

# Multifeed Emulsion Polymers: The Effects of Monomer Feed Sequence and the Use of Seed Emulsion Polymers

L. W. MORGAN, *S. C. Johnson and Son, Inc., Polymer Research Department, Racine, Wisconsin 53403*

## Synopsis

The core/shell concept of emulsion polymerization postulates particle formation during the reaction in such a way that macromolecules formed in the early stages of the reaction are in the core or center of the final particles and latter-formed macromolecules are located in a shell layer around the core. This paper describes work done on model hard/soft and soft/hard two-stage, emulsion polymer systems. Variables studied included seed levels, monomer type, monomer addition sequence, surfactant level, and initiator level. Emulsion optical densities were used as estimates of particle size. Minimum film formation temperatures (MFT) were correlated with the above variables. Ratio of seed polymer/added monomer and initiator levels were found to markedly affect MFT.

## INTRODUCTION

The location of the first-formed polymer molecules in a particle in relation to the location of the latter-formed polymer molecules is an essential question raised in the discussion of emulsion particle morphology.

In the commonly used incremental monomer addition technique, the monomers are usually converted to polymer nearly as fast as they are added. In a sequential multifeed addition (one in which two or more different monomer feeds are added sequentially with a short hold period between additions), two or more different polymer compositions should be formed in the same particle. In most cases there will be little blocking and grafting unless first stage polymers contain unsaturation such as butadiene copolymers.<sup>1</sup> Several possibilities for location of early- A, and late- B, formed macromolecules in the particle are: (1) a random mixture of A and B; (2) a core of A interpenetrated with B; (3) a core of A with a uniform shell of B around it; (4) a core of A with domains of B; and (5) a separation of A and B into hemispheres or "dumbbells."

Excellent work in recent years indicate that case 1 is not typical. Most possible configurations are attainable by control and selection of variables. Several key papers and reviews describing different emulsion particle morphologies are listed in the bibliography.<sup>2-9</sup>

The multistage polymer emulsions studied were made to gain knowledge of the relationship between performance properties and the methods of polymer preparation. Emulsion minimum film-formation temperature (MFT) was chosen to follow the variable effects. Model systems were studied using methyl methacrylate (MMA) and styrene (S) as the "hard" monomers and ethyl acrylate (EA) and butyl acrylate (BA) as the "soft" monomers. MMA and EA comprise a relatively hydrophilic pair. S and BA are more hydrophobic due to their higher

hydrocarbon content. The pairs were comparatively evaluated. All polymers had a total of 3% methacrylic acid (MAA) uniformly incorporated. Experiments employing seeded and nonseeded techniques were conducted. Optical density measurements were used as simple, crude estimates of particle size.

## EXPERIMENTAL

### Materials

Commercial polymerization grade monomers were used without purification or inhibitor removal:

Methyl methacrylate	(MMA)	60 ppm HQ	Rohm & Haas
Ethyl acrylate	(EA)	200 ppm MEHQ	Union Carbide
Styrene	(S)	15 ppm TBC	Koppers
Butyl acrylate	(BA)	15 ppm MEHQ	Celanese
Methacrylic acid	(MAA)	200 ppm MEHQ	Rohm & Haas

Here HQ is hydroquinone, MEHQ is monomethyl ether of hydroquinone, and TBC is tertiary butyl catechol.

Emulsifiers were commercially available and used as received:

Sodium lauryl sulfate—Maprofix 563	Millmaster Onyx
Sodium alkylaryl polyether sulfate—Triton X-301	Rohm & Haas
Sodium alkylaryl polyether sulfonate—Triton X-200	Rohm & Haas
Alkylphenol polyglycol ether—Neutronyx 675	Millmaster Onyx

Reagent grade ammonium persulfate (APS) from J. T. Baker Chemical Co. was used as the initiator in all experiments. Water was purified by passage through a mixed anion/cation exchange resin column.

### Preparation of Emulsion Polymers

#### *Unseeded Emulsions*

The general emulsion polymerization procedure used for the unseeded emulsions was as follows: Anionic surfactants were added to the water in the stirred reactor and heated to 80–82°C under nitrogen. Reactions used 1 wt % initiator based on the monomer weight and were carried out at 35% nonvolatile. The nonvolatile is considered to be every ingredient except water—the monomers ultimately being converted to polymer. The initiator was added, and then the first monomer feed was begun. A 30-min monomer feed schedule was used. The reaction was then held 5 min to complete most of the polymerization. The second monomer feed was also added over 30 min, and the emulsion then held 30 min to complete the reaction.

#### *Preparation of the Seed Polymer*

A fine particle size acrylic emulsion polymer was prepared for use as the seed polymer.

The monomer feed was 70 wt % MMA/27 wt % EA/3 wt % MAA.

The polymerization was carried out at 25 wt % nonvolatile and 80°C, under

nitrogen, and used a 1-h monomer addition with a 30-min hold. 0.5 wt % initiator was used based on the monomer weight. The emulsifier was 3 wt % sodium lauryl sulfate based on monomer. 5% of the monomer mixture was precharged to the stirred 80°C surfactant solution 2 min before the initiator was added. The monomer precharge *in situ* seed technique results in narrower particle size distribution.

### *Seeded Emulsion Polymers*

The general emulsion polymerization procedure used for preparing the seeded emulsions was to add 0.1 wt % of the nonionic Neutronyx 675, based on the monomer feed weight, to water in the stirred reactor, and then to heat the solution to 80–82°C under nitrogen. The seed emulsion and then the initiator were added. The monomer feeds were added using the same timing as in the unseeded emulsions, but they differed in that they were added as 70/30 wt % W/O monomer emulsions using 0.5 wt % active of Triton X-301 based on monomer weight as the emulsifier. The purpose of the nonionic is to minimize destabilization of the seed polymer by the initiator. The selection of the type, level, and programming of the anionic surfactant is designed to minimize new particle formation by surfactant starvation while still stabilizing the growing seeded particles. The nonvolatiles of seeded emulsions varied from 17% to 35%. Initiator levels varied from 0.25 to 0.5 wt % based on monomer concentrations.

## **Emulsion Characterization**

### *Minimum Film-Formation Temperature*

Minimum film-formation temperature (MFT) measurements were run on a temperature gradient bar "that is a modification of the type" described by the Rohm & Haas Co.<sup>10</sup> MFTs were measured on unneutralized, 15.0% nonvolatile dilutions. MFTs were normally measured within 30 h of preparation.

### *Optical Density*

Optical Density (OD) measurements were taken on 1.0% nonvolatile unneutralized dilutions for the unseeded emulsions at 500 nm in 0.5-in. cells. OD measurements were taken at 0.1% nonvolatile, unneutralized dilutions for both the seed and the seeded emulsion polymers at 500 nm in 0.5-in. cells.

## **RESULTS**

### **Unseeded Emulsions**

The first experiments were carried out with unseeded emulsion polymers. Initially, a simple 2<sup>2</sup> experimental design was set up using 2 wt % sodium lauryl sulfate and 1 wt % Triton X-200 (100% active level) based on the total monomer weight, 1 wt % ammonium persulfate, and 35.0% nonvolatile as constants. Table I shows the variables selected for the sequential monomer feeds. This led to the four experiments and results shown in Table II.

The optical densities indicated, as expected, that the feed sequence had little

TABLE I  
Experimental Design Variable and Level Assignments

Variable		(-)	(+)
$X_1$	Hard/soft (high/low $T_g$ ) order sequence	Hard	Soft
$X_2$	Hydrophilicity of monomer pair	Hydrophilic	Hydrophobic

effect on particle size. The hydrophilic emulsions had lower optical densities (finer particle size) than the hydrophobic ones. The MFT data did not indicate any effect of the monomer order sequencing such as core/shell morphology.

One possible explanation for the lack of an observed MFT orientation effect was the fine particle size of the emulsions. If a pure core/shell effect existed, the shell would only be calculated to be 20% of the radius. This type of emulsion characteristically is about 50 nm in diameter so a shell would only be about 5 nm thick. Such a shell might be inadequate to dominate MFT in a dynamic film forming process. Alternatively, a shell might never have formed. Formation of a shell could have been disrupted by other orienting forces such as methacrylic acid groups or initiator end groups equilibrating with the surface. To estimate this possibility the series was repeated using lower surfactant levels (Table III).

Reducing the surfactant levels changed the optical densities as expected. MFTs were also changed. The slight increase of MFT of the hydrophilic emulsions and the appreciable reduction of MFT in the hydrophobic emulsions would not be expected from the coalescence of particles of homogeneous composition. The MFT data did not indicate core/shell morphology. One possibility that might account for both the change in optical density and the lack of MFT/sequence effect would be particle size distributions so broad as to allow enough thin shells to obliterate an observable MFT effect.

TABLE II  
2<sup>2</sup> Experimental Design Runs and Effect of Variable on MFT and Optical Density

Emulsion no.	Mon. feed #1 (48.5%/1.5%)	Mon. feed #2 (48.5%/1.5%)	MFT (°C)	Optical density
1	MMA/MAA	EA/MAA	39	0.32
2	EA/MAA	MMA/MAA	35	0.26
3	S/MAA	BA/MAA	17	0.60
4	BA/MAA	S/MAA	17	0.50

TABLE III  
2<sup>2</sup> Experimental Design Repeated at Low Surfactant Levels To Produce Thicker Shelled, Larger Particles

Emulsion no.	Mon. feed #1 (48.5%/1.5%)	Mon. feed #2 (48.5%/1.5%)	Surfactant level	MFT (°C)	Optical density
5	MMA/MAA	EA/MAA	0.5% NaLS	43	2.0+
6	EA/MAA	MMA/MAA	0.5% NaLS	42	1.4
7	EA/MAA	MMA/MAA	0.4% NaLS	46	2.0+
8	S/MAA	BA/MAA	1.0% NaLS	≤0	1.8
9	BA/MAA	S/MAA	1.0% NaLS	≤0	1.4

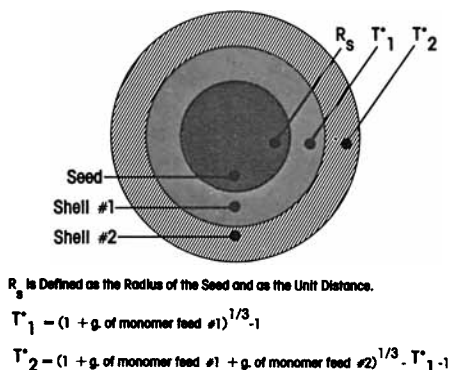


Fig. 1. A visualization of the two concentric shelled seeded emulsion particle model.

### Seeded Emulsions

To preclude the above possibility, seeded, narrow particle size range emulsions were examined. The preparation of these emulsions is discussed in the Experimental section. The narrow size distributions result from forcing polymerization to take place on the seed emulsion particles by "surfactant starvation," thus minimizing new nucleation. The tendency is for the growing seed particles to approach the same size.

The fine particle size seed emulsion was made several times (for example, see emulsion no. 10) and was characterized as having MFTs of  $63^\circ\text{C} \pm 3^\circ\text{C}$  and optical densities of  $0.08 \pm 0.03$ . Sequential monomer feed polymers were then prepared in the presence of the seed emulsion. Monomers were added as emulsions.

Single feed, seeded, terpolymer emulsions were made for comparison with the sequential feed, seeded copolymer emulsions. In this set the single feed consisted of a mixture of the same monomers in the same proportions, as was used in both feeds of the analogous, sequential hard/soft and soft/hard polymers. These are designated "average uniform copolymers." Various weight ratios of seed polymer to monomer were investigated.

The seed polymer technique yielded emulsion polymers showing the expected effects. MFT was affected by the sequencing and the ratios of monomers feeds. Optical densities correlated with particle size. Although this was not conclusive proof of pure core/shell effects, it is useful to examine the polymers using the following model and assumptions:

Assuming the particles remain spherical, with no significant interpenetration of the layers (see Fig. 1), additive volumes yield the following relationships. In these equations the dimensionless quantity,  $T_i^*$ , is calculated from the additive volumes.  $T_i^*$  is equal to the ratio  $T_i/R_s$ , where  $T_i$  is the thickness of the  $i$ th shell and  $R_s$  is the radius of the seed particle.

A single-shell, seeded, polymer particle has a volume  $V_{\text{total}_1}$  after adding  $g_1$  g of monomer feed # 1 and is related to the volume of the seed,  $V_s$ , by:

$$1. \quad V_{\text{total}_1} = V_s + g_1/\rho_1$$

where  $\rho_1$  is the density of the polymer made from monomer feed # 1

2. Dividing by  $V_s$ , substituting  $V_{\text{total}_1} = \frac{4}{3} \pi (R_s + T_1)^3$  and  $V_s = \frac{4}{3} \pi R_s^3$ , and simplifying, we obtain

$$(1 + T_1/R_s)^{1/3} = (1 + g_1/\rho_1 V_s)^{1/3}$$

3. Substituting
- $T_1^*$
- ,

$$(1 + T_1^*)^{1/3} = (1 + g_1/\rho_1 V_s)^{1/3}$$

4. Solving for
- $T_1^*$
- ,

$$T_1^* = (1 + g_1/\rho_1 V_s)^{1/3} - 1$$

Similarly, the volume after adding  $g_2$  g of monomer feed #2 is related to  $V_s$  as follows:

5.  $V_{\text{total}_2} = V_s + g_1/\rho_1 + g_2/\rho_2$

where  $\rho_2$  is the density of the polymer made from monomer feed #2.

6. Dividing by
- $V_s$
- ,

$$V_{\text{total}_2}/V_s = 1 + g_1/\rho_1 V_s + g_2/\rho_2 V_s$$

7. Substituting
- $V_{\text{total}_2} = 4/3 \pi (R_s + T_1 + T_2)^3$
- and
- $V_s = 4/3 \pi R_s^3$
- and simplifying,

$$\left(1 + \frac{T_1}{R_s} + \frac{T_2}{R_s}\right)^3 = 1 + \frac{g_1}{\rho_1 V_s} + \frac{g_2}{\rho_2 V_s}$$

8. Substituting
- $T_1^*$
- and
- $T_2^*$
- and solving for
- $T_2^*$
- ,

$$T_2^* = (1 + g_1/\rho_1 V_s + g_2/\rho_2 V_s)^{1/3} - T_1^* - 1$$

Assuming that the volume of the seed and the densities of the polymers in the shells are both unity (e.g., PMMA,  $\rho = 1.195$ , and PS,  $\rho = 1.065$ );

9.  $T_1^* = (1 + g_1)^{1/3} - 1$  and

10.  $T_2^* = (1 + g_1 + g_2)^{1/3} - T_1^* - 1$ .

The remainder of the work reported here utilized only the hydrophilic hard, soft, and acid monomers. The hard shell was always 48.5 wt % MMA/1.5 wt % MAA, and the soft shell was always 48.5 wt % EA/1.5 wt % MAA. Styrene and butyl acrylate were not examined further at this time.

In the following tables the order of the experiments is based on monomer sequences—"hard" shell last, "soft" shell last, average uniform copolymer composition, and finally, for comparison, the composition of the seed polymer. Seed and shell thicknesses are calculated as well as the total particle radius. The MFT and optical densities are shown. The tables demonstrate the effects of the seed to shell ratios and of the feed composition sequence order.

Table IV shows the calculations for particle shell thicknesses and particle sizes, the observed MFTs, and the optical densities for the first set of seeded emulsions. In this set the weights of seed to shell #1 to shell #2 are in the ratio 1/2.5/2.5.

TABLE IV  
The Effects of the 1/2.5/2.5 Seed/Shell #1/Shell #2 Weight Ratio and Feed Composition Sequence Order

Emulsion no.		Particle calculations ( $R_s$ )					
		Seed	$T_1^*$	$T_2^*$	Total	MFT (°C)	Optical density
11	Hard shell last	1.0	0.52	0.29	1.81	38	0.06
12	Soft shell last	1.0	0.52	0.29	1.81	53	0.06
13	Average uniform copolymer	1.0	0.81	—	1.81	25	0.06
10	Seed polymer	1.0	—	—	1.0	63	0.05
	Relative weight ratio	1	2.5	2.5			

TABLE V  
The Effects of the 1/10/10 Seed/Shell #1/Shell #2 Weight Ratio and Feed Composition  
Sequence Order

Emulsion no.		Particle calculations ( $R_s$ )					
		Seed	$T_1^*$	$T_2^*$	Total	MFT ( $^{\circ}\text{C}$ )	Optical density
14	Hard shell last	1.0	1.22	0.54	2.76	67	0.18
15	Soft shell last	1.0	1.22	0.54	2.76	5	0.19
16	Average uniform copolymer	1.0	1.76	—	2.76	24	0.20
10	Seed polymer	1.0	—	—	1.0	63	0.05
	Relative weight ratio	1	10	10			

The effect of monomer feed sequencing was first observed in this set. MFTs were not in the expected order. The hard shell last emulsion produced a lower MFT than the soft shell last. This effect will be discussed later. The MFTs of emulsions 11 and 12, however, were markedly different from those of the average uniform copolymer or the seed polymer. Note that the seed-based average uniform copolymer is really a single shell with thickness equal to the sum of shell #1 and shell #2 in the sequential feed emulsions. Optical densities of all seeded emulsions were similar and slightly larger than that of the seed emulsion.

Table V presents the data for a second set of seeded emulsions in which the ratio of the weights of seed to shell #1 to shell #2 is increased to 1/10/10. The calculated outer shell thickness has increased from 0.29 to 0.54  $R_s$ . The outer shells are expected to be the most influential in film formation as the particles pack together and coalesce. The Table V MFT data shows a pronounced core/shell effect in the expected direction. The MFT of the average uniform copolymer is essentially unchanged by the shell thickness increase. The optical densities increased, as expected, and are similar for all the seeded emulsions in the set.

Table VI presents the data for a third set of seeded emulsions in which the ratio of the weights of seed to shell #1 to shell #2 is increased to 1/50/50. The calculated outer shell has thus increased from a thickness of 0.29 to 0.54 to 0.95  $R_s$ —an outer shell more than three times as thick as in the lowest seed to shell ratio. The total radius has increased from 1.81 to 2.76 to 4.66  $R_s$ . The set shows the sequencing MFT effect even more strongly. The single-shell average uniform copolymer MFT did not change. Optical densities are again very similar within the set, indicating similar particle size distributions. The magnitude of the optical densities increased in the three sets from about 0.06 to 0.19 to 0.65.

Figure 2 is a graph summarizing the effect of the seed/shell #1/shell #2 ratios

TABLE VI  
The Effect of the 1/50/50 Seed/Shell #1/Shell #2 Weight Ratios and Feed Composition  
Sequence Order

Emulsion no.		Particle calculations ( $R_s$ )					
		Seed	$T_1^*$	$T_2^*$	Total	MFT ( $^{\circ}\text{C}$ )	Optical density
17	Hard shell last	1.0	2.71	0.95	4.66	75	0.61
18	Soft shell last	1.0	2.71	0.95	4.66	$\leq 0$	0.67
19	Average uniform copolymer	1.0	3.66	—	4.66	26	0.65
10	Seed polymer	1.0	—	—	1.0	63	0.05
	Relative weight ratio	1	50	50			

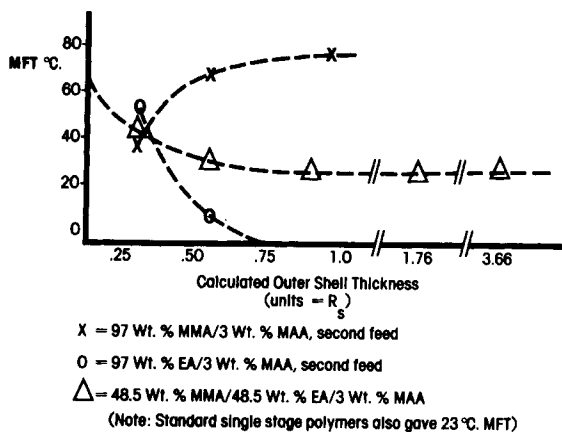


Fig. 2. MFT ( $^{\circ}\text{C}$ ) vs. calculated outer shell thickness.

on MFT. The crossover region was unexpected and was investigated further. The graph also includes the MFT results of thinner shelled uniform seeded terpolymer emulsions. This data is discussed later.

The MFTs of many of the emulsions were rechecked. All tended to replicate readily except for emulsions 11 and 12. The MFTs of these changed from  $38^{\circ}\text{C}$  and  $53^{\circ}\text{C}$  to  $47^{\circ}\text{C}$  and  $45^{\circ}\text{C}$ , respectively. These MFTs were measured when the emulsions had aged 5 days. The emulsions were prepared again, and MFTs were run on the first and fifth days. They were found to vary during these first days before reaching an equilibrium MFT range of about  $45\text{--}47^{\circ}\text{C}$ . Unexpectedly, these thinnest-shell emulsion polymers were exhibiting age dependence. MFTs of thicker shell emulsions were stable for at least several weeks. The equilibrium temperature range of  $45\text{--}47^{\circ}\text{C}$  is not the result of a blend of two emulsion polymers. The 50/50 blend has been shown in other unpublished data to have an MFT of less than  $8^{\circ}\text{C}$ —i.e., a matrix effect as reported earlier.<sup>10,11</sup>

Additional seeded average uniform copolymers were prepared with single-shell thicknesses calculated to be 0.29 and  $0.54 R_s$ . These are equivalent to the outer shell of emulsions 13 and 16, respectively. Table VII summarizes this data which was also included in Figure 2 above.

Optical densities do not show much variation with seed/shell weight ratios below 1/10/10 (i.e., Table IV). Particle size data (discussed later in the Particle Size subsection) indicates that growth is taking place on all seeded polymers by

TABLE VII  
 The Effect of the Seed/Shell Weight Ratio on Single Shell Average Uniform Copolymer Compositions

Emulsion no.	Seed	$T_1$	Total	Particle calculations ( $R_s$ )		Optical density
				MFT ( $^{\circ}\text{C}$ )		
				1 day	5 days	
10	1.0	—	1.0	63	63	0.05
20	1.0	0.29	1.29	42	—	0.04
21	1.0	0.54	1.54	30	—	0.06
13	1.0	0.81	1.81	25	25	0.06
16	1.0	1.76	2.76	24	24	0.20



TABLE VIII  
The Effect of Initiator Concentration on Multifeed Sequence/MFT Effects in Unseeded Emulsions

Emulsion no.	Mon. feed #1 (48.5%/1.5%)	Mon. feed #2 (48.5%/1.5%)	Initiator level (%)	MFT (°C)
22	EA/MAA	MMA/MAA	0.25	77
23	MMA/MAA	EA/MAA	0.25	≥0
25	EA/MAA	MMA/MAA	1.0	43

the polymerization method used, even though OD data shows some variance in the lowest region.

The MFT data of Table VII plotted in Figure 2 indicates that at shell thicknesses of about  $0.75 R_s$  or greater these uniform composition shells on the seed reach constant MFT. As the shell thickness decreases below this level, MFT increases and approaches that of the seed polymer. No MFT age dependence was found in this set of thin, single-shell compositions prepared on the preformed seed.

### The Effect of Initiator Concentration

Up to this point MFT evidence of structure within particles had only been observed within "seeded," multifeed, sequenced emulsion polymers. Additional unseeded experiments were run to determine if other variables were important. Table VIII shows the unexpected importance of initiator level on MFT.

It seems reasonable to speculate that the multifeed MFT effect with low initiator may be due to restricted mobility of macromolecules of higher molecular weight in the particle or, possibly, to the lower concentration of orienting water-soluble hydroxyl and sulfate initiator end groups.

### Particle Size

The use of optical densities as estimates of particle size was checked on four emulsions. Particle size distributions were obtained by hydrodynamic chromatography.<sup>12,13</sup> The data is shown in Table IX.

The seed emulsion had an average particle size of 25 nm with a range of 21–35 nm. Emulsions 14 and 18 were considered to have very narrow distributions. Narrowing of particle size distribution is typical for surfactant-starved emulsion

TABLE IX  
Hydrodynamic Particle Sizes of Seeded Emulsions

Emulsion no.	Seed emulsion/shell I/shell II	Observed particle size <sup>a</sup> (nm)	Theoretical calculated particle size (nm)
10	1/0/0	25	—
13	1/2.5/2.5	48	38
14	1/10/10	79	72
18	1/50/50	120	121

<sup>a</sup> Taken from peak of an approximately Gaussian absorption curve.

polymers. Calculations of particle sizes were made using 13 nm as the radius of the seed ( $R_s = 13$  nm). Good agreement between calculated and observed particle sizes justified our use of optical density as estimates of particle size.

### SUMMARY

Model seeded and unseeded sequential multifeed emulsions polymers were prepared and particle morphology variations were correlated with MFT changes. Properties associated with core/shell structure were observed in seeded and unseeded systems. MFT data correlated well with calculated shell thicknesses. Monomer feeds/seed ratios were shown to markedly affect observed MFT. With some low feed/seed ratio multifeed emulsions, MFT was found to be age dependent. This may indicate that a large quantity of final stage polymer relative to first stage polymer is required to attain a stable core/shell particle configuration.

*Note:* Portions of this study were presented at the 181st National Meeting of the American Chemical Society (Atlanta, GA, 1981).

The author wishes to express his gratitude to Professors M.S. El-Aasser and C. Silebi of the Emulsion Polymer Institute at Lehigh University for the hydrodynamic chromatography.

### References

1. T. Sakuma and I. Nakamura, U.S. Pat. 3,336,417 (1967).
2. M. R. Grancio and D. J. Williams, *J. Poly. Sci. A-1*, **8**, 2617 (1970).
3. R. A. Dickie, M. Cheung, and S. Newman, *J. Appl. Poly. Sci.*, **17**, 45-94 (1973).
4. J. W. Vanderhoff, "Core-Shell: Morphology in Emulsion Polymerization," presented at the Third Annual Water-borne Symposium in New Orleans, La. (1976).
5. T. Matsumoto, M. Okubo, and S. Shibao, *Kobunshi Ronbunshu Eng. Ed.*, **5**(10) 784 (1976).
6. S. Yamazaki, S. Hattori, and M. Hamashima, *Kobunshi Ronbunshu Eng. Ed.*, **5**(11), 893 (1976).
7. S. Yamazaki et al., Ref. 6.
8. D. I. Lee, *ACS Prepr., Org. Coatings Plastic Chem. Div.*, **43**, 622 (1980).
9. K. L. Hoy, *J. Coatings Technol.*, **51**(651), 21 (1979).
10. T. F. Protzman and G. L. Brown, *J. Appl. Poly. Sci.*, **4**, 81 (1960).
11. J. T. Taylor and M. D. Hurwitz, *Am. Digest., Repr.*, **51**, 636 (1962).
12. H. Small, *J. Colloid Interface Sci.*, **48**, 147 (1974).
13. C. A. Silebi and A. J. McHugh, *Emulsions, Lattices, and Dispersions*, P. Becher and M. N. Yudenfreund, Eds., Marcel Dekker, New York, 1978, p. 155.

Received October 13, 1981

Accepted December 8, 1981