Why is miniemulsion polymerization a suitable candidate for nanoencapsulation of clays?

Nano fillers in powder form are very unstable with respect to their particle size due to agglomeration caused by high surface energy. As a result, incorporation of nano fillers in powder form into the coatings is unlikely to prove effective in delivering the desired properties. Therefore the nanoparticles have to be either generated in-situ during dispersion process or externally added in the pre-dispersed form. For preparing a stable pre-dispersion of nanoparticles, the technique of nanoencapsulation by emulsion polymerization can be adopted. This intermediate material in turn can be used in formulation of the coatings.

There are several techniques in emulsion polymerization such as:

- Conventional emulsion polymerization
- Mini emulsion polymerization
- Suspension polymerization
- Dispersion polymerization
- Microemulsion polymerization

From the view point of particle size and monomer types used in coatings, conventional and miniemulsion polymerizations appear as potential candidates. The following Table 1 compares and contrasts these two approaches.

No	Aspect	Conventional emulsion polymerization	Mini- emulsion polymer
1.	Definition	Polymerization brought about in the surfactant micelles in water such that polymerization and particle growth are concurrent	Pre-dispersion of monomer into droplets in water using shear, microfluidics or ultrasonic energy; followed by polymerization in the droplets
2	Particle size range	200~600 nm	100~700 nm

3	Site of polymerization	Surfactant micelle	Monomer droplet
4	Monomer transport	Dynamic: From monomer droplets to micelles.	Static: Monomer pre-exists in the dispersed droplets
5	Highly hydrophobic monomer	Difficult to nucleate	Can be initially incorporated in the droplets
6	Particle size control	Dependent on surfactant type, concentration and rate of initiation	Predetermined by monomer droplet size
7	Particle size distribution	Generally narrow	Wide because of monomer dispersion process
8	Initiators	Only water soluble initiators like sodium or potassium persulfates	Both water soluble and solvent soluble(initiators like AIBN)
9	Surfactants types	Combination of non-ionic or anionic surfactants	Combination of anionic surfactant (SDS) and a co-stabilizer like cetyl alcohol or hexdecane are used
10	Surfactant concentration	Necessarily higher than CMC	Can be lower than CMC
11	Solids	Typically 50~55 %	Higher solids possible due to wider particle size distribution
12	Process	Semi-continuous	Semi-continuous

Table 1: Conventional emulsion and miniemulsion polymerization

It is quite apparent from the above features that miniemulsion polymerization satisfies the following requirements for the encapsulation of nanoclay particles.

- Polymer particle size should be big enough to completely encapsulate the clay particle with its high aspect ratio

- All the clay particles should be covered with the polymer to prevent their agglomeration
- There should be no monomer transport process during polymerization which disrupts contact between the monomer and the clay particles. (Figure 1).
- Encapsulated nano clay emulsion should be stable for several months
- Wide choice of hydrophobic monomers should be workable.
- Higher solids emulsions should be possible

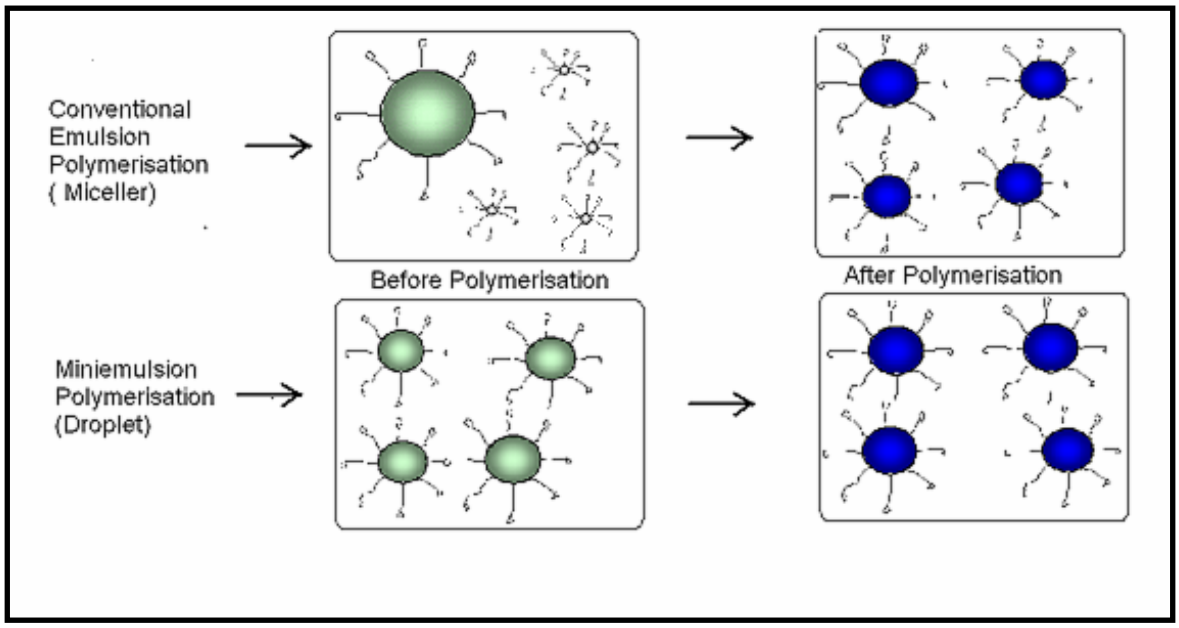

Fig 1: Particle formation in conventional and miniemulsion polymerization

The schematic of encapsulation of nanoclay by miniemulsion polymerization is shown in Figure 2

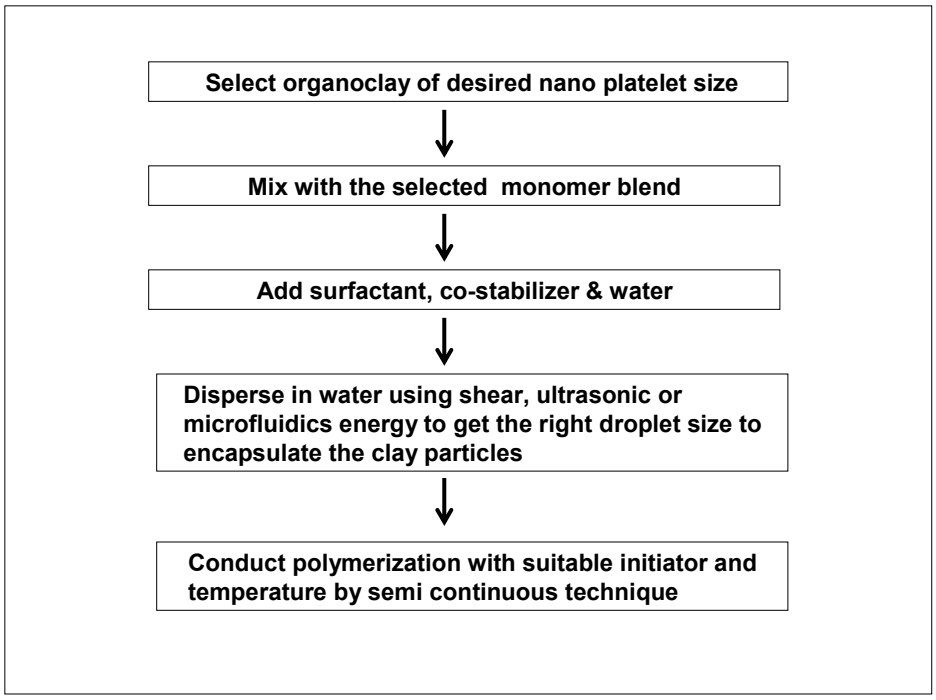

Fig 2: Encapsulation by miniemulsion polymerization.

(Ref: Zhaohui Tong; Water based suspension of polymer nanoclay composite via mini-emulsion polymerization)