

# MICROEMULSION COPOLYMERIZATION OF VINYL ACETATE/BUTYL ACRYLATE USING A MIXTURE OF ANIONIC AND NON-IONIC SURFACTANTS

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## Abstract

The monomer mixture of vinyl acetate (VAc):butyl acrylate (BuA) was polymerized in batch reactions at 60 °C with potassium persulfate as the initiator in microemulsions consisting of VAc:BuA (85:15 w/w) /water / sodium dodecyl sulfate (SDS): Polyoxyethylene (23) dodecyl ether (Brij-35) (3:1 w/w). The effect of the concentration of the monomer mixture on the kinetics was studied for 2, 3 and 4% (w/w) monomers with respect to the total reaction mixture. It was found that as the monomer concentration increases the polymerization rate ( $R_p$ ) increases and that the maximum polymerization rate,  $R_{pmax}$ , is proportional to  $[VAc+BuA]^{1.26}$ . Particle size increases with the monomer mixture concentration also. Final particle sizes were less than 50 nm. Particle number is independent of the monomer concentration and it was observed some coagulation at the end of the polymerization.

## Introduction

Microemulsion polymerization has gained importance only since the last two decades mainly due to the necessity to obtain water-based lattices (particle diameters smaller than those obtained by emulsion polymerization) to be used as adhesives and coatings. The homopolymers and copolymers of VAc are prepared industrially by emulsion polymerization. Today it is not known to the authors whether microemulsion polymerization is carried out commercially or not. This polymerization method could have some advantages not yet investigated; for example, the effects of nanometric sizes of polymer particles on film formation, adhesives, mechanical and physical properties of the films. Although microemulsion and miniemulsion homopolymerizations have been studied recently [e. g., 1-3], the copolymerization of monomers of industrial interest like VAc and BuA have not. A limitation to extend the industrial application of microemulsion polymerization, in general, is the low ratio of polymer content in the final latex to tensoactive used to stabilize it, for homopolymers as well as for copolymers.

The purpose of this work is to study the kinetics of the batch microemulsion copolymerization of the VAc/BuA system using a 3:1 (w/w) mixture of SDS/Brij-35 as emulsifier to provide the required data for a future comparative study with semibatch microemulsion copolymerization.

## Experimental section

Potassium persulfate (KPS), hydroquinone (HQ) and the non-ionic surfactant Brij-35 were purchased from Aldrich (> 99%). VAc and BuA monomers from Aldrich were purified washing with an aqueous solution of NaOH (10% weight). Monomers were dried with anhydrous magnesium sulfate for 12 hours before distillation at 35 and 50 °C, respectively, at reduced pressure and were stored at 4 °C. Water was deionized tridistilled grade obtained from an ionic interchange column from Cole-Parmer Instruments-Company and the argon was ultra-high purity from Infra.

### *Partial phase diagram*

The determination of the water - rich o/w microemulsion region for the system VAc:BuA (85:15 w/w)/H<sub>2</sub>O/SDS:Brij-35 (3:1 w/w) at 60 °C was made by titration of mixtures of different surfactants/water ratios with the monomer mixture. The microemulsion boundaries were detected visually for each constant composition surfactants/water line. Within this region, microemulsions are transparent and nonbirefringent (when examined through cross polarizers).

### *Polymerizations*

Polymerizations were carried out in a 250 mL glass reactor with magnetic stirring at 60 °C. The mixture of surfactants, water and KPS (2% weight with respect to the monomer mixture) were charged to the reactor, cooled, vacuum degassed and saturated with argon. The previously degassed and saturated with argon monomer mixture was added to the reactor to initiate the polymerization. The reacting system was continuously stirred during the entire reaction and purged with argon each time that a sample was taken. Conversion was followed gravimetrically: samples were withdrawn from the reacting system at given times and put in vials (of known weight) immersed in an ice bath containing 0.5 g of an aqueous hydroquinone solution (0.4%). Samples were then weighed and freeze-dried. The weight of polymer was estimated by subtracting the known weights of surfactants and hydroquinone from the total weight of the freeze-dried sample.

### *Characterization*

Particle size was measured in a Malvern 4700 quasielastic-light-scattering (QLS) apparatus equipped with an argon laser ( $\lambda = 488$  nm). Measurements were performed at 25 °C at an angle of 90°. Copolymer samples were purified washing with hot water (to remove most of the surfactants), vacuum dried at 40 °C and then dissolved in chloroform and precipitated with anhydrous ethyl ether and finally vacuum dried for 24 hours. Copolymer compositions were determined from <sup>1</sup>H-NMR recorded on an FTNMR Gemini 200, Varian (200MHz) using 10 mg/mL sample solution in deuterated chloroform. Average molar masses and molar mass distributions (MMD) were measured with a Hewlett-Packard series 1100 gel permeation chromatograph equipped with a refractive index detector and using HPLC-grade tetrahydrofuran (Aldrich) as mobile phase. For the copolymers the weighted averages of the Mark-Houwink *K* and  $\alpha$  values were calculated using the cumulative copolymer composition data obtained earlier using <sup>1</sup>H-NMR spectrometry [4].

### **Summary of results and discussions**

Figure 1 shows the o/w microemulsion region for the system VAc:BuA (85:15 w/w)/H<sub>2</sub>O/SDS:Brij-35 (3:1 w/w), in which the compositions selected to make the batch copolymerizations can be seen, corresponding to 2, 3 and 4% of monomer content with respect to the total reaction mixture.

Final latex characteristics and copolymer properties, as well as reaction rate depend on initial monomer concentrations in the reactor. Figure 2 presents experimental conversion vs. time data for different monomer concentrations. High conversions and fast reaction rates were observed. Initially clear microemulsions turned bluish and translucent at the early stages of reaction and became opaque at the end. These latexes are very stable and no phase separation or precipitation was observed after nine months of storage. Polymerization rate and conversion increase when monomer concentration is increased.

The polymerization rates are shown in Figure 3. It can be seen two periods of polymerization which is typical in microemulsion polymerization systems [5]. The first period corresponds to polymer particle formation and growth until a maximum in  $R_p$  is reached around 18% conversion, and then begins to decrease because the monomer is being depleted. The next change in the slope of  $R_p$  occurs between 25 and 30% of conversion which is due to the disappearance of the more reactive monomer (BuA). From this point on  $R_p$  is controlled by VAc consumption. From a plot of maximum polymerization rate,  $R_{p_{max}}$ , vs. natural logarithm of monomer concentration (VAc+BuA) it was found a relationship of  $R_{p_{max}} \propto [\text{VAc+BuA}]^{1.26}$ , which is different to that reported by Torres-Plata [6] who found  $R_{p_{max}} \propto [\text{VAc+BuA}]^{1.65}$  using V-50 (2,2 –azobis[2-amidinopropane] 2HCl) as initiator and AOT as surfactant. Figure 4 shows the evolution of particle size as a function of conversion at different monomer concentrations. It can be seen that particle size increases as monomer concentration and conversion increase. This result is typical of microemulsion homo and copolymerization kinetics.

In Figure 5, molecular weight,  $M_w$ , and molecular weight distribution (MWD) versus conversion are shown. Average molecular weight decreases as conversion increases with a maximum value around 20% conversion. This behavior has been observed in other copolymerization systems [7]. The MWD shows at least two populations at low conversions and the high molecular weight population almost disappears when conversion increases. More details will be given at the meeting.

## Conclusions

The copolymerization kinetics of the monomer mixture VAc/BuA in the system VAc:BuA (85:15 w/w)/H<sub>2</sub>O/SDS:Brij-35 (3:1 w/w) presents the typical behavior of microemulsion polymerization reactions. Average molecular weight decreases as the reaction progresses and the MWD shows at least two populations at low conversions and the high molecular weight population almost disappears when conversion increases.

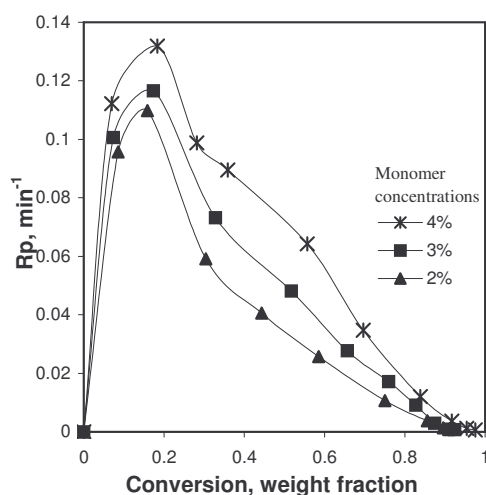


Figure 3. Polymerization rates of batch microemulsion copolymerization initiated at 60°C with 2% (w/w) of KPS (respect to monomers content) at three initial monomers concentrations. VAc:BuA (85:15 w/w) using a 3:1 (w/w) mixture of SDS/Brij-35 as emulsifier.

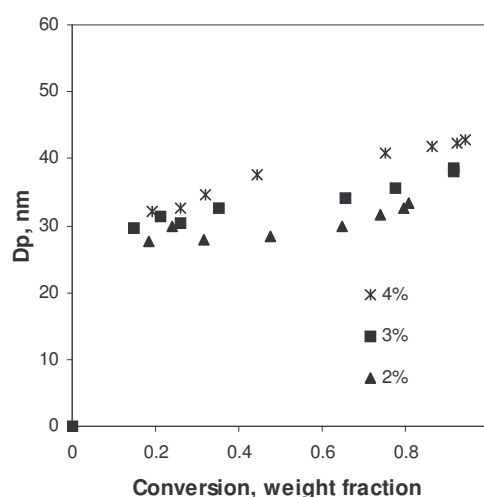


Figure 4. Particles size vs. conversion of microemulsion copolymerization at three monomer concentrations. VAc: BuA (85:15 w/w); 3:1 (w/w) mixture of SDS/Brij-35 as emulsifier. Reactions initiated at 60°C with KPS (2 % respect to monomer content).

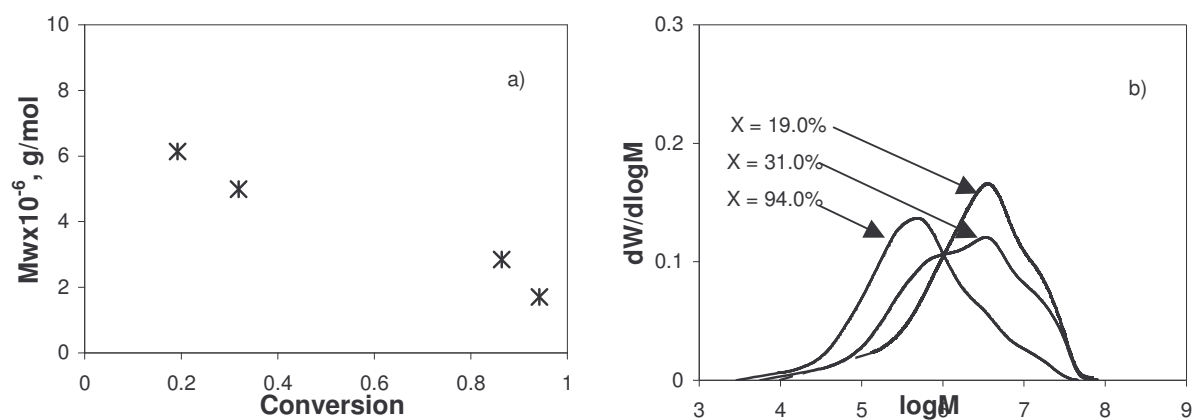


Figure 5. a) Molecular weight vs. conversion and b) Molecular weight distribution of batch microemulsion copolymerization at 60°C with 2% (w/w) of KPS with respect to the monomer content and 4% of monomer mixture VAc:BuA (85:15 w/w) in the initial charge.

## References

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