N89-20318

THE FIRST PRODUCTS MADE IN SPACE: MONODISPERSE LATEX PARTICLES

J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale,
E. D. Sudol, C.-M. Tseng, and H.-R. Sheu
Emulsion Polymers Institute and Departments
of Chemistry and Chemical Engineering
Lehigh University
Bethlehem, Pennsylvania 18015

and

D. M. Kornfeld
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

ABSTRACT

The monodisperse polystyrene latexes widely used for calibration and other scientific uses are made by seeded emulsion polymerization, i.e., by polymerizing styrene in a previously prepared monodisperse latex, to grow the particles to larger size while maintaining their uniformity. The emulsifier concentration is critical: too little results in coagulation of the latex; too much, in the nucleation of a new crop of particles. Monodisperse latexes of 0.1-2.0 μm particle size have been available for some years. Larger sizes are difficult to prepare: the extent of coagulation increases with increasing particle size above 2 μm to complete coagulation at 10 μm. Brownian motion ceases for particles larger than 2 μm, and the large sticky monomer-swollen particles cream and the polymerized particles settle; this creaming or settling is offset by stirring the emulsion polymerization, but the monomer-swollen particles are sensitive to coagulation by mechanical shear, so that the amount of coagulum increases with increasing particle size. Polymerization in space eliminates the settling or creaming, so that the latex need be stirred only enough to give good heat transfer and mixing, thus alleviating or eliminating the coagulation by mechanical shear. Thus twenty monodisperse polystrene latexes were prepared in the MLR flight hardware on the STS-3, STS-4, STS-6, STS-7, and STS-11 flights of the Shuttle. Two polymerizations were small-particle-size controls. Of eighteen large-particle-size latex polymerizations, four on STS-4 failed owing to malfunction of the flight hardware, one on STS-6 owing to a broken heating wire, and one on STS-11 owing to a broken stirrer shearpin. The remaining twelve monodisperse latexes of 4-30 μm size had narrower particle size distributions (coefficients of variation 0.9-1.4%) than the ground-based control latexes (coefficients of variation 2-5%) and contained fewer offsize larger particles. The flight polymerizations produced only negligible amounts of coagulum; the ground-based control polymerizations produced increasing amounts with increasing particle size, and so were discontinued for latexes larger than 18 μm. The polymerization rates in space were the same as on earth within experimental error. The 10 μm STS-6 (coefficient of variation 0.9%) and the two 30 μm STS-11 (coefficients of variation 1.3%) latexes were accepted by the National Bureau of Standards as Standard Reference Materials, the first products made in space for sale on earth. Moreover, these particles were more

PRECEDING PAGE BLANK NOT FILMED

perfect spheres than the ground-based control particles. Thus the original rationale of the experiments was confirmed unequivolcally by: 1. the negligible amounts of coagulum formed in the flight polymerizations; 2. the smaller number of offsize larger particles in the flight latexes; 3. the broadening of the particle size distribution and the formation of more larger offsize particles during the completion on earth of the polymerization of the partially-converted STS-4 flight latexes. The unanticipated advantages were: 1. the better uniformity of all flight latexes 4 μm or larger in size; 2. the more perfect sphericity of the 10 and 30 μm flight particles. More recent ground-based polymerizations gave monodisperse particles as large as 100 μm with tolerable levels of coagulum; however, their coefficient of variation (2.5%) was greater than those of the flight latexes. Monodisperse nonspherical particles (symmetric and asymmetric doublets, ellipsoids; egg-shaped, pear-shaped, ice cream cone-shaped, popcorn-shaped particles) were prepared by careful control of the polymerization recipe.

INTRODUCTION

Since 1947 monodisperse polystyrene latexes have found wide application as calibration standards and other scientific uses [1]. Series of monodisperse latexes were prepared by seeded emulsion polymerization, i.e., by polymerizing monomer in a previously-prepared monodisperse latex [2,3]; the particle size distribution was self-sharpening at small particle sizes [4-6]. The emulsifier concentration was critical: too little resulted in flocculation of the latex, too much, in nucleation of a new crop of particles [6].

The first series of monodisperse latexes ranged in average diameter from 88 nm (standard deviation σ 8.0 nm) to 340 nm (σ 5.2 nm) to 1171 nm (σ 13.3 nm) [3]. These standard deviations included not only the width of the particle size distributions, but also the errors involved in measuring the individual particle images of the electron micrographs and the difference in magnification from one exposure to another [3]. A later series showed improved monodispersity: the average particle diameters ranged from 91 nm (σ 5.8 nm) to 176 nm (σ 2.3 nm) to 1100 nm (σ 3.5 nm) to 2020 nm (σ 13.5 nm) [7].

Even larger sizes were prepared in the laboratory, i.e., up to 5.6 μm in 100-gm quantities and 10-12 μm in much smaller quantities [8]. The quantities were small because the polymerizations produced increasing amounts of coagulum, giving complete coagulation of the 10-12 μm sizes. The range of emulsifier concentrations which gave neither coagulum nor a new crop of particles was relatively broad at submicroscopic particle sizes [6], but narrowed with increasing size, so that duplicate polymerizations yielding 2 μm particles gave either stable latexes contaminated with a new crop of smaller particles or relatively unstable monodisperse latexes [8].

Particles larger than 2 μm in size show little or no Brownian motion; polystyrene (1.050 gm/cc) seed latex particles swollen with styrene monomer (0.905 gm/cc) cream and the polymerized particles settle. Of course, creaming or settling of the particles can be offset by stirring, which is always used in emulsion polymerizations; however, the large, soft, sticky monomer-swollen particles are sensitive to mechanical shear and thus are easily coagulated by too-

vigorous stirring. The result is that the larger the particle size, the faster must be the stirring to avoid creaming and settling; however, too-fast stirring gives mechanical coagulation, so that it is difficult to prepare large-particle-size latexes without excessive coagulum.

In space, the particles show no tendency to cream or settle; therefore, the polymerization need be stirred only well enough to ensure good heat transfer and mixing (for the latex to be monodisperse, each particle must have the same temperature-time history, as the rate of polymerization increases with increasing temperature). Thus seeded emulsion polymerization in space would allow growth of the particles to larger sizes without excessive coagulum [9]; moreover, such a system would comprise an ideal model of a heterogeneous chemical reaction in space. This paper describes such polymerizations carried out on the STS-3 and STS-4 flights of the Columbia, and the STS-6, STS-7, and STS-11 flights of the Challenger.

EXPERIMENTAL DETAILS AND PROCEDURES

The flight hardware comprised the Monodisperse Latex Reactor (MLR; General Electric Space Sciences Laboratory) and the Support Electronics Package (SEP; Rockwell International). The MLR comprised four stirred 100-cc stainless-steel piston-cylinder dilatometers [10] (see Figure 1) in a sealed cylindrical container; the polymerization conversion-time curves were measured from the decrease in volume using a linear-variable-differential-transformer (LVDT); the temperatures in each dilatometer were measured by four three-pellet diodes in: 1. a probe in the center of the dilatometer; 2. the top of the reactor (piston face); 3. the wall midway between the top and bottom; 4. the bottom near the stirrer shaft. The SEP comprised the requisite DC voltage converters, electronic equipment, and data tape cassette in a sealed rectangular container. Both containers, connected with cables, were mounted on the forward bulkhead of the mid-flight deck of the Shuttle in place of three locker-drawers. The dilatometers were loaded with the monomer-swollen seed latexes and mounted on the circular base. Both containers were sealed, flushed with helium to detect leaks, and then with nitrogen to give an inert atmosphere. The sealed containers were mounted in the Shuttle 24-48 hours before launch.

The dilatometers were operated in preprocessing and processing modes. The preprocessing mode comprised intermittent stirring for 90 sec every 30 min (STS-3, STS-4, STS-6) or continuous stirring (STS-7, STS-11). The processing mode comprised continuous stirring while the contents were heated to 70° for 10.5 or 17.0 hrs, according to the flight, and then to 90° for 0.75 hrs, to complete the polymerization. The intermittent preprocessing stirring was used from the time of loading until the astronauts switched to processing at the predetermined time in orbit, and between the end of the processing and the recovery of the flight hardware on earth; the continuous preprocessing stirring was used from the time of loading until the Shuttle was in orbit, after which it was discontinued. After recovery from the Shuttle, the MLR was either stirred in the preprocessing mode until it was unloaded, or it was left unstirred and inverted periodically to redisperse the settled particles.

The polymerization recipes comprised seed latex, styrene monomer, azo initiator, inhibitor, and emulsifier. These recipes were developed after extensive ground-based research on the kinetics of seeded emulsion polymerization using oil-soluble azo and water-soluble persulfate ion initiators [11,12] and development of a three-component (sulfonated monomer or sulfonate emulsifier-carboxylated oligomer-water-soluble polymer) emulsifier mixture (instead of the single sulfonate emulsifier used earlier) to give better stability during polymerization [13]. The small-particle-size control polymerizations comprised 0.19 µm seed latex, styrene monomer, potassium persulfate initiator, and sodium bicarbonate buffer. The styrene monomer was distilled twice just before use to remove inhibitor; the desired amount containing initiator and inhibitor was added to the seed latex, and the mixture was agitated gently for 20 hrs; the monomer not absorbed by the latex was separated, and the monomer-swollen latexes were degassed and loaded into the dilatometers.

After the flight, the dilatometers were unloaded and cleaned, and ground-based control polymerizations were carried out using the same seed latex, monomer, and temperature-time schedule, except for STS-3 in which another seed latex of the same size was used for the control polymerizations and for STS-11 in which the control polymerizations were not run because of excessive coagulum. The data tape cassettes were processed by computer, to give the conversion-time curve and the four temperature-time variations for each dilatometer. The latexes were examined by optical microscopy immediately after unloading to gain an impression of their monodispersity, and later by transmission electron microscopy (Philips Model 400) or scanning electron microscopy (ETEC Autoscan) to determine the particle size distributions. The distributions were measured using the Zeiss MOP-3 Modular System for Quantitative Digital Analysis, and the offsize larger particles were counted.

EXPERIMENTAL RESULTS AND DISCUSSION

Several preliminary descriptions of the flight experiments were given earlier [14-17]. Four polymerization experiments were carried out on STS-3; three used a 2.52 µm monodisperse seed latex with nominal 2:1, 4:1, and 10:1 monomer-polymer ratios; the fourth control polymerization used a 0.19 µm monodisperse seed latex with a 2:1 monomer-polymer ratio. The polymerization time at 70° was 10.5 hrs. For 24-48 hrs before opening, the MLR was inverted periodically to redisperse the settled latex particles and then the stirrers were turned on. The rotation of the stirrer of flight latex 2 dilatometer was restricted, so it was turned off.

Figure 2 shows electron micrographs of the seed latexes and the large-particle-size flight latexes prepared on STS-3, STS-6, STS-7, and STS-11, and Table I gives the nominal monomer-polymer (M-P) ratio, preprocessing/processing agitation rates, initiator concentration [I], number-average diameter D_n, standard deviation σ, number of particles measured n, coefficient of variation σ/D_n in percent, and the number of offsize larger particles relative to the number in the main distribution. Except where noted, all latexes were completely polymerized when removed from the dilatometers, as determined by the absence of styrene odor. The flight latex 2 dilatometer contained a small lump of hard coagulum adhering to the wall, which

TABLE I

Particle Size Distributions

Latex	Flight	Nominal M-P Ratio	rpm	[I] mM	D_n μm	σ μm	n	σ/D_n	Offsize Larger Part*
seed	STS-3	---	---	---	2.52	0.046	1024	1.84	-----
flight 1	STS-3	2:1	13/13	3.9	3.44	0.064	2777	1.87	1/264
ground 1	STS-3	2:1	13/13	3.9	3.72	0.057	1363	1.54	1/339
flight 2	STS-3	4:1	13/13	6.6	4.08	0.069	2256	1.69	1/207
ground 2	STS-3	4:1	13/13	6.6	3.93	0.077	913	1.96	1/172
flight 3	STS-3	10:1	13/13	12.6	4.98	0.082	2095	1.64	1/99
ground 3	STS-3	10:1	13/13	12.6	4.74	0.167	1232	3.51	1/65
seed	STS-6	---	---	---	5.63	0.073	328	1.30	1/168
flight 9	STS-6	2:1	13/13	2.5	7.94	0.122	829	1.53	1/267
ground 9	STS-6	2:1	13/13	2.5	7.86	0.137	675	1.74	1/220
flight 11	STS-6	6:1	13/13	5.3	9.96	0.115	1102	1.15	1/106
ground 11	STS-6	6:1	13/13	5.3	10.04	0.281	1059	2.80	1/93
seed**	STS-7	---	---	---	7.94	0.046	1024	1.53	1/267
flight 13	STS-7	6:1	13/13	5.3	13.12	0.149	327	1.13	1/360
ground 13	STS-7	6:1	13/13	5.3	13.89	0.371	308	2.67	1/120
seed	STS-7	---	---	---	10.30	0.135	300	1.31	1/130
flight 14	STS-7	4:1	13/13	4.1	16.64	0.201	322	1.21	1/90
ground 14	STS-7	4:1	13/13	4.1	17.17	0.394	326	2.29	1/50
flight 15	STS-7	6:1	13/6	5.3	17.81	0.210	321	1.18	1/70
ground 15	STS-7	6:1	13/6	5.3	17.68	0.949	275	5.37	>1/50
flight 16	STS-7	6:1	6/3	5.3	18.18	0.200	321	1.10	1/110
ground 16	STS-7	6:1	6/3	5.3	16.97	0.778	361	4.58	-----
seed***	STS-11	---	---	---	17.81	0.210	321	1.18	1/70
flight 17	STS-11	5:1	13/6	5.5	30.42	0.41	310	1.35	1/30
flight 18	STS-11	5:1	6/3	5.5	30.92	0.44	320	1.42	1/25
seed	STS-11	---	---	---	10.30	0.135	300	1.31	1/130
flight 19	STS-11	6:1	13/6	5.5	18.4	-----	---	----	----
flight 20	STS-11	6:1	6/3	5.5	19.44	0.24	256	1.22	1/66

   * relative to the main distribution
  ** flight latex 9 from STS-6
 *** flight latex 15 from STS-7

restricted the motion of the stirrer; the other flight latexes contained negligible amounts of coagulum.

Figure 2a shows the three monodisperse flight latexes. Table I shows that there were subtle differences in particle size distribution between the three flight latexes and the corresponding ground-based control latexes. The coefficients of variation were about the same for all latexes except for ground-based control latex 3, which was broader in particle size distribution. The standard deviations increased only slightly with increasing particle size; however, they express not only the breadth of the particle size distribution, but also the errors in measuring the particle images of the electron mi-

crographs and the variation in magnification from one exposure to another. For the 2.52 μm seed latex, measurement of the same particle image twenty times gave a standard deviation of 0.015-0.018 μm (coefficient of variation 0.6-0.7%). Earlier, it was shown that the standard deviation of the averages of 24 exposures of 1.17 μm-size particles was 0.0092μm (coefficient of variation 0.8%) [3]. The contributions of these two sources of error to the standard deviations are significant.

These latexes contained a small number of particles which were 30-80% larger than those of the main distribution. Table I shows that the relative numbers of the larger offsize particles increased with increasing monomer-polymer ratio. Moreover, the number was slightly smaller for ground-based latex 1 and slightly larger for ground-based latexes 2 and 3, as compared with those of the corresponding flight latexes. Polymerizations of latexes of these sizes on earth gave relative numbers of 1/60 at best, greater that those of flight latexes 1 and 2 and slightly greater than that of the flight latex 3.

These larger offsize particles were attributed to the coalescence of two or more monomer-swollen seed particles or the presence of a few larger offsize particles in the seed latex which grew proportionately during the polymerization. The coalescence of two particles of the main distribution would give a particle of 26% larger diameter, three a 44% larger diameter, four a 59% larger diameter, five a 71% larger diameter, and six an 82% larger diameter. These larger offsize particles are difficult to remove because their sizes are only slightly larger than those of the main distribution.

The smaller offsize particles can be removed completely by repeated sedimentation-decantation or serum replacement [18]. The number of these smaller particles was not determined accurately; however, their relative number was small and increased with increasing monomer-polymer ratio. Some were about the same size as the original seed latex particles, which suggests that the latexes became contaminated by unpolymerized seed latex particles which were lodged in the entry ports of the dilatometers.

Figure 3 shows the conversion-time curves of the large-particle-size latexes. The data points were 1-min averages of the tape data, which formed a continuous line on this scale. For all three monomer-polymer ratios (Figure 3a), the conversion-time curves of the flight and ground-based control polymerizations were parallel; however, these curves virtually coincided when shifted slightly along the ordinate. The initial dips in these curves were attributed to the errors in the calibration of the dilatometers. The lab prototype dilatometer, which had been calibrated more rigorously, showed no such dips in the conversion-time curves. The leveling-off of the conversion-time curves was attributed to the formation of a gas bubble or sticking of the dilatometer; the nitrogen formed by decomposition of the azo initiator may have exceeded its solubility in the latex and thus formed a bubble; since gas bubbles are compressible, the dilatometer reading beyond this point would not change. Sticking of the dilatometer would also give such a leveling-off.

Despite these discrepancies, the conversion-time curves of the

flight polymerizations were essentially the same as those of the corresponding ground-based control polymerizations: the 2:1 ratio gave a significant upward deviation from linearity indicative of autoacceleration, the 4:1 ratio only a slight upward deviation from linearity, and the 10:1 ratio a near-linear variation. Since the critical particle size for the transition from emulsion polymerization kinetics to bulk polymerization kinetics is ca. 1.3 µm for the styrene-polystyrene system at 70° [19], the polymerization rate should be proportional to the monomer concentration and the square root of the initiator concentration in the absence of autoacceleration. The upward deviation from linearity began earlier, the lower the monomer-polymer ratio, as expected from the higher viscosity of the particles.

Four polymerizations were carried out on STS-4; all used a 5.5 µm ground-based monodisperse polystyrene seed latex with nominal 2:1, 4:1, 6:1, and 8:1 monomer-polymer ratios in flight polymerizations 5, 6, 7, and 8, respectively, and preprocessing/processing stirring rates of 13/13 rpm. The polymerization of all four latexes was incomplete as evidenced by the odor of styrene; moreover, the data tape cassette yielded only meaningless numbers for the dilatometer volume and temperature readings. A DC voltage converter in the SEP had failed, with the consequent failure of other electrical components, so that the temperature-time variation of the monomer-swollen latexes was not known and the voltage signals to the data tape cassette were inconsistent and nonrepresentative. The conversions were 48-67% by gravimetric measurement and 54-73% by ultraviolet absorbance of isooctane extracts. Optical microscopy showed that the latex particles were monodisperse with only a few offsize larger particles; moreover, their size was that expected from the stoichiometry of the seeded polymerizations, i.e., 7.2, 8.6, 9.5, and 10.4 um, respectively, for the 2:1, 4:1, 6:1, and 8:1 monomer-polymer ratios. The residual monomer in these latex particles made them useless as calibration standards. Moreover, completion of the polymerizations on earth gave a broader particle size distribution and an increased number of larger offsize particles, the result of further coalescence of the monomer-swollen particles during polymerization.

Four polymerizations were carried out on STS-6; three used a 5.63 µm ground-based monodisperse polystyrene seed latex with nominal 2:1, 4:1, and 6:1 monomer-polymer ratios, and the fourth control polymerization used the 0.19 µm seed latex with a 2:1 monomer-polymer ratio. Flight latex 10 displayed a strong odor of styrene; this sample had not polymerized owing to a broken wire in the heating circuit. It is not known whether the wire broke before or during the launch; however, the reactor functioned satisfactorily in the test polymerizations carried out two weeks before the flight.

Figure 2b shows electron micrographs of the two flight latexes. Table I shows that the coefficients of variation for the flight latexes were slightly smaller than for the ground-based control latexes. The values of the standard deviations were similar for the two flight latexes and slightly greater than that of the seed latex; these values were slightly smaller than those of the ground-based latexes, especially for flight latex 11.

All of the STS-6 latexes contained a small number of offsize

larger particles. Their numbers were slightly smaller for flight and ground-based latexes 9, and slightly greater for flight and ground-based latexes 11, as compared with the number for the seed latex; moreover, the numbers for the flight latexes were slightly smaller than for the ground-based latexes.

In summary, both flight latexes 9 and 11 were clearly superior in uniformity to the ground-based control latexes. Flight latex 11 (D_n 9.96 μm; σ 0.115; σ/D_n 1.15%) was accepted by the National Bureau of Standards as a Standard Reference Material and placed on sale in July 1985, to make it the first product made in space for sale on earth. These particles were also found to be more perfect spheres than the ground-based particles [20]. The Bureau gave average diameters of 9.886$\pm$0.029 μm (σ 0.09 μm; σ/D_n 0.91%) by metrology electron microscopy, 9.89$\pm$0.04 μm by optical-microscopic center-distance-finding, and 9.90 μm by resonance light scattering. The Lehigh 9.96 μm value was in excellent agreement with these values.

Figure 3b shows that the conversion-time curves were similar for the flight and ground-based latexes. The leveling-off of the conversion-time curves of the flight latexes was attributed to the formation of a nitrogen bubble or sticking of the dilatometer. The curves for the flight and ground-based latexes 9 showed a significant upward deviation from linearity, indicative of autoacceleration; those for latexes 11 showed near-linear variations. The conversion-time curves of the flight polymerizations leveled-off at a relatively early stage, which was more likely due to sticking of the dilatometer than to the formation of a nitrogen bubble. The curves for the flight and ground-based polymerizations were similar up to this point, with the flight polymerizations showing slightly faster polymerization rates. The disparity was attributed to the poorer mixing of the ground-based latexes, which would give a greater temperature gradient and thus a greater variation in polymerization rates. The upward deviation from linearity began earlier, the lower the monomer-polymer ratio, as expected from the higher viscosity of the monomer-swollen particles. The failure of the curves for latexes 11 to show upward deviations from linearity was attributed to sticking of the dilatometers or formation of nitrogen bubbles before the polymerizations reached the autoacceleration stage.

Four polymerizations were carried out on STS-7; three used a 10.30 μm ground-based monodisperse polystyrene seed latex with nominal 4:1, and 6:1 monomer-polymer ratios; the fourth used the 7.94 μm flight latex 9 as seed with a 6:1 monomer-polymer ratio. Figure 2c shows electron micrographs of the four monodisperse flight latexes. Table I shows that the coefficients of variation of the flight latexes were slightly smaller than those of the seed latexes, 1.13% for flight latex 13 as compared to 1.53% for the flight latex 9 seed, and 1.21, 1.18, and 1.10% for flight latexes 14, 15, and 16, respectively, as compared to 1.31% for the 10.30 μm seed latex; the values for the ground-based control latexes were 2.67%, and 2.29, 5.37, and 4.58%, respectively, significantly greater than for the flight latexes. All latexes contained a small number of larger and smaller offsize particles. The numbers of offsize larger particles were slightly smaller for the flight latexes than for the ground-based control latexes and increased with increasing particle size

and monomer-polymer ratio.

Figure 3c shows that the conversion-time curves of flight latexes 13 and 16 virtually coincided with those for the ground-based control polymerizations; the curves for the flight latexes 14 and 15 fell slightly above those for the control latexes. The leveling-off of the conversion-time curves was attributed to the formation of a nitrogen bubble or sticking of the dilatometer. The temperature gradients between the wall and center of the dilatometer increased with increasing latex particle size and monomer-polymer ratio. The differences in temperature gradient between the flight and ground-based control polymerizations ranged from 0.46° for latexes 13 to 2.85° for latexes 15.

Four polymerizations were carried out on STS-11; two used the 10.30 μm ground-based seed latex used on STS-7; two used the 17.81 um flight seed latex 15 prepared on STS-7 flight with a nominal 5:1 monomer-polymer ratio. For several hours before unloading, the MLR was inverted periodically to redisperse the settled latex particles. When the stirrers were turned on, the movement of the flight latex 19 stirrer was restricted; therefore, it was turned off immediately; the dilatometer had a broken stirrer-shaft shear-pin, and it contained a mass of coagulum between one side of the stirrer blade and the wall. It is not known whether the formation of coagulum stalled the stirrer and broke the shear pin or the failure of the shear pin caused the formation of coagulum: flight latex 20, which was identical except for the stirring rates, contained no coagulum, yet failure analysis of the broken shear pin showed no evidence of fatigue failure. Ground-based control polymerizations were not carried out for this series because the STS-6 and STS-7 control polymerizations showed that the coagulum increased so strongly with increasing particle size that the valuable seed latex would have been wasted.

Figure 2d shows electron micrographs of the two seed latexes and three flight latexes, and Table I shows that the coefficients of variation of the flight latexes were about the same or slightly greater than those of the seed latexes. The standard deviations were slightly greater than those of the seed latexes.

All of the STS-11 latexes contained smaller and larger offsize particles. The smaller offsize particles were removed by repeated sedimentation-decantation. The numbers of offsize larger particles determined by particle counts in the optical microscope were about twice those of the seed latexes. Flight latexes 17 and 18 (30 μm) were accepted by the National Bureau of Standards as a Standard Reference Material, to make them the second product made in space for sale on earth. These particles were also found to be more perfect spheres than the ground-based particles [20].

Figure 3d shows that initially the conversion-time curves of the flight latexes virtually coincided, but that flight latexes 17 and 18 showed a slightly greater upward deviation from linearity than flight latexes 19 and 20, which was attributed to the higher monomer-polymer ratio and hence lower viscosity delaying the onset of autoacceleration.

The monomer-swollen seed latexes used in the STS-11 experiments

creamed at the preprocessing stirring rates used (their stability during polymerization was satisfactory, however), and it was feared that flight polymerization of larger particles would fail because of this creaming. Therefore, an extensive investigation was carried out to develop recipes that would give better stability before and during polymerization. This investigation included: 1. the use of denser monomers, e.g., chlorostyrene, to make the monomer-swollen particles neutrally buoyant; 2. the use of divinylbenzene crosslinking monomer to make the particle-particle collisions more elastic; 3. the use of higher-molecular-weight water-soluble polymer to enhance its adsorption on the particles; 4. the optimization of the buffer electrolyte system to keep the pH at a value where the carboxylated oligomer was near-completely ionized. The result was a series of polymerizations [21] in which 0.2-μm particles were grown in eighteen steps to 100 μm particles (Figure 4) with tolerable levels of coagulum. Their coefficient of variation was 2.5%, typical of ground-based latexes and significantly greater than that of flight latexes. Thus these new recipes enhance the probability of success in making monodisperse 100-μm latexes in future flights.

These experiments also showed that spherical lightly-crosslinked particles swollen with styrene containing small concentrations of divinylbenzene sometimes became nonspherical during polymerization. The second crosslinked network polymerized in the first crosslinked network became incompatible and separated [22]. The tendency to separate was determined by the balance between: 1. the osmotic swelling force; 2. the elastic retractile force of the network; 3. the interfacial tension between the particles and the medium. By careful control of the divinylbenzene concentration and the other parameters of the system, uniform nonspherical particles of various shapes were made. Figure 5 shows scanning electron micrographs of uniform: (a) egg-shaped particles; b. ellipsoids; c. asymmetrical doublets; d. symmetrical doublets; e. ice cream cone-shaped particles; f. popcorn-shaped particles. These particles will find application in fundamental studies of rheology, sedimentation, electrophoresis, and other hdyrodynamic phenomena.

CONCLUSIONS

The preparation of large-particle-size 3-30 μm monodisperse latexes in space confirmed the original rationale unequivocally: 1. the flight polymerizations formed negligble amounts of coagulum as compared to increasing amounts for the ground-based polymerizations; 2. the number of offsize larger particles in the flight latexes was smaller than in the ground-based latexes; 3. the particle size distribution broadened and more larger offsize particles were formed when the polymerizations of the partially converted STS-4 latexes were completed on earth. Polymerization in space also showed other unanticipated advantages: 1. the flight latexes had narrower particle size distributions than the ground-based latexes; 2. the particles of the flight latexes were more perfect spheres than those of the ground-based latexes. The superior uniformity of the flight latexes was confirmed by the National Bureau of Standards acceptance of the 10 μm STS-6 latex and the 30 μm STS-11 latexes as Standard Reference Materials, the first products made in space for sale on earth. The polymerization rates in space were the same as those on earth within experimental error. Further development of the ground-

based polymerization recipes gave monodisperse particles as large as 100 μm with tolerable levels of coagulum, but their uniformity was significantly poorer than that of the flight latexes. Careful control of the polymerization parameters gave uniform nonspherical particles: symmetrical and asymmetrical doublets, ellipsoids, egg-shaped, ice cream cone-shaped, and popcorn-shaped particles.

ACKNOWLEDGMENTS

REFERENCES

1. J. W. Vanderhoff, Org. Coatings Plastics Chem. 24(2), 223 (1964).
2. T. Alfrey, Jr., E. B. Bradford, J. W. Vanderhoff, and G. Oster, J. Opt. Soc. Am. 44, 603 (1954).
3. E. B. Bradford and J. W. Vanderhoff, J. Appl. Phys. 26, 864 (1955).
4. E. A. Willson, J. R. Miller, and E. H. Rowe, J. Phys. Colloid Chem. 53, 357 (1949).
5. J. W. Vanderhoff, J. F. Vitkuske, E. B. Bradford, and T. Alfrey, Jr., J. Polym. Sci. 20, 225 (1956).
6. E. B. Bradford, J. W. Vanderhoff, and T. Alfrey, Jr., J. Colloid Sci. 11, 135 (1956).
7. J. W. Vanderhoff, M. S. El-Aasser, and F. J. Micale, Abstracts, 175th Meeting, ACS, Anaheim, March 13-17, 1978, COLL-110.
8. J. W. Vanderhoff, unpublished research, Dow Chemical Co., 1958-1962.
9. J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale, and D. M. Kornfeld (to NASA), U. S. Patent 4,247,434, January 27, 1981.
10. E. D. Sudol, F. J. Micale, M. S. El-Aasser, and J. W. Vanderhoff, Rev. Sci. Instruments 57 2332 (1986).
11. E. D. Sudol, M. S. El-Aasser, and J. W. Vanderhoff, J. Polym. Sci., Part A: Polym. Chem. 24 3499 (1986).
12. E. D. Sudol, M. S. El-Aasser, and J. W. Vanderhoff, J. Polym. Sci., Part A: Polym. Chem. 24 3515 (1986).
13. J. W. Vanderhoff, C.-M. Tseng, and M. S. El-Aasser, U.S. Patent Application Ser. No. 682,181, filed December 17, 1984.
14. J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale, E. D. Sudol, C.-M. Tseng, A. Silwanowicz, D. M. Kornfeld, and F. A Vicente, J. Dispersion Sci. Technol. 5 231 (1984).
15. J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale, E. D. Sudol, C.-M. Tseng, A. Silwanowicz, and D. M. Kornfeld, Polym. Materials Sci. Eng. 54 587 (1986).
16. J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale, E. D. Sudol, C.-M. Tseng, H.-R. Sheu, and D. M. Kornfeld, Preprint 04.4, Fall Meeting, Materials Research Society, December 1-6, 1986, Boston; to be published in J. Materials Res.
17. J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale, E. D. Sudol, C.-M. Tseng, H.-R. Sheu, and D. M. Kornfeld, Preprint AIAA-87-0389, AIAA 25th Aerospace Sciences Meeting, January 12-15,

1987, Reno; submitted to J. Spacecraft Rockets.

18. V. Lowry, M. S. El-Aasser, and J. W. Vanderhoff, Graduate Research Progress Reports, Emulsion Polymers Institute, Lehigh University 14 13 (1980); *ibid*. 15 13 (1981); *ibid*. 16 23 (1981).

19. J. W. Vanderhoff and E. B. Bradford, Tappi 39, 650 (1956).

20. T. E. Lettieri, National Bureau of Standards, private communication, 1986.

21. H.-R. Sheu, M. S. El-Aasser, and J. W. Vanderhoff, Graduate Research Progress Reports, Emulsion Polymers Institute, Lehigh University 26 6 (1986).

22. H.-R. Sheu, M. S. El-Aasser, and J. W. Vanderhoff, Graduate Research Progress Reports, Emulsion Polymers Institute, Lehigh University 26 11 (1986).

a.

STS-3

2.5 μm Seed

2/1   4/1   10/1

3.4 μm   4.1 μm   5.0 μm

c.

STS-7

7.9 μm Seed   10.3 μm Seed

6/1   4/1   6/1   6/1

13.1 μm   16.6 μm   17.8 μm   18.2 μm

b.

STS-6

5.6 μm Seed

2/1   6/1

7.9 μm   9.96 μm

d.

STS-11

10.3 μm Seed   17.8 μm Seed
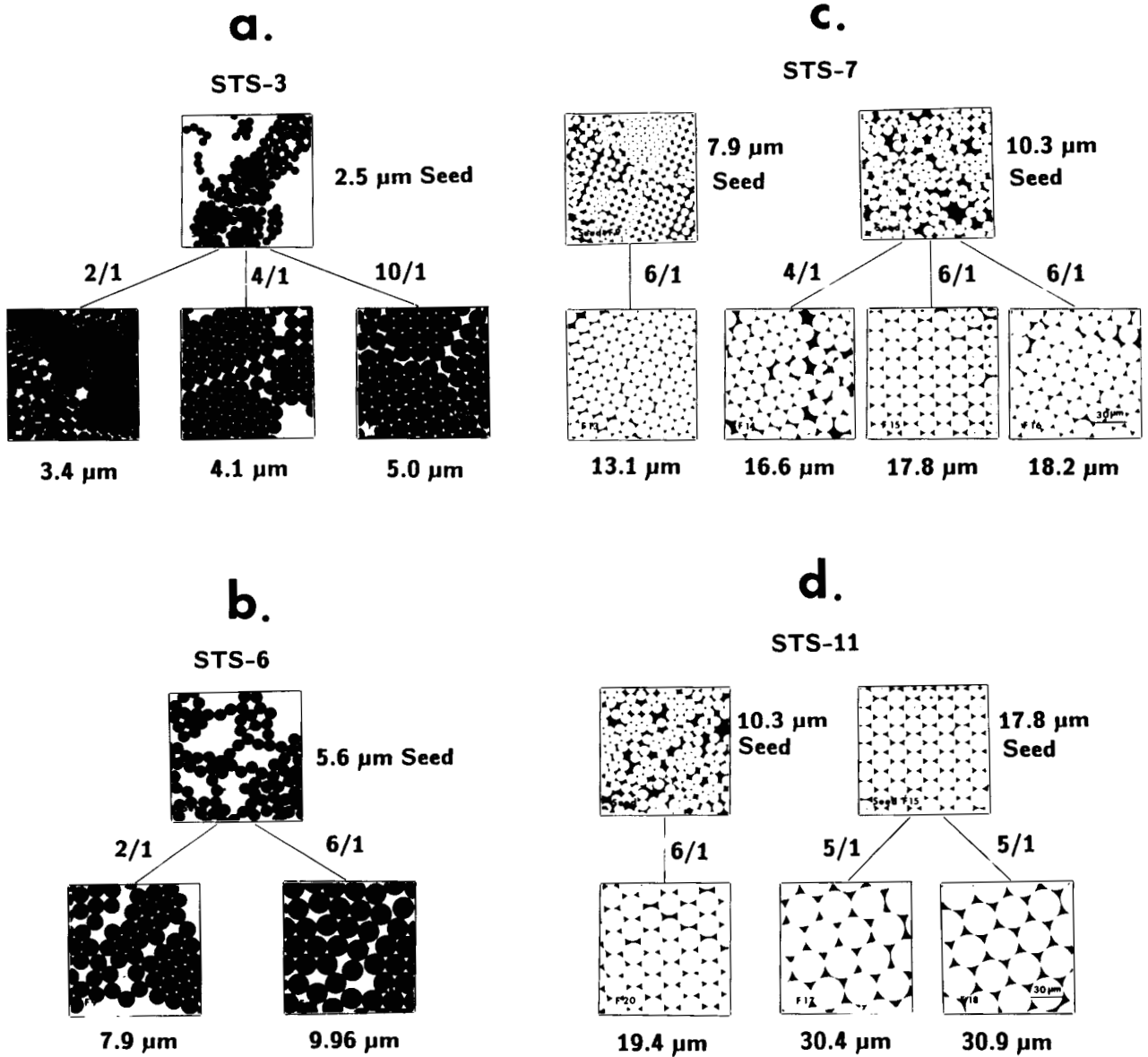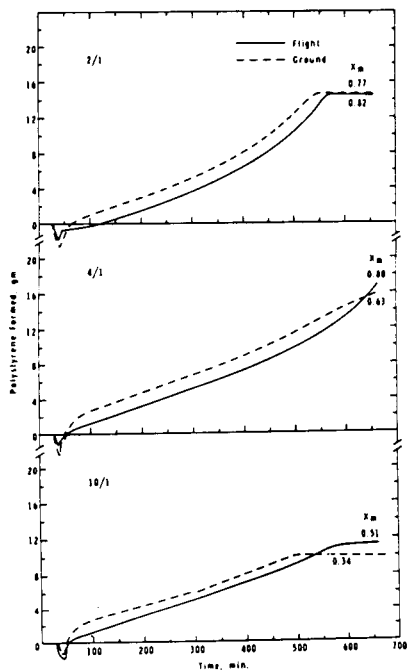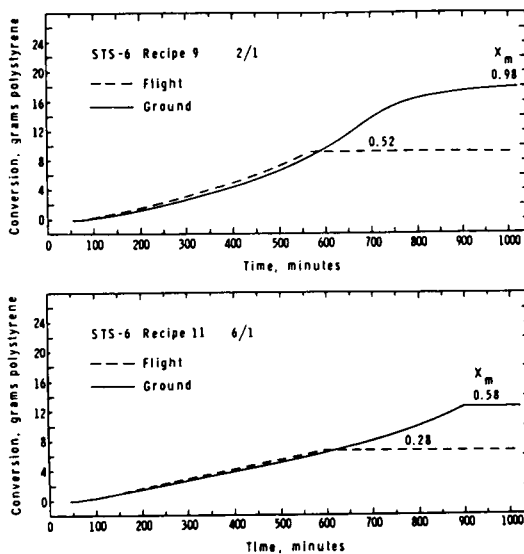
6/1   5/1   5/1

19.4 μm   30.4 μm   30.9 μm

Figure 2. Electron micrographs of the seed and flight latexes.
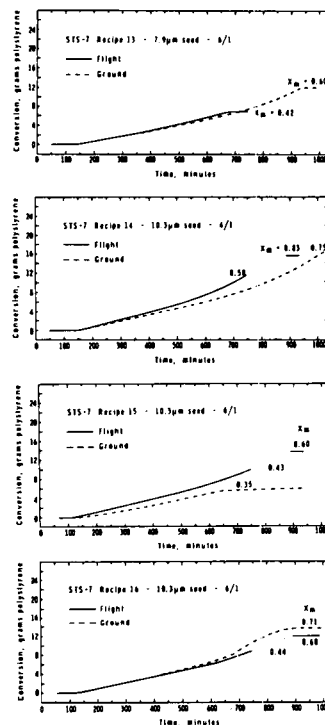
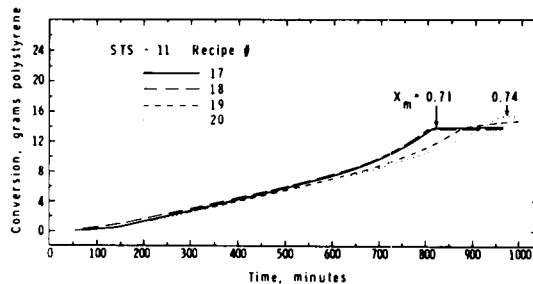# a.
STS-3

c.
STS-7

b.
STS-6

d.
STS-11

Figure 3.   Variation of conversion with time for
the flight and ground-based control latexes.

786

ORIGINAL PAGE IS
OF POOR QUALITY

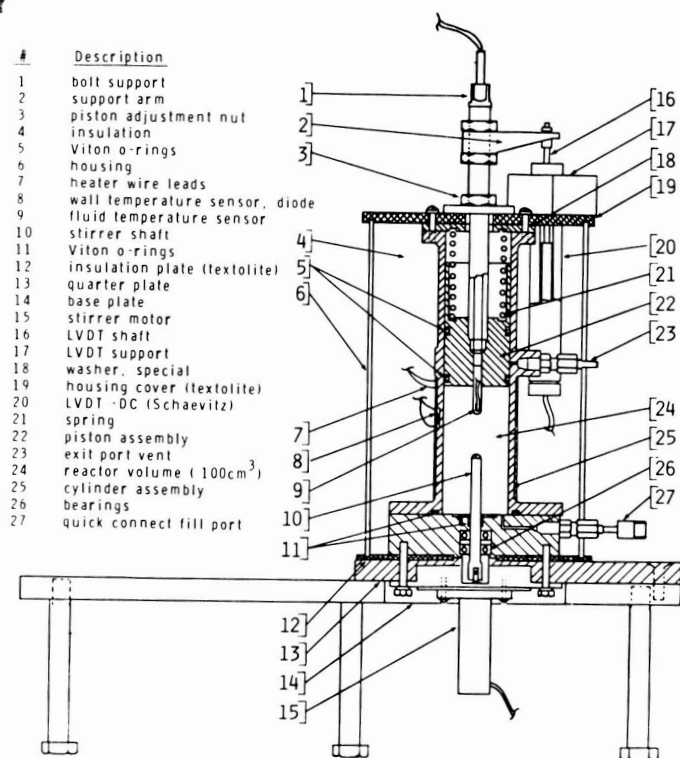| #	Description
1	bolt support
2	support arm
3	piston adjustment nut
4	insulation
5	Viton o-rings
6	housing
7	heater wire leads
8	wall temperature sensor, diode
9	fluid temperature sensor
10	stirrer shaft
11	Viton o-rings
12	insulation plate (textolite)
13	quarter plate
14	base plate
15	stirrer motor
16	LVDT shaft
17	LVDT support
18	washer, special
19	housing cover (textolite)
20	LVDT -DC (Schaevitz)
21	spring
22	piston assembly
23	exit port vent
24	reactor volume ($100 cm^3$)
25	cylinder assembly
26	bearings
27	quick connect fill port

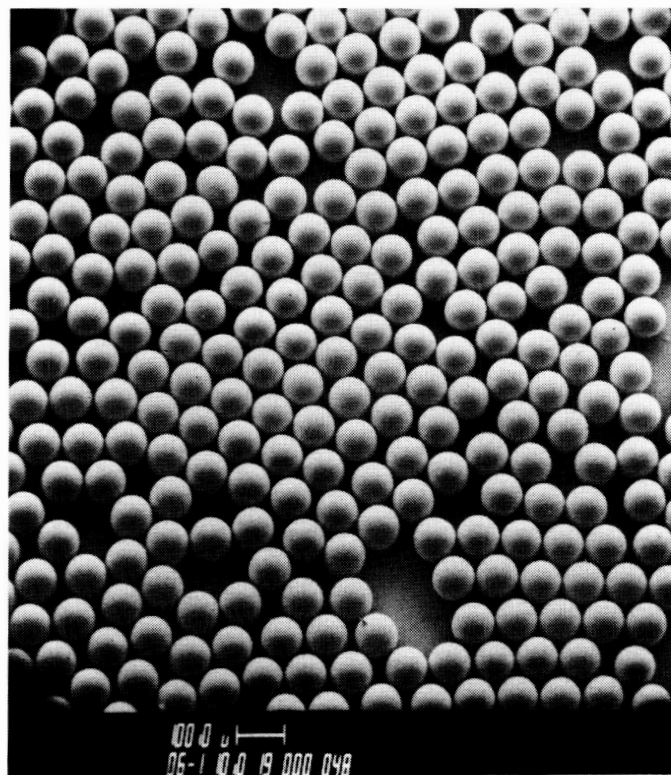Figure 1.   Schematic diagram of the flight dilatometer.

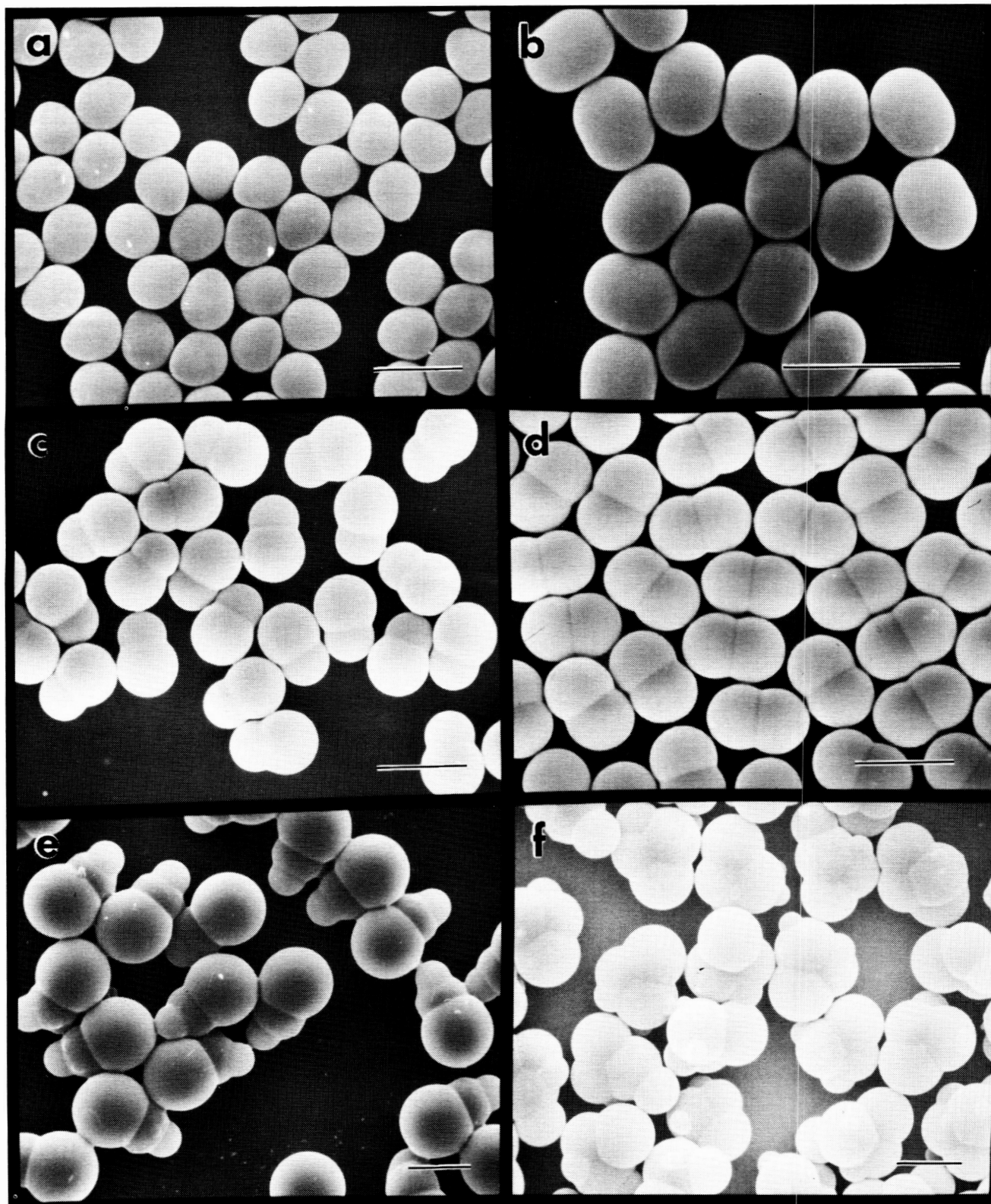Figure 4.   Scanning electron micrograph of 100-µm particles

787

Figure 5.   Scanning electron micrographs of
uniform nonspherical particles (bar = 10 μm).