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Suspension Graft Polymerization of Methyl Methacrylate onto Selected Backbones

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ABSTRACT

Methyl methacrylate was grafted onto poly(vinyl oxazoline ester) and poly(stearyl methacrylate) by a chain transfer suspension polymerization method to produce specialty polymeric products. These graft polymers should find application in powder coating, toner resin, and for encapsulating electronic components.

INTRODUCTION

Suspension polymerization, an offshoot of bulk polymerization, is used to produce enormous volumes of polymers and polymeric products. 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.

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 describe a background of suspension, bulk, and emulsion polymerization processes, and a treatment of colloidal stability and instability.

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SUSPENSION, BULK, AND EMULSION POLYMERIZATIONS

Suspension polymerization has a common feature with emulsion polymerization in that soap and suspension stabilizers are used. However, bulk kinetics are essentially followed in suspension polymerization. Bulk, suspension, and emulsion polymerization processes are schematically shown below.

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

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

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

Kinetics treatment will give the following results:

$$\overline{X}_n \propto 1/[I] \qquad \text{(in emulsion polymerization)}$$

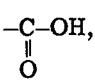
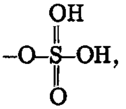
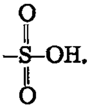
$$\overline{X}_n \propto 1/[I]^{1/2} \qquad \text{(in bulk and suspension polymerizations)}$$

where $\overline{X}_n$ is the degree of polymerization and [I] is the initiator concentration.

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 $\frac{3}{2}kT$. Dispersions of neutral colloidal particles flocculate rapidly as a result of long-range attractive forces. In particle dispersions, the total potential is the sum of energies of attraction and 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 [1].

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  $-\underset{\overset{\|}{O}}{C}-OH$,  $-O-\overset{\overset{OH}{\|}}{\underset{\overset{\|}{O}}{S}}-OH$, and  $-\overset{\overset{O}{\|}}{\underset{\overset{\|}{O}}{S}}-OH$. If particles approach to a point where attractive forces overcome electrostatic forces, flocculation will occur.

Steric Stabilization

The word "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. The compression produces a change in the free energy, given by the Gibbs-Helmholtz equation [2].

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

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 a negative ΔF_R is needed for recovery of the polymer and better coagulation (see Table 1).

EXPERIMENTAL

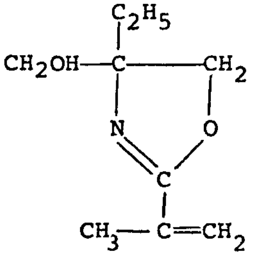
The type and rate of agitation determines particle size in suspension recipes. Thus, experimentation in a bottle polymerizer can yield information on composition and kinetics only.

TABLE 1. Schemes for Positive Change in Free Energy during Suspension Polymerization for Colloidal Stability

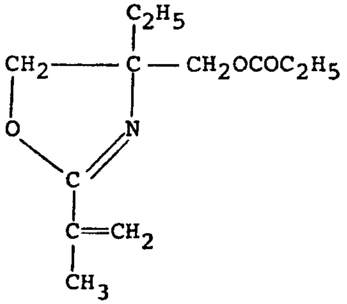
ΔH_R	ΔS_R	$\Delta H_R/T\Delta S_R$	Type	Temperature effect
-	-	< 1	Entropic	If temperature decreases, less positive ΔF_R and less stability, i.e., colloidal system will flocculate
+	+	> 1	Enthalpic	If temperature increases, less positive ΔF_R and more instability, i.e., colloidal system flocculate
- or +	+ or -	$\gtrless 1$	Hybrid	Increase of temperature can produce either stability or instability

Homopolymerization of Vinyl Oxazoline and Its Ester

Vinyl oxazoline (I) was polymerized with 2% azobisisobutyronitrile at 80 ± 2°C in toluene for 4 h. 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, and 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%



I



II

di-t-butyl peroxide at 125 ± 2°C in xylene for about 30 h. The resin solution was dried in a vacuum oven at 100 ± 2°C for 72 h. The polymer was a sticky solid, light lemon in color, soluble in aromatic hydrocarbons, and moderately soluble in acrylic ester monomers.

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 h. 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-fluid oz Coke bottle. The monomer/polymer/initiator syrup (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 h. After polymerization the polymer was recovered by the usual method of filtration, washing, and drying.

RESULTS AND DISCUSSION

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 dimethylcyanomethyl radicals are not resonance stabilized. Benzoyl peroxide that produces the benzyl radical was found to be a suitable initiator. Azocumene produces the dimethylphenylmethyl 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 very 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.

CONCLUSIONS

Poly(vinyl oxazoline ester) and poly(stearyl methacrylate) gave most promising results as alien polymers in suspension recipes to graft methyl methacrylate. Azocumene was found to be a suitable grafting initiator. Methyl methacrylate/poly(vinyl oxazoline ester) or poly(stearyl methacrylate) (90/10 wt%) graft compositions that we have prepared should find application in powder coating, toner resin, and for encapsulating electronic components.

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