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Suspension Graft Polymerization

Suspension Graft Polymerization by Chain Transfer

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Summary

Poly(vinyl oxazoline ester) and poly(stearyl methacrylate) were found to be good alien polymers for grafting of methyl methacrylate by suspension polymerization whereas poly(tridecyl methacrylate) was not a good backbone. Azobisisobutyronitrile was found to be an inefficient grafting initiator where azocumene that produces highly resonance and hyperconjugated stabilized dimethyl phenyl methyl radical was a superior initiator to benzoyl peroxide for grafting. Poly(stearyl methacrylate) was found to be a suitable polymeric stabilizer for nonaqueous suspension polymerizations.

Introduction

This paper describes suspension graft polymerization of methyl methacrylate onto poly(vinyl oxazoline ester) and poly(stearyl methacrylate) by a chain transfer method to produce specialty polymeric products. We also report nonaqueous suspension polymerization of acrylic esters. Background of suspension, bulk and emulsion polymerization processes, treatment of colloidal stability and instability as well as a pictorial description of micellization have also been provided.

Suspension, Bulk and Emulsion Polymerizations

In suspension polymerization, monomers essentially insoluble in water are suspended as globules. These globules are then converted to polymeric globules by heat and/or suitable chemicals. Suspension polymerization has a common feature with emulsion polymerization in that soap and suspension stabilizers are used. Bulk kinetics are essentially followed in suspension polymerization however. Bulk, suspension and emulsion polymerization processes are schematically shown below:

$$M \longrightarrow M_p \qquad \text{(Bulk)}$$

$$M \longrightarrow M_{droplet} \longrightarrow M_{monomeric\text{-}polymeric} \longrightarrow M_p \qquad \text{(Suspension)}$$

$$M \longrightarrow M_{droplet} \longrightarrow M_{aq} \longrightarrow M_p \qquad \text{(Emulsion)}$$

Micellization

The soap above the critical micelle concentration (cmc) is molecularly dispersed whereas it will have the micelle structure below the cmc. It is inside the micelle that the monomer gets solubilized in emulsion polymerization. In nonaqueous systems the micelle structure is reversed as shown in Fig. 1.

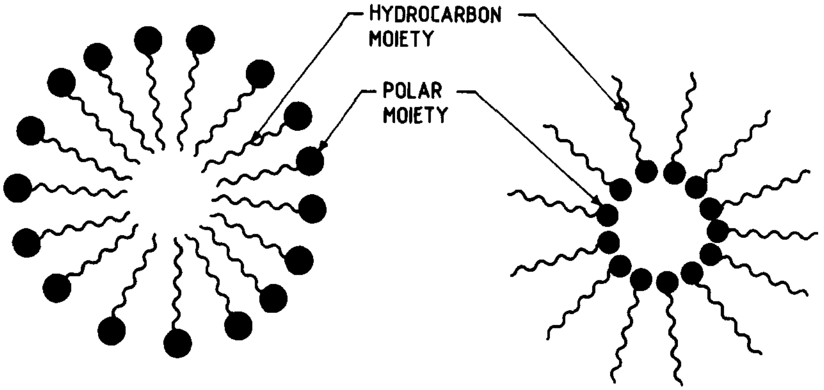
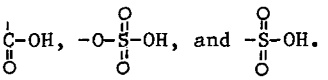


Fig. 1. Structure of micelles in aqueous phase (left) and nonaqueous phase (right).

Colloidal Stability and Instability

Colloidal stability is important in suspension and emulsion polymerizations. For colloidal dispersions to be stable, it is essential to provide a repulsive barrier between the particles so that the London and van der Waals attractive energies do not overcome the energy of thermal motion which is 3/2 kT. Dispersions of neutral colloidal particles flocculate rapidly as a result of the long-range attractive forces. In particle dispersions, the total potential is the sum of energies of attraction and the energies of repulsion. When the potential energy maximum is quite large as compared to the thermal energy, then dispersions of such particles display long-term stability. In order to achieve a potential energy maximum, it is necessary to provide a repulsive potential energy between particles. This is achieved by electrostatic or steric stabilization.

Electrostatic Stabilization

Interparticle repulsion due to Coulombic forces between two particles is a function of the dielectric constant of the continuous medium. The surface potential develops by adsorption of potential determining ions, e.g., soaps and by ionization of ion-bearing groups such as  $\underset{\underset{O}{\|}}{\overset{|}{C}}\text{-OH}$, $\text{-O-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-OH}$, and $\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-OH}$. If particles approach to a point where attractive forces overcome electrostatic forces, flocculation will occur.

Steric Stabilization

The term steric is not used in the organic chemical sense of the restriction of movement; rather, it has thermodynamical implications. Interpenetration of particles due to Brownian motion results in compression of the nonionic hydrocolloid polymer or its chain segments (Fig. 2). The compression produces a change in the free energy, given by the Gibbs-Helmholtz equation.

$$\Delta F_R = \Delta H_R - T\Delta S_R$$

There are three possibilities regarding the change of free energy;
Case 1: $\Delta F_R = 0$; if no nonionic hydrocolloid is present.
Case 2: $\Delta F_R = +$; hydrocolloid stabilizes the particles and does not sensitize them. Case 3: $\Delta F_R = -$; hydrocolloid sensitizes the particles and destabilizes them.

In suspension as well as emulsion polymerization a positive ΔF_R is important for stability during formation. However, a less positive or negative ΔF_R is needed for recovery of the polymer and better coagulation (see Table 1)[1].

Table 1 Schemes for Positive Change in Free Energy During Suspension Polymerization for Colloidal Stability

ΔH_R	ΔS_R	$\Delta H_R/$ $T\Delta S_R$	Type	Temperature effect
-	-	<1	entropic	if temperature decreases, less positive ΔF_R and less stability, i.e., colloidal system will flocculate
+	+	>1	enthalpic	if temperature increases, less positive ΔF_R and more instability, i.e., colloidal system flocculates
- or +	+ - 	>1 < 	hybrid	increase of temperature can produce either stability or instability.

Aqueous Suspension Polymerization

The type and rate of agitation determines particle size in suspension recipes. Thus, experiment in the bottle polymerizer can yield information on composition and kinetics only.

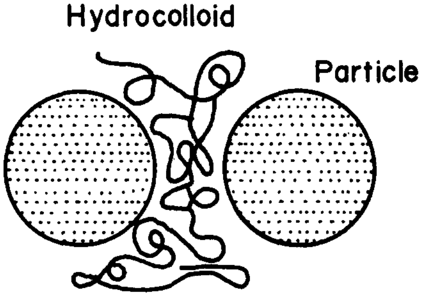
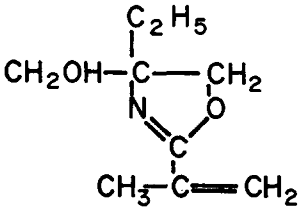


Fig. 2. Interpenetration of particles results in compression of hydrocolloid.

Homopolymerization of Vinyl Oxazoline and Its Ester

Vinyl oxazoline (I) was polymerized with 3% azobisisobutyronitrile at 80±2°C in toluene for 4 hr. The polymer was recovered by drying in a vacuum oven at 100°C to constant weight. The powder was light buff in color, readily soluble in aromatic solvents, moderately soluble in common acrylic ester monomers. The vinyl oxazoline ester (II) was found to be quite resistant to free radical polymerization in comparison to vinyl oxazoline. The ester was polymerized with 2% di-t-butyl peroxide at 125 ± 2°C for 72 hr. The polymer was a sticky solid, light lemon in color, soluble in aromatic hydrocarbons and moderately soluble in acrylic ester monomers.



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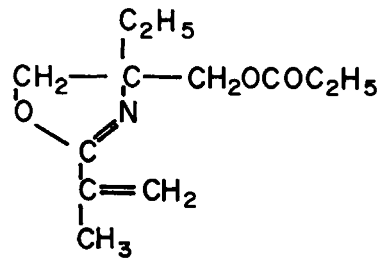

II

Homopolymerization of Stearyl and Tridecyl Methacrylates

Stearyl and tridecyl methacrylates were homopolymerized in an isoparaffinic hydrocarbon with 1% azobisisobutyronitrile at 80±2°C for 5 hr. The solid was recovered by the usual method of vacuum drying.

Graft Polymerization by Chain Transfer

Under suitable processing conditions the introduction of an alien homo- or copolymer in a free radical polymerization mass leads to the formation of a graft polymer. The alien polymer (backbone) was dissolved in the grafting monomer, namely, methyl methacrylate (10/90 wt.%) along with 2% free radical initiator, e.g., azocumene (based on total polymerization mass). Water (continuous phase, 60%) and surfactant (e.g., sodium lauryl sulfate at 0.00 or 0.03% based on aqueous phase) were transferred into a 6 fl.oz. coke bottle. The monomer/polymer/initiator sirup (dispersed phase, 40%) was then transferred to the bottle. The bottle was sealed with a septum and cap. The contents in the bottle were sparged with nitrogen and polymerized in a bottle rotating water bath at 70±2°C for 6 hr. After polymerization the polymer was recovered by the usual method of filtration, washing and drying. A very large number of suspension recipes were prepared. Typical grafted samples were resolved and analyzed. We will present a capsule of the results obtained.

Grafting Initiator

Azobisisobutyronitrile was found to be an inefficient grafting initiator because the dimethyl cyno methyl radicals are not reasonance stabilized.[2] Benzoyl peroxide that produces benzyl radical was found to be a suitable initiator. Azocumene produces dimethyl phenyl methyl radical which is highly stabilized by resonance and hyperconjugation. Azocumene was found to be a superior initiator to benzoyl peroxide for grafting.

Alien or Backbone Polymers

Poly(tridecyl methacrylate) is not a good alien polymer for graft suspension polymerization as compared to poly(stearyl methacrylate) and poly(vinyl oxazoline ester). Poly (tridecyl methacrylate) is a viscous liquid whereas poly(stearyl methacrylate) is a sticky solid at room temperature, but the latter appears to be a very good steric stabilizer. Therefore suspension recipes can be run without any soap. Poly(vinyl oxazoline) has poor solubility in methyl methacrylate and therefore its utility as a backbone polymer is limited for grafting methyl methacrylate. Poly(vinyl oxazoline ester) is an excellent steric stabilizer.

Nonaqueous Suspension Polymerization

Aliphatic hydrocarbons and alcohols do not offer the advantage of water as a continuous phase in suspension and emulsion polymerizations. Also monomers, e.g., methyl methacrylate and styrene are soluble in aliphatic hydrocarbons and alcohols whereas the polymers are not soluble. Thus in such systems combination of suspension and solution polymerizations occur concurrently. Nonaqueous suspensions may be used as are or they can be converted into powders for solventless systems. Two methods of polymerization were investigated.

Polymeric stabilizer

Polymerization conducted in presence of a polymeric stabilizer that contain solvated and non-solvated components will lead to dispersion polymerization. Particle growth takes place around the non-solvated component. A typical recipe is butyl methacrylate (5.0M), stearyl methacrylate (0.25M) acrylic acid (0.2M), benzoyl peroxide (0.75% based on total monomer), and high flash mineral spirits (half of total formula by weight). Monomer-initiator was added to hot mineral spirits at 130 ± 2°C over a two-hour period. The reaction mass was held for an additional 6 hr to complete polymerization. The viscosity of the dispersion was 13 stokes.

Macro-monomer

A copolymer containing acidic pendant group, at complete or partial conversion is allowed to react with a basic monomer, e.g., t-butylaminoethyl methacrylate, dimethylaminoethyl methacrylate or 4-vinyl pyridine thus producing a macro-monomer. Additional monomers can be added and dispersion polymerization is completed by usual method. A typical recipe is isobutyl methacrylate (3.0M), stearyl methacrylate (0.5M), methyl methacrylate (1.0M), and acrylic acid (0.5M) polymerized at 100 ± 2°C in V&MP naphtha to 80% conversion. To this 0.5M dimethylaminoethyl methacrylate was added along with 2% di-t-butyl peroxide based on total unpolymerized monomer. Dispersion polymerization was conducted at 90 ± 2°C for 6 hr. The viscosity of dispersion was 42 Kreb unit at 40% solid.

Applications

Compositions that we have described in the paper should find application in powder coating, toner resin, automotive finishes and for encapsulating electronic components.

Acknowledgement

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2. A.M. Usmani and I.O. Salyer, J. Elast. Plast., 13, 90 (1981).

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