Emulsion Polymerization of Hydrophobic Monomers

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Summary: Emulsion polymerization is the most important industrial polymerization process for manufacturing water based polymers. The heterogeneous nature of the process requires the diffusion of monomers from the emulsified droplets, through the aqueous medium, into the polymer particles where the polymerization takes place. Adequate solubility of the monomer is necessary for the diffusion process to occur effectively. Consequently, very hydrophobic monomers cannot be readily incorporated by emulsion polymerization. The use of a catalytic level of cyclodextrin allows the use of very hydrophobic monomers in emulsion polymerization.[1] The mechanism of the process is believed to involve a catalytic cycle in which cyclodextrin acts as a "Phase Transport Catalyst", continuously complexing and solubilizing the hydrophobic monomers and releasing them to the polymer particles. The kinetics and thermodynamics are favorable for the reaction to proceed.

Introduction

There are three major aqueous based polymerization processes that account for the majority of commercial water based polymers. These include solution, emulsion and suspension polymerization. It would be very desirable to be able to choose from any one of these processes for the synthesis of a polymer; however, the choice is very much dictated by the water solubility of the monomers and the corresponding polymers. As depicted in *Table 1*, solution polymerization is useful when both monomers and polymers are fully soluble in water, while suspension polymerization is utilized when both are insoluble in water. The most intricate process among them is emulsion polymerization, in which monomers are semi-soluble and the polymers are insoluble in water.

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Table 1. Aqueous polymerization processes with respect to monomer and polymer solubility.

	Polymerization Processes		
	Solution	**Emulsion**	**Suspension**
Monomer	Soluble	Semi-soluble	Insoluble
Polymer	Soluble	Insoluble	Insoluble

Emulsion polymerization is an extremely important process for the synthesis of a wide variety of latex polymers on a commercial scale. The advantages of emulsion polymerization include favorable kinetics, safety, environmental, compositional control, high solids level and conversion.[2] The emulsion polymerization process is a free radical reaction carried out under heterogeneous conditions as shown in *Figure 1.*

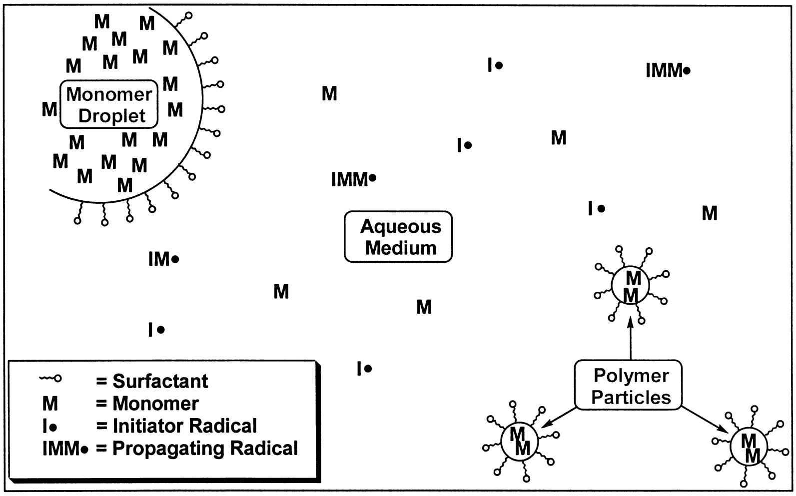


Figure 1. Schematic representation of an emulsion polymerization.

During the reaction, three separate phases coexist in the reaction medium:

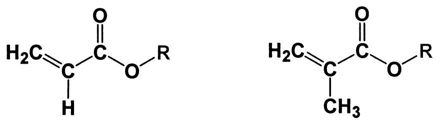
- the monomer exists as emulsified droplets
- the growing polymer particles
- the continuous water phase

The polymerization process requires the continuous diffusion of monomers from the emulsified droplets through the aqueous medium into the polymer particles. The monomers are subsequently polymerized by free radical initiators in the polymer particles. All the monomers are consumed at the completion of the polymerization, and the resulting latex is supplied as a stable colloidal suspension of polymer particles in water. Typical latex polymer particles are between 50-1000 nm in diameter, and the latex has the appearance of a milky, white fluid.

Monomers that are suitable for use in emulsion polymerization include C_1-C_8 alkyl esters of acrylic and methacrylic acid (acrylates and methacrylates), styrene, vinyl acetate, and many other functional monomers. All these monomers have a finite solubility in water *(Table 2)* which allows facile diffusion from the droplets to the growing particles. The family of acrylic and styrene-acrylic copolymers leads to an enormous range of accessible compositions and physical properties, such as glass transition temperature and solubility characteristics. The versatility of these polymers allows them to be used in a broad range of applications including adhesives, coatings, textiles, non-woven fabrics, floor polishes, etc.

The diffusion of monomers through the aqueous phase into the polymer particles requires the monomers to have a finite level of solubility, and the ability to partition into and swell the polymer particles. All the monomers listed in *Table 2* except for the ones with lauryl and stearyl groups can be readily incorporated under conventional emulsion polymerization conditions. It is highly desirable to increase the hydrophobicity of the polymers since many of the uses of latex polymers are designed to protect the substrate against water. Although very hydrophobic monomers such as lauryl methacrylate and stearyl methacrylate (LMA and SMA) are available commercially, their very low water solubilities render them unsuitable to be polymerized by emulsion polymerization. Polymerizing LMA and SMA by a conventional emulsion process often results in poor conversion; formation of suspension polymer particles; and poor compositional control in copolymers. This solubility barrier creates a limitation for the synthesis of hydrophobic polymers by emulsion polymerization.

Table 2. Solubility of acrylates and methacrylates in water.



	Solubility in Water (g/100g at 25?C)	
R	Acrylate	Methacrylate
Methyl	5	1.5
Ethyl	1.5	Low
Butyl	0.2	Low
2-Ethylhexyl	0.01	---
Lauryl ($C_{12}H_{25}$)	<<0.01	<<0.01
Stearyl ($C_{18}H_{37}$)	<<0.01	<<0.01

Cyclodextrin as "Phase Transport Catalyst"

We overcame the solubility barrier in emulsion polymerization with the recent discovery of cyclodextrin as a "Phase Transport Catalyst". Cyclodextrins (CD) are cyclic polyglucoses whose physical structures resemble a truncated cone.[3] The interior of the cavity is hydrophobic and the exterior is hydrophilic. These unique features make it possible for the water soluble CD to act as a host, enveloping less polar guest molecules, and rendering them more water soluble as a complex. The complexation of the hydrophobic guest is reversible, allowing the release of the guest molecule under suitable conditions. The transport mechanism in emulsion polymerization is believed to involve a catalytic cycle, as depicted in *Figure 2*.

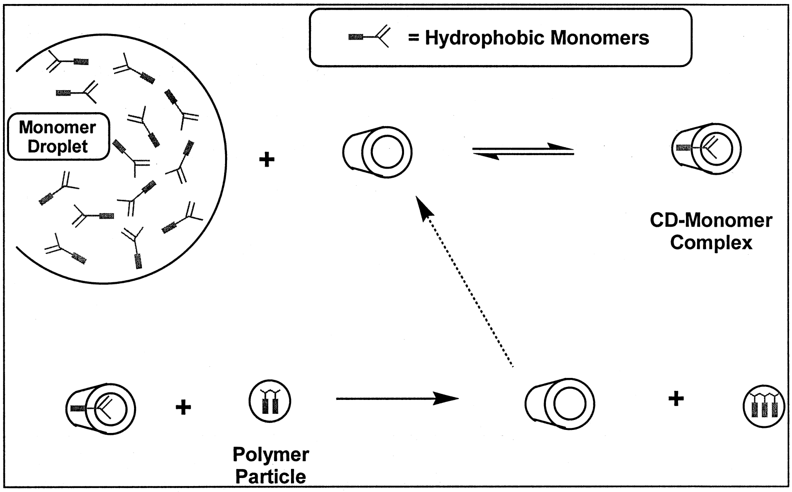


Figure 2. Proposed mechanism of phase transport cycle in emulsion polymerization.

Our proposed mechanism involves the solubilization of the hydrophobic monomer through complexation with CD, followed by diffusion across the aqueous medium and release into the polymer particle. Subsequent polymerization of the monomer eliminates the reverse process. After the release of the monomer, the CD is free to participate again in the transport cycle. The transport process overcomes the solubility barrier of hydrophobic monomer. The catalytic nature of the process allows the use of low levels of CD (<2% by weight based on total monomer) in the emulsion polymerization of LMA and SMA. The preferred CD useful for LMA and SMA transport is Methyl-ß-Cyclodextrin.

Using CD as "Phase Transport Catalyst", long chain hydrophobic monomers such as LMA and SMA can be incorporated to produce hydrophobic latex polymers. The new class of hydrophobic latex polymers, trade-named Lipacryl^{TM}, has been designed for wide ranges of applications by considering the following aspects:

- Compositionally, Lipacryl^{TM} contains hydrophobic monomers including LMA, SMA and fluorinated acrylic monomers.[4]

- Copolymers containing other monomers such as butyl acrylate, methyl methacrylate and styrene can be incorporated to achieve desirable property balances such as hydrophobicity, hardness, and self crosslinking capability.
- Lipacryl™ with high levels of hydrophobic monomers exhibits crystalline characteristics and properties, displaying a melting point due to its "waxy" nature.[5]
- Lipacryl™ exhibits very similar colloidal property balances compared to conventional latex polymers, making it suitable for use in most typical latex applications.

Attributes of Lipacryl™ Polymers

Lipacryl™ polymers have been shown to be useful in a broad range of applications. The catalytic level of CD involves in the polymerization process have no undesirable effect on the applications and no isolation is needed. The attributes that associate with the hydrophobic nature of the polymer include

- Superior water repellency
- Low water absorption and sensitivity
- Low water vapor permeability
- High contact angle
- Superior adhesion to hydrophobic surfaces
- Crystallinity of SMA-rich polymer provides waxy-like properties

Conclusion

As demonstrated in this paper, a new, patented emulsion polymerization technique has been developed which permits, for the first time, the facile incorporation of hydrophobic monomers. A mechanism was proposed but yet to be elucidated. We believe the ability to transport hydrophobic molecules through an aqueous medium by a catalytic level of cyclodextrin has far more reaching utilities in other aqueous system beyond that of emulsion polymerization, and these are being explored.

Acknowledgement

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[2] (a) R.G. Gilbert, Emulsion Polymerization, A mechanistic Approach, Academic Press, 1995. (b) P.A. Lovell, M.S. El-Aasser, Emulsion Polymerization and Emulsion Polymers, Chapter 18, Wiley, 1997
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[4] Hsing-Yeh Parker, Willie Lau, Erik S. Rosenlind, US Patent Number 5969063, October 19, 1999.
[5] Willie Lau, Michael D. Kelly, Dennis P. Lorah, David R. Heinley, US Patent Number 6040409, March 21, 2000.