# Novel Industrial Application of Miniemulsion Polymerization – Use of Alkali Soluble Resin as Surfactant in Miniemulsion Polymerization

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**Summary:** Nowadays, the great versatility of the miniemulsion polymerization technique to synthesize novel and high value added materials attracts great interest from both the academic and the industrial community. Recently, a novel process based on the use of alkali soluble resin (ASR) as sole surfactant in miniemulsion polymerization for high solids content latexes has been disclosed. This new technology opens a vast field for the production of high performance latexes for industrial applications, as well as an interesting topic for future academic research. This work presents the key factors influencing the use of ASR in aqueous polymer dispersions, highlighting the differences in terms of types and concentrations of ASR used in conventional and miniemulsion polymerization. The effects of type of initiator, ASR concentration and type, as well as solids content on the miniemulsion polymerization of styrene and acrylic monomers are presented.

**Keywords:** alkali soluble resin; latex; miniemulsion polymerization; process

## Introduction

Amphiphatic macromolecules are widely employed in conventional emulsion polymerization processes in order to obtain aqueous polymer dispersions with improved colloidal properties and enhanced end-use performances.[1-6] These are polymers with a proper hydrophobic-hydrophilic balance, produced either by emulsion, bulk or solution polymerization, which are commonly added in the initial charge of semi-continuous emulsion polymerization processes. Low molar mass alkali-soluble resins (ASRs) have been used as colloidal stabilizers in commercial applications since the 70s, especially in latexes used for waterborne printing inks. ASRs are commonly used at high levels (>20 wt% on dry polymer basis) compared to standard non-polymeric surfactants. The incorporation of ASRs is considered to bring many advantages, such as more Newtonian

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rheological behavior, excellent freeze-thaw and shear stability, good pigment dispersion, good wetting properties, ease of printing machine cleaning, and good rewet characteristics. [7,8]

Miniemulsions are distinguished from conventional emulsions by their high stability (combination of surfactant and costabilizer) droplets in the range of 50-500 nm and swelling capacity; they have been exploited to develop new and high value added products not available by conventional emulsion polymerization processes.[9-11] Accordingly, several different kinds of surfactant have been used in miniemulsion polymerization; however, few studies have been dedicated to the use of polymeric surfactant.

In the present work, the use of ASR as sole surfactant in miniemulsion polymerization is presented. First, two different commercial types of ASR were employed in low solids miniemulsion polymerization. General characteristics of the use of ASR were assessed by varying several experimental conditions. Next, after mapping the experimental conditions, the synthesis of high solids content latexes is briefly discussed.

## Experimental

### *Materials*

All reactants, technical grade monomers butyl acrylate (BuA), methyl methacrylate (MMA), and styrene (Sty) containing 10-20 ppm of methyl-ethyl hydroquinone and with purity of 99% minimum (Quimidroga S.A., Spain), C18-C22 acrylate Norsocryl (Atofina), a mixture of long chain acrylates, which acted as costabilizer, ammonium and potassium persulfate (Fluka), Luperox 256 (Atofina), a tert-amyl tert-butyl perester, were used as supplied. Morez 101 and Morez 300, random copolymers of styrene, α-methyl styrene and acrylic acid, were kindly supplied by Rohm&Haas, France. The main characteristics of the ASR were the average molecular weight, the glass transition temperature and the acid number, which are 6500, 93 °C and 205 mg KOH/g, and 1200, 70 °C and 235 mg KOH/g for Morez 101 and Morez 300, respectively. ASRs were neutralized with a 35 wt% solution of $NH_4OH$ in order to obtain a 30 wt% ASR aqueous solution, with a pH in the range of 8.2 to 8.5. In the remaining part of the text, the mention to ASR, or the respective brand name, refers to the neutralized aqueous solution of ASR at 30 wt%. Doubly deionized water (DDI) was used throughout the work.

### *Miniemulsification and Polymerization Procedure*

Miniemulsions were prepared by first dissolving the costabilizer in the organic phase. Next, the monomer solution was mixed with the ASR aqueous solution by means of a magnetic stirrer for 5 minutes at 1000 rpm. The coarse monomer dispersion was then sonicated for 5 minutes at 8 output control and 80% duty cycle (Branson Sonifier 450). Table 1 shows the formulation employed in each experiment. Batch polymerizations were carried out in glass bottles of 80 mL volume put inside a water bath with controlled temperature. The bottles were tumbled end-over-end. Alternatively, a 500-mL reactor equipped with reflux condenser, stainless steel stirrer, sampling device and nitrogen inlet was employed. Control of the reaction temperature was carried out by means of Camile TG®. All polymerizations were carried out at 70 °C, and good control of the reaction temperature was obtained in all reactions. Conversion was measured by gravimetry and coagulum level was measured by collecting any lump of polymer left in the bottles or in the reactor and after the latex filtration.

Table 1. Formulation used in the batch miniemulsion polymerizations.

| Run | Monomer/ Costabilizer | ASR wt% * | Initiator wt% * | Organic vol. frac. (%) |
|---|---|---|---|---|
| 1 | Sty / HD | Morez 101, 5 | KPS, 0.5 | 20 |
| 2 | Sty / HD | Morez 300, 5 | KPS, 0.5 | 20 |
| 3 | Sty / HD | Morez 300, 20 | KPS, 0.5 | 20 |
| 4 | St / HD | Morez 300, 1.5 | APS, 1 | 40 |
| 5 | St / HD | Morez 101, 2 | Luperox 256, 2 | 50 |
| 6 | BuA / HD | Morez 300, 2 | Luperox 256, 2 | 50 |
| 7 | MMA / HD | Morez 101, 4 | Luperox 256, 2 | 40 |
| 8 | BuA / HD | Morez 101, 2 | VA-086, 2 | 50 |
| 9 | BuA / Norsocryl | Morez 300, 2 | Luperox 256, 2 | 50 |

* Based on the total weight of monomer.

### *Droplet and Particle Size Measurement*

Miniemulsion droplet size and latex particle size were measured by QELS (Coulter N4 Plus). An aliquot of the monomer miniemulsion was diluted with DDI water, and the droplet size was assessed within 10 min of its preparation. Capillary hydrodynamic fractionation (CHDF 2000, Matec) was used to measure latex particle size distribution (PSD). Carrier fluid 1X, supplied by Matec, was used as received. The qualitative analysis of the PSD by transmission electron microscopy was carried out by the analysis of microphotographies of latex samples previously dried. Samples were prepared by first diluting the latex with DDI water. Next, a droplet of the sample was placed on a copper grid, previously coated with poly(vinyl formaldehyde) and dried in a protected atmosphere at room temperature. Images were obtained with a Hitachi H-7000 FA.

## Results and Discussions

The results obtained in the batch miniemulsion polymerization experiments are given in Table 2. The first two runs indicated the possibility of producing stable latexes with concentrations of ASR lower than the concentrations employed in conventional emulsion polymerization, which are usually higher than 30 wt% based on the monomer. Alkali soluble resins could be used as sole surfactant in miniemulsion polymerization, and different types of ASR gave similar results. The results obtained in runs 1 and 2 indicated a rather similar droplet and particle size, suggesting that particles were mainly formed by droplet nucleation. The complexity of the system, where ASR can form aggregates of detectable sizes, and hence may promote particle bridging, prevents us from accurately determining the prevailing nucleation mechanism through the analysis of droplet and particle size. It is interesting to remark that the particle sizes obtained are significantly larger than the ones usually obtained in conventional emulsion polymerization employing ASR as surfactant (usually smaller than 80 nm). [12,13]

Latex with poorer stability was obtained when the concentration of ASR was increased to 20 wt% based on the monomer (run 3). Under such high concentration of surfactant, the early stages of the polymerization was likely marked by the competition between micellar and droplet nucleation. The generation of an increased number of particles due to micellar nucleation, could have led to a point where the total surface area was too large to be covered by the surfactant present in the reaction media. This would possibly explain why poorer stability results were obtained when the ASR concentration was increased. On the other hand, the miniemulsion prepared with formulation 3 was stable, as checked by visual inspection, although contrary to what was expected, larger droplet sizes were obtained when the concentration of ASR was increased. This aspect is further explored in the last part of this work.

Synthesis of latex with low solids content is a useful strategy to gain knowledge on process and product characteristics. However, in industrial application, polymerization of concentrated aqueous polymer dispersions is mandatory, since low solids content latexes are not economically viable for most applications. Run 4 illustrates the attempt to produce latexes of higher solids content. The formulation employed was similar to Run 2, but increasing the organic volume fraction and reducing the concentration of the ASR. Coarse coagulation was obtained in this run. The reason for this behavior was not clear, but it was speculated that four main factors could influence the results: the higher organic volume fraction; the lower ASR concentration, the solubility of the ASR in the monomer phase; and the charge of the radical entering the particles.

The decomposition of the salt of persulfate decreased the pH of the medium, [14] lowering the emulsifying capacity of the ASR. The pH of runs 1-4 was below 7.5, whereas pH values between 8.3 and 8.5 were found in runs 5 to 9. It was speculated that the presence of sulfate groups on the particles' surface could also influence the stability of the system.

Table 2. Results obtained from the miniemulsion polymerization experiments. Droplet and particle size obtained by QELS.

| Run | Droplet size (nm) | Particle size (nm) | Solids content (%) |
|---|---|---|---|
| 1 | 191 | 176 | 18.6 |
| 2 | 177 | 163 | 18.7 |
| 3 | 200 | 99 | 16.6 * |
| 4 | 170 | - | - |
| 5 | 172 | 203 | 19.8 * |
| 6 | 162 | 280 | 49.8 |
| 7 | 114 | 222 | 40.3 |
| 8 | 180 | 368 | 50 |
| 9 | 180 | 340 | 50.5 |

* Formation of coagulum observed in Runs 3 and 5.

The influence of the type of initiator on the latex stability was studied by replacing APS, which generates ionic species, by oil-soluble initiators. Run 5, initiated with Luperox 256, showed better stability than Run 4, initiated with APS, although a substantial amount of coagulum was collected. On the other hand, no coagulum was detected in Runs 6 and 7, where the styrene was replaced by BuA and MMA, respectively. It is interesting to remark that stable latexes at high solids content were obtained by miniemulsion polymerization using only a small fraction of the ASR concentration employed in conventional emulsion polymerization processes. [12,13] Styrene is the major component in the chemical composition of both Morez 101 and Morez 300. As a result, in styrene miniemulsion polymerization part of the ASR could be buried inside the monomer droplets, and the effective concentration of surface active molecules in the polymerization media would be lowered. In Run 5, carried out with oil-soluble initiator and with styrene as monomer, coarse coagulation was observed, indicating that the solubility of the ASR in the monomer droplets could indeed reduce the concentration of surfactant to stabilize the polymer particles.

A similar behavior has also been documented in conventional emulsion polymerization using non-ionic surfactants, where the solubility of the surfactant in the monomer droplets reduced the effective concentration of surfactant in the aqueous phase. [16-18] Although some affinity between on the one hand MMA or BuA, and on the other Morez 101 or Morez 300 could be expected, the solubility of the ASR in the miniemulsion monomer droplets did not affect the latex stability, within the limits of the experimental conditions assessed.

Comparing the final values of the particle size with the experiments carried out with low solids content, it could be observed that in Runs 6 and 7 particles were larger than the initial droplets. It is believed that the results are influenced by an enhanced bridging of the particles due to the higher concentration of the dispersed phase, and that droplet nucleation might be the main particle nucleation mechanism under these experimental conditions.

In order to further investigated the effect of the initiator type on the miniemulsion polymerization using ASR, Run 8 was carried out using an azo initiator that is water soluble and upon thermal decomposition generates non-ionic radicals. [15] The results obtained in Run 8 are given in Table 2. A coagulum-free latex was obtained. Comparing with a polymerization carried out in the presence of oil-soluble initiators a larger particle size was obtained. The reasons for this behavior were not clear.

As described previously, no clear and direct correlation between the miniemulsion droplet size and the latex particle size could be obtained. A sample of the latex obtained in Run 8 was analyzed by TEM in order to gain further understanding on the aspect of the latex particle size distribution. Figure 1 illustrates a representative micrograph obtained in the analysis of the particles. The particle size distribution of the latex was also analyzed by means of CHDF, and is shown in Figure 2.

A rather broad and complex PSD can be observed in Figure 1. The result was corroborated from CHDF analysis, as observed in Figure 2. It is important to remark that the micrograph gives a less than perfect representation of the PSD given the low Tg of the latex. A dark layer is seen surrounding the particles, and in some regions dark agglomerates are observed, which are interpreted as ASR molecules. In the case of the agglomerates is also observed that their sizes roughly corresponded to the size measure by CHDF of the pure ASR dispersion, which was found to be in the range of 20-30 nm, as observed in Figure 3. Within the detection limits of the CHDF techniques, both Morez 101 and Morez 300 gave aggregates of similar size. The analysis of the aggregate size by light scattering gave similar values. Figure 2 shows the weight distribution of the latex particle size distribution, and in spite of the influence of the large particles on the distribution, smaller ones can still be seen in the initial part of the distribution. The average particle size observed by CHDF was shifted to a higher value than the average observed by light scattering. This lack of correlation was probably influenced by the broadness of the PSD, which limits the accuracy of the value obtained by QELS.

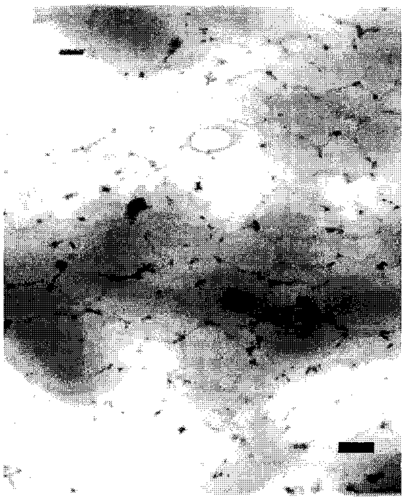

Figure 1. TEM micrograph of the latex obtained in Run 8. The bar on the lower part of the figure corresponds to a scale of 300 nm.

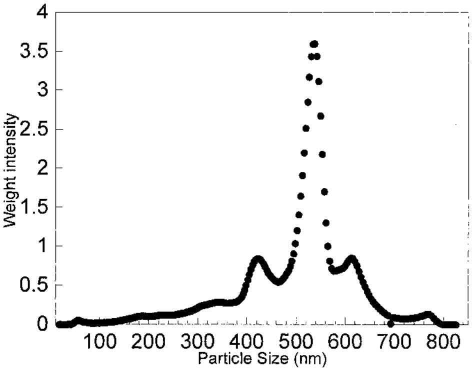

Figure 2. Particle size distribution obtained by CHDF of Run 8.

In view of the production of commercial products by miniemulsion polymerization, it is desirable to avoid the presence of non-reactive costabilizers, which would remain in the polymer particles, and could influence the end-use properties. [19] Using a formulation similar to Run 6, hexadecane, which may impart deleterious properties to the dried polymer, was replaced by a reactive costabilizer, Norsocryl C18-C22. The sonication time was extended to 10 minutes since a larger volume of miniemulsion was prepared, in order to avoid variation of the monomer droplet size due to volume changes of the flat-bottom beaker used in the sonication. [20]

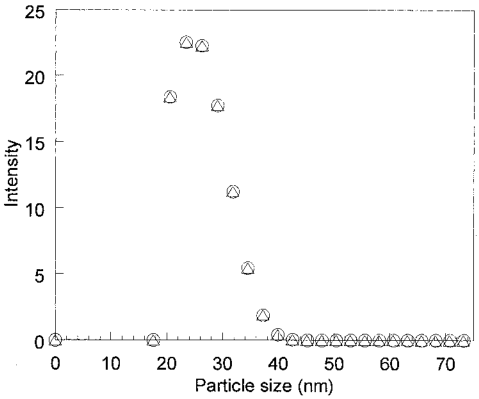

Figure 3. Determination the aggregate size of ASR. Morez 101 (o), Morez 300 (Δ).

A stable and coagulum-free latex was obtained in Run 9. Monomer droplet and latex particle sizes were similar to the values previously observed in Run 6, as given in Table 2. This indicates that the reactive costabilizer C18-C22 acrylate Norsocryl could successfully replace hexadecane in the miniemulsion formulation.

The polymerization temperature could be controlled at 70 °C throughout the reaction, and no thermal runaway was observed. Complete conversion was achieved within a period of less than three hours. The results indicate that some precautions need to be taken when upscaling the batch miniemulsion polymerization using ASR as sole surfactant. Industrial reactors have an inferior capacity to remove heat, when compared to laboratory scale reactors. Consequently, it might be risky to work under batch conditions with miniemulsions with a monomer concentration around 50 wt%. Possibly, working in semi-continuous conditions would be a safer strategy for large scales. This topic is currently under investigation. [21]

## Conclusions

Miniemulsion polymerization offered the possibility of drastically reducing the amount of ASR needed to generate a stable latex. Conventional emulsion polymerization processes employ up to 30 – 45 wt% (based on the total monomer) or ASR, whereas with 2 wt% the polymerization could be carried out in miniemulsion. [22]

A great advantage of the miniemulsion process was that different types of ASR were suitable as sole surfactant in aqueous polymer dispersion. Stable latexes were polymerized in the presence of Morez 300. High solids content latexes were produced. Under such conditions lack of stability was observed for systems using ammonium persulphate as initiator. Probably, this was caused by the charged species generated by the decomposition of the initiator. Changing the initiator to either oil-soluble or water-soluble azo initiator led to stable latexes at high solids. Solubilization of ASR into the monomer droplets may also play a relevant role. Further investigation is needed to understand the mechanism of particle nucleation and stabilization.

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