Experimental observations in the preparation of microsphere polymer dispersions

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ABSTRACT: Stable microsphere polymers result from minimum interfacial tension between monomers and aqueous suspending agent solution. Surfactant selection to improve the microsphere stability and control particle size is critical. Particle size distribution depends on vessel configuration, agitation, interfacial tension, and the weight ratio of the reacting medium to the immiscible aqueous solution. Average particle size is inversely proportional to stirring rate. There is an empirical formula to predict average particle size at a given stirring rate when other factors are constant.

KEYWORDS: Dispersions, microspheres, polymerization, polymers, surfactants.

Polymerization in a heterogeneous, aqueous suspension system offers many advantages leading to its widespread commercial use. The technique is ideal for the preparation of polymeric materials in bead form. Such bead polymers have wide application as molding, ion exchange, and chromatographic resins as well as flocculating agents. Earlier papers by other researchers have discussed the basic aspects of suspension polymerization (*1, 2*). Further investigation by others (*3*) leads to the assumption that polymerization kinetics are similar to those of a respective bulk or solution polymerization, depending on the absence or presence of a solvent during the reaction.

It is possible to extend the principles of suspension polymerization to reverse bead polymerization such as the manufacture of a water soluble polymer. The technique is an inverse suspension polymerization (*4–6*). One example is an acrylamide polymer. Some applications of these water soluble polymers include recirculating heating and cooling systems, thickening agents, cutting fluids, textile sizes, and fire fighting media. There also are strategic uses such as flame–retardant additives to reduce fuel atomization.

Historically, the introduction of bead–type suspension polymerization met specific manufacturing requirements. The extensive patent literature indicates substantial progress in the art and application of suspension polymerization. Most of this work covers development of a bead polymer with a particle size having a diameter ranging from 100 to 2000–3000 μm. It was not until 1972 that a patent (*7*) taught the preparation of a microsphere polymer with a particle size of 10–100 μm using suspension polymerization for a particular coating application. There is no elucidation of that technique in the literature, however.

In this paper we report the complete details of the particle size and particle size distribution associated with reactor design and the selection of stabilizers, including both suspending agents and surfactant. There also is information on the rate of agitation with emphasis on the technical aspects of suspension polymerization and the preparation of microspheres for coating applications. This extension of microsphere polymer technology may offer some useful knowledge to add to conventional bead polymerization techniques for many applications.

Experimental

Materials

2–Ethylhexyl acrylate, butyl acrylate, isobutyl acrylate, methyl acrylate, ethyl acrylate, and acrylic acid are technical-grade monomers which are satisfactory for direct use in polymerization without further purification. Suspending agents in this study include partially hydrolyzed polyvinyl

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alcohol (PVA), fully hydrolyzed PVA, starch, and the sodium salt of an acid-containing acrylic copolymer. Useful surface-active agents are ethoxylated alkyl ammonium sulfate, ethoxylated alkyl sodium sulfate, and alkylaryl sodium sulfonate. Initiators include benzoyl peroxide, azo–bis–isobutryl nitrile (AIBN), lauroyl peroxide, t–butylperoctoate, and t–amylperoxy–2–ethylhexanoate.

A strobotac unit monitored the rate of agitation during polymerization. A tensiometer measured the interfacial tension between the two immiscible media at room temperature.

Suspension polymerization procedure

Suspension polymerization takes place when there is an organic phase consisting of acrylic monomer mixture and initiator dispersed in an aqueous solution containing surfactant and stabilizer. Since oxygen is a strong inhibitor, special care must be taken to remove it before introducing the initiator. We applied heat to initiate the reaction and allowed the temperature to rise to its peak. There was vigorous stirring during the entire reaction. At the end of the polymerization, we removed a sample to analyze for particle size and particle size distribution. The microsphere polymer received additional formulation as necessary for specific coating applications.

Particle size analysis

A centrifugal-type automatic analyzer determined particle size distribution of the particulate samples. It used a noncontact measuring method based on liquid–phase sedimentation. It allowed analyses of samples as small as 2.5 mL. The rotational speed of 1000 rpm in the centrifugal sedimentation unit enabled rapid measurement of the microsphere particles. A computer software program provided automatic printing of the measurement of the average diameter.

Results and discussion

Particle size distribution

The configuration of the polymerization vessel largely determines the size distribution of the microspheres in a suspension polymerization. In our studies, a cylindrical vessel with side baffles produced particle sizes smaller than those prepared from a vessel without side baffles. **Figure 1** provides photographs of these vessels.

At a stirring speed of 200 rpm, vessel A with side baffles gave microspheres with an average diameter of 37 μm. Vessel B, without side baffles, produced particles of an average diameter greater than 60 μm at the same speed. This phenomenon is exactly the same as that in making bead polymers (*8*). All attempts to make small-particle-size microsphere polymers using vessel B by substantially increasing both the surfactant and suspending agent failed. The 60-μm or large-particle-size microspheres which always resulted from this vessel without side baffles would have very limited use in coating applications. We therefore chose vessel A (with side baffles) to study the effect of stirrer speed on the size of microspheres produced by suspension polymerization.

Stirring rate

The rate of stirring varied to obtain microsphere polymers in the range of 10 μm to 60 μm. All factors except the rate of stirring remained constant in this study. **Table I** shows average particle diameters with different stirring speeds. **Figure 2** shows the cumulative particle size distribution at different rates of agitation. As the rate of agitation increases, the cumulative particle size distribution changes to a smaller size. Alternatively, the cumulative particle size distribution shifts to a larger size as the rate of agitation decreases. The nearly parallel lines of the cumulative particle size distribution plotted against the rate of agitation further suggest that the average size of the microspheres from suspension polymerization is inversely proportional to the stirring speed. Equation 1 defines this relationship:

$$\bar{D} \propto \frac{1}{R} \qquad (1)$$

where

$\bar{D}$ = average particle diameter, mm

R = stirring speed, rpm

A plot of the average particle diameter vs. the rate of stirring produces the straight line with a negative slope of **Fig. 3**. This quantitative relationship provides a useful guide to save considerable experimental effort. For example, if one knows the average particle size at a certain rate of agitation, the rate of stirring to obtain a desirable particle size derives from Eq. 2:

$$D_i\bar{D}/D_j\bar{D} = R_j/R_i \qquad (2)$$

where

$D_i\bar{D}$ = average particle diameter for polymer i, μm

$D_j\bar{D}$ = average particle diameter for polymer j, μm

R_j = stirring rate for polymer j, rpm

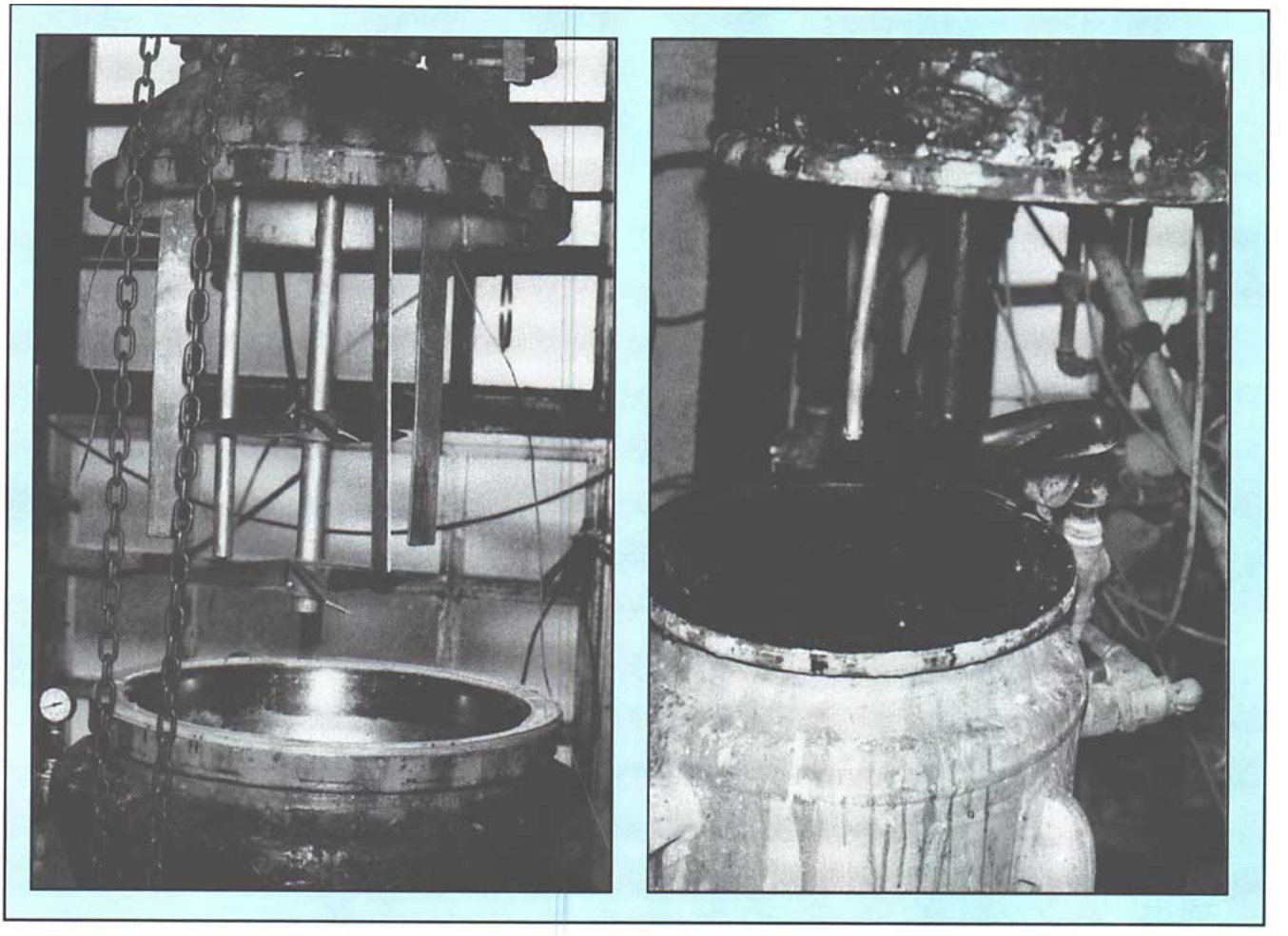
R_i = stirring rate for polymer i, rpm

As Table I indicates, the calculated $D_i\bar{D}/D_j\bar{D}$, which is based on R_j/R_i, is nearly equal to the experimental value. This observation from our experiments again demonstrates that stirrer speed should usually be the first choice for adjusting particle size with all other factors remaining constant, since it is by far the easiest method. However, our studies pertain only to suspension polymerization having microspheres with a size of 10–60 μm.

Stabilizers and surfactants

In suspension polymerization, mechanical agitation causes the liquid monomer mixture to disperse as droplets in the aqueous solution. To prevent the coalescence of these droplets during reaction, it is necessary to add suspending agents or protective colloids to the system.

1. Suspension polymerization apparatus with vessel A on the left containing baffles and vessel B on the right containing no baffles



I. Calculated and experimental average particle diameter ratios at different rates of agitation

Rate of agitation, R, rpm	*Average particle size, D, μm*	*Calculated D_i/D_j*	*Experimental D_i/D_j*
290	22.2	-	-
255	29.6	1.1	1.3
211	36.2	1.4	1.6
171	43.4	1.7	1.9
121	56.0	2.4	2.5

The selection of a suspending agent for a given reacting system is a time consuming, trial and error technique. It is usually necessary to undertake a complete polymerization reaction to test the effectiveness and efficiency of a particular suspending agent. In our study to prepare microsphere polymers, we investigated two types of suspending agents. One type was an organic polymer such as partially hydrolyzed PVA, fully hydrolyzed PVA, or starch. The other was the alkali salt of an acid containing, crosslinked acrylic copolymer. These water-soluble polymeric suspending agents, with a very small amount of a surface-active agent to help further stabilize the microsphere and control the particle size, are an important aspect of our investigation.

The amount of surfactant in a suspending aqueous solution must be below the critical micelle concentration. Larger amounts of surface-active agents will prevent formation of the microsphere by promoting emulsion polymerization and latex formation.

Table II summarizes the interfacial tensions between acrylic monomers and suspending agents in an aqueous solution. The partially hydrolyzed PVA and the aqueous solution of the alkali salt of the acid containing, crosslinked acrylic copolymer have the lowest interfacial tensions. They produce the ideal microsphere polymers for practical coating applications. The other suspending agents exhibit higher interfacial tensions and produce shapeless polymers or lumps regardless of surfactant incorporation.

Apparently, the fully hydrolyzed PVA and starch are too hydrophilic.

They do not seem to adsorb strongly enough at the monomer and water boundary to form a coherent film, which will prevent drop coalescence. On the contrary, the partially hydrolyzed PVA and the alkali salt of the acid containing, crosslinked acrylic copolymer are more surface active and adsorb more strongly at the monomer and water interface. This is clear from the values of the interfacial tensions of Table II. These experimental facts save time when selecting a suspending agent.

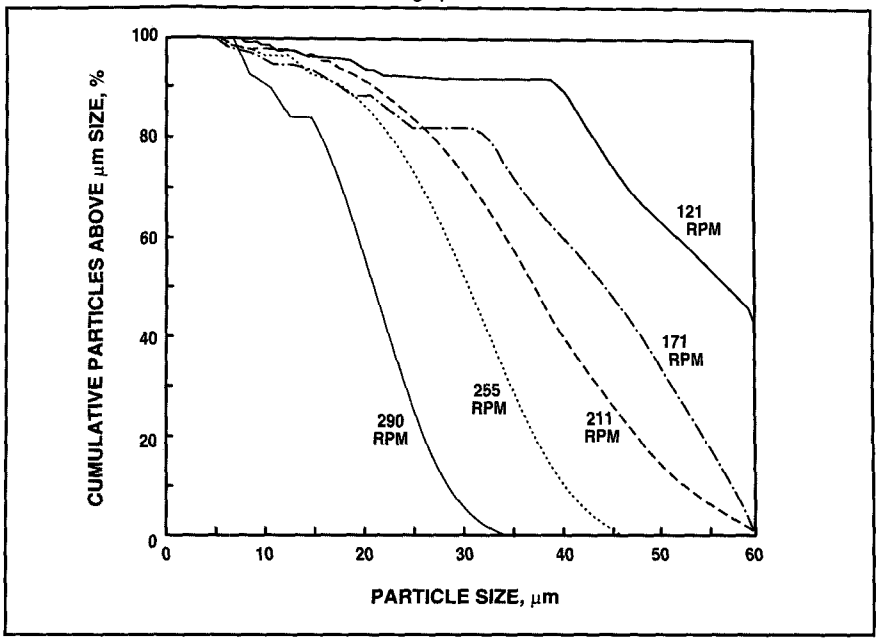
The selection of a surfactant to use in conjunction with either the partially hydrolyzed PVA or the alkali salt of the acid containing, crosslinked acrylic polymer is intricate and interesting. **Table III** shows that the aqueous polymerization phase, consisting of an ammonium salt of ethoxylated surfactant and partially hydrolyzed PVA, produces the ideal microsphere polymer. If the sodium salt of the same ethoxylated surfactant replaces the ammonium ethoxylated surfactant, particle agglomeration occurs and produces a shapeless bulk polymer. Similarly, use of the alkali salt of the acid containing, crosslinked acrylic copolymer with the sodium salt of an alkylaryl sulfonate surfactant, where no ethoxylated moiety is present in the molecule, yields microsphere polymers without any problem. When the ammonium ethoxylated surfactant replaces the sodium counterpart, the reaction produces polymers of large particle sizes and some lumps.

Evidence indicates that an ethoxylated surfactant containing polyethylene oxide chains has a significant impact on a polymer, depending on the kind of cation salt present in the reaction system. The alkali salt seems to present polymerization problems in the presence of an ethoxylated surfactant.

The problem disappears if the surfactant has no ethylene oxide. An example would be an alkaline salt of alkylaryl sulfonate. The interaction between alkali metal ions and the ethylene oxide moiety may contribute to this unusual phenomenon. Perhaps the complex of ethylene oxide with alkali metal ion causes a decrease of chain transfer reactivity of the ethoxylated emulsifiers. This may in turn increase the molecular weight of the polymer. Ammonium ions fail to form such a complex with the ethylene oxide chain. One research group reported that a chain transfer reaction occurs on the polyethylene oxide chains present in polyoxyethylene (4 moles) nonylphenol (*9*), probably on a methylene group which the proximity of an oxygen atom activates. More studies and investigation are necessary to clarify this explanation.

The effect of suspending agent and surfactant concentration on particle size is not quite as appreciable as one might imagine. In a typical experiment, when both suspending agent and surfactant concentration increased two-fold, the particle size and particle size distribution showed no significant change. **Figure 4** indicates the effects of stabilizer concentration on the particle size distribution. Curve A and curve B almost overlap, even though the concentrations of the stabilizer and surfactant in curve A are two times less than that for curve B. Remember, however, that this study only covers suspension polymerization where the surfactant concentration must be below the critical micelle concentration.

2. Particle size distribution at different stirring speeds



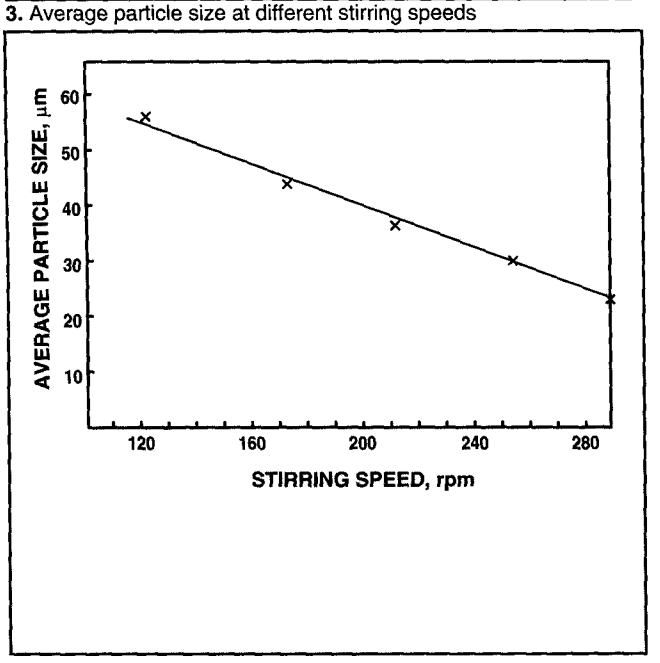
II. Interfacial tension between monomers and aqueous suspending agent solutions for various suspending agents with the results of their suspension polymerization

Suspending agents	*Interfacial tension, dynes/cm*	*Product*
Partially hydrolyzed PVA	2.3	Microsphere polymer
Fully hydrolyzed PVA	7.3	Shapeless bulk
Starch	10.9	Shapeless bulk
Sodium salt of acid containing acrylic copolymer	0.7	Microsphere polymer

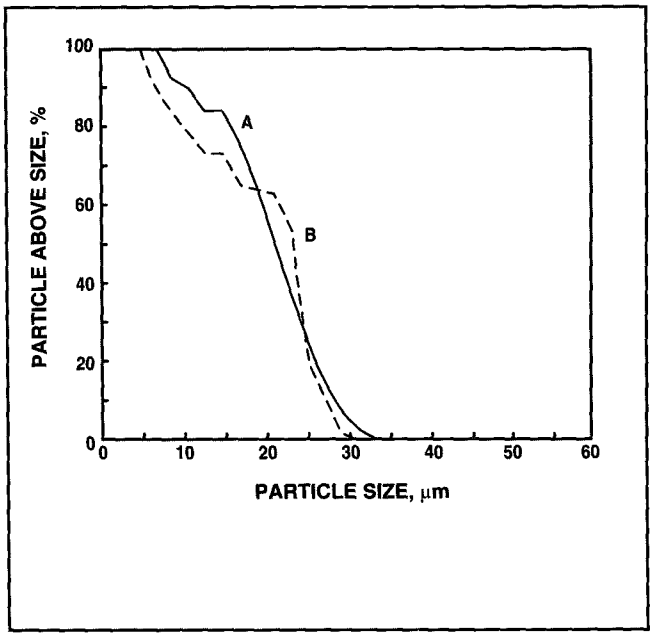
Initiator selection

Chemical initiation of the polymerization reaction most often occurs with free radical azo or peroxide species. Their location can be in the dispersed aqueous or in the continuous mono-

3. Average particle size at different stirring speeds



4. Effect of stabilizer concentration on particle size distribution at 290 rpm



III. Suspension polymerization results using different combinations of suspending agent and surfactant

Suspending agent	*Surfactant*	*Product*
Partially hydrolyzed PVA	Ethoxylated ammonium sulfate	Microsphere polymer
Partially hydrolyzed PVA	Ethoxylated sodium sulfate	Lump and shapeless
Sodium salt of acid containing acrylic copolymer	Ethoxylated ammonium sulfate polymer	Lump and large size
Sodium salt of acid containing acrylic copolymer	Sodium alkylaryl sulfonate	Microsphere polymer

mer phase. Oil-soluble initiators are common, since they generate higher molecular weight and offer better thermal stability.

Particle size dependence

The polymerization mixture consists of an acrylic monomer mixture in water. The organic phase weight fraction of this mixture is the total amount of organic material divided by the sum of the organic material and water. This varied in our work from 0.1 to 0.6. As the weight ratio of the organic phase increases, the particle size of the polymer becomes larger, and the suspended particles tend to coalesce. It is therefore necessary to increase substantially the rate of agitation. This propels the crowded organic phase and breaks the larger droplets into smaller ones before they can polymerize to form a large particle. On the other hand, as the weight ratio of the organic phase decreases, the polymer particles become smaller. A low rate of agitation is necessary to obtain a desirable particle size for microsphere polymers.

Particle size control

Suspension polymerization involves the formation of small droplets of monomers in an immiscible suspension medium with the direct conversion of the individual droplets into the corresponding polymer particles. A more uniform distribution of the mixing force throughout the suspension mixture produces a narrower droplet size distribution with concomitant final polymer particle production. Various parameters control the average size of the droplets in a two-phase suspension system. Our investigations and observations indicate that the weight ratio of the two immiscible phases, the speed of mixing, the design of the vessel, and the interfacial tension between the two immiscible media have a major role in controlling

the particle size of the microsphere. Stabilizer and surfactant concentration seem to have a smaller role. Equation 3 provides a semiquantitative, empirical basis for formation of microsphere particles and a useful guide for preparation of microsphere polymers:

$$\bar{D} \propto A \cdot \frac{Y \cdot W}{R} \qquad (3)$$

where

A = vessel design, stirrer, or other parameter

Y = interfacial tension between the two immiscible phases

W = weight ratio of the droplet phase to the suspension medium

The magnitude of the various parameters in this equation, however, may vary appreciably from one suspension system to another. Similarly, some of the variables may fall within relatively narrow or rather broad limits, depending on the magnitude of other variables. For instance, our specific investigation reveals that the average particle size of microspheres in suspension polymerization is inversely proportional to the stirring speed, as described in Eq. 1, when A, Y, and W remain constant. The substantial experimental data collection necessary to determine the influence of other factors is beyond the scope of our current study. Nevertheless, selection of a surfactant along with the suspending agents also can affect the particle size of the product. The effect in this case, however, is mainly through chemical interaction to alter the kinetic polymerization. It is not possible to modify Eq. 3 to include this effect.

Conclusion

Microspheres of a particle size in the range of 10 μm to 60 μm prepared by suspension polymerization are particularly useful for coating applications. The vessel design, speed of agitation, weight ratio of the monomers to aqueous solution, and interfacial tension between the two immiscible media control the particle size. The average particle size is inversely proportional to the rate of agitation, provided other factors remain constant. Adding a small amount of surfactant to the suspending medium can help to control further the particle size as well as stabilize the microsphere polymer. This is not true, however, in the case where ethoxylated surfactant with alkaline metal cation is present. This effect may result from the ability of polyethylene oxide to complex with alkaline metal ions and cause a change in the shape and size of polymerized particles.

Literature cited

1. Hohenstein, W.P. and Mark, H. H., J. Polym. Sci. 1(2): 127(1946).
2. Trommsdorff, E., Kohle, H., and Lagally, P., Makromol Chem. 1:169(1948).
3. Munzer, M. and Trommsdorff, E., High Polym. 29:106: 106(1977).
4. Baade, W. and Reichert, K. H., Eur. Polym. J. 20(5): 505(1984).
5. Vanderhoff, J. W., Distefano, F. V., El-Aasser, M. S., *et al.*, J. Dispers. Sci. Technol. 5(3&4): 323(1984).
6. Kim, K. J. and Ruckenstein, E., Macromol. Chem. Rapid Commun. 9(6): 285(1988).
7. Silver, S. F., U.S. pat. 3,691,140 (Sept. 12, 1972).
8. Burger, J. J., Tomlinson, E., Mulder, E. M., *et al.*, Int. J. Pharm. 23(8): 333(1985).
9. Dimonie, M. V., Boghina, C. M., Marinescu, N. M., *et al.*, Eur. Polym. J. 18: 639(1982).

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