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Mechanism and Modeling of Emulsion Polymerization: New Ideas and Concepts – 1. Particle Nucleation

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Summary: New experimental data for nucleation in emulsion polymerization prove that the process is heterogeneous in nature so that water-borne oligomers precipitate at the surface of monomer drops. The particle morphology at the early stage of the process is strongly influenced by the initiator concentration. The hydrophilicity of the monomer is less important as methyl methacrylate, styrene, and 4-tert-butyl styrene show similar behaviour.

Keywords: emulsion polymerization; hydrophilicity of monomers; particle nucleation; spontaneous emulsification

Introduction

This contribution summarizes new experimental results on particle nucleation during batch ab-initio emulsion polymerization in water. This is the most complicated and least understood technical version of emulsion polymerization (EP) and characterized by most drastic changes in the course of the reaction particularly during particle nucleation.

Experimental Part

4-tert-butylstyrene (Alfa Aesar, 94% purity) was purified by passing over activated alumina columns and the other monomers (styrene and methyl methacrylate) by distillation under reduced pressure. Potassium peroxydisulfate (KPS) from Fluka was used as received. The water was taken from a Seral purification system (PURELAB Plus) with a conductivity of 0.06 μS/cm and degassed prior to use for polymerization.

The experimental setup and the procedure to investigate particle nucleation have been described elsewhere.[1,2] In brief, the all-Teflon reactor was filled with 400 g of water. Then 4.9 g of monomer was placed on top of the water confined in a glass funnel maintaining a constant monomer-water interface. The stirrer speed is so slow that the monomer phase is not comminuted but the water phase is thoroughly mixed. The polymerizations were started by injection 10 ml initiator solution at 70 °C. The amount of initiator in the reaction mixture was varied between 0.05 and 6 mM. For molecular weight and morphology characterization samples were taken from polymerizations in all-glass reactor at different times. The molecular weight distribution (MWD) was determined by size exclusion chromatography (SEC) in tetrahydrofuran according to standard procedure. Particle morphology was checked by transmission electron microscopy (TEM) (Zeiss EM 912 Omega microscope operating at 100 kV, suspension preparation).

New Experiments Contributing to Understand Particle Nucleation

Particle nucleation is the most important step in any heterophase polymerization as it generates the loci of main monomer conversion. Despite its importance it was

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the least understood step in EP. There are two major reasons for this condition. Firstly, particle nucleation in batch *ab-initio* EP takes place at very low monomer conversions, it is extremely fast and hence, its experimental investigation is tremendously challenging. Secondly, as it is finished at quite low monomer conversion it is only of minor importance for understanding and investigating the monomer conversion including particle growth during the remaining almost 99% of the reaction. Nevertheless, a complete description of the mechanism of EP requires also understanding of particle nucleation.

The assumption that micelles are precursors of polymer particles lacks experimental verification. In contrast, recently we were able to show experimentally that particle nucleation is not altered by micelles. Only seed particles are able to influence particle nucleation and they even can suppress it, if present above a concentration limit.[2] A key to understand the mechanism of particles nucleation in EP, independent of the emulsifier concentration, is the state of the monomer in the aqueous phase. Experimental results show that there is not a pure solution of single monomer molecules in water but monomer droplets exist even at concentration below the saturation concentration.[3] Meanwhile there is a lot of experimental support for that what is called spontaneous emulsification.[4] Spontaneous emulsification happens in both the absence and presence of emulsifiers immediately after bringing two immiscible liquids in contact even without any shear forces. In styrene emulsion polymerization these droplets participate in the nucleation process as sites where the water-born oligomers nucleate. Within the frame of classical nucleation theory, the presence of any external species (emulsifiers, seed particles, and monomer droplets) can facilitate particle formation by decreasing the free energy barrier.[5] This scenario is impressively proven by electron microscopy images as exemplarily shown in Figure 1. After nucleation, the water-born oligomeric particles precipitate at the droplet water interface and cause the formation of hollow particles by templating the monomer drops (Figure 1A, C). At later stages (Figure 1B, D), solid particles are formed as the polymerization is gradually more and more shifted into the particles.

The particle morphology during the nucleation period is governed by the initiator concentration that determines the properties of the nuclei, that is, whether or not they are soluble in the monomer, cf..[2]

Here we report new results of surfactant-free emulsion polymerization of 4-*tert*-butylstyrene (tBS), a much more hydrophobic monomer than styrene for which also spontaneous emulsification has been observed.[4] There is a report saying that unlike styrene, emulsifier-free polymerization of tBS is not possible however, polymerization starts immediately after emulsifier addition.[6] In contrast to these results, we were able to polymerize tBS under emulsifier-free conditions in an experimental setup especially designed to follow particle nucleation.[1] Due to the higher hydrophobicity one might expect a different nucleation behavior than for styrene, especially a higher probability of droplet nucleation due to entry of oligomers into monomer drops. The polymerizations were evaluated with our standard procedure[2] that is conductivity measurement during the reaction, electron microscopy, and size exclusion chromatography of samples withdrawn from the reactor.

Spontaneous emulsification of tBS[4] leads to droplets possessing quite a broad size distribution. The image of Figure 2 was taken with a digital light microscope (Keyence, Japan). The droplets are stable as long as the two phases exist and gathering in the vicinity of the water – tBS interface. Of course, the droplets size distribution might be influenced by the mild stirring applied during the polymerization but, this does not change the scenario basically.

The droplet size distribution is extremely broad and reaches from about 10 μm down to a few nanometers. The existence of the smallest droplets, that are normally not

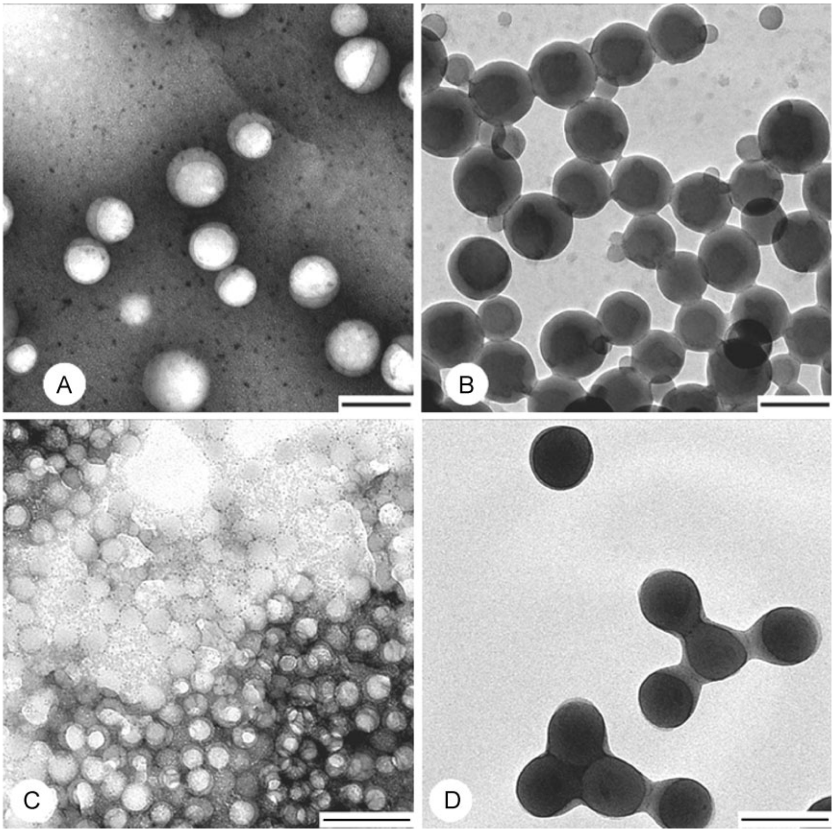

Figure 1.
TEM images polystyrene (upper row) and PMMA particles (lower row) showing the development of particles' morphology during surfactant-free EP; images A and B after polymerization time of 10 and 150 min with monomer equilibration time in water of 180 min; images C and D after polymerization time of 2 and 8 min with monomer equilibration time of 120 min; experimental conditions styrene: all-glass reactor, non-stirred, 70 °C, 20 ml of monomer, 562.5 g of water, 8.22 mM KPS; MMA: all-glass reactor, stirring 50 rpm, 70 °C, 20 ml of monomer, 410 g of water, 0.244 mM KPS the bar indicates 200 nm.

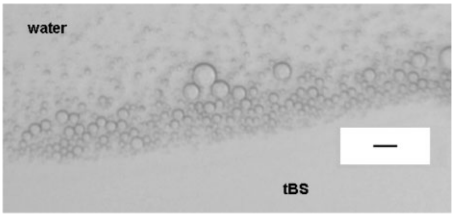

Figure 2.
Light microscopy image of spontaneously formed tBS drops after contact with water; tBS was carefully placed on top of water in an optical cuvette of 1 mm thickness; the image was taken about 12 hours after preparation; bar: 10 μm.

directly visible by light microscopy, is concluded due to a special illumination technique of the Keyence microscope, that allows the detection of the scattered light similar to the action of an ultramicroscope.[7] Satpathy & Dunn came during their study[6] on emulsion polymerization of highly water insoluble monomers (octadecyl methacrylate, ODMA, and tBS) to an interesting inference. As the reported water solubility of ODMA is with 0.24% almost double that of methyl methacrylate (MMA) they concluded mainly micellar solubility assuming the monomer might be weekly surface active. Also a saturated

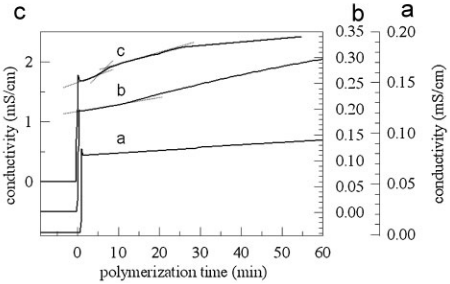

Figure 3.

Change of the aqueous phase conductivity during surfactant-free *ab-initio* emulsion polymerization of *tert*-butyl styrene with low (curve a,), intermediate (curve b) and high (curve c) KPS concentration; time zero marks the start of the polymerization by initiator addition; a – 0.058 mM KPS, b – 0.58 mM KPS, c – 5.8 mM KPS.

styrene in water solution (2.1.mM at 25 °C) contains droplets despite that the solution appears absolutely clear to the naked eye.[3,8] For styrene it is rather the hydrophobic effect than the surface activity that causes droplet formation. Mechanism of droplet formation has been discussed in.[4] In the same line of arguments ODMA micelles can be considered as monomer droplets (melting point of ODMA is about 18–20 °C). The importance of spontaneous emulsification for particle nucleation in emulsion polymerization of tBS becomes clear by the following experimental results.

According to previous experimental findings a bend in the conductivity time curve marks the onset of particle nucleation[1,2] by precipitation of water-born oligomers. The bend is caused by the capture of protons (these are the species with the highest mobility contributing most to the conductivity) in the electrical double layer of the just generated particles. The bend does not appear if no particles are generated that is, if enough water-born oligomers are captured by existing colloidal objects (seed particles, droplets, or micelles) that already possess an interface surrounded by an electrical double layer.

For styrene a single bend appears over a wide range of persulfate concentration.[2] However, for tBS the shape of the conductivity - time curves clearly depends on the initiator concentration (Figure 3). Immediately after adding KPS the conductivity jumps and peroxodisulfate decomposition causes it to increase, resulting in a period of constant slope. Both the slope and the duration of this period depend on the KPS concentration. The higher is the concentration the larger the slope and the shorter this period. For the lowest initiator concentration (curve a) a bend can only be hardly identified after about 30 min with, however, only a minor change in the slope. For the intermediate KPS concentration (curve b) the first period lasts about 13 minutes and thereafter the slope is gradually decreasing. This behavior might be explained with almost continuous nucleation after the bend. The highest initiator concentration (curve c) is characterized by the appearance of multiple bends. The first occurs after about 7 minutes and is followed by a period with larger slope for only two minutes. Then two more bends appear followed by periods with decreasing slopes. This behavior points to multiple nucleation events occurring at certain times after the necessary supersaturation has been built up repeatedly. The time to reach the supersaturation regarding the oligomers in the continuous phase increases from bend to bend which makes sense as existing particles can capture oligomers.

TEM images of the final latexes reveal that also the particle morphology is strongly dependent on the KPS concentration (cf. Figure 4a and 4b). The observed morphologies correlate nicely with both the different nucleation behavior indicated by the conductivity-time curves and the KPS concentration.

Both images of Figure 4a show solid sphere morphology whereas with the lowest initiator concentration (image A) much less but larger particles are observed than for the intermediate amount of KPS (image B). In the latter case the particles are much smaller and their shape appears better defined. In general, the solid sphere morphology already indicates droplet nucleation. The larger number of particles

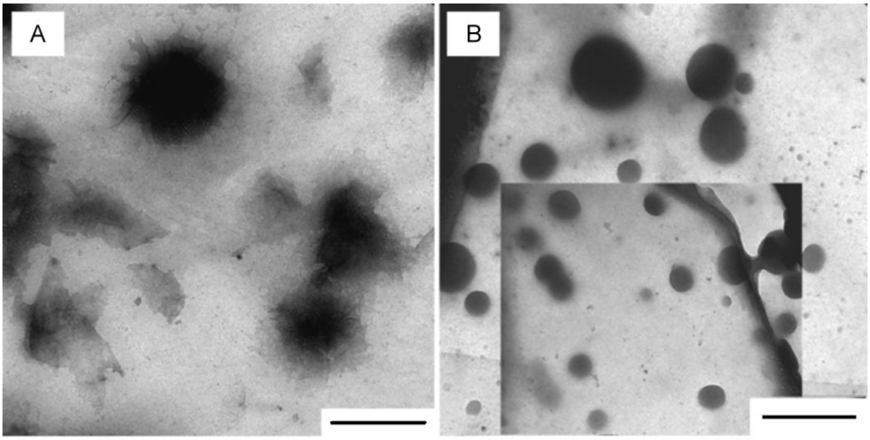

Figure 4a.
TEM images of the particles obtained by surfactant-free emulsion polymerizations of tBS with low (image A, bar: 500 nm) and intermediate (image B, bar: 1000 nm, composite image) KPS concentration; image A and B corresponds to curves a and b of Figure 3.

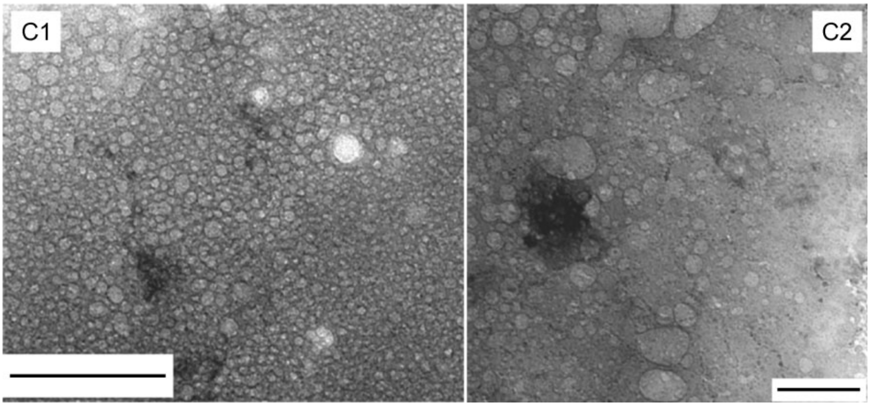

Figure 4b.
TEM images of the particles obtained by surfactant-free emulsion polymerizations of tBS with high KPS concentration (curve c of Figure 3, C1 bar: 200 nm, C2 bar: 100 nm).

and the broad size distribution seen for the intermediate initiator concentration support an almost continuous nucleation. In contrast, the images of Figure 4b (polymerization with the highest KPS concentration) show a completely different morphology. These particles do not possess solid sphere morphology but show spheres with dark edges and much brighter interior resembling hollow spheres. This corresponds to multiple nucleation events where the water-born oligomeric particles after nucleation adhere only to the droplet interface without being hydrophobic enough to enter the droplets completely.

The TEM images of Figure 5 show that also for the intermediate KPS concentration hollow particles are generated initially and solid particles appear only later. For the lowest initiator concentration samples taken 10 minutes after initiation already show solid particles.

Changing the initiator concentration influences strongly the particle morphology and the molecular weight of the oligomers/polymers as already shown for styrene.[2]

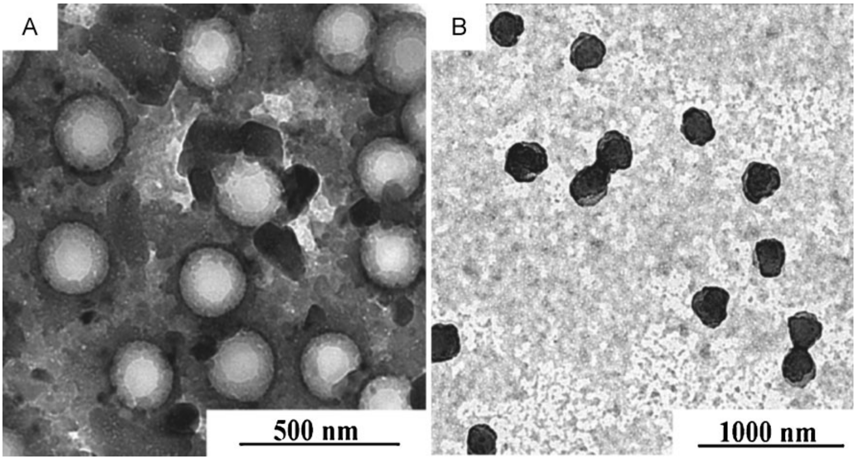

Figure 5.
TEM images of the particles obtained by surfactant-free emulsion polymerization of tBS in an all glass reactor; KPS concentration 0.58 mM, sampling time image A and B 30 and 45 min after initiation, respectively.

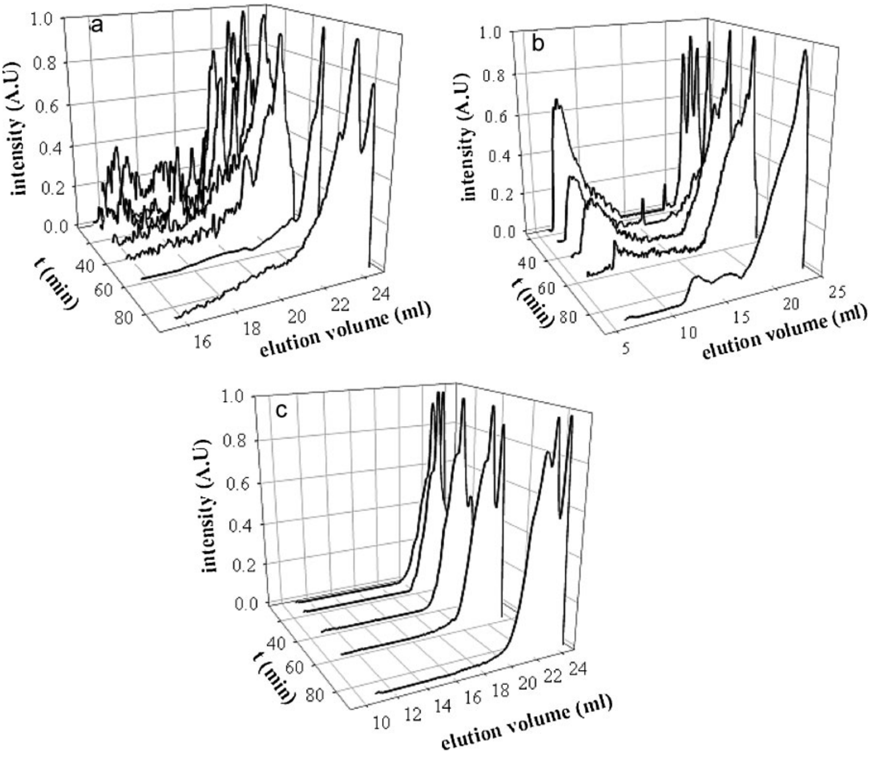

Figure 6.
Development of the MWD during surfactant-free emulsion polymerizations of tBS initiated with low (a), intermediate (b), and high (c) concentration of KPS.

Figure 6 shows similar behavior for tBS and additionally, an astonishing effect regarding the time dependence of the MWD. For both the lower initiator concentrations (graphs a and b of Figure 6) the estimated average molecular weight decreases with time whereas it increases for the highest amount of KPS (graph c). The surprising result is the decrease of the average molecular weight with time. For typical emulsion polymerization one would expect an increase with time after particle nucleation because the reaction loci with the high monomer concentration need to be built up in the course of the reaction. Such behavior is observed for tBS only for the highest KPS concentration but it was found also for styrene over the entire range of KPS concentrations studied.[2]

The data of Figure 5 (graphs a and b) show an extremely broad MWD. The samples taken between 10 and 60 minutes are basically bimodal with peaks in the high and low molecular weight region (lowest and highest elution volume, respectively). In the course of the polymerization the relative intensity of the peak in the high molecular weight region decreases and that of the peak in the low molecular weight region broadens and shifts towards higher molecular weights. The bimodality of the MWD clearly reveals the existence of two reaction loci that differ greatly regarding the monomer concentration. Knowing about spontaneous emulsification it is straightforward to identify these loci as monomer droplets (high tBS concentration) and the aqueous phase (low tBS concentration). Thus, experimental evidence is presented that tBS surfactant free EP is characterized by two nucleation mechanisms (cf. Figure 6) – droplet nucleation and heterogeneous aggregative nucleation – taking place simultaneously, at least at KPS concentration below or equal to 0.577 mM.

MMA, styrene, and tBS are monomers that differ in their water solubility by about four orders of magnitude, but they show absolutely comparable behavior regarding particle nucleation (cf. Figure 7). At higher initiator concentration hollow spheres are formed due to heterogeneous nucleation of water-born oligomers on the surface of monomer droplets. In the course of the polymerization when the polymerization is

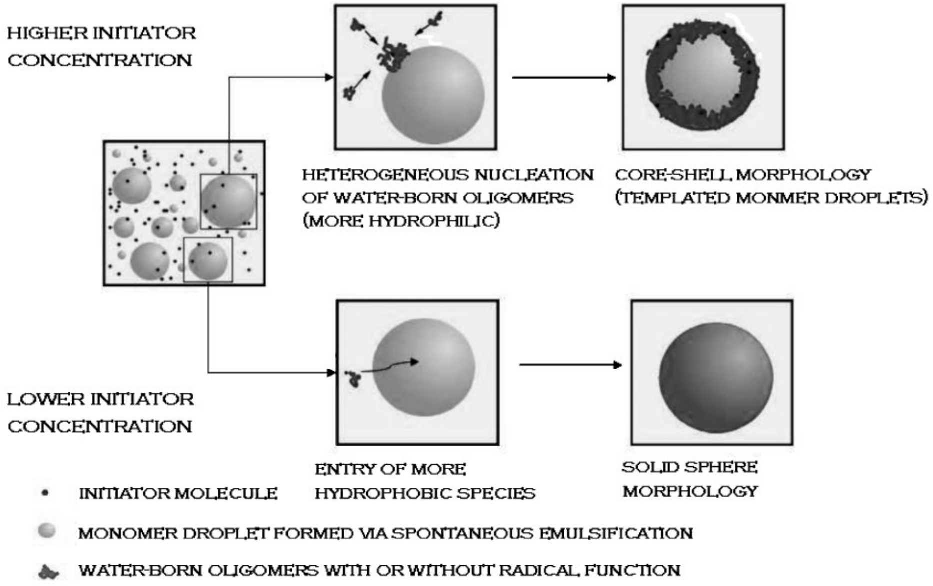

Figure 7.
Sketch of particle nucleation in dependence on initiator concentration for tBS.

shifted inside the spheres the morphology changes to solid particles. At lower initiator concentrations solid spheres are generated from the very beginning as the longer and hence more hydrophobic oiligomers in the nucleated aggregates are able to enter the monomer droplets quicker. In conclusion, the fact that MMA, styrene, and tBS behave similarly supports greatly the quality of being general of the presented ideas regarding particle nucleation in EP.

Summary and Conclusions

During the last years progress has been made towards a consistent mechanistic description of ab-initio batch emulsion polymerization. The discovery of spontaneous emulsification, that is, the experimentally proven fact that a monomer-in-water solution is characterized by the existence of aggregates of monomer molecules (droplets of any size between nanometers and micrometers depending on the emulsification time), is an essential key to better understanding. Particle nucleation is heterogeneous in nature as water born oligomers precipitate at the interface of the monomer droplets.

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