depended on the type of clay at low concentrations corresponding to adsorption as a monolayer. Adsorption of clay particles as multilayers was observed for all the grades above a certain concentration under the considered ionic strength (mainly due to the initiator ionic species). The stabilization efficiency of these clays was investigated during the polymerization reaction (free of any other stabilizer). The clays did not have the same effect on stabilization, which was

related to differences in their compositions and in their adsorption isotherms. The different grades led to different polymer particles sizes, and therefore to different polymerization reaction rates. Laponite RDS and S482 gave similar results, ensuring the best stabilization efficiency and the fastest reaction rate; the number of particles increased as the clay concentration increased. Stabilization with Laponite XLS gave the same particles size and number as the latter two clays at low clay concentrations; but it reached an upper limit in the number of nucleated polymer particles at higher concentrations indicating a decrease of stabilization efficiency at high concentrations. Laponite JS did not ensure a sufficient stability of the polymer particles, as the polymerization results were comparable to a stabilizer-free polymerization system.

KEYWORDS. Pickering emulsion polymerization, clay, Laponite, stabilization, adsorption.

1. Introduction

Polymer nanocomposites allow combining polymer properties (*e.g.* stiffness, toughness) with those of inorganic materials (*e.g.* resistance to ignition) which enhances the end-use product properties (*e.g.* barrier properties, fire resistance or optical properties) while reducing their cost.[1] Among inorganic materials, Laponite® [2] clay (BYK Additives Ltd) can be easily exfoliated in water as a colloidal suspension, making it particularly interesting for the stabilization of emulsions[3] or latex particles.[4–6] Therefore, Laponite clay has been widely used to stabilize polymer particles during emulsion polymerization without any other stabilizing agent, which we refer to as Pickering emulsion polymerization in this work.

Pickering emulsion polymerization is a classical emulsion polymerization process, but where the conventional emulsifier is replaced by solid inorganic particles/platelets that adsorb at the surface of polymer particles during the course of the polymerization. It is a free radical polymerization (of styrene in the present case) initiated by a water-soluble initiator (potassium persulfate in the present case). The monomer is emulsified as coarse droplets, so that polymerization takes place in the aqueous phase and inside the monomer-swollen polymer particles after such particles have nucleated. It is to be distinguished from Pickering miniemulsion polymerization where a miniemulsion of monomer of sub-micron droplets is prepared such that the radicals generated in the aqueous phase are efficiently trapped by the monomer droplets; hence, the polymerization takes place in the monomer droplets and the final polymer particles correspond to the initial monomer droplets if coagulation is prevented.

The term Laponite is a brand that includes quite a large number of materials.[2] In the framework of clay chemistry, Laponite is a synthetic hectorite.[7] It is chemically composed of magnesium

silicates (the neutral equivalent is talc) where part of the magnesium atoms has been substituted by monovalent lithium atoms. Such isomorphic substitution causes a departure from electrical stoichiometry that provides a negative surface charge to the platelets balanced by sodium cations. The charge is related to the substitution rate of Mg by Li being in the 5-10 mol% range. Physically, this clay is made of disc-shaped crystals (*i.e.* platelets) of approximately 25 nm diameter and 0.92 nm thickness.[8] Its density is 2570 kg m^{-3} [9] and it has a melting point of 900 °C. Each elementary particle is a crystal composed of about 1500 unit cells, and each cell is composed of six octahedrally coordinated atoms, either divalent magnesium or monovalent lithium, sandwiched between two layers of four tetrahedral silicon atoms. These groups are balanced by twenty oxygen atoms and four hydroxyl groups. In the powder form, the crystals share interlayer Na^+ ions forming stacks.

Though there are several grades of Laponite, many articles in the literature do not specify the studied grade, preventing a discussion with regards to the type of Laponite. Nevertheless, Laponite RD has been the most frequently used in emulsion or miniemulsion polymerizations or for the formation of gels.[10] Laponite RDS was found to be an efficient stabilizer of polymer particles produced by surfactant-free emulsion polymerization with[11] or without addition of an auxiliary polar (macro)monomer.[10] Increasing the clay concentration increased the number of nucleated polymer particles, and hence decreased their final size. Moreover, Laponite RDS platelets adsorbed as multilayers on the surface of the polymer particles during the polymerization reaction as well as during adsorption experiments performed at room temperature on previously formed latex particles.[10]

The objective of this work is to investigate the effect of different Laponite clay grades on the reaction rate and stabilization of polymer particles synthesized by surfactant-free emulsion

polymerization. Four different grades were investigated: Laponite RDS, S482, XLS and JS. Such Laponite grades have been selected because they can be dispersed in water as individual nano-platelets with no significant aggregation up to rather high concentrations, and present a long-term stability due to the stabilization of the rims by a peptizing agent. The character "S" in the grade name signifies that they are all sol-forming grades specifically designed to produce low viscosity dispersions in water through the addition of a so-called peptizing agent. The role of the peptizing agent is to avoid gel formation when dispersing the clay in water (more details are given below).

2. Materials and Methods

2.1. Materials

The monomer, styrene (Acros Organics, 99% extra pure, stabilized) and the initiator, potassium persulfate (KPS, Sigma-Aldrich, minimum 99%) were stored in a fridge until use. The four Laponite® clays: RDS, XLS, JS and S482, were kindly donated by Rockwood additives (now BYK Additives Ltd). Deionized water of 18 MΩ cm resistivity was used throughout the work.

2.2. Laponite clays

In this work, three grades of Laponite were selected among the temporary sol-forming grades that are: Laponite RDS, XLS and JS. These clays can be well dispersed in water below 10 wt%. Also, Laponite S482 was selected as a permanent sol-forming grade. Fluid dispersions can be prepared up to 30 wt% concentration in water. All used clays are in powder form and contain a peptizing agent to prevent the formation of a thixotropic gel structure when dispersed in water.

The anionic peptizing agent adsorbs to the positively charged rims of the clays platelets. Charge reversal of the rims into negative charges avoids the electrostatic attraction between the rims and the faces. Tetrasodium pyrophosphate ($Na_4P_2O_7$) is used as peptizing agent for Laponite RDS, XLS and JS whereas (1-hydroxyethylidene)bisphosphonate ($C_2H_8O_7P_{2.4}Na$) (CAS # 7414-83-7) is used for the stabilization of Laponite S482. Laponite JS is a fluorohectorite that has its MgOH groups partly fluorinated (*i.e.* the OH groups are substituted by F atoms). The mean chemical compositions of these clays provided by the suppliers' product data sheet are presented in Table 1.

Table 1. Chemical composition of the Laponite grades used in this study

Chemical composition (%, dry basis)		**Laponite RDS**	**Laponite S482**	**Laponite XLS**	**Laponite JS**
CAS #		53320-86-8		53320-86-8	64060-48-6
Components	SiO_2	54.5	54.5		50.2
	MgO	26.0	26.0		22.2
	Li_2O	0.8	0.8		1.2
	F	0	0		4.8
Water (loss on ignition)		8.0	ns	8.2	8.7
x		0.5		0.5	0.75
y		0	0	0	2.4
Surface area ($m^2\ g^{-1}$)		330	370	330	300
pH of a 2% suspension		9.7	9.8	9.7	10.0
Peptizing agent	Na_2O	5.6	ns	5.6	7.5
	P_2O_5	4.4	ns	4.1	5.4

*ns = non specified

Ideal Laponite has the following chemical formula:[12,13]

$$Na_x^+\left[\left(Si_8Mg_{6-x}Li_xF_y\right)O_{20}(OH)_{4-y}\right]^{-x}$$

Though the chemical compositions given by the supplier do not fit the general chemical formula, the values of *x* and *y* have been tentatively estimated in Table 1 from the chemical compositions. Besides, Laponite powder contains around 8 wt% water which should be either eliminated before weighing (by heating) or taken into consideration in the calculation of the concentration.

2.2.1 Laponite dispersion in water

Laponite platelets are hydrophilic. Their dispersion in water leads to pH = 8-9. The release of the Na^+ ions from the clay surface generates a strongly negative charge on their basal faces (700 elementary charges). A weakly positive charge present on the rim of the disks[4] causes destabilization and gel formation in the absence of specific stabilizer of the rims.[14] The Laponite clays used in this work contain a peptizing agent: tetrasodium pyrophosphate (10 wt% based on clay) adsorbed onto the positively charged rims (edges); the tetravalent negatively charged pyrophosphate ions neutralize the rim charge and decrease electrostatic attractions between the positively charged rims and the negatively charged faces, and therefore avoid gelation. Reducing such interactions contributes to a longer stability of the dispersions in water. Laponite S482 is stabilized by the (1-hydroxyethylylidene)bisphosphonate that acts by the same mechanism as sodium pyrophosphate. Note that neutral low molar mass polyethylene oxide molecules have also been reported to delay Laponite aggregation by forming a steric barrier which prevents contact between platelets.[10] Dispersion of Laponite RDS in water has previously been investigated in order to determine the efficiency of dispersion and the time period before aging starts.[10,15–17] TEM and cryo-TEM images indicated that the dispersion mainly contained isolated particles and only few stacks of two to six platelets, with an interlayer thickness of 1 nm.

2.2.2 Clay suspension aging

Aqueous Laponite suspensions undergo chemical aging, which is characterized by leaching of Mg^{2+} ions taking place according to the following chemical reaction in acidic medium.

$$Si_8Mg_{6-x}Li_xH_4O_{24}Na_x + 12\ H^+ + 8\ H_2O \rightarrow x\ Na^+ + 8\ Si(OH)_4 + (6-x)\ Mg^{2+} + x\ Li^+$$

This reaction takes place in contact with CO_2 which dissolution in water generates an acidic medium (carbonic acid). It can be avoided by working under inert atmosphere.[8] Conductometry indicated full dispersion in 1 hour and no aging (via the release of lithium and magnesium ions) after 4 days at ambient temperature, which provides an estimate of the time period during which the non-aggregated dispersion can be safely used for polymerization.

2.3 Emulsion polymerization experiments

2.3.1 *Ab initio* semi-continuous polymerization experiments

A 1 L reactor was used with mechanical stirring at 400 rpm using a three blades Bohlender propeller. The polymerization reaction started by a batch period for polymer particles nucleation followed by a semi-continuous part for their growth. First, a known amount of clay was dispersed in 800 g of water for 30 min under stirring in the reactor at ambient temperature, degassed using nitrogen, and heated to 70 °C using a thermostated bath. Then, 40 g of styrene were added and the polymerization was initiated by adding 1.6 g of KPS dissolved in a small amount of degassed water. During the reaction, the stream of nitrogen was moved upwards off the reaction medium to maintain saturation of the gaseous atmosphere with nitrogen. At the end

of the batch reaction, semi-continuous monomer addition was started where 160 g of monomer was added at a flow rate of 0.02 g s^{-1}. Samples were withdrawn at specific time intervals to measure the solids content (SC, *i.e.* mass fraction of solid) using a thermogravimetric balance and the particle size, which allowed calculating the particle number density. The solids content was used to calculate the amount of polymer and the monomer conversion (after subtracting the mass of clay and initiator). The coverage of the polymer particles surface by clay platelets was calculated as the ratio of the surface area of platelets' faces discs (of 25 nm diameter) to the polymer particles' area assuming spherical shape and full clay dispersion.

2.3.2 Surfactant-free polystyrene seed latex

The seed latex was synthesized for the adsorption analyses. It was prepared batch-wise using 4 g of KPS in 800 mL degassed water and 3 wt% of styrene (with respect to water). The final latex had a mean particle size of 300 nm and was concentrated under reduced pressure in a Rotavapor® up to 20 wt% solids content. Such high concentration is required since the adsorption study using analyses by inductively coupled plasma - atomic emission spectroscopy (ICP-AES) involves diluting the latex with a dispersion of clay. Then, the latex was cleaned about 10 times with ion exchange resins (Dowex® Marathon™ MR3) to eliminate free ionic species resulting from initiator decomposition and water-soluble species. The washing steps were repeated until a constant conductivity was obtained.

2.4. Characterizations

2.4.1 Particle size measurements

Particle mean size and size distribution were measured by dynamic light scattering (Zetasizer, Nano ZS, Malvern) at 25 °C at a fixed scattering angle of 173° after dilution in water. The *z*-average hydrodynamic diameter (d_p, nm) is defined as $d_p = \sum n_\mathrm{i} d_\mathrm{pi}^6 / \sum n_\mathrm{i} d_\mathrm{pi}^5$, where n_i is the number density of particles of diameter d_pi. The measured particle size was corrected to get the diameter of unswollen polymer particles with monomer but was not corrected with regards to the adsorbed platelets thickness. Indeed, it has previously been observed that the platelets laid flat on the polymer particles and therefore did not significantly contribute to the measured particle size, due to their small thickness (1 nm) compared to the particles diameter (of the order of 200 nm).[10]

2.4.2 Zeta potential measurements

Zeta potentials of the Laponite platelets, dispersed at 1 g L^{-1} concentration in pure water, were measured by electrophoresis using a Nano ZS Zetasizer, (Malvern). The electrophoretic mobility (μ_E) was measured in a U-shaped sample holder equipped with two electrodes (Malvern folded capillary cells DTS 1070). It was converted into zeta potential (ζ) using the Henry equation $\mu_\mathrm{E} = \frac{2}{3}\frac{\varepsilon_0 \varepsilon\ \zeta}{\eta}\ f(\kappa a)$ with the Smoluchowski approximation: $f(\kappa a) = 3/2,$ valid for ionic strength such that the Debye length ($1/\kappa$) is shorter than the particle size ($\kappa a > 1$), where ε and ε_0 are the permittivities of water and vacuum respectively, η is the viscosity and κa is the ratio of particle radius to double layer thickness.

2.4.3 Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

Adsorption of clay platelets on polystyrene latex was investigated by measuring the residual magnesium (Mg), silicon (Si) and lithium (Li) in water. A titration method was employed using at least two distinct wavelengths for each element: 279.8 nm, 280.3 nm and 285.2 nm for Mg; 252.9 nm, 255.6 nm and 288.2 nm for Si, and finally 610.4 nm and 670.8 nm for Li. First, a dispersion of clay in water was gently stirred for 24 h, then added to the surfactant-free seed described above and allowed to equilibrate for 12 h. Deionized water was added to reach the same solids content (5 wt%) for all samples, with different clay concentrations. Separation of polystyrene polymer particles from free clay platelets was ensured by two methods: 1) filtration through a syringe filter of 200 nm pore diameter or 2) centrifugation at 40 000 rpm during 20 min. To ensure that the separation method did not impact the results of adsorption; a test was done to validate that the particles did not pass through the filter while the clay did. In the centrifugation test, a test was also done to validate that clay platelets did not sediment while the particles did.[10] Each series of experiments was repeated four times.

3. Results and discussion

3.1. ζ potentials of the Laponite clay platelets

Electrophoresis measurements of ζ potential of clay platelets were performed in order to assess relevant data pertaining to the stabilization ability of clay platelets (as their elemental composition is not available). The ζ potential depends on the ionic strength of the aqueous medium. The adsorption isotherms of clay platelets on the surface of polymer particles were also

found to depend on the ionic strength (by the comparison between cleaned latex using ion exchange resins and uncleaned latex).[10] The ionic species present in the aqueous phase during emulsion polymerization come from thermal decomposition of the KPS initiator, so that the ionic strength varies during the course of the polymerization. Pure water was however selected for the measurement of the ζ potential as the dispersion was more stable in this case.

The calculation of the ζ potential from the measured electrophoretic mobility, μ_E, depends on the ionic strength and the shape of the particles. The Henry factor, $f(\kappa a)$, in the Henry equation: $\mu_E = \frac{2}{3}\frac{\varepsilon_0 \varepsilon\ \zeta}{\eta}\ f(\kappa a)$, assumes two limiting values for spherical particles depending on the ionic strength described by the width of the double electrical layer or the Debye length, κ^{-1}, with respect to the particle radius a: $f(\kappa a) = 1$ for $\kappa a \ll 1$ corresponding to low ionic strength, and $f(\kappa a) = 3/2$ for $\kappa a \gg 1$, at high ionic strength. Though pure water was used as liquid medium, the ionic strength was fairly high because the Laponite platelets released ionic species in water upon dispersion. Indeed, the chemical compositions of the Laponite clays reveal an excess of sodium with respect to the substitution of lithium for magnesium x. The high ionic strength was revealed by a high electrical conductivity of the samples. The electrical conductivity measured during the electrophoresis experiments was between 0.1 and 0.4 mS cm^{-1}, which corresponded to an NaCl concentration of 0.01 M and a Debye length κ^{-1} = 3 nm, much shorter than the size of the clay platelets. Therefore, the Smoluchowki approximation where the thin double layer is not deformed by the electric field was valid and $f(\kappa a)$ was taken equal to $3/2$.

The non-spherical shape of the Laponite clay platelets is another matter of concern. Such issue has been addressed both by theoretical calculations and experimental studies.[18] According to the calculations by Loewenberg[19] and comparative experimental studies on spherical and platelet-

shaped particles,[20,21] the application of the theoretical expressions valid for spherical particles to non-spherical particles is of acceptable accuracy as long as the surface conductivity of the particles remains low, which is the case here. Since such topic might be a matter of controversy, both the experimental electrophoretic mobilities and the calculated ζ potentials are reported in Table 2.

Table 2. Electrophoretic mobility and ζ potential of 1 g L^{-1} suspensions of Laponite in water.

	Laponite RDS	**Laponite S482**	**Laponite XLS**	**Laponite JS**
Electrophoretic mobility (m^2 V^{-1} s^{-1})	-3.1×10^{-8}	-3.4×10^{-8}	-3.0×10^{-8}	-4.8×10^{-8}
ζ potential (mV)	- 40	- 44	- 38	- 62

The ζ potentials of Laponite RDS, XLS and S482 were found to be similar in magnitude. This is not surprising owing to the close chemical compositions of Laponite RDS and XLS; the chemical composition of Laponite S482 is proprietary information of the manufacturer. Note that the ζ potential of the clay is reduced when measured in NaCl solution; for instance for Laponite RD at a concentration of 10 g L^{-1} in the presence of sodium pyrophosphate and NaCl (10^{-3} M), the ζ potential is –29.5 mV. The ζ potential of the fluorohectorite Laponite JS is significantly higher than the three other Laponite grades. This is related to its electrical charge and the ionic adsorbed species, namely the pyrophosphate peptizing agent, and not to the substitution of F for OH that should not affect electrical charges. Thus, the substitution of lithium for magnesium is 50% higher for Laponite JS than for other grades (x = 0.75 against 0.50), which increases the electrical charge of platelets by the same amount. The amount of peptizing agent is also 50% higher in Laponite JS, causing larger negative charge. In summary, ζ potential measurements

showed that the Laponite JS clay was different from the others, not only because it is a fluorohectorite, but also because it is more negatively charged. The later character is an important consideration with regards to its adsorption and the stabilization of latex particles.

3.2. Clay adsorption on polystyrene

Figure 1 shows the adsorption isotherm of Laponite clay platelets on surfactant-free polystyrene polymer particles. First of all, for all clay grades it can be noticed that the adsorption isotherms show two distinct regimes as a function of the clay concentration. For clay concentrations lower than 0.6 g L^{-1} (which corresponds to 0.35 g L^{-1} of residual clay in water), the clay platelets partitioned between the latex surface and bulk water. In this dilute regime, the adsorbed amount was lower than the amount allowing full coverage of the polymer surface. Above this clay concentration, adsorption rose almost vertically, showing that clay platelets in excess fully adsorbed onto the latex particles. In the concentrated regime, the adsorbed amount exceeded the limit of one dense monolayer. Such results strongly suggest that the clay was adsorbed as a monolayer for concentrations lower than 0.6 g L^{-1} but started forming multilayers for higher concentrations. With the used polymer seed with $d_p = 300$ nm at SC = 5%, the surface area of polymer particles can be calculated (assuming spherical polymer particles) and compared to the surface area of adsorbed clay platelets to estimate the surface coverage. At a clay concentration of 0.6 g L^{-1}, the adsorbed amount of clay is 0.25 g L^{-1}, which gives a surface coverage of polymer particles of 40%. Full coverage can be attained (so multilayer formation can start) when the adsorbed amount of clay is 1.0 g L^{-1}, which corresponds to a total concentration of about 1.3 g L^{-1}.

The formation of multilayers is not due to the formation of aggregated stacks in water upon increasing the clay concentration. Indeed, cryo-TEM analysis of the clay suspensions before adsorption showed full clay dispersion as individual platelets. Moreover, a linear increase of the conductivity was observed when increasing the clay concentration in pure water, which indicated that the added clay was well dispersed.[10]

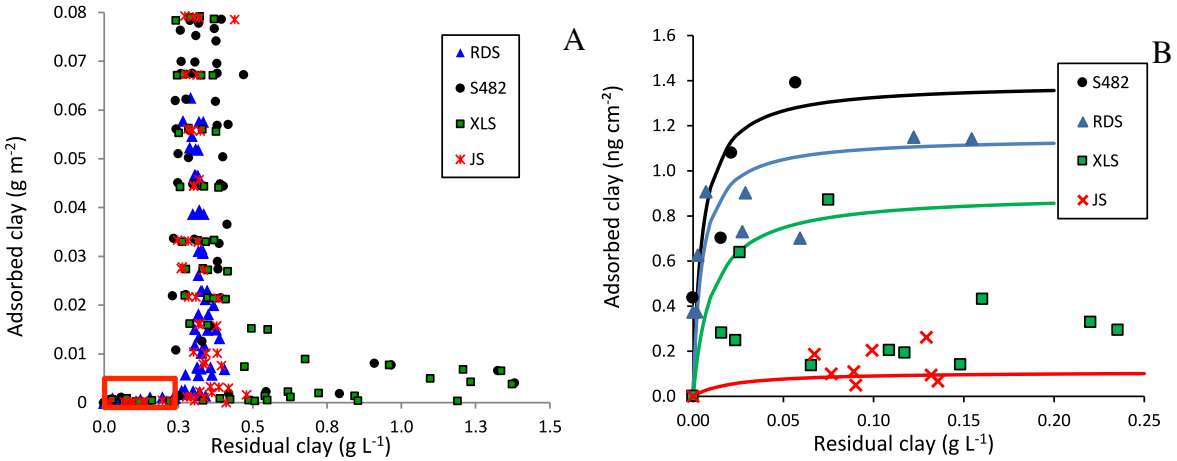


Figure 1. A: Adsorption isotherm of Laponite clay platelets on preformed polystyrene latex particles (with 5 wt% solids content and mean diameter 300 nm) measured using ICP-AES based on Si analysis and B: Zoom of the selected zone in Figure A with Langmuir fits (continuous line).

Note that few measurements in the adsorption isotherms of Laponite S482 and XLS followed an unusual behavior. Thus, the concentration of residual clay in water could be as high as 1.2 g L^{-1} when the introduced clay concentration was at 3 g L^{-1}; the formation of multilayers on the polymer surface started at higher concentration and the residual clay in water became similar as the other clays (at maximum 0.35 g L^{-1}) leading to similar adsorption isotherms. This phenomenon might have been attributed to slow micro-gel formation that is concentration-dependent. However, according to the supplier and our observations, gel formation starts few

days after the dispersion and the samples in this work were only 1 to 2 days old. Another explanation is that the samples were not at equilibrium. While adsorption can be assumed to be fast for Laponite RDS and Laponite JS thus ensuring fast equilibrium (~ 5 min for Laponite RDS), the adsorption would be slower for Laponite S482 and Laponite XLS.[10] Therefore, the data with residual clay concentrations higher than 0.5 g L^{-1} were discarded in fitting a theoretical model of adsorption isotherm to the experimental data.

A closer look at the dilute regime (Figure 1B), revealed significant differences between the adsorption isotherms of the clays. Laponite JS had the lowest adsorption to the particles surface, and Laponite RDS and S482 had similar first layer isotherms while the trend of the adsorption isotherm was less obvious for Laponite XLS. The noisy measurements of Laponite XLS can be due to a higher difficulty in fully dispersing this clay, especially at higher clay concentrations or to its non-equilibrium characteristics (which indicates slower adsorption). A Langmuir isotherm was nevertheless fitted to this part of the experimental data at low coverage. Note that the Langmuir isotherm assumes monolayer adsorption with no lateral interactions or steric hindrance between the adsorbed species:[22]

$$\frac{q}{q_m} = \frac{K_S C_{eq}}{1+K_S C_{eq}} \tag{1}$$

where C_{eq} (g L^{-1}) is the equilibrium concentration in the liquid medium, q (mg m^{-2}) the surface density of adsorbed species, q_m (mg m^{-2}) the adsorbed amount at the plateau (maximum surface density for monolayer coverage) and K_S the associated equilibrium constant (L mg^{-1}). The Langmuir model was fitted to the adsorption isotherms in Figure 1B and the corresponding adsorption parameters are given in Table 3. The equilibrium constants K_S are comparable for Laponite RDS and Laponite S482. A much lower value of K_S was estimated for Laponite JS

indicating lower binding strength of Laponite JS to the surface of polystyrene particles. The estimated K_S parameter is lower for Laponite XLS, but this estimation should be considered with precaution due to the noisy measurements related to this clay. The adsorbed amount at full monolayer coverage q_m was of similar magnitude for all Laponite clays, which was expected owing to their similar particle size.

Table 3. Adsorption parameters of the Langmuir model ($\boldsymbol{q_m}$ and $\boldsymbol{K_S}$) and BET model ($\boldsymbol{q_m}$, $\boldsymbol{K_S}$ and $\boldsymbol{K_L}$) for each Laponite grade investigated in this study

Clay	$\boldsymbol{q_m}$ (mg m^{-2})	$\boldsymbol{K_S}$ (L mg^{-1})	$\boldsymbol{K_L}$ (L mg^{-1})
Laponite RDS	1.1	212.8	3.1 10^{-3}
Laponite S482	1.4	204.9	3.1 10^{-3}
Laponite XLS	0.9	98.0	3.1 10^{-3}
Laponite JS	0.2	31.6	3.1 10^{-3}

In order to describe multilayer adsorption, the Brunauer–Emmett–Teller (BET) isotherm was used.[23] This model, originally developed for adsorption from the gas phase, is an extension of the Langmuir theory under the additional hypothesis that molecules can also physically adsorb by binding to already adsorbed molecules, resulting in the formation of multilayers with no limit regarding the number of layers. Therefore, the model allows describing monolayer and multilayer adsorption behaviors:

$$\frac{q}{q_m} = \frac{cX}{(1-X)(1-X+cX)} \tag{2}$$

where X is the ratio of the partial pressure of the adsorbate to its saturation partial pressure at the system temperature and q_m is the surface density of adsorbed species for a hypothetic monolayer

at full coverage. c is the BET constant defined as $c = \exp\left(\frac{E_1 - E_N}{k_B T}\right)$ where E_1 is the heat of adsorption for the first layer and E_N is that for the higher layers. The BET model was applied to liquid phase adsorption by substituting the partial pressure of the adsorbate by its concentration in the liquid phase ($X = C_{eq}/C_S$).[24,25] In this case, equation 2 has three degrees of freedom (q_m, c and C_S). In order to estimate the adsorption energies corresponding to the different layers, Ebadi *et al*.[24] expressed the BET constant as the ratio of the equilibrium constants of the adsorption equilibria for the first layer and the higher layers: $c = \frac{K_S}{K_L}$, which led to the following equation:

$$\frac{q}{q_{\mathrm{m}}} = \frac{K_S C_{\mathrm{eq}}}{(1 - K_{\mathrm{L}} C_{\mathrm{eq}})[1 - K_{\mathrm{L}} C_{\mathrm{eq}} + K_{\mathrm{S}} C_{\mathrm{eq}}]} \tag{3}$$

where K_{S} becomes the adsorption equilibrium constant of the 1st layer and K_{L} the adsorption equilibrium constant of upper layers. Based on this assumption, the model parameters were fitted to the data and are given in Table 3. It can be seen that K_{s} is higher than K_{L}, which indicates that the formation of multilayers takes place by means of stronger interactions in the first layer contacting polystyrene than for the upper layers (among clay platelets). K_{L} takes the same value for all the studied Laponite clays. On the contrary, K_{s} is much smaller for Laponite JS, which points the lower adsorption of Laponite JS on polystyrene.

3.3. Role of the clay in semi-continuous *ab initio* emulsion polymerization

Surfactant-free emulsion polymerization of styrene was carried out in the presence of increasing amounts of clay for each of the four Laponite grades by semi-continuous monomer addition in

ab initio mode. The objective of these experiments was to investigate the effect of the clay concentration on the number density and stability of the nucleated particles.

3.3.1. Effect of Laponite RDS concentration

Investigation of Laponite RDS in *ab initio* semi-continuous emulsion polymerization was reported by Brunier *et al* (Figure 2).[10] The number of particles increased with increasing the clay concentration, but the increase slowed down at higher concentrations, although a clear leveling off was not observed. Increasing the clay concentration (for a fixed solids content of 20 wt%) thus led to an increase in the reaction rate due to the formation of smaller particles. In addition, the clay platelets were quite efficient in ensuring particles' stability since the particles number remained constant until the end of the reaction, revealing that neither coagulation nor nucleation of new polymer particles took place. At the beginning of the polymerization, for clay concentrations higher than 0.5 g L^{-1}, the area of platelets was enough to cover the full surface area of particles and a significant excess of clay platelets was present. By the end of the reaction, as the particles grew, the amount of clay became insufficient to cover the full polymer particles' surface area, except for 10 g L^{-1} clay. The stabilization of polymer particles by adsorbed clay platelets is probably caused by the formation of a rigid coating around the polymer particles, which prevents the latex particles from close contact and coagulation. This is the main mechanism put forward for the stabilization of Pickering emulsions.[26,27]

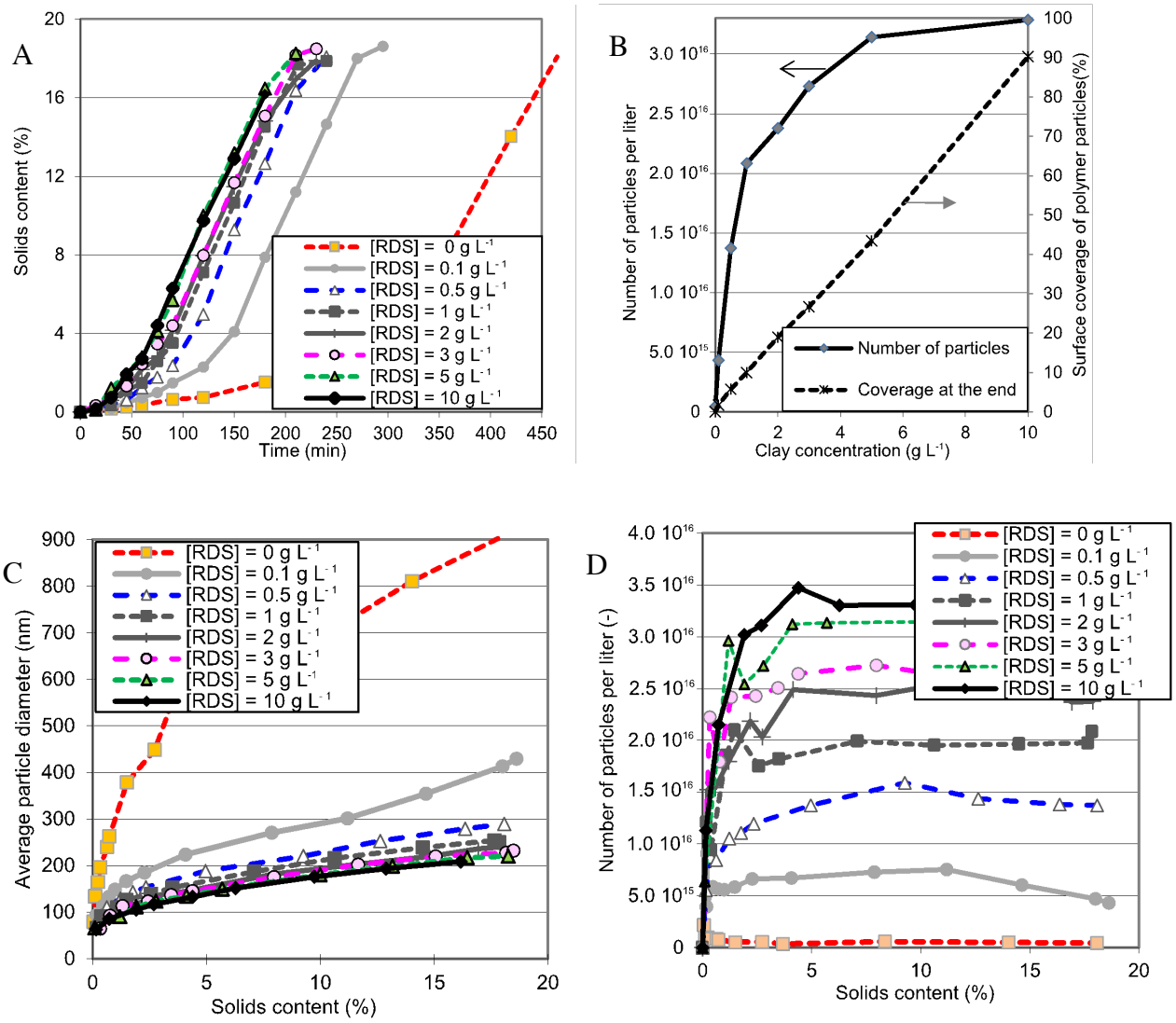


Figure 2. Pickering *ab initio* semi-continuous emulsion polymerization of styrene stabilized by different amounts of Laponite RDS. *Reprinted with permission from Langmuir, 2016, 32, 112−124, copyright 2016 American Chemical Society*.

3.2.2. Effect of Laponite S482 concentration

A similar trend was observed for Laponite S482 (Figure 3). At the beginning of the reaction, the number of particles increased during the nucleation period, which lasted between 45 and 90 min.

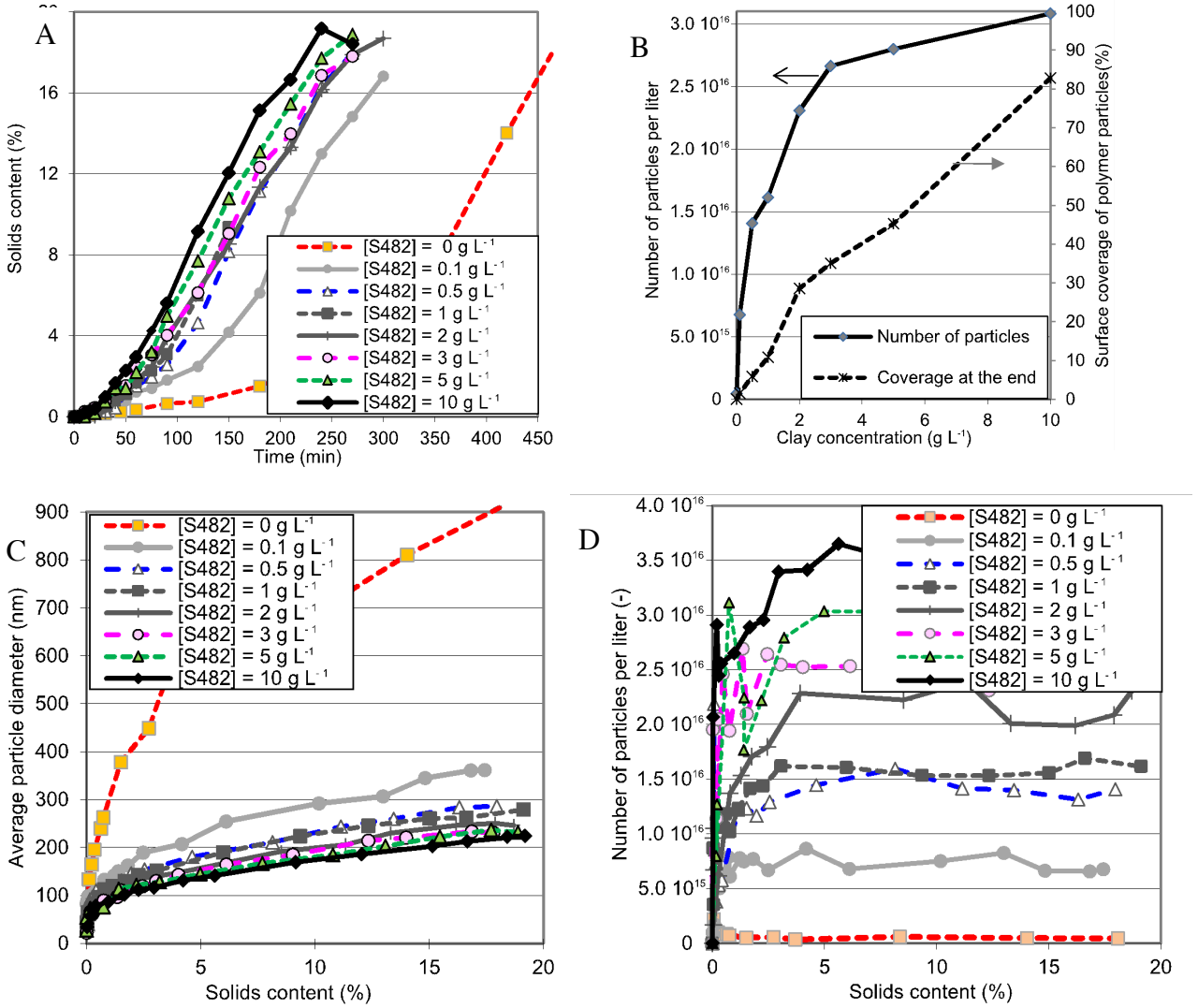


Figure 3. Pickering *ab initio* semi-continuous emulsion polymerization of styrene stabilized by different amounts of Laponite S482.

The higher the clay concentration, the longer was the nucleation period. The number of particles also increased with increasing clay concentration. At high concentrations, the increase in the particles size slowed down a little, without leveling off. This led to an increase in the reaction rate and to the formation of smaller particles when increasing the clay concentration (at the same solids content). The efficiency of this clay to stabilize the polymer particles could therefore be demonstrated as a small amount of clay (0.1 g L^{-1}) was enough to reduce the particles size

significantly compared to the clay-free experiment and the number of particles remained constant until the end of the reaction, with SC = 20%.

For clay concentrations higher than 0.5 g L^{-1}, the area of platelets was enough to cover the total surface of particles and a significant excess of clay platelets was present until 30 min of polymerization. As the particles grew, this amount became insufficient to cover the full polymer particles' surface. It can be noticed that the number of particles in some samples decreased during the very beginning of the reaction for high concentrations of clays. This suggests a coagulative nucleation mechanism.[28] It is worth mentioning that this phenomenon was not observed for Laponite RDS.

3.3.3. Effect of Laponite XLS concentration

Figure 4 shows the results of *ab initio* emulsion polymerization using different concentrations of Laponite XLS. Laponite XLS behaved similarly as Laponite RDS and Laponite S482 up to 2 g L^{-1} (*i.e.* 0.05 % of clay based on monomer mass). Above 4 g L^{-1}, the influence of the clay concentration became small and the particles number density levelled off to around 2×10^{16} particles per liter. At this stage, the mean diameter of polymer particles was about 300 nm for a solids content of 20%. A similar levelling-off of the latex particle size was observed by Bon and coworkers[29] during Pickering emulsion copolymerization of styrene and *n*-butyl acrylate using also Laponite XLS as stabilizer. It can also be noticed that the number of particles increased and then decreased during the very beginning of the reaction, which is again indicative of coagulative nucleation. This effect was more pronounced for Laponite XLS than for Laponite S482 and as a reminder, it was not observed for Laponite RDS.

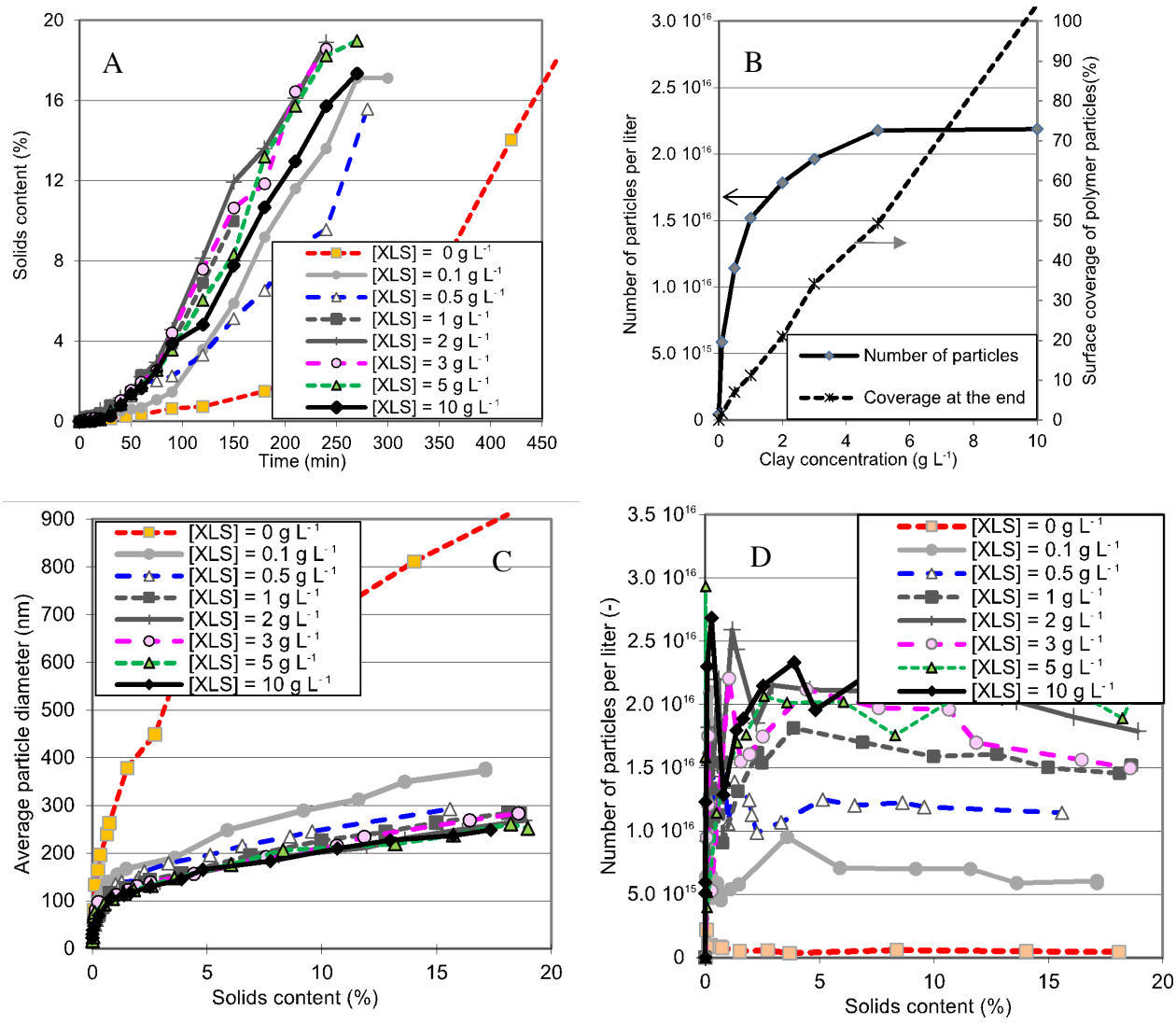


Figure 4. Pickering *ab initio* semi-continuous emulsion polymerization of styrene stabilized by different amounts of Laponite XLS.

3.3.4. Effect of Laponite JS concentration

Similarly to Laponite RDS and Laponite S482, increasing the amount of Laponite JS led to the formation of smaller particles (i.e., an increase in the number of particles) for the same solids content (Figure 5). However, the obtained latex particles were much bigger and the particles

number density was almost 10 times lower than for the other clays, (i.e., close to the clay-free experiment), which led to lower reaction rates. The nucleation rate was also lower, which extended the nucleation period from 60 to 120 min. Laponite JS was therefore less efficient for stabilizing polystyrene particles in emulsion polymerization. A deeper comparison and analysis of the different clays is done in the next section.

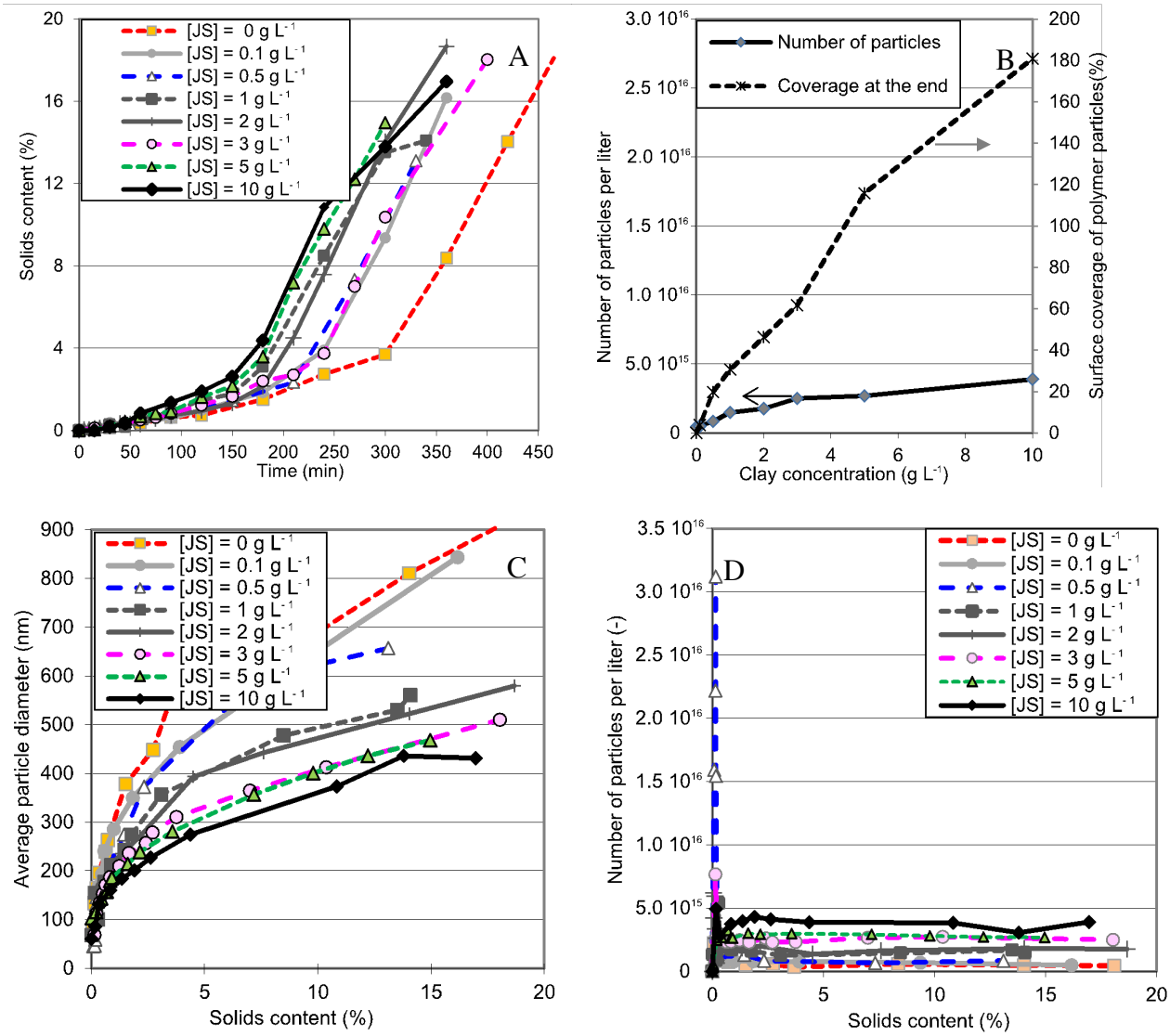


Figure 5. Pickering *ab initio* semi-continuous emulsion polymerization of styrene stabilized by different amounts of Laponite JS.

3.3.5. Comparison of the different Laponite clays grades

Figure 6 compares the behavior of the different clay grades for different clay concentrations with time and Figures 7 summarizes the resulting particles number density at the end of these reactions.

First of all, it is important to remind that all clays showed multilayer adsorption isotherm for high clay concentrations but differed at low concentrations where Laponite JS and Laponite XLS adsorb less on the particle surface. Second, all the clays had a similar ζ potential except Laponite JS that had a much more negative ζ potential. Finally, the stabilization by clay platelets depends on the surface coverage. Based on the last point, two different stabilization mechanisms can be put forward depending on surface coverage by clay platelets. Firstly, the predominant stabilization comes from formation of a dense coating of solid material at the surface of the polymer particles makes a rigid shell around the particles that prevents coagulation and coalescence; this is the standard picture put forwards regarding the steric stabilization of Pickering emulsions when a large amount of clay platelets is adsorbed. However, a low coverage by the clay platelets is much less efficient in stabilizing the polymer particles since the polymer particles can go to close contact at the parts of their surface that are not covered by clay platelets. It is presumed that the main stabilization mechanism switches from steric to electrostatic due to the strong negative surface charges of the clay (700 elementary charges, due to the release of the Na^+ ions from the surface). ~~The Na^+ counter ions dispersed in the solution screen the negative charges of the faces forming an electrical double layer composed of~~

~~a Stern and a diffuse layer. Charges of the rims are screened by the adsorption of the peptizing agent.~~

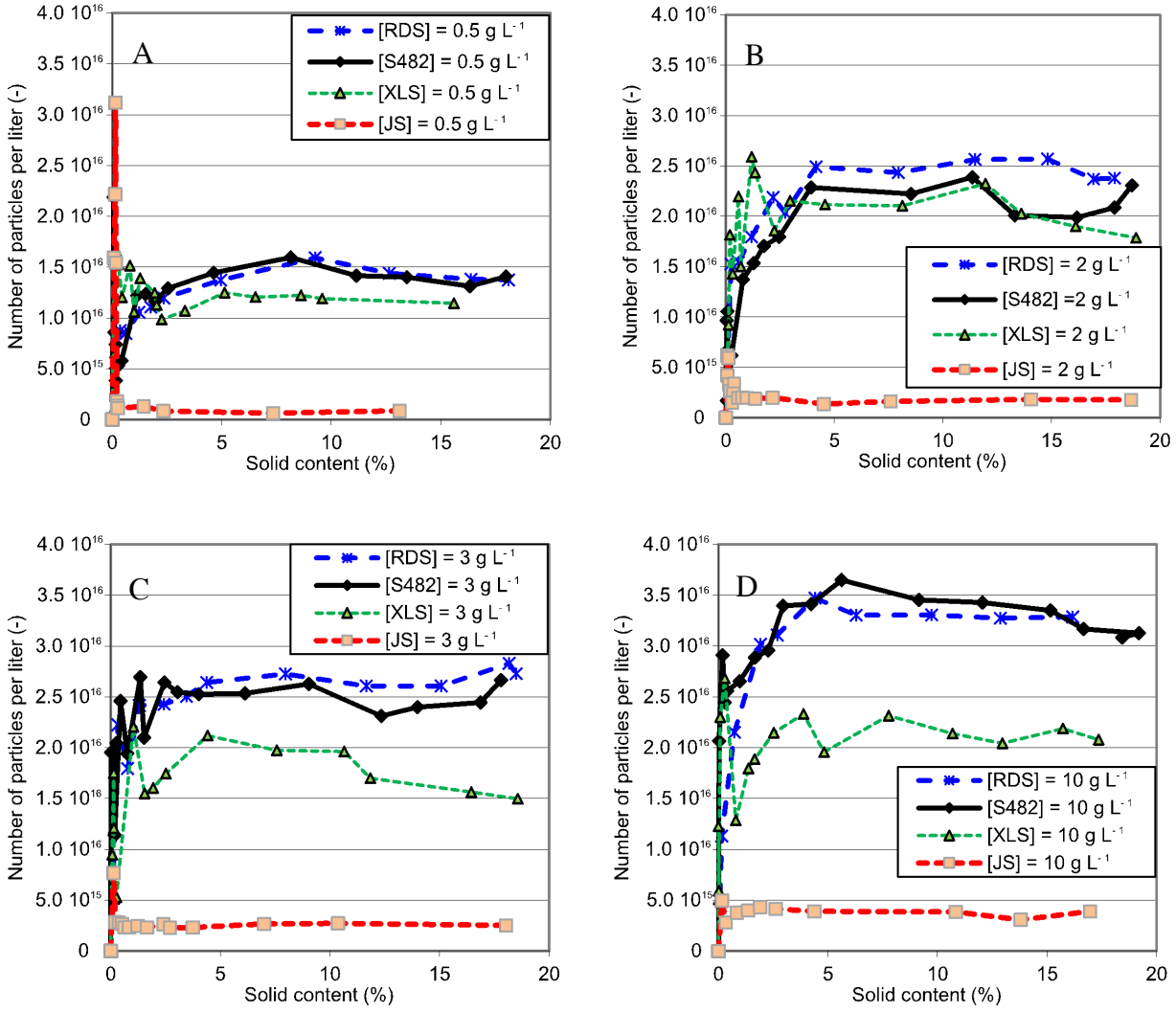


Figure 6. Comparison of the different clay grades in Pickering *ab initio* semi-continuous emulsion polymerization of styrene for different amounts of Laponite: (A) 0.5 g L^{-1}, (B) 2.0 g L^{-1}, (C) 3.0 g L^{-1}, and (D) 10.0 g L^{-1}.

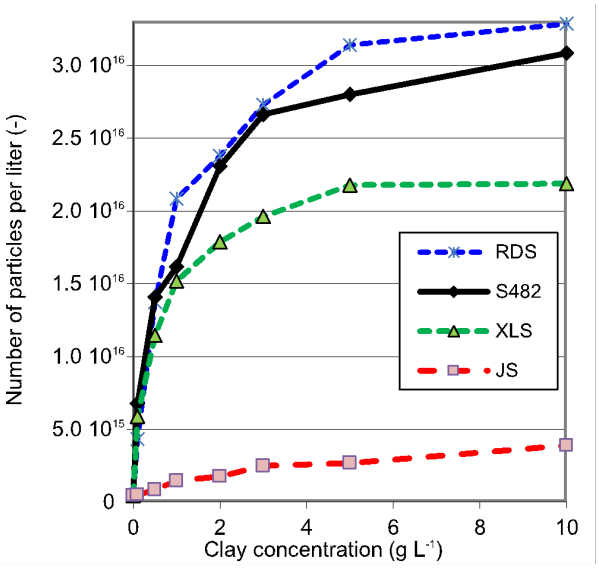


Figure 7. Comparative summary of the behaviors of the four Laponite clays in emulsion polymerization.

The nucleated number of particles was almost identical for the three grades Laponite RDS, S482 and XLS, for the two low concentrations (0.5 and 2 g L^{-1}), (and much higher than for Laponite JS). This indicates similar surface charge for these grades. For higher concentrations, the number of particles continued to increase with increasing the clay concentration for Laponite RDS and S482 while it stayed constant for Laponite XLS. This might be due to the formation of some clay aggregates of Laponite XLS platelets at high concentrations, which reduces its stabilization efficiency. Another explanation would be that Laponite XLS adsorbs more slowly on the surface of particles, which is in agreement with the non-equilibrium characteristic of this clay observed in the adsorption isotherm measurements.

Laponite JS led to the generation of the lowest number of particles at all clay concentrations. This clay contains fluorine (4.8%), contrary to the other clays, and a higher amount of lithium (1.2% vs 0.8% for the other clays). It is therefore the most charged clay among the four studied

ones in this work. This was confirmed by ζ potential measurements. Saunders *et al.*[13] also reported that clays with higher Li and F levels had a higher (more negative) basal surface charge and a lower (less positive) edge charge.[30,31]

The electrostatic repulsions may have a double effect: the adsorption of charged clay platelets increases the charge of the polymer particles and improves their stability against coagulation; but, electrostatic repulsions between the clay and the polymer particles, both negatively charged, may prevent the adsorption of the clay which hinders stabilization of polymer particles.

Such paradoxical role of electrostatic repulsions has already been reported in the case of oil/water Pickering emulsions (of liquid oil droplets instead of polystyrene particles).[30,31] For example, silica particles have a very hydrophilic surface and are negatively charged at pH above the isoelectric point (iep = pH 2). As a consequence, silica particles are poor stabilizers of Pickering emulsions because they do not adsorb enough: the negative charge generated by the adsorption of few silica particles makes the oil droplets negatively charged, so that they repel other silica particles and prevent further adsorption. Every phenomenon that weakens such electrostatic repulsions allows a larger and faster adsorption of silica particles and improves the stabilization of oil droplets against coalescence. For instance, the addition of electrolytes (especially multivalent cations) increases the adsorption of silica particles and causes the aggregation of silica particles at the surface of oil droplets, thereby improving the stabilization of emulsions.[32] Similarly, lowering the pH closer to the isoelectric point of silica or the addition of polymers that cause bridging flocculation of the silica sol also weaken electrostatic repulsions.[33]

Accordingly, it is presumed that the weak stability against coagulation taking place during emulsion polymerization in the presence of Laponite JS is caused by the weak adsorption of clay

platelets due to the strong electrostatic repulsions between clay platelets and polystyrene particles partially covered by clay particles. Weak adsorption of Laponite JS has been observed at equilibrium in the concentration domain where monolayer adsorption takes place.

At higher concentrations, the adsorption isotherm showed that Laponite JS did adsorb at the surface of polymer particles; their adsorption should have generated enhanced electrostatic repulsions between polymer particles and prevented coagulation. However, during the course of emulsion polymerization, the rapidity of adsorption also becomes an important parameter, while the adsorption isotherm of this clay indicated a possible non-equilibrium characteristic, which suggested a slower adsorption. Indeed, efficient stabilization of nucleated polymer particles by clays requires that the rate of adsorption be faster than the rate of coagulation. Thus, a too large electrical charge of clay platelets may create electrostatic repulsions that make adsorption slower than coagulation, causing inefficient stabilization of the newly nucleated polymer particles within the time scale of coagulation. This involves non-equilibrium adsorption phenomena that may be studied using for instance Quartz Crystal Microbalance measurements.

4. Conclusions

Information about the ζ potential and adsorption isotherms was combined with the data of the different clay compositions, in order to elucidate Laponite stabilization behavior during Pickering emulsion polymerization:

- The chemical compositions of Laponite RDS, Laponite XLS and Laponite JS are comparable, except for Laponite JS, which is a fluorohectorite (MgOH groups partly fluorinated, as the OH

groups are substituted by F atoms). The composition of Laponite S482 is proprietary information of the manufacturer and it contains a different peptizing agent than the other clays.

- The ζ potential of Laponite JS was higher in magnitude than the other studied clays, due to a higher substitution of lithium for magnesium (50% higher than the other clays).
- The adsorption isotherm could be divided into two concentration regimes: at high clay concentrations, all clays followed a similar multilayer adsorption mechanism whereas at low clay concentration, the adsorption of the first layer of clay on the particle surface was larger for Laponite RDS and Laponite S482 than for Laponite XLS and Laponite JS. A non-equilibrium characteristic for Laponite XLS and Laponite JS was observed.

During the course of the polymerization:

- Laponite RDS and Laponite S482 were very similar in that increasing the clay concentration was found to increase the number of particles.
- Laponite JS was found the least efficient for stabilizing the latex particles, among the studied clays. At low clay concentrations, this can be explained by the lower adsorption (as shown by the adsorption isotherm), as a result of an increased repulsion between the clay and the polymer particles surface due to the higher charge of the clay. At higher concentrations, the adsorption isotherm showed that the clay adsorbed similarly as the other ones. However, a non-equilibrium characteristic was presumed in this isotherm, which suggested a slower adsorption of this clay than the other ones. The rapidity of adsorption is critical during the course of emulsion polymerization, and should be faster than the coagulation rate.
- Laponite XLS followed a similar behavior as Laponite RDS and Laponite S482 at low clay concentrations. This indicates that, for the three clays, individual platelets had the same surface charge (indeed the surface charge is better assessed under dilute conditions where the clay

platelets do not interact with each other). But, a kind of saturation was observed for Laponite XLS at higher concentrations, and the nucleated number of particles reached a limit at a clay concentration of about 3 g L^{-1}. Increasing further the clay concentration did not affect the particles number. As the concentration of all clays on the particles surface was the same, this might be due to slower adsorption of this clay similarly to Laponite JS or to the formation of aggregates of Laponite XLS at high concentrations making it less efficient in stabilization.

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