



HAL
open science

A “Limited Aggregation Model” to Predict the Size of Acrylamide-Based Microgels Synthesized with Ionic Surfactants

Antoine Brézault, Véronique Schmitt, Valérie Ravaine, Patrick Perrin, Nicolas Sanson

► **To cite this version:**

Antoine Brézault, Véronique Schmitt, Valérie Ravaine, Patrick Perrin, Nicolas Sanson. A “Limited Aggregation Model” to Predict the Size of Acrylamide-Based Microgels Synthesized with Ionic Surfactants. *Macromolecular Chemistry and Physics*, 2023, pp.2300372. 10.1002/macp.202300372 . hal-04485303

HAL Id: hal-04485303

<https://hal.science/hal-04485303>

Submitted on 1 Mar 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

A “Limited Aggregation Model” to Predict the Size of Acrylamide-Based Microgels Synthesized with Ionic Surfactants

Antoine Brézault, Véronique Schmitt, Valérie Ravaine, Patrick Perrin, and Nicolas Sanson*

The size of acrylamide-based microgels can be decreased by addition of ionic surfactants during the classical dispersion polymerization. Nevertheless, the mechanism of such syntheses is not well understood yet. Here, a “Limited Aggregation Model” is proposed by analogy with the limited coalescence mechanism occurring for Pickering emulsion stabilization. In such a model, nuclei aggregate until a constant, high enough surfactant surface coverage is reached, which ensures colloidal stability. Consequently, the total surface of the growing particles, linked to the inverse of their size, is linearly dependent on the surfactant concentration. This law is verified if the surfactant/polymer particle interaction is high enough to guarantee a “total adsorption” of the surfactants onto the particles. This simple model fits very well with all the data extracted from the literature, including very different synthesis conditions. Finally, it not only permits to predict the microgels size, but it is also an interesting tool to investigate the role of each synthesis parameter like initiator, solvent or polymer. For instance, it shows that the surfactant role is not linked to its charge, proving that a phenomenon complementary to the electrostatic repulsion, related to the surfactant tail, ensures the colloidal stability of the growing collapsed microgels.

1. Introduction

Microgels are defined as colloidal particles made of tridimensional macromolecular crosslinked networks swollen by a solvent. Usually, their size varies from a few dozens of nanometers to micrometer in the swollen state and they form colloidal dispersions in water. Since their discovery in 1986 by Pelton et al.,^[1] microgels have garnered significant attention from the scientific community owing to their wide-ranging applications in various fields.^[2,3] They serve as drug carriers in the biomedical field,^[4,5] have the ability to adsorb at interfaces to stabilize Pickering emulsions or foams,^[6–8] find utility in the field of photonics,^[9,10] and can be assembled to create larger smart materials.^[11,12] In all these cases, microgels are of great interest since they can response to diverse *stimuli* and especially temperature. Indeed, the most famous responsive microgels are poly(*N*-isopropylacrylamide) (PNIPAM)-based ones. The PNIPAM polymer chains exhibit a Lower Critical Solution


Temperature (LCST) behavior in water which endows the microgels with an ability to collapse when the temperature is raised above 32 °C. Such property is not only useful for many applications but also permits the synthesis of these microgels by dispersion polymerization. Indeed, in this process the synthesis reaction takes place at a temperature higher than the LCST of PNIPAM, temperature at which the growing polymer chains collapse in water, and bound together thanks to a crosslinker, to form microgel precursor particles. Then, microgels grow, by addition of other chains and monomers or by aggregation. By adjusting the synthesis conditions, the size of the microgels can be fine-tuned, which is of paramount importance for numerous applications.

Pelton was the first to prove that the size of PNIPAM-based microgels could be efficiently tuned by adding an ionic surfactant like Sodium Dodecyl Sulfate (SDS) during the dispersion polymerization.^[13] Following Pelton’s pioneering works, numerous fundamental studies have been conducted to understand the mechanism involved in these syntheses.^[14–19] It is a general trend that surfactants decrease the size of formed microgels. They obviously contribute to the stabilization of growing particles, which consequently reduce their size by limiting their growth. It is generally admitted that the charges coming from the ionic

A. Brézault, V. Schmitt
 Centre de Recherche Paul Pascal
 Université de Bordeaux
 CNRS UMR 5031, 115 Avenue Dr Albert Schweitzer, Pessac 33600,
 France

A. Brézault, V. Ravaine
 Bordeaux INP
 ISM
 Université de Bordeaux
 CNRS UMR 5255, 16 Avenue Pey Berland, Talence 33400, France

A. Brézault, P. Perrin, N. Sanson
 Soft Matter Sciences and Engineering
 ESPCI
 PSL University
 Sorbonne Université
 CNRS UMR 7615, 10 rue Vauquelin, Paris Cedex 05, Paris 75231, France
 E-mail: nicolas.sanson@espci.fr

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/macp.202300372>

© 2023 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/macp.202300372

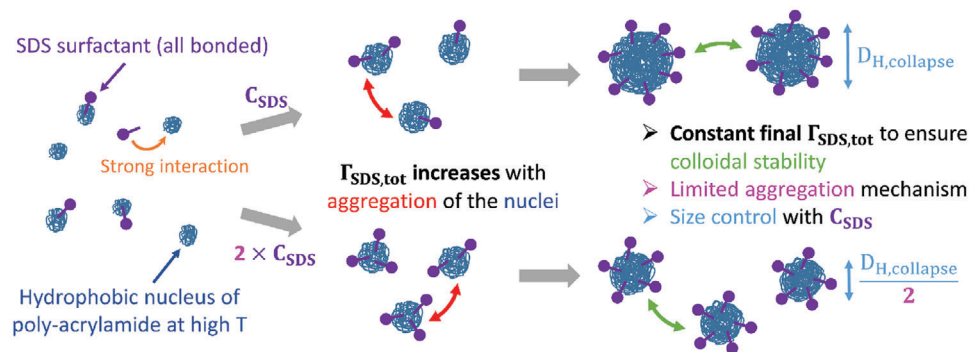


Figure 1. Scheme of the growth of particles during the synthesis of microgels according to a model of nuclei aggregation limited by the surfactant surface coverage $\Gamma_{\text{SDS,tot}}$. In such model the final size of the collapsed microgels $D_{\text{H,collapse}}$ is inversely proportional to the concentration of surfactant C_{SDS} .

surfactants and initiators can promote colloidal stability of the collapsed microgels through electrostatic repulsion. More recently, Hellweg suggested that interfacial tension could also play an important role to explain the colloidal stability.^[20] Nevertheless, to the best of our knowledge, a general model which links the size of the microgels to the surfactant concentration does not exist yet. Besides, the understanding of which effect(s) allow(s) reaching the colloidal stability during the synthesis is not achieved yet. Even for surfactant-free synthesis, the effects of initiator, salt, crosslinker, polymer content, temperature, on the size of the resulting microgels is not entirely clarified despite some well-conducted studies.^[21,22]

In this paper, we focus on the synthesis of PNIPAM microgels conducted with SDS and develop a simple general model which fits very well with our data as well as all the data extracted from the literature. To do so, we base our arguments on an analogy between the growth of hydrophobic particles stabilized by SDS during the microgels synthesis, and the limited coalescence of oil droplets stabilized by particles in the case of Pickering emulsions (**Figure 1**). For Pickering emulsions, in the particle-poor regime, the oil droplets coalescence after stirring cessation stops when a constant, high enough, particle surface coverage is reached, meaning that the total area of the droplets and consequently their size is directly linked to the number of particles.^[23,24] Similarly, we propose that the growth of hydrophobic microgels during the dispersion synthesis stops, as soon as a constant surfactant surface coverage, required to ensure colloidal stability, is reached. Consequently, the total surface area of the growing particles that is given by the inverse of their size is linearly related to the surfactant concentration. Of course, such model is based on strong hypotheses, such as a total adsorption of the surfactants on the polymer particles, which will be discussed in this article. To test our model, we performed systematic experimental studies to investigate both the roles of surfactant and initiator in the colloidal stability of the formed microgels. The influence of both the crosslinker content and the solvent on the surfactant ability to stabilize the growing particles has also been studied. We think that such general Limited Aggregation Model could be of great interest to investigate the mechanism of microgels synthesis and to foresee the sizes of the resulting microgels.

2. The Proposed “Limited Aggregation Model” to Fit and Analyze all the Data from the Literature

2.1. Description of the “Limited Aggregation Model”

Here, we develop a model to explain the influence of the surfactant concentration in the reaction mixture on the final size of collapsed microgel. The model is based on an analogy with the well-known limited coalescence process happening for Pickering emulsions stabilized by particles, in the particle-poor regime.^[23,24] Similarly, we call it “Limited Aggregation Model.” As illustrated in Figure 1, according to this model, the mechanism of the dispersion polymerization synthesis of microgels in the presence of surfactant is described as follows: at the early stage of the synthesis that is performed at $T > \text{LCST}$ of PNIPAM, nuclei are formed and SDS molecules begin to adsorb on the hydrophobic collapsed NIPAM polymer chains. If SDS molecules are not enough numerous to stabilize all the nuclei, these last aggregate to form precursor particles as shown in literature.^[15] Due to such aggregation, the total number of particles decreases, leading to a decrease of the total surface between hydrophobic particles and water during the synthesis. It means that the SDS surface coverage proportionally increases, if we assume that all the SDS molecules are totally adsorbed at the interface (see the part 3.4. Limits of the Limited Aggregation Model). Then, particles can grow until the SDS surface coverage is high enough to ensure the colloidal stability. A limited growth of the particles is the only way to explain the formation of well monodisperse microgels while aggregation is occurring. To validate such mechanism, $\Gamma_{\text{SDS,tot}}$, the final total SDS surface coverage should be constant for syntheses performed with various SDS concentrations. Consequently, if the SDS initial concentration is increased, the surface which can be covered with the same $\Gamma_{\text{SDS,tot}}$ is proportionally increased and therefore the size of the collapsed microgels is proportionally decreased. More generally, according to this model, the hydrodynamic diameter of the collapsed microgels $D_{\text{H,collapse}}$ should be inversely proportional to the concentration of surfactant C_{SDS} . The calculation explaining how data are plotted according to this model is detailed in the following section.

2.2. Calculation Quantities of the Model

In this study, both the literature and our new experimental data will be analyzed simultaneously. The objective of our study is to determine if the proposed Limited Aggregation Model for the microgels synthesis is general. Such model permits to link easily $D_{H,collapse}$, the final diameter of the collapsed microgels (measured by Dynamic Light Scattering at the end of the synthesis), and C_{SDS} , the millimolar concentration of SDS surfactant used during the synthesis, through the final total SDS surface coverage, $\Gamma_{SDS,tot}$. The following calculation permits to establish such link.

By definition, $\Gamma_{SDS,tot} = \frac{N_{SDS}}{S_{tot}}$, where S_{tot} is the total surface of the particles-solvent interface, and N_{SDS} is the number of SDS molecules adsorbed at this interface. Assuming that all the SDS molecules adsorb to the interface, we obtain $N_{SDS} = C_{SDS} \times V \times N_a$ with N_a the Avogadro constant and V , the volume of the reaction mixture. Besides, $S_{tot} = N_{\mu G} \times \pi D_{H,collapse}^2$ with $N_{\mu G}$ the final number of microgels. $N_{\mu G}$ can be estimated thanks to Lele's formula: $N_{\mu G} = \frac{6m_{pol}}{\pi D_{H,collapse}^3} \times (\frac{1}{\rho_{pol}} + \frac{0.29}{0.71\rho_{water}})$, with the mass of polymer m_{pol} , $\rho_{pol} = 1.269 \times 10^{-21}$ g/nm³ and $\rho_{water} = 0.988 \times 10^{-21}$ g/nm³ the respective polymer and water densities.^[25] It leads to this equation:

$$\frac{\alpha}{D_{H,collapse}} = C_{SDS} \times \frac{1}{\Gamma_{SDS,tot}} \quad (1)$$

where $\alpha = \frac{6m_{pol}}{V \times N_a} \times (\frac{1}{\rho_{pol}} + \frac{0.29}{0.71\rho_{water}})$ is a constant parameter for each set of synthesis proportional to the polymer concentration. Since a total conversion of the monomer is expected and that all measurements are performed without allowing the possible free chains to unbind the particles, one can assimilate the mass of polymer to the initial mass of monomer. In this case, for the sets of syntheses we performed in this study, $\alpha = 119.7$ mM.nm³.

2.3. Validation of the Model by Fitting all the Data from the Literature

To validate the proposed Limited Aggregation Model we use data extracted from the literature. The PNIPAM microgels are most often chemically crosslinked using the *N,N'*-methylenebis(acrylamide) (BIS). During the dispersion polymerization, initiation is usually ensured at high temperature by a water-soluble thermally-activated initiator like persulfate or an

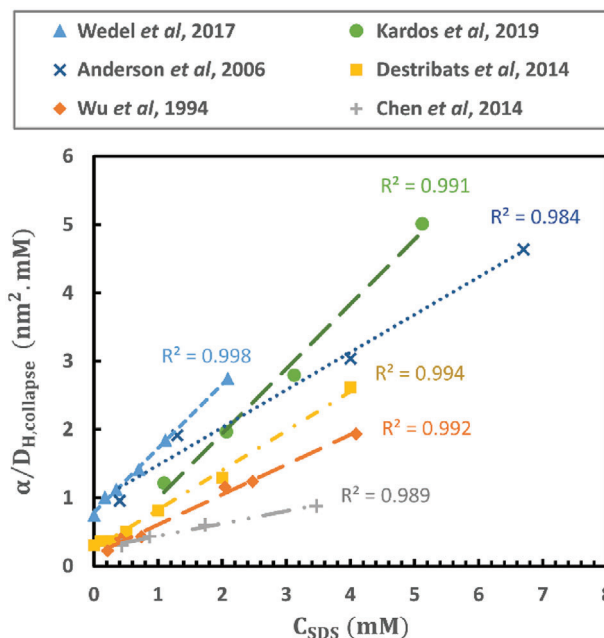


Figure 2. Compilation of the data extracted from the literature in which the final size of collapsed PNIPAM-BIS microgels is tuned by addition of SDS surfactant. The data are plotted according to a Limited Aggregation Model (Equation (1)) which predicts a linear variation of the inverse collapsed size, $D_{H,collapse}$, with the SDS concentration, C_{SDS} . The synthesis conditions and the references of each data set are reported in Table 1.

azo-based one. The initiator remains grafted on the chains and brings some electrostatic charges to the particles. We will first focus on this precise type of microgels to study the effect of SDS surfactants on the final size of the collapsed microgel. Being negatively charged, SDS is used in combination with potassium persulfate (KPS) or ammonium persulfate (APS) as anionic initiators. According to the model proposed previously, we plot $\alpha/D_{H,collapse}$ as a function of C_{SDS} for different sets of synthesis reported in the literature (Figure 2 and Table 1).

The obtained straight lines in Figure 2 prove that the Limited Aggregation Model fits very well the experimental data of all the references reported in the literature irrespective of the synthesis conditions. It also proves that the SDS molecules totally adsorb to the surface of the PNIPAM growing particles. However, in contrast with the limited coalescence mechanism observed with the case of Pickering emulsions, affine and not linear

Table 1. Synthesis conditions and references for all the data extracted from the literature in which the collapsed size of PNIPAM microgels is tuned by addition of SDS surfactants.

Author, date	Reference	NIPAM [wt% vs water]	Initiator [mol% vs NIPAM]	BIS [mol% vs NIPAM]	T [°C]	Γ_{SDS}^a [SDS molecules.nm ⁻²]
Wedel et al., 2017	14	0.9	5.7 mol% APS	5.4	70	1.1
Kardos et al., 2019	16	1.5	1.5 mol% APS	3.3	80	1.1
Andersson et al., 2006	17	1.5	1.5 mol% KPS	3.2	70	1.8
Destribats et al., 2014	6	0.7	4 mol% KPS	2.5	70	1.7
Wu et al., 1994	19	1.4	1.6 mol% KPS	7.3	70	2.3
Chen et al., 2014	18	8	0.6 mol% KPS	Crosslinker free	60	5.4

^{a)} The value of Γ_{SDS} is extracted from the slope on Figure 2 using Equation (2).

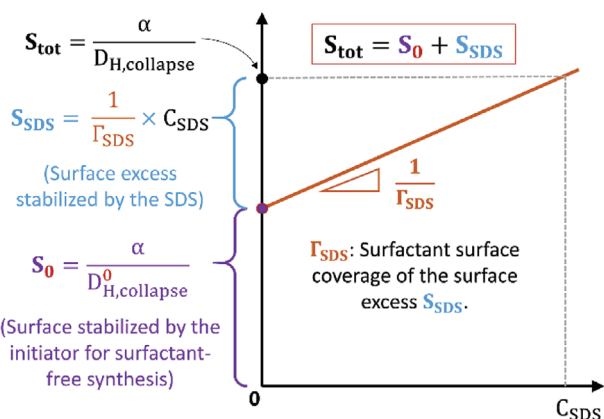


Figure 3. Scheme of the information extracted from the affine variation of the inverse diameter of the collapsed microgels $\frac{\alpha}{D_{H,collapse}}$, as a function of the surfactant concentration C_{SDS} , according to our “Limited Aggregation Model.”

variations of $\alpha/D_{H,collapse}$ as a function of C_{SDS} are observed. This can be reasonably explained as monodisperse microgels can actually be obtained in surfactant-free synthesis. Thus, the model can be slightly adapted by considering that the Y-intercept is inversely proportional to the diameter of microgels which would have been synthesized without any surfactant, $D_{H,collapse}^0$ (see **Figure 3**). In other words, a total surface $S_0 = \alpha/D_{H,collapse}^0$ between particles and water is stabilized at the end of the surfactant-free synthesis, probably thanks to the charges of the initiator. The use of surfactants allows the stabilization of a surface excess, S_{SDS} , in addition to S_0 . Finally, a total surface $\alpha/D_{H,collapse} = S_{SDS} + S_0$ can be stabilized. S_{SDS} is directly proportional to C_{SDS} , according well to the obtained affine relationship. The slope of the affine variations are the inverse of the SDS surface coverage of this supplementary surface stabilized by SDS, S_{SDS} . Finally, Equation (1) can be rewritten:

$$\frac{\alpha}{D_{H,collapse}} = \frac{\alpha}{D_{H,collapse}^0} + \frac{1}{\Gamma_{SDS}} \times C_{SDS} \quad (2)$$

where $D_{H,collapse}$ is the true hydrodynamic diameter of the collapsed microgels measured by DLS, $D_{H,collapse}^0$ is the hypothetical hydrodynamic diameter of the collapsed microgels synthesized without surfactant (calculated from the Y-intercept of each set of data), and Γ_{SDS} is the SDS surface coverage of the excess of surface stabilized by SDS (calculated from the slope of each set of data) (See **Figure 3**).

Thanks to the Limited Aggregation Model, we can now separate the effect of the initiator (influence on the Y-intercept) and the effect of the SDS (influence on the slope).

For instance, from the slopes, one can extract the adsorption of the surfactant. Very different values of Γ_{SDS} are obtained ranging from 1.1 to 5.4 SDS molecule.nm⁻² (Table 1). This is not surprising as the synthesis conditions are different (temperature, type of initiation, ionic strength) and adsorption depends on several experimental parameters that are not always accessible in the published papers. In order to shed the light on possible growing

Table 2. Ionic strength due to KPS and K₂SO₄ for the three different sets of syntheses described in **Figure 4**.

KPS [mol% vs NIPAM]	K ₂ SO ₄ [mol% vs NIPAM]	Ionic Strength [mM] ^{a)}
2	0	5.3
4	0	10.7
2	2	10.7

^{a)} The SDS concentrations have not been taken into account in the calculation of ionic strength since we will use it to focus on the Y-intercept and on the hypothetical size of the microgels reached without any SDS.

mechanisms, we carried out experiments in which key parameters are systematically varied.

3. Results and Discussion

In this part, we discuss the experimental results obtained for our dispersion syntheses of PNIPAM microgels, in the presence of surfactants. The discussion is divided into five paragraphs aiming at answering the corresponding questions, in order to shed light on the mechanism of microgel formation during the dispersion synthesis:

- What is the effect of electrostatic repulsion on the microgel colloidal stability? Indeed, charges coming from the initiator and from the surfactant could both allow colloidal stability and consequently be responsible for the “Limited Aggregation.”
- Is there another effect able to explain the surfactant ability to decrease the final size of the microgels? Indeed, as mentioned before by Wedel et al., surface tension should also be taken into account to explain the role of the surfactant.^[14]
- What is the role of other synthesis parameters in the synthesis mechanism? In other words, can the solvent properties or the crosslinker content affect the limited aggregation of the growing particles?
- What are the limits of this new Limited Aggregation Model? Indeed, such model proves that the SDS molecules totally adsorb to the PNIPAM interface contrary to what is usually observed with surfactants.
- Can we combine surfactants and initiators of opposite charges to reach colloidal stability and is our model still valid in this original case? In literature, microgels are always synthesized with surfactant and initiator of same charge. Here, we show that a broader microgel size range can be reached by using oppositely charged initiator and surfactant.

3.1. Effect of the Electrostatic Interactions on the Microgel Colloidal Stability

It is widely accepted that electrostatic charges play a role in the colloidal stability of microgels in collapsed state. To re-investigate the role of charges, experiments were carried out by varying initiator (KPS from 2 to 4 mol% versus NIPAM) and salt (K₂SO₄ from 0 to 2 mol% versus NIPAM) concentrations (**Table 2**). K₂SO₄ salt have been used to tune the ionic strength because it has the same charges than KPS without being able to initiate the polymerization. Measurements of the final collapsed size $D_{H,collapse}$

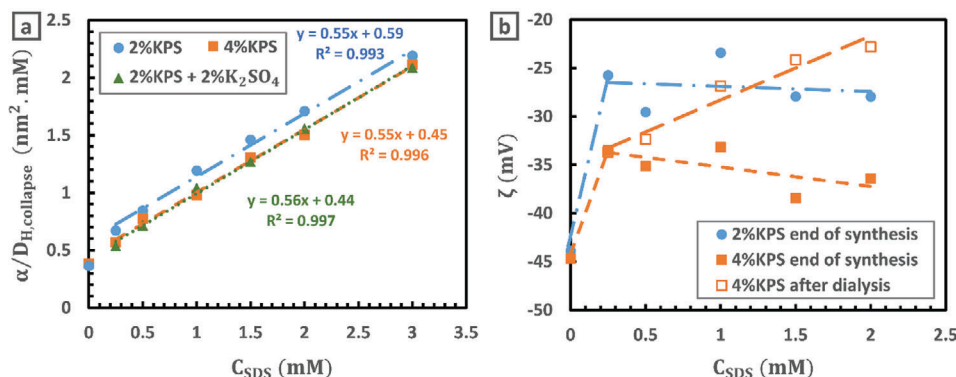


Figure 4. a) Plots of $\alpha/D_{H,collapse}$ for collapsed microgels as a function of the SDS concentration for three different experiments: concentration of KPS equal to 2 mol% NIPAM (filled blue circles); concentration of KPS equal to 4 mol% NIPAM (filled orange squares); concentration of KPS equal to 2 mol% NIPAM and concentration of K₂SO₄ equal to 2 mol% NIPAM (filled green triangles). Lines are fits to Equation (2). b) Zeta potential measurements ζ for syntheses performed at different SDS concentrations and for initiator concentrations equal to 2 mol% NIPAM (filled blue circles) or 4 mol% NIPAM (filled orange squares). ζ have been measured both for unpurified microgels at the end of the synthesis (filled orange squares) and for microgels purified by dialysis (empty orange squares). Measurements were performed at NaCl concentration equal to 10⁻³M. Dashed lines are only guide for the eyes.

by Dynamic Light Scattering (DLS), allow to plot $\alpha/D_{H,collapse}$ as a function of C_{SDS} , to test the “Limited Aggregation Model” as shown in Figure 4a. The zeta potentials measurements (ζ) for each microgels in the collapsed state at the end of the synthesis before and after purification have also been reported in Figure 4b. It is important to notice that the salt concentration was kept constant for each measurement and that unpurified microgels have not been allowed to swell between the end of the synthesis and the measurements.

3.1.1. The Limited Aggregation Model is not Adapted to Surfactant-Free Syntheses

As predicted by the “Limited Aggregation Model,” affine variations of $\alpha/D_{H,collapse}$ with C_{SDS} are observed for all syntheses and Equation (2) fits very well our data. Let us focus on the Y-intercept. We note that the experimental value of $\alpha/D_{H,collapse}$ at $C_{SDS} = 0$ is different from the value of the intercept between the Y-axis and the straight line fitting the experimental data of the 2 mol% of KPS syntheses. Indeed, the real diameter obtained for surfactant free synthesis is $D_{H,collapse} = 327 \pm 5$ nm whereas the Y-intercept corresponds to a smaller hypothetical diameter $D_{H,collapse}^0 = 203$ nm. We then come to the conclusion that the stabilization mechanism of the microgel with presence and absence of surfactant are different. This result is confirmed by zeta potential measurements (ζ) (Figure 4b). Indeed, the zeta potential absolute values reached at the end of the surfactant-free syntheses ($\zeta \approx -45$ mV) are much higher than those obtained in the presence of surfactant ($\zeta \approx -25$ or -35 mV). Consequently, the colloidal stability does not seem to be reached in the same way if SDS are used or not during the synthesis. We should notice that the decrease of ζ for syntheses performed with SDS, cannot be attributed to the loss of surfactants before the measurements for unpurified microgels. Indeed, we notice a decrease of ζ after the dialysis (empty symbols compared with filled ones), proving that SDS is still adsorbed to the surface when zeta potential measurements were conducted on unpurified microgels. By the way, as expected, this decrease of ζ after purification is higher as more

SDS is used during the synthesis, in agreement to the idea that SDS molecules remain adsorbed to the interface before the dialysis.

Since our model only describes syntheses performed in the presence of SDS, we can put aside the experimental data obtained without SDS to focus on the Y-intercepts representing the inverse of the hypothetical $D_{H,collapse}^0$.

3.1.2. The Hypothetic Size Obtained without Surfactant $D_{H,collapse}^0$ is Linked to Electrostatic Interactions

If the role of initiator would be solely related to the addition of charges on the particles, one could speculate that doubling the concentration of charged initiator could enhance the colloidal stability and would lead to smaller microgels. Indeed, the zeta potential measurements for unpurified microgels from the 4 mol% KPS set ($\zeta \approx -35$ mV, orange full squares) were higher than those performed for unpurified microgels from the 2 mol% KPS set ($\zeta \approx -25$ mV, blue discs). It proves that the amount of initiator modifies the charge density on the particle surface. Nevertheless, $D_{H,collapse}^0$ obtained for 4 mol% KPS (orange squares) is higher than $D_{H,collapse}^0$ obtained for 2 mol% KPS (blues discs) (Figure 4a). It surprisingly means that, in this case, using more KPS leads to more aggregation and larger particles. It seems that KPS is screening the electrostatic repulsion instead of strengthening it. As shown in Table 2, the ionic strength is indeed increased when more KPS is used. To understand better the 4 mol% KPS set, we performed a third set by keeping constant the ionic strength thanks to the addition of 2 mol% of K₂SO₄, but using only 2 mol% of KPS (green triangles). The results superimposed perfectly with the 4 mol% KPS set. It proves that, at least in such concentration conditions, KPS is behaving as salt. It screens the electrostatic interactions, leading to higher aggregation and larger $D_{H,collapse}^0$ (the Debye length λ_D is equal to 4.1 nm and 2.9 nm for the ionic strength of 5.3 and 10.7 mM, respectively). Thus, even if the results is surprising, it is still possible to analyze the Y-intercept with electrostatic interactions arguments.

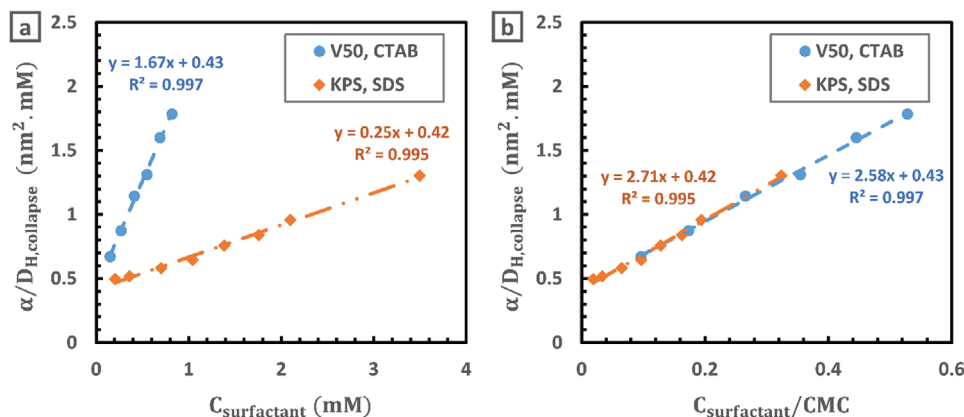


Figure 5. a) Plots of the inverse hydrodynamic diameter for collapsed microgels, $\alpha/D_{H,collapse}$, as a function of the surfactant concentration for two different experiments. For syntheses performed with CTAB surfactant, the concentration of the positively charged initiator V50 is equal to 0.25 mol% compared to NIPMAM monomers (blue circles). For syntheses performed with SDS surfactant, the concentration of the negatively charged initiator KPS is also equal to 0.25 mol% compared to NIPMAM monomers (orange diamonds). In both cases, the concentration of crosslinker BIS was equal to 5.3 mol% compared to NIPMAM monomers. b) Same plot, except that the surfactant concentrations is normalized by the CMC of the surfactant, which leads to a master curve. CMC = 10.8 mM for SDS, while CMC = 1.55 mM for CTAB at a temperature of synthesis equal to 70 °C.

3.1.3. Surfactant Surface Coverage Γ_{SDS} , is not Linked to Electrostatic Interactions

Let's now focus on the slopes of the three sets (Figure 4a). From the slope obtained at 2 mol% of KPS, we can calculate $\Gamma_{\text{SDS}} = \frac{1}{\text{slope}} \approx 1.8 \text{ SDS molecule} \cdot \text{nm}^{-2}$. Interestingly, this value is really close to the maximum surfactant coverage of the heptane-water interface, $\Gamma_m \approx 1.74 \text{ SDS molecule} \cdot \text{nm}^{-2}$.^[26] Surprisingly, the slopes of the three experiments are exactly the same meaning that changing the concentration of the initiator or the ionic strength do not affect the final surfactant surface coverage Γ_{SDS} . Contrary to the Y-intercept and $D_{H,collapse}^0$, Γ_{SDS} and hence, the SDS ability to stabilize the interface, is not related to electrostatic considerations, at least in the range of investigated concentrations. This result is consistent with zeta potential measurements (Figure 4b). Indeed, the zeta potential values are much smaller (in absolute values) in the presence of SDS than in surfactant-free syntheses, indicating that SDS surfactant is able to stabilize the interface more efficiently than just simple charges, contrary to the initiators.

To conclude this part, the evolution of $D_{H,collapse}^0$ (linked to the Y-intercepts) can be analyzed using general arguments about electrostatic interactions in relation to charged initiator concentration, ionic strength and charge screening. However, the surfactant ability to stabilize a surface excess, is surprisingly not linked to its charge. In the next paragraph, we aim at finding the parameters responsible for the size control of the microgel by SDS.

3.2. Is the Surfactant Ability to Decrease the Microgels Size Linked to Interfacial Tension Effects?

Since electrostatic interactions are not the predominant effect which controls Γ_{SDS} , we focus now on the ability of surfactants to decrease interfacial tension between hydrophobic growing particles and water. For this purpose, we refer to a study published by

von Nessen et al. in 2013.^[20] In this work, authors have shown that the size of poly(*N*-isopropylmethacrylamide) (PNIPMAM) microgels can be tailored by the addition of either cationic or anionic surfactants. They also have linked the surfactant efficiency to decrease the size of microgels to the Critical Micellar Concentration (CMC) of the surfactant. To do so, they have performed two sets of syntheses varying the concentration of surfactant. In the first set, syntheses were initiated by an anionic initiator (KPS) whereas an anionic surfactant (SDS) was used to decrease the size of PNIPMAM microgels. Similarly, in the second set, syntheses were performed with both a cationic initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (V50) and a cationic surfactant, the cetyltrimethylammonium bromide (CTAB). Thus, in both cases, the charges of the initiator and surfactant are the same. By combining von Nessen et al. data and the Limited Aggregation Model, we aim at understanding better the relationship between the surfactant concentration and the final size of the collapsed microgels (Figure 5a).

First, the obtained straight lines show that our model can still be applied for PNIPMAM-based microgels. It can even be applied to CTAB surfactants using a positive initiator like V50. Second, the Y-intercept is the same if the concentration of the initiator is kept constant irrespective of the charge sign of the initiator, positive for CTAB-V50 experiments and negative for SDS-KPS experiments. Changing the couple initiator-surfactant is not affecting $D_{H,collapse}^0$. However, changing the surfactant is highly affecting the slope of the straight lines ($\Gamma_{\text{SDS,NIPMAM}} = 4.0 \text{ SDS molecules} \cdot \text{nm}^{-2}$ and $\Gamma_{\text{CTAB,NIPMAM}} = 0.6 \text{ CTAB molecule} \cdot \text{nm}^{-2}$). The huge difference of surface coverage for the two surfactants, while their absolute charge is the same, confirms that surfactants do not stabilize the colloidal dispersion via electrostatic charge effect. The stabilization due to surfactants most probably comes from their amphiphilicity and their ability to decrease surface tension. The longer is the chain length, the more efficiently surfactants can stabilize the particle/water interface, the lower is the final surfactant surface coverage and the higher is the slope on our model.

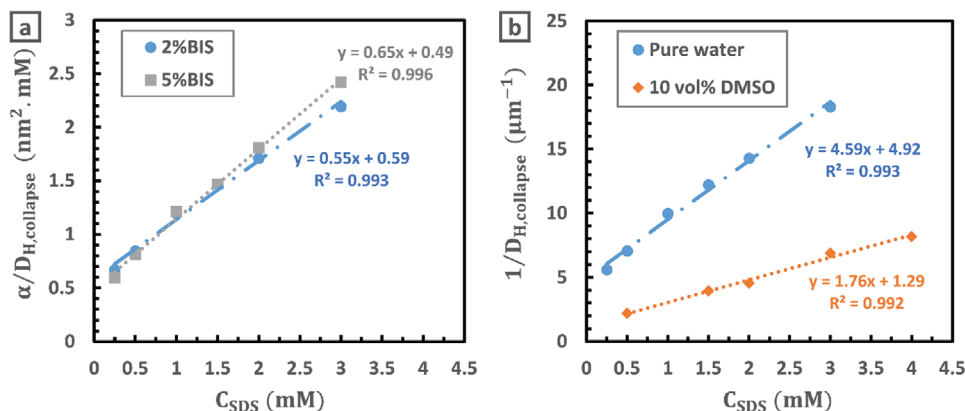


Figure 6. a) Plots of the inverse hydrodynamic diameter for collapsed microgels, $\alpha/D_{H,collapse}$, as a function of the surfactant concentration (C_{SDS}) according to our model. Syntheses are conducted in pure water with a BIS crosslinker concentration equal to 2 mol% compared to NIPAM monomers (blue circles) or 5 mol% compared to NIPAM monomers (grey squares). b) For the last set, syntheses are conducted in pure water (blue circles) or in a mix of water (90 vol%) and DMSO (10 vol%) with a BIS crosslinker concentration equal to 2 mol% compared to NIPAM monomers (orange diamonds). In this case, $1/D_{H,collapse}$ is plotted against C_{SDS} because α is unknown in presence of DMSO.

As similarly done by Hellweg et al., the surfactants concentrations have been normalized by their CMC to obtain, in this particular case, a master curve in Figure 5b. This master curve is surprising since the assembly of surfactants in bulk is not easily linked to its ability to stabilize the polymer/water interface. We can only roughly assume that a lower CMC is obtained for a surfactant with a higher hydrophobic tail, and that a more hydrophobic surfactant is more efficient to stabilize a surface by decreasing its interfacial energy. Nevertheless, we think that the most relevant normalization would not be to divide $C_{Surfactant}$ by the CMC of the surfactant but to normalize Γ by the value of $(\frac{\partial \gamma}{\partial \ln C_{Surfactant}})_{C_{Surfactant} \rightarrow CMC}$ where γ is the surface tension between collapsed particles and the solvent of reaction. It would normalize the surfactant surface coverage by the true surfactant ability to stabilize the interface between collapsed microgels and the solvent of the reaction. Unfortunately, even by approaching γ with the surface tension of a classical oil-solvent interaction, the experimental measurement of such parameter in the exact synthesis conditions is challenging. Such approach is actually in progress.

In any event, these results indicate that surface tension arguments have to be taken account to understand the role of surfactants. The hydrophobic chain length of the surfactants has a predominant role, much more important than its ionic head, in their ability to stabilize particles-water interface and control the size of the microgels.

3.3. Effect of Different Synthesis Parameters

To identify the synthesis parameters able to affect the surfactant surface coverage we have performed two other sets of syntheses varying the crosslinker content and the solvent properties (Figure 6). In a first set, the crosslinker concentration has been increased from 2 to 5 mol% versus NIPAM. In the other one, syntheses have been conducted in a different solvent by mixing water and dimethylsulfoxide (DMSO, 10 vol%). In both sets, straight lines are once more time obtained, confirming the proposed model.

3.3.1. Effect of the Crosslinker Content

When the crosslinker content is increased from 2 to 5 mol% compared to NIPAM monomers, $D_{H,collapse}^0$ is slightly increased (244 nm > 202 nm) and Γ_{SDS} is slightly decrease (1.5 SDS molecule. nm^{-2} < 1.8 SDS molecule. nm^{-2}) (Figure 6a). The differences are small, likely because the crosslinker has not a strong impact on the colloidal stability, but its effect can still be analyzed regarding the literature.^[21] Two hypotheses can be made to explain the increase of $D_{H,collapse}^0$ with an increase of crosslinker content. First, increasing the crosslinker content probably facilitates aggregation by permanently binding the precursor particles, resulting in higher final sizes. Second, the crosslinkers could restrict the mobility of the bound charges and trap them in the interior of the particles, preventing them to contribute to colloidal stability. Here, we also see that Γ_{SDS} is decreased, meaning that the protection of the interface is slightly enhanced by the crosslinkers. Less surfactant is needed to stabilize the same surface which seems contradictory with the hypothesis of trapped surfactants. However, we also admit that it is not easy to explain the slight slope variation with interfacial tension arguments.

3.3.2. Effect of the Solvent Properties

When DMSO is mixed to water during the synthesis, $D_{H,collapse}^0$ is much larger (798 nm \gg 202 nm) and the slope is smaller than in pure water (Figure 6b). The increase of $D_{H,collapse}^0$ can be explained with electrostatic interactions. In a DMSO-water solvent, the counter ions are less dissociated from the charged initiator than in pure water. The electrostatic repulsion between particles is consequently much smaller, leading to higher aggregation and larger microgel sizes. One can note that using a mix of solvent could be of great interest to synthesize monodisperse microgels of very large size.

The slope is also highly affected by a change of solvent. Nevertheless, in this case, the slope cannot be used to directly calculate Γ_{SDS} since α is probably affected by the use of DMSO (see

part 1.2). Indeed, we can guess that the Lele's formula cannot be applied anymore since the presence of DMSO probably affects the PNIPAM chains hydration, even if the DMSO content have been chosen to keep constant the LCST of PNIPAM chains.^[27] However, it can be qualitatively seen that Γ_{SDS} is higher in the presence of DMSO. More surfactant molecules are required to stabilize a same surface, proving that the ability of SDS to stabilize the particles-solvent interface is much smaller. As before, this could be explained through surface tension arguments since the CMC of SDS is indeed higher in the presence of DMSO than in pure water.^[28] We can also guess that if γ is already lowered by the presence of DMSO, $(\frac{\partial \gamma}{\partial \ln C_{\text{SDS}}})_{C_{\text{SDS}} \rightarrow \text{CMC}}$ and the SDS ability to decrease γ will be much smaller than in the case of pure water. The measure of such value in the conditions of the syntheses would be therefore interesting. Finally, since γ is already lowered by the presence of DMSO we could also guess that surface tension is no more a predominant argument to explain the role of surfactant and that electrostatic interactions have to be taken account now. We could therefore explain the need of a higher surfactant surface coverage, by a decrease of the electrostatic repulsion between ionic heads of the surfactants due to the presence of DMSO.

Finally, the effect of DMSO on the surfactant ability to stabilize the colloidal dispersion can be qualitatively understood both with surface tension and electrostatic repulsion arguments but is not quantitatively demonstrated yet.

3.4. Limits of the "Limited Aggregation Model"

To study the limits of this model, and especially its hypothesis of a strong interaction between the polymer and the surfactant, we investigate different acrylamide-surfactant couples thanks to data extracted from the literature (Figure 7).^[14]

In all experiments presented until now, straight lines were obtained when the inverse diameter of collapsed microgels was plotted as a function of the surfactant concentration. Changing the solvent, the initiator charge or concentration, the ionic strength and the crosslinker content did not break down the Limited Aggregation Mechanism, therefore showing its strength and generality. We recall that the model relies on one main assumption: surfactant molecules have to be all adsorbed at the solvent-particle interface. Contrary to particles which irreversibly adsorb to the interface in Pickering emulsions, surfactant distribution is always presented like a dynamic equilibrium between the surface and the volume, depending on the surfactant-interface and surfactant-bulk interactions. Here, such equilibrium is apparently broken and all the surfactants adsorb to the interface, since straight lines are always obtained in our model. It can be explained by a particular huge attractive interaction between PNIPAM or PNIPMAM chains and surfactant molecules already reported in the literature.^[29–31] At least, strong interactions have been evidenced when the surfactant concentrations are smaller than the CMC or even smaller than the Critical Aggregation Concentration (CAC) of the surfactant-polymer couple as discussed by Kardos et al.^[16] That's why, in all the experiments, low concentration of surfactants have been used.

As proven by the Figure 7, when surfactants with a smaller hydrophobic tail like sodium decyl sulfate (SDeS) is used, straight lines are no more obtained. We hypothesize that the polymer-

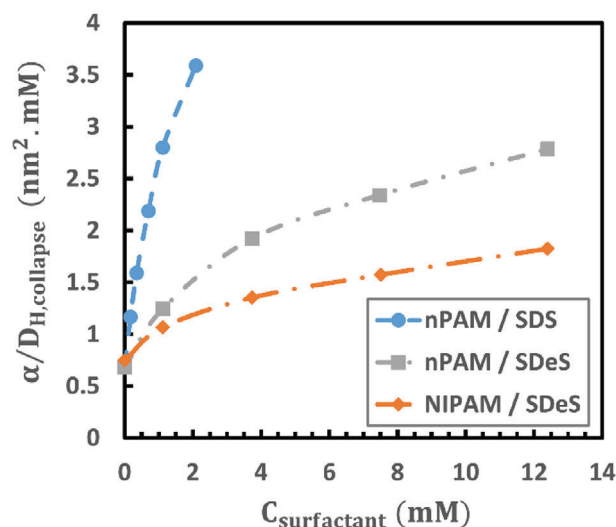


Figure 7. Plots of the inverse hydrodynamic diameter for collapsed microgels, $\alpha/D_{H,\text{collapse}}$, as a function of the surfactant concentration (C_{SDS}) according to our model for three different acrylamide-surfactant couples: N-n-propylacrylamide (nPAM) / SDS (blue circles); nPAM / Sodium Decyl Sulfate SDeS (grey squares); and NIPAM / SDeS (orange diamonds). The initiator and crosslinker concentrations are kept constant for each sets. Dashed lines are guide for the eyes.

surfactant interaction is not strong enough to validate the hypothesis of a total adsorption of the surfactant at the interface so that the Limited Aggregation Model does not apply anymore. Similarly, when another acrylamide like N-n-propylacrylamide (nPAM) is used, straight lines are not observed, likely originating from a less strong surfactant-polymer binding unable to ensure irreversible adsorption.

3.5. Syntheses with Oppositely-Charged Initiators and Surfactants

In literature, authors always combine surfactant and initiator with the same charge. Originally, we finally performed a set of syntheses in which initiator and surfactant are of opposite charges (Figure 8). This allows studying the condition of obtaining monodisperse microgels and permits to test the robustness of our model. To do so, we combined the positively charged initiator V50 and the negatively charged surfactant SDS (Figure 8a).

In all the syntheses, the concentration of charges coming from the initiator is equal to 3.5 mM. For low C_{SDS} (0 and 1 mM), when surfactant molecules are not enough numerous to hide the charges coming from the initiators, monodisperse microgels are obtained without any aggregation. The final surface charge ζ is positive, meaning that the colloidal stability is reached thanks to electrostatic repulsion and to the charges dominated by the initiator ones. When C_{SDS} increases, ζ decreases, proving that the positive charges coming from the initiators are gradually hidden by the negatively charged SDS. When the charges are entirely hidden ($\zeta = 0$ mV and $C_{\text{SDS}} = 2$ mM), the colloidal stability cannot be reached again, showing the importance of electrostatic repulsions (at low surfactant concentrations) and microgel aggregation occurs as proven by the large diameter (superior to 1.2 μm) and the high PDI value (0.4) obtained. As soon as C_{SDS} is high

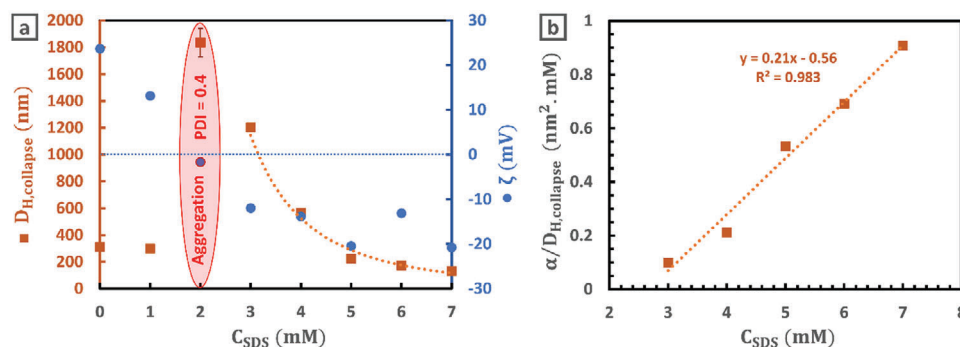


Figure 8. a) Plots of the hydrodynamic diameter (orange squares) and zeta potential measurements (blue circles) for collapsed microgels as a function of the SDS concentration. Syntheses are conducted in pure water with a BIS crosslinker concentration equal to 2 mol% compared to NIPAM monomers and a concentration of the positively charged initiator V50 equal to 2 mol% compared to NIPAM monomers. Dashed lines are guide for the eyes. b) Plots of the inverse hydrodynamic diameter for collapsed microgels as a function of the surfactant concentration according to our model. The data comes from (a), when the SDS concentration is high enough to obtain stable colloidal dispersions ($C_{SDS} \geq 3$ mM).

enough to ensure a final negative zeta potential ($\zeta \sim -15$ mV and $C_{SDS} \geq 3$ mM), well monodisperse microgels are obtained and limited aggregation occurs. The obtained collapsed sizes are much larger than those obtained by classical dispersion polymerization. Thus, very large ($D_{H,collapse} \sim 1$ μ m) and highly monodisperse (PDI < 0.1) microgels can be synthesized with this new type of synthesis combining surfactant and initiators of opposite charge. Indeed, surfactants are able to screen the charges coming from the initiators and consequently prevent them to participate to colloidal stability. Besides the size of these large microgels can still be decreased by using a higher concentration of surfactants. Then, we can apply our model to these points (Figure 8b). Straight line is once more obtained, showing that a limited aggregation mechanism occurs. In this case, Γ_{SDS} is larger (4.8 SDS molecule.nm⁻² > 1.8 SDS molecule.nm⁻²). It means that surfactants are less efficient to stabilize the interface. It can be understood by the presence of electrostatic pairs between the positive initiators and negative SDS which probably disturb the adsorption of other SDS responsible for the stabilization. It can be also understood thinking that, in this special case, some SDS molecules are probably trapped inside the particles because of the electrostatic attraction by the positively charged initiator. These trapped surfactants do not participate to the stabilization of the interface and fictively increase Γ_{SDS} .

4. Conclusion

A “Limited Aggregation Model” is proposed, to explain the dispersion polymerization syntheses of acrylamide-based microgels, in the presence of charged surfactants. This model predicts that the successive aggregation between nuclei involves a reduction of the interfacial area between the growing particles and the solution. In presence of charged surfactant, smaller particles are obtained since an additional interfacial area is created. This additional interfacial area is found to be proportional to the amount of surfactant, as proven by the affine relation between the inverse microgels diameter and the surfactant concentration, obtained for both our new data and data extracted from the literature. This phenomenon is analogous to the limited coalescence process occurring in Pickering emulsions. It involves that the successive aggregation steps would stop once a given surfactant coverage is

reached, which also implies that all the surfactant are anchored to the interface.

By analyzing the dependence between the interfacial area and the surfactant concentration, the surfactant adsorption could be determined. In the case of SDS/PNIPAM system, it was found to be consistent with the values at the heptane-water interface. The adsorption does not depend on the ionic strength, showing that the surfactant ability to decrease the size of the particles is not due to its charge. However, the adsorption was found to strongly depend on the surfactant tail length and the chemical nature of the polymer. Thus, the surface energy of the system is an important parameter that drives the surfactant ability to stabilize the growing particles. Contrarily to the limited coalescence process, the diameter did not tend to infinity in absence of surfactant. This owes to the fact that other parameters, such as the charges induced by initiator, could stabilize the growing particles in the absence of surfactant.

Finally, the model reveals to be a very good tool to predict the final size of the particles in a dispersion polymerization process in presence of surfactant. It was possible to transfer it to very different conditions including various ionic strengths and solvent mixtures. It was also possible to apply it to a combination of oppositely charged couple of initiator/surfactant. In this case, the addition of surfactant did not only control the size due to interfacial energy considerations, it also neutralized the surface charges. In overall, this combination resulted in a broadening of the accessible size range of particles. In few cases, the model was not valid, likely due to a lower adsorption energy of the surfactant, and thus its reversible binding at the interface.

In summary, most dispersion polymerizations can be viewed through the prism of this “Limited Aggregation Model.” Although the mechanisms are not fully deciphered, it turns out that the main ingredients, involving charges for the initiators and polymer-surfactant interaction tuning the amount of necessary surfactant, were highlighted. More work is actually in progress to propose a full understanding about these complex systems.

5. Experimental Section

Materials: All materials were purchased from Sigma-Aldrich. The monomers *N*-isopropylacrylamide (NIPAM, > 97%) and

N-isopropylmethacrylamide (NIPMAM, > 97%) were recrystallized from *n*-hexane and dried in vacuum at 25 °C. The cationic initiator 2,2'-azobis(2-amidinopropane) dihydrochloride (V50, purity 97%), the anionic initiator potassium peroxydisulfate (KPS, purity 99%), the crosslinker *N,N'*-methylenebis-acrylamide (BIS, 99%), and the anionic surfactant Sodium Dodecyl Sulfate (SDS) were used as received. Potassium sulfate K₂SO₄ (> 99%) was used to adjust the ionic strength during the synthesis. 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO, 98%) was used to quench the radical polymerization. Sodium chloride (> 99%) was used to keep ionic strength constant for the zeta potential measurements. Milli-Q water (Millipore, France) with a resistance of 18 MΩ cm and a total organic content (TOC) < 10 ppb was employed for the synthesis, purification and characterization process of the microgels. Dimethyl sulfoxide (DMSO, > 99%) has been mixed (10 vol%) to water to modify the properties of the solvent.

Synthesis of the Microgels: The microgel synthesis was performed via free-radical dispersion polymerization in water. For all the syntheses, water was purged with nitrogen for 1 h before use. All polymerizations were conducted in a 100 mL three-necked double-wall flask equipped with a reflux condenser, a mechanical rotor (250 rpm), and a nitrogen inlet. The monomer NIPAM or NIPMAM (302 mg, 1 wt% versus water) was dissolved in 8 mL of purged water in the flask. The crosslinker BIS (8.2 mg, 2 mol% versus the monomer) and various amount of SDS were added in the flask and the volume of solution in the flask is 29 mL. Except if mentioned, the final concentrations of SDS varies from 0 to 3 mM for each set of synthesis. Afterward, the temperature was raised to 70 °C thanks to the circulation of water in the double-wall flask. After an equilibration time of 30 min, the polymerization reaction was started by rapid addition of the initiator KPS (14.4 mg, 2 mol% versus the monomer), preliminarily dissolved in 1 mL of water (the final volume of the reaction mixture is 30 mL). The initially transparent reaction mixture became turbid within the first 10 min after the addition of the initiator. The polymerization reaction was allowed to proceed for 4 h.

Sample Preparation: A quenching solution was prepared by dispersing NaCl salt (10⁻³ mol L⁻¹) and radical quencher TEMPO (280 mg L⁻¹, i.e. 50 equivalents versus initiator after the dilution) in 50 °C milli-Q water. At the end of the synthesis, microgels are kept at a temperature higher than 50 °C to avoid any swelling, or loss of free chains, before measurements. To do so, 20 μL of the reaction mixture was added to 2 mL of a 50 °C quenching solution. The resulting solutions of microgels were then analyzed directly by Dynamic Light Scattering (DLS) and Zeta Potential measurements at 50 °C. It can be noticed that the dilution of the synthesized microgels was high enough to both allow DLS measurements in the diluted regime (simple scattering) and allow Zeta Potential measurements at a constant salt concentration of 10⁻³ mol L⁻¹. Besides, as proven by comparing Zeta Potential measurements before and after purification, the SDS surfactants were not pulled off from the surface of the microgels by the dilution at high temperature.

Dynamic Light Scattering: Dynamic Light Scattering was performed on an ALV goniometer (ALV/CGS-3) with a He/Ne laser operated at a wavelength of λ = 633 nm, in combination with an ALV/LSE-5003 correlator at 50 °C. For each sample, six measurements with 60 s duration were performed. The obtained data were evaluated using a second order cumulant fit. A classical standard deviation was calculated to obtain the uncertainties on both the size of the microgels in the collapsed state and on its polydispersity. Except if mentioned, all samples were highly monodisperse as proven by the very low polydispersity index (PDI) always inferior to 0.05.

Zeta Potential Measurement: Zeta Potential (ζ) measurements were performed on a Zetasizer Nano-ZS93 (Malvern) at 50 °C. Six measurements were done to calculate the uncertainty on ζ for each sample before and after a purification of the microgels. The aqueous microgel dispersions were purified by dialysis (Biotech CE 1000000 MWCO 31 mm) during 10 days in water to remove oligomers, unreacted monomers and surfactant molecules. The preparation of the sample for zeta potential measurement after purification was exactly the same as before, by dispersing 20 μL of the aqueous purified microgel dispersion into 2 mL of the quenching solution. It can be reminded that the quenching solution is at constant salt concentration of 10⁻³ mol L⁻¹.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

dispersion polymerization, limited aggregation model, microgel, precipitation polymerization, surface coverage, surfactant, synthesis mechanism

Received: October 10, 2023

Revised: November 23, 2023

Published online:

- [1] R. H. Pelton, P. Chibante, *Colloids Surf.* **1986**, *20*, 247.
- [2] F. A. Plamper, W. Richtering, *Acc. Chem. Res.* **2017**, *50*, 131.
- [3] M. Karg, A. Pich, T. Hellweg, T. Hoare, L. A. Lyon, J. J. Crassous, D. Suzuki, R. A. Gumerov, S. Schneider, I. I. Potemkin, W. Richtering, *Langmuir* **2019**, *35*, 6231.
- [4] M. Mackiewicz, J. Romanski, K. Drabczyk, E. Waleka, Z. Stojek, M. Karbarz, *Int. J. Pharm.* **2019**, *569*, 118589.
- [5] E. Waleka, M. Mackiewicz, J. Romanski, A. Dybko, Z. Stojek, M. Karbarz, *Int. J. Pharm.* **2020**, *579*, 119188.
- [6] M. Destribats, M. Eyharts, V. Lapeyre, E. Sellier, I. Varga, V. Ravaine, V. Schmitt, *Langmuir* **2014**, *30*, 1768.
- [7] T. Zhang, T. Ngai, *Langmuir* **2021**, *37*, 1045.
- [8] Y. Horiguchi, H. Kawakita, K. Ohto, S. Morisada, *Adv. Powder Technol.* **2018**, *29*, 266.
- [9] R. Contreras-Cáceres, A. Sánchez-Iglesias, M. Karg, I. Pastoriza-Santos, J. Pérez-Juste, J. Pacífico, T. Hellweg, A. Fernández-Barbero, L. M. Liz-Marzán, *Adv. Mater.* **2008**, *20*, 1666.
- [10] C. D. Sorrell, M. C. D. Carter, M. J. Serpe, *Adv. Funct. Mater.* **2011**, *21*, 425.
- [11] J. Es Sayed, C. Lorthioir, P. Banet, P. Perrin, N. Sanson, *Angew. Chem., Int. Ed.* **2020**, *59*, 7042.
- [12] L. A. Lyon, Z. Meng, N. Singh, C. D. Sorrell, A. St John, *Chem. Soc. Rev.* **2009**, *38*, 865.
- [13] W. McPhee, K. C. Tam, R. Pelton, *J. Colloid Interface Sci.* **1993**, *156*, 24.
- [14] B. Wedel, T. Brändel, J. Bookhold, T. Hellweg, *ACS Omega* **2017**, *2*, 84.
- [15] Y. Nishizawa, H. Minato, T. Inui, T. Uchihashi, D. Suzuki, *Langmuir* **2021**, *37*, 151.
- [16] A. Kardos, T. Gilányi, I. Varga, *J. Colloid Interface Sci.* **2019**, *557*, 793.
- [17] M. Andersson, S. L. Maunu, *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 3305.
- [18] Y. Chen, S. Sajjadi, *J. Appl. Polym. Sci.* **2014**, *131*, 40781.
- [19] X. Wu, R. H. Pelton, A. E. Hamielec, D. R. Woods, W. McPhee, *Colloid Polym. Sci.* **1994**, *272*, 467.
- [20] K. Von Nessen, M. Karg, T. Hellweg, *Polymer* **2013**, *54*, 5499.
- [21] O. L. J. Virtanen, H. M. Ala-Mutka, W. Richtering, *Macromol. Chem. Phys.* **2015**, *216*, 1431.
- [22] O. L. J. Virtanen, M. Brugnoli, M. Kather, A. Pich, W. Richtering, *Polym. Chem.* **2016**, *7*, 5123.
- [23] S. Arditty, C. P. Whitby, B. P. Binks, V. Schmitt, F. Leal-Calderon, *Eur. Phys. J. E* **2003**, *11*, 273.
- [24] B. P. Binks, S. O. Lumsdon, *Langmuir* **2001**, *17*, 4540.
- [25] A. K. Lele, M. M. Hirve, M. V. Badiger, R. A. Mashelkar, *Macromolecules* **1997**, *30*, 157.

- [26] F. Van Voorst Vader, *Trans. Faraday Soc.* **1960**, *56*, 1067.
[27] R. O. R. Costa, R. F. S. Freitas, *Polymer* **2002**, *43*, 5879.
[28] S. A. Markarian, L. R. Harutyunyan, R. S. Harutyunyan, *J. Solution Chem.* **2005**, *34*, 361.
[29] A. Durand, D. Hourdet, *Polymer* **2000**, *41*, 545.
[30] J. Chen, H. Xue, Y. Yao, H. Yang, A. Li, M. Xu, Q. Chen, R. Cheng, *Macromolecules* **2012**, *45*, 5524.
[31] L.-T. Lee, B. Cabane, *Macromolecules* **1997**, *30*, 6559.