

**SYNTHESIS OF AN IMPACT MODIFIER BY EMULSION
POLYMERISATION**

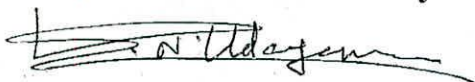
**By
Ravindra Udagama**

December 2005

M.Sc. Polymer Science and Technology

Declaration

The work described in this thesis was carried out by me under the supervision of Prof. Timothy McKenna at LCPP-CNRS/ESCPE, Lyon – France and the report on the same has not been submitted to any university for another degree.



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We certify that the above statement made by candidate is true and this thesis is suitable for submission to the university for the purpose of evaluation.



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Ravindra Udagama**

This thesis was submitted in partial fulfillment of the requirement for the Master's Degree in Polymer Science and Technology for the University of Sri Jayawardanepura, Sri Lanka.

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2005

To
My Dearest
Parents

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1.INTRODUCTION

By definition a latex is a stable, homogeneous dispersion of sub-micron polymer particles in a continuous aqueous phase. Synthesis of latex by Emulsion Polymerisation presents different advantages. A few of them are: (1) the continuous medium is water, which is non-polluting and relatively inexpensive; (2) the use of water as the continuous phase makes it easier to remove the heat generated by the reaction than in solution polymerisation; (3) the reaction mechanisms involved in emulsion polymerisation allow us to reach very high molecular weight and low amounts of residual monomer hence a higher % conversion at the end of reaction; (4) the low viscosity of the dispersion makes the product easy to manipulate. Therefore, synthesis of latex by Emulsion Polymerisation has become industrially important. The latex applications are diverse and numerous. They are widely used in coating applications such as paints, inks, adhesives, paper coatings. They can also be used in medical applications as vectors for drug delivery, or even as an additive in the synthesis of other products, such as cements.

The quality parameters of a given latex directly depend on the final application of it. In some applications such as impact modifiers, good mechanical properties like absorption of impact energy could be achieved by high solid content lattices with a controlled particle size and low viscosity. But as will be explained in the next chapter, the viscosity of a latex increases sharply when particles begin to enter into contact. Therefore, during the synthesis of a high solid content latex, the effect of viscosity and particle size have to be strongly considered.

If we assume that a latex is composed of spherical particles, there is an upper limit on the amount of polymer that can be packed into a given space. If the particles are packed in a Face Centered Cubic (FCC) array, they will occupy at most 74% of the volume. Randomly packed identical spheres will have a volume fraction of 64%. In either case, all of the spheres would be in contact at the maximum packing fraction, and the apparent viscosity of the system

would be infinite. In a real latex, one must also take into consideration the space occupied by the stabilizers situated on the surface of the particles, and must also avoid excessively high viscosities. For these reasons, the solid content of industrial latexes rarely exceeds 55 to 60% when the products have a monomodal Particle Size Distribution (PSD) [4]. The dependence of the viscosity (η) of a latex on its solid content (SC) is illustrated in Figure 1.

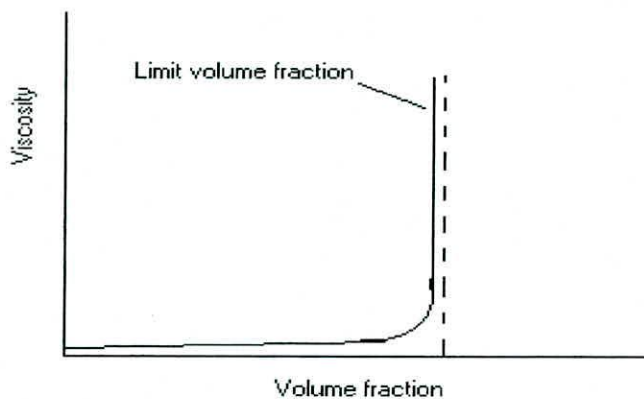


Figure 1 Dependence of viscosity of a latex upon its solid content

At low SC, the particles have relatively weak interactions, so the viscosity remains low. As the SC increases η increases slowly at first, then more and more rapidly as the SC approaches its maximum value (i.e. where the particles begin to touch). At this point η increases extremely quickly. The behaviour in Figure 1 is qualitatively the same regardless of the PSD of the latex, only the value of the limiting SC changes.

1.1. Objective

The objective of this experiment is to develop a Poly Butyl Acrylate latex coated with Poly Methyl Methacrylate by emulsion polymerisation to be used as an impact modifier.

The expected quality parameters of the latex are:

- (1) Total Solid Content > 45%**
- (2) Particle size is in the range of 90 – 200nm**
- (3) Viscosity lower than 150cps.**

The specific reasons for having above quality parameters for the impact modifier developed in this research project were not revealed by the industrial partner.

But as mentioned earlier, to develop an impact modifier with good mechanical properties it is necessary to manipulate a latex with high solid content because many mechanical properties directly depend on the solid content of a latex. But as we have discussed here the increase of solid content is limited by the sharp increase of viscosity. Therefore it is necessary to maintain viscosity at a low level while increasing the solid content. This can be achieved by controlling the particle size of the latex because interactions between particles depend on the particle size also. Poly Methyl Methacrylate coat around poly butyl acrylate polymer particles gives good shock absorbing properties and hence the stability of the latex is increased.

1.2 Basic science of emulsion polymerisation

In the work presented in this thesis, emulsion polymerisation refers to the creation of an aqueous dispersion of sub-micron polymer particles via free radical polymerisation. In this section we will discuss some of the basics of emulsion polymerisation, and will then focus on one of the most delicate aspects of the emulsion polymerisation: particle nucleation.

1.2.1 Description of the radical emulsion polymerisation

Classically, an unpolymerised emulsion is composed of an organic phase (monomer(s)), a continuous phase, and amphiphilic molecules (surfactants(s)). Most often the continuous phase is water, so we will refer to it as the aqueous phase throughout the rest of the study. Depending on the nature of the monomer(s), part of the organic phase can be dissolved in water. The surfactants, or emulsifier molecules, are composed of hydrophobic and polar moieties, and ensure the homogeneous dispersion of monomer droplets in the aqueous phase. If the concentration of surfactant is above the critical micellar concentration (CMC), emulsifier molecules form micelles. The addition and decomposition of the initiator in the aqueous phase provides free radicals, which initiate the polymerisation reaction. In a radical emulsion polymerisation polymerisable free radicals are created in the continuous phase, and are then transferred to the organic phase.

One of the first attempts at understanding the process of emulsion polymerisation is attributed to Harkins [1,2,3]. This model, proposed in 1947, is understandably simplified but remains a useful starting point for understanding how an emulsion polymerisation proceeds. According to this model, the rate of homopolymerisation can be quantified as described by Equation 1:

$$R_p = K_p \times [M]_p \bar{n} \times N_p / N_A \quad (1)$$

R_p : polymerisation rate ($\text{mol} \cdot \text{min}^{-1} \cdot \text{L}^{-1}$)

K_p : propagation rate constant ($\text{L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$)

$[M]_p$: The concentration of Monomer in the particles

\bar{n} : Average number of radicals per particle

N_p : number of polymer particles per litre of emulsion

N_A : Avagadro's number

Changes in the rate of polymerisation during a batch reaction can be roughly placed in one of three intervals shown schematically in Figure 1, and described below.

Interval 1

This stage begins with the initiation of the polymerisation by free radicals generated in the aqueous phase, and corresponds to the phase of polymer particle formation, usually referred to as nucleation. In this model, polymer particles form when a free radical enters a micelle swollen with monomer, thus beginning the polymerisation. This interval is characterized by an increasing polymerisation rate due to an increase of the number of polymer particles. The end of this stage corresponds to the end of micellar nucleation, which is the only means of particle formation considered by Harkins. We will see below that this is an oversimplified view.

Interval 2

During this stage the number of polymer particles remains stable and the reactor contains growing polymer particles, dispersed monomer droplets, and surfactant dissolved in the water and adsorbed on the surface of the organic phases. The concentration of monomer in the polymer particles ($[M]_p$) is constant at a value referred to as the saturation, or critical concentration ($[M]_{pSAT}$).

This value varies from monomer to monomer for reasons to do with thermodynamic considerations, and as long as monomer droplets are present $[M]_p = [M]_{pSAT}$. Thus, if no polymer particles are nucleated or consumed by flocculation, the polymerisation rate is constant during this interval. This interval is often characterised by the term “flooded”, since there is more monomer in the reactor than the growing polymer particles can absorb. This interval is said to end when the monomer droplets disappear.

Interval 3

Theoretically, during this interval, the number of polymer particles remains constant and the concentration of monomer in polymer particles decreases since there are no longer any droplets to replenish them. For this reason the system is often referred to as being in “starved” conditions. The polymerisation rate can either decrease as the monomer is consumed, or increase if the resulting increase of the local viscosity inside the polymer particles leads to a reduction in the mobility of the macro radicals in the polymer particles. If the latter phenomenon is significant, the rate of termination decreases and \bar{n} increases. This is called the gel, or Tromsdorff effect.

This model makes a number of useful points, notably that the rate of polymerisation depends on certain parameters that we can not totally control, such as kinetic constants, or saturation concentrations of monomers, and others over which we have some influence, in particular the number of polymer particles.

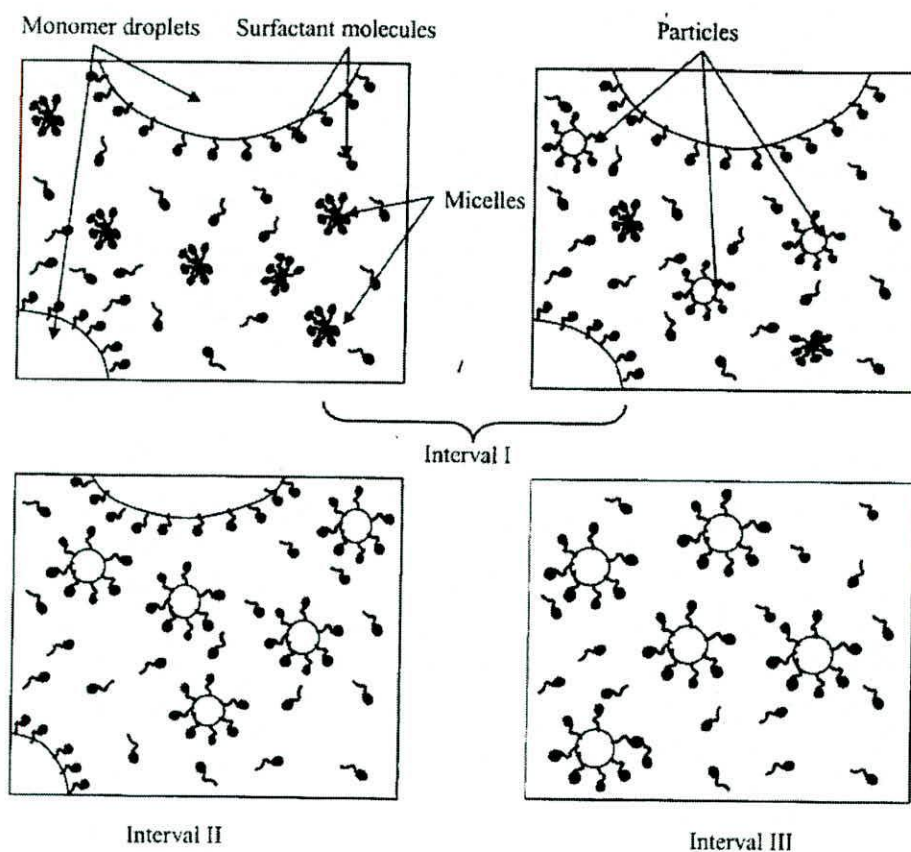


Figure 2: Scheme of the evolution of an emulsion during polymerisation

As mentioned in the introduction to this thesis, controlling the number and size of the polymer particles during the process is the key to achieving the objective of the research project. It is therefore important to understand how polymer particles are formed and stabilised during the polymerisation process. We will look at these two points in the following sections.

1.2.2 Nucleation

Particle nucleation is one of the most hotly debated topics in emulsion polymerisation. This is due in large part to the difficulty of experimentally exploring this phenomenon. First of all, it is very rapid and particles typically form in less than one second [4, 5]. Also, as will be discussed in section 1.4, measuring the particle size and PSD is technically very challenging, especially when small and large particles coexist in the same sample. This is true even under static conditions.

Nevertheless, it is widely accepted that micellar nucleation is not the only way that particles can be formed. Indeed, emulsion polymerisations can be run with a concentration of surfactant below the CMC, or even without surfactant [6,7]. Three main mechanisms are usually described for particle formation: micellar, homogeneous and coagulative. However, in particular conditions we can observe monomer droplet nucleation (mini-emulsion, microemulsion), and the formation of new particles in presence of a first population. The latter phenomenon is called secondary nucleation.

1.2.2(A) Micellar nucleation

Harkins was the first to describe this phenomenon [1,2,3], then Smith and Ewart[8] proposed a more quantitative description of micellar nucleation. Obviously this mechanism occurs in presence micelles, which means that the surfactant concentration must be greater than the CMC. When the reaction begins in the aqueous phase, radicals react with monomer dissolved in water and form oligoradicals. As oligoradicals grow they are less and less water-soluble and once they attain a certain length “z”, they are sufficiently hydrophobic that they can be captured by monomer swollen micelles, which have a hydrophobic core [3, 8, 9, 10]. Not all of the micelles are nucleated, and some of them play the role of a reservoir of surfactant that is used to stabilise growing particles. Indeed, there are typically $10^{20} - 10^{21}$ micelles per litre of emulsion, which is 100 to 1000 times more than polymer particles at the end of the reaction [11].

1.2.2(B) Homogeneous nucleation

As we said previously, it is well known that emulsion polymerisations can be carried out with a surfactant concentration below the CMC, or even without emulsifier [6,7]. In 1952, Priest [12] proposed an explanation for this observation. He said that particle nucleation could take

place directly in the aqueous phase. Recall that the polymerisation begins with the formation of oligoradicals in the aqueous phase. Once these oligoradicals reach their limit of water solubility (critical length of the chain " j_{crit} " > "z"), they precipitate and form primary particles. These particles can be stabilised by dissolved surfactant molecules, or by charges situated at the end of the polymeric chain that comes from initiators such as persulphates. Depending on what is present in the reaction medium, these primary particles can also flocculate on to larger particles already present in the latex. This will be discussed in section 1.2.

1.2.2 (C) Coagulative and aggregative nucleation

The mechanism of coagulative nucleation, proposed by Lichti et al. [13], is derived from homogeneous nucleation theory. In this case, the primary particles formed by oligoradical precipitation are essentially stabilised by the charges provided by the initiator. However, the surface area developed by such small particles is very high, so in order to maintain a sufficient density of charges for their stabilisation, the primary particles reduce their surface area by coagulating with each other, or onto larger particles already present. It is worth noting that this mechanism requires the use of an initiator that provides charged radicals.

More recently, Tauer et al. [14] developed a model for aggregative nucleation based on a thermodynamic approach of the phenomena. This model can be used to predict nucleation behaviour based on the assumption that waterborne oligomers form stable nuclei under critical conditions. The authors introduced the concept of super saturation, which is the ratio of the concentration of oligomers to their water solubility. This parameter is estimated using the Florry-Huggins interaction parameter, which can be deduced by gas-liquid chromatography measurements. A critical value of the super saturation is required for particle nucleation. The predictions of the model are in good agreement with the experimental data obtained by surfactant free polymerisation with different monomers (styrene, MMA and vinyl acetate-VAC). The results clearly show the influence of monomer water solubility on the