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HETEROGENEOUS CHEMICAL REACTIONS: PREPARATION OF MONODISPERSE LATEXES

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ABSTRACT

The feasibility study summarized in this Final Report has demonstrated that a photoinitiated emulsion polymerization can be carried out to a significant conversion in a SPAR rocket prototype polymerization vessel within the six minutes allowed for the experiment. The initial work was carried out in a flat cell assembled at Lehigh which lead to the preliminary recipes and final specifications for the General Electric cell. The GE polymerization vessel, which is the laboratory version of the SPAR rocket prototype, consists of a cylindrical cell which utilizes dilatometry to measure the rate of conversion. The percentage of conversion was determined by both dilatometry and gravimetric methods with good agreement. The experimental results lead to the following conclusions concerning the emulsion polymerization for the preparation of latexes within a six-minute period in the GE laboratory prototype of the SPAR rocket polymerization vessel.

1. Emulsion polymerizations can be carried out to conversions as high as 75%, using a stable micellized styrene-SLS system plus photoinitiator.

2. Dilatometry can be used to accurately determine both the rate and conversion of polymerization.

3. Thermal expansion due to the light source and heat of reaction is small and can be corrected for if necessary.

4. Although seeded emulsion polymerizations are unfavorable in photoinitiation, as opposed to chemical initiation, polymerizations can be carried out to at least 15% conversion using 7940Å seed particles, with 0.05% solids.

5. Photoinitiation should be used to initiate polymerization in the SPAR rocket experiments because of the mechanical simplicity of the experiment.

This report was prepared by Lehigh University and General Electric Company under Contract NAS8-32399, "Heterogeneous Chemical Reactions: Preparation of Monodisperse Latexes" for George C. Marshall Space Flight Center of the National Aeronautics and Space Administration.

I. INTRODUCTION

The objective of this work was to further define and develop the scientific base, flight hardware requirements, and experiment operating conditions for the proposed SPAR flight investigation of the preparation of large-particle-size monodisperse latexes in microgravity. This objective was accomplished by demonstrating that a photoinitiated emulsion polymerization could be carried out to a significant conversion within 5 minutes in a laboratory prototype polymerization vessel of the same configuration as that proposed for SPAR. The Lehigh University (LU) contribution was to establish the polymerization recipes and experimental operating parameters such as ultraviolet light source and critical polymerization vessel dimensions. The approach used was to measure the rate of polymerization in a simple, flat quartz-window cell as a function of ultraviolet radiation intensity, cell thickness, and concentration of ingredients in polymerization recipe. The General Electric Company (GE) contribution was to construct the laboratory prototype polymerization vessel which comprised two concentric cylinders, of which the inside one was quartz, irradiated with a mercury lamp aligned along the axis of the cylinders inside the quartz cylinder, and which used a capillary to measure the conversion rate by dilatometry instead of the pressure-sensing device proposed for the SPAR experiments. The GE prototype polymerization vessel was subsequently used by LU to carry out photoinitiated emulsion polymerizations in short time periods.

The SPAR rocket experiments furnish an excellent opportunity to demonstrate the feasibility of carrying out emulsion polymerizations in microgravity. The 5-minute duration would restrict the polymerization experiments to the fast-polymerizing small-particle-size latexes; however, these results could be compared with those of ground-based experiments to determine if there are any differences between ground-based and microgravity polymerizations. The SPAR rocket experiments, therefore, are intended as a prelude to the Spacelab/Space Shuttle production system. The longer duration of the Orbital Flight Test and Space Transportation System missions of the 1979-81 period would allow the investigation of the slower-polymerizing large-particle-size monodisperse latexes. Therefore, we submitted two proposals to NASA which are intended as a logical continuation of this work to its ultimate end, viz. the production of kilogram quantities of large-particle-size monodisperse latexes under the sponsorship of the appropriate industrial organization. The proposals which were submitted are: 1. "Heterogeneous Chemical Reactions: Preparation of Large-Particle-Size Monodisperse Latexes", in response to NASA A.O. No. OPPI-76-1 "Orbital Flight Test"; and 2. "Production of Large-Particle-Size Monodisperse Latexes", in response to NASA A.O. No. OA-77-3 "Space Processing Investigation for STS Missions". These proposals include the two necessary phases for completion of this program: 1. determination of the rates of polvmerization of the large-particle-size monodisperse latexes as a function of particle size and the other parameters of the polymerization system; and 2. development of a production facility for operation in microgravity.

II. BACKGROUND AND JUSTIFICATION

A. Development and Marketing of Monodisperse Latexes

Synthetic polymer latexes which comprise colloidal dispersions of submicroscopic polymer spheres in water are used in large-tonnage quantities for synthetic rubber, latex paints, paper coatings, carpet backing, textile sizings, binders for non-woven fabrics, and reinforcement of portland cement mortar and concrete. These latexes usually have a relatively broad distribution of particle sizes, e.g., an average diameter of 0.20μm and a standard deviation of 0.05μm.

Monodisperse latexes are those in which the particle-size distribution is extremely narrow. The first monodisperse latex was the famous 580G Lot 3584 polystyrene latex which was prepared in the pilot plant of The Dow Chemical Company in 1947. The monodispersity of this latex was discovered by accident (1), and it was considered to be anolamous because other batches prepared using the same recipe had broader particle-size distributions. The supply of 580G Lot 3584 was divided into 375 samples, which were distributed to scientists who measured its particle size (average diameter 0.259μm; standard deviation 0.005μm) by electron microscopy, light scattering, ultracentrifugation, and small-angle X-ray scattering (2). Beginning in 1951, one of us (JWV) undertook the deliberate preparation of monodisperse latexes and soon reproduced the 580G Lot 3584 preparation. In addition, he applied the concept of "seeding" (3), i.e., the growing of previously prepared latex particles to a larger size without initiating a new crop of particles, to the preparation of a series of monodisperse polystyrene and polyvinyltoluene latexes in the size range 0.088-1.172μm (4, 5). The seeding reaction is self-sharpening, i.e., the particle-size distribution of the seed latex can be narrowed by growth under controlled conditions (6-8).

In 1955, Dow offered a series of ten different particle sizes (0.088-1.172μm) to interested scientists without charge (5). These latexes were used for calibration of scientific measuring instruments (e.g., electron microscopes, light scattering instruments, ultracentrifuges, electronic particle counters), counting of virus particles, determination of pore size, medical serological tests (e.g., rheumatoid arthritis, human pregnancy, trichinosis, histoplasmosis) and studies of the reticulo-endothelial system (9).

The demand for these latex samples grew until Dow had to assess a handling charge for each sample and, eventually, a sales price to offset the cost of production. The sales continued to increase until monodisperse latexes became a profitable business. The use of these latexes increased dramatically after the first latex particle diagnostic test for rheumatoid arthritis was developed (10). The increase in the use of monodisperse latexes for this application was shown by a review (11) published 5 years later which contained 78 references to the use of these latexes. By the early 1970's, the annual sales of latex particle diagnostic test kits were $30,000,000.

Presently, monodisperse latexes are available in the size range 0.1-2.0μm.

Monodisperse particle sizes larger than 2µm are not available, yet there is an unsatisfied demand for monodisperse latex particles between 2µm and the smallest size that can be separated by sieving or elutriation, 40-50µm. Both Dow and Polysciences, Inc. (which has recently entered the business) have expressed interest in marketing these large particle sizes once they become available (see Appendix A for copies of letters from Dow and Polysciences). The current sales price (Dow) is $50 for 15 ml of 5% solids latex or $30,000/lb ($67,000/kg) of polymer.

The greatest benefit of the preparation of these 2-40µm-diameter monodisperse latexes is not economic, however, but scientific. The availability of these larger sizes would stimulate an enormous outpouring of research. Gram quantities of 3.0 and 5.6µm-diameter latexes have been laboriously prepared by one of us (JWV) by recovering the stable residues from polymerizations that produced mostly coagulum. These latexes have never been offered for sale because their preparation was not suited for the requisite scale for sampling. Nevertheless, these small samples were used to good advantage in several studies, e.g., in a study of glaucoma where the exit channels of human eyes were sized accurately -- 1.2µm or smaller particles perfused through the exit channels without hindrance, 1.8 and 3.0µm sizes perfused with some hindrance, and the 5.6µm size which did not perfuse at all (12). Similar benefits would accrue in the calibration of measuring instruments. Almost every hospital and medical research center now counts blood cells using a Coulter Counter or some other electronic particle counter. These particle counters are usually calibrated with less-than-satisfactory samples -- monodisperse latex particles of 2µm diameter, fixed red blood cells which are not measured by an independent method, or ragweed pollen spores of 20µm diameter which are spherical but not smooth-surfaced. At present, independently-measured calibration standards of the same size as red blood cells, 7µm, are not available.

Recently, several small companies have advertised the availability of monodisperse latexes in the size range of 2-40µm. These companies have been contacted and, with one exception, their claims are that the standard deviations of the particles exceeds 10% of the diameter. The exception is Duke Scientific Corporation of Palo Alto, California, which offers for sale polystyrene particles with diameters of 5, 10, and 20μm with standard deviations of 1.4% to 1.6% at a price which varies from $200 to $13,000/gm. Small samples of each of these particle sizes were obtained for particle size analysis. Preliminary microscopic examination shows that these samples have standard deviations far greater than the claimed values. For the 20μm sample, particles larger than 30μm are present in number concentrations of about 5% and particles smaller than 10μm are present at higher concentrations. Electron microscopic examination of the 5μm sample shows the presence of submicroscopic particles in number concentrations which are higher than the specified particles. Apparently, this company reports standard deviations which bear no resemblance to the actual values. A complete particle size analysis of all three samples is now in progress and will be reported later.

B. Problems in the Preparation of Monodisperse Latexes

Monodisperse polystyrene latexes are prepared by emulsion polymerization, i.e., by mixing styrene monomer, water, emulsifier, initiator, and buffer, and heating to the polymerization temperature (13). The monodispersity is achieved by maintaining the particle nucleation stage short relative to the particle growth stage. Once a small-particle-size monodisperse latex (e.g., of 0.1μm diameter) has been prepared, it can be grown to larger sizes by seeded emulsion polymerization, i.e., by adding monomer and initiator to the seed latex and growing these particles to a larger size without initiating a new crop of particles (3-8). This seeded emulsion polymerization technique can be used to grow 0.1μm-size monodisperse latex particles in sequential steps to a size of 2μm (4,5,7,8).

The problems encountered in this seeded emulsion polymerization limit the largest practical particle size to about 2μm. The difficulty lies in the sensitivity of the latexes to emulsifier concentration and mechanical shear. If the added emulsifier is insufficient to stabilize the latex particles, they will flocculate to form coagulum. If too much emulsifier is added, a new crop of particles will be formed, and the latex particle-size distribution will be bimodal rather than monodisperse (7,8). The range of operable emulsifier concentration range is relatively broad at small particle sizes, e.g., from 1.00 to 2.57% for a seed latex of 0.257μm diameter (7,8), but with increasing particle size the operable range becomes more and more narrow until at sizes above 1μm, the polymerization becomes a "knife"edge" operation, i.e., duplicate polymerizations may give either a partially-flocculated monodisperse latex or a stable latex containing a new crop of particles.

Moreover, with increasing particle size, there is an increasing tendency for the particles to cream or settle out during polymerization because of the decreasing intensity of Brownian motion and the density difference between the particles and the aqueous phase. As the polymerization proceeds, styrene (density 0.905 gm/cc) is converted to polystyrene (density 1.050 gm/cc). The critical size for settling of polystyrene particles in water is 0.65μm from theoretical calculations and 0.5-0.8μm from experimental measurements. The critical size for creaming of a polystyrene particle swollen with 2 parts monomer/part polymer is about the same. Thus the latex particles tend to cream at low conversions and to settle out at high conversions. This creaming-settling tendency can be offset by increasing the agitation rate, but these large-particle-size latexes are often sensitive to mechanical shear, so that such an increase often results in the formation of coagulum.

Some improvement is obtained by substituting vinyltoluene for the styrene. The density of polyvinyltoluene is 1.027 gm/cc, which allows the preparation of 2μm-diameter particles instead of the maximum of about 1.5μm for polystyrene. However, even in this case, the particles tend to cream at low conversions, even though the tendency to settle is less at high conversions. Similarly, vinyltoluene-tert-butylstyrene copolymer particles of density 1.00 gm/cc have been prepared, but these particles also tend to cream at low conversions during polymerization. The density of the aqueous phase can be altered by addition of electrolytes or non-electrolytes, but these compounds often affect the latex stability adversely; moreover, the density of the particles cannot be matched at both low and high conversions. Thus, with all available improvements, the largest particle size monodisperse latex that can be prepared in even the small-kilogram quantities needed for calibration standards and serological diagnostic tests is 2μm.

C. Advantages of Preparation in Microgravity

Polymerization in microgravity would allow the preparation of latexes with particle sizes larger than 2μm in practical quantities. In the seeded emulsion polymerizations, the emulsifier concentration could be reduced below the level required to generate a new crop of particles without endangering the stability of the latex by flocculation or by settling or creaming. Moreover, the effect of the density increase during polymerization on the creaming or settling of the particles would be obviated. The agitation rate could be reduced to the minimum level required for good heat transfer, thus minimizing flocculation by mechanical shear. The small-kilogram quantities of these latexes that could be prepared in microgravity would be sufficient to serve a wide variety of calibration, diagnostic, and research purposes. The price for which they could be sold would justify the cost of production. Moreover, companies such as Dow and Polysciences are interested in adding these larger-particle-size latexes to their already-existing product lines.

We propose a five-stage program to develop a suitable production process for microgravity:

1. demonstration of feasibility of carrying out emulsion polymerizations in microgravity in the SPAR rocket experiments;
2. determination of the kinetics of seeded emulsion polymerization of large-particle-size monodisperse latexes, to furnish a basis for the design and operation of the production process;
3. development of a production facility for operation in microgravity that will produce 1500-2000 cc quantities of 30% solids latexes (1.0-1.3 lbs or 0.45-0.60 kg polymer);
4. scale-up of the production facility to a 5-10-fold larger capacity that will produce 7500-20,000 cc quantities of latex (5.0-13 lbs or 2.3-6.0 kg polymer);

5. transfer of responsibility for manufacture and marketing to an interested company.

III. EXPERIMENTAL

In order to determine the critical dimensions required for construction of the GE prototype polymerization vessel, a simple reaction cell for the photoinitiated polymerization was designed and constructed. The details of the cell are presented in Figure 1. The cell consists of a circular flat quartz window on the side exposed to the UV radiation while the far side is Plexiglas having three thermistors imbedded so that the temperature at the top, middle and bottom of the polymerization medium can be monitored. The cell thickness is 0.091 cm and this dimension can be varied by replacement with other Teflon blocks machined to a specified thickness. The polymerization medium in the cell is connected to a capillary, which is used to monitor reaction kinetics and conversions by dilatometry. The entire apparatus is illustrated in Figure 2 where a catheometer is used to measure the fall in the liquid level in the capillary. The ultraviolet lamp used for activation of the photoinitiator is a low-pressure mercury vapor lamp (Model C-15-61, Oriel Corporation), 5 cm long, having a power of 4.6 watts. The distance between the lamp and the cell can be varied to a minimum of 3.7 cm from the quartz window.

The objectives of the experiments in the LU flat cell were: 1. to establish the critical dimensions of the GE laboratory prototype polymerization vessel; 2. to evaluate a preliminary polymerization recipe consisting of styrene monomer, sodium lauryl sulfate (SLS), co-emulsifier, and diethyoxyacetophenone (DEAP); and 3. to determine the problems associated with determining the percent conversion of the polymerization by capillary and gravimetric techniques. The latter two objectives will be discussed in IV. Results and Discussion. The degree of conversion in the LU cell was found to be a critical function of the distance between the lamp, the cell, and the cell thickness, with the conversion increasing with decreasing lamp distance and cell thickness. Decreasing both of these dimensions in the circular

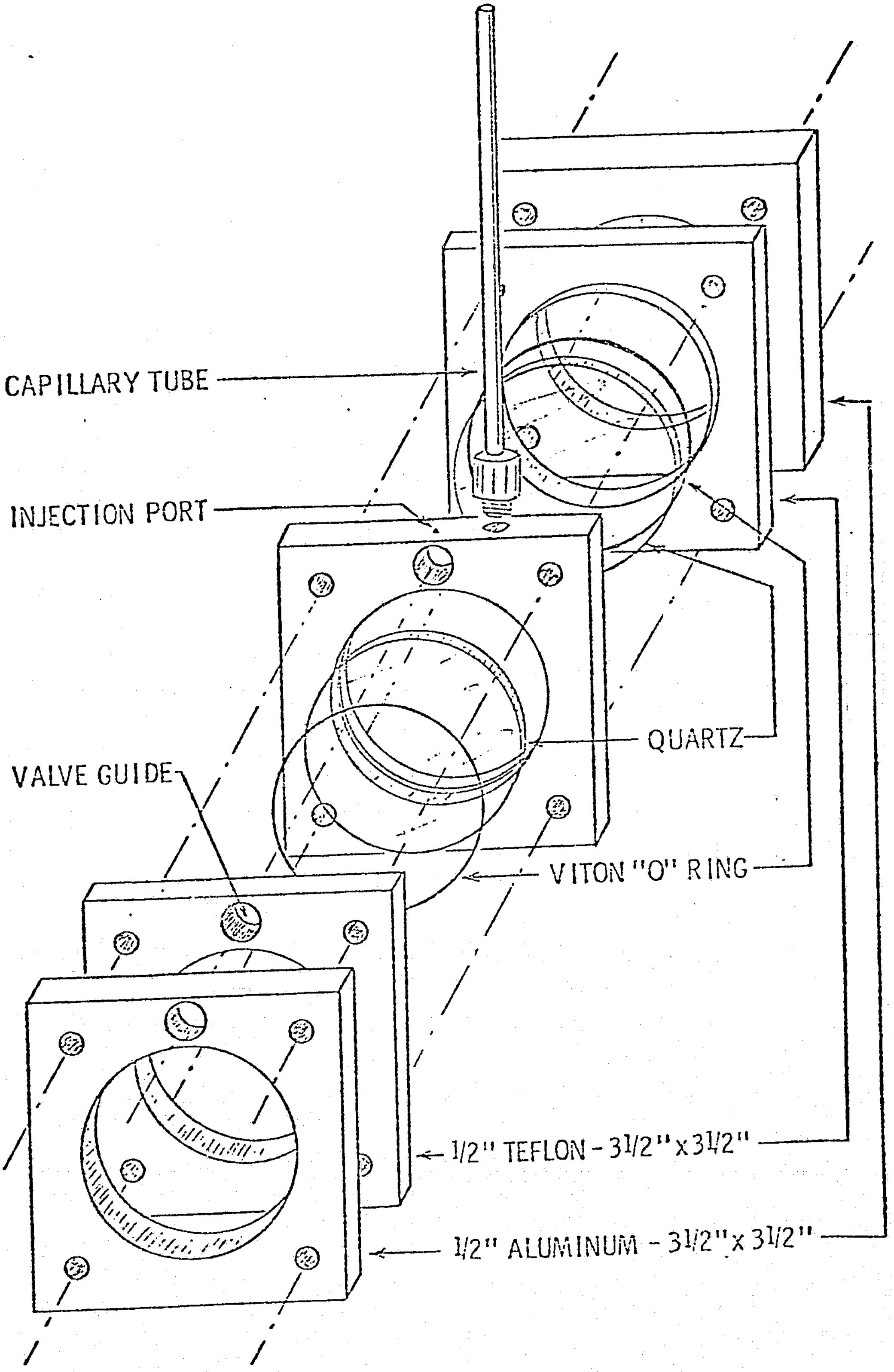

Figure 1. LU laboratory polymerization vessel - exploded diagram.

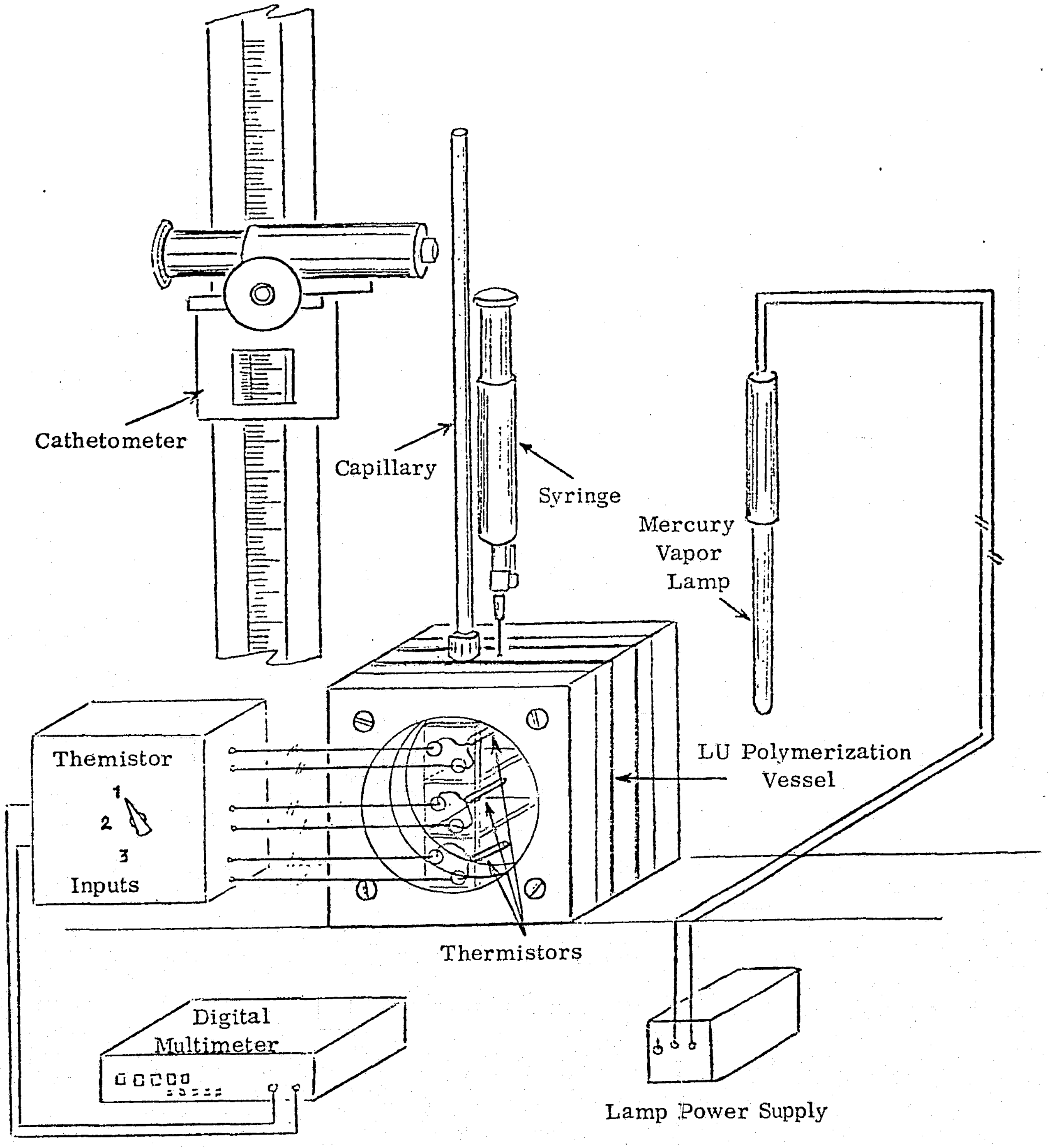

Figure 2. Schematic of the LU cell with accompanying equipment.

configuration proposed for the GE cell, however, results in a decreasing sample volume, which affects the sensitivity and usefulness of the experiment. The results with the LU cell indicated that increasing the sample thickness above 0.1 cm greatly reduced the conversion and calculation showed that a convenient sample volume would be 8 ml. These two requirements, along with the GE design shown in Figure 3, resulted in the sample being confined between a 5cm-long quartz tube with an OD of 5.4 cm and a stainless steel cylinder with an ID of 5.6 cm. These dimensions result in a sample thickness and volume of 0.1 cm and 8.6 ml, respectively. Photographs of the GE cell are shown in Figure 4.

The rates of polymerization, for both the LU and GE cells, were determined by dilatometry, while the final conversions were determined by both dilatometry and a gravimetric method. The gravimetric method consists of collecting the sample after completion of the experiment, evaporating a known volume to dryness, and weighing the product. Since the dried product consists of polymer and an unknown amount of photoinitiator, the results are reported in terms of minimum and maximum percent conversion by assuming that all of the photoinitiator is trapped in the polymer and that all of the photoinitiator evaporates with the solvent, respectively. The actual conversion lies between the two extremes.

The capillary data were corrected for the thermal expansion of the fluid due to heating by the UV source. Water was used as the medium to test this thermal expansion. Figure 5 shows that the error due to this expansion is very small. The capillary rise because of expansion of the fluid is compensated for by expansion of the cell itself. The temperature measured by a thermistor rises linearly and fluid expansion only predominates at exposure times greater than 10 minutes. This result is important because conversion will be measured only by dilatometry in the SPAR experiments.

One possible problem that may arise is that some polymerization may occur in the dark prior to UV irradiation. Experiments have shown that, within 4 days, polymerization samples containing photoinitiator show conversions of about 15%.

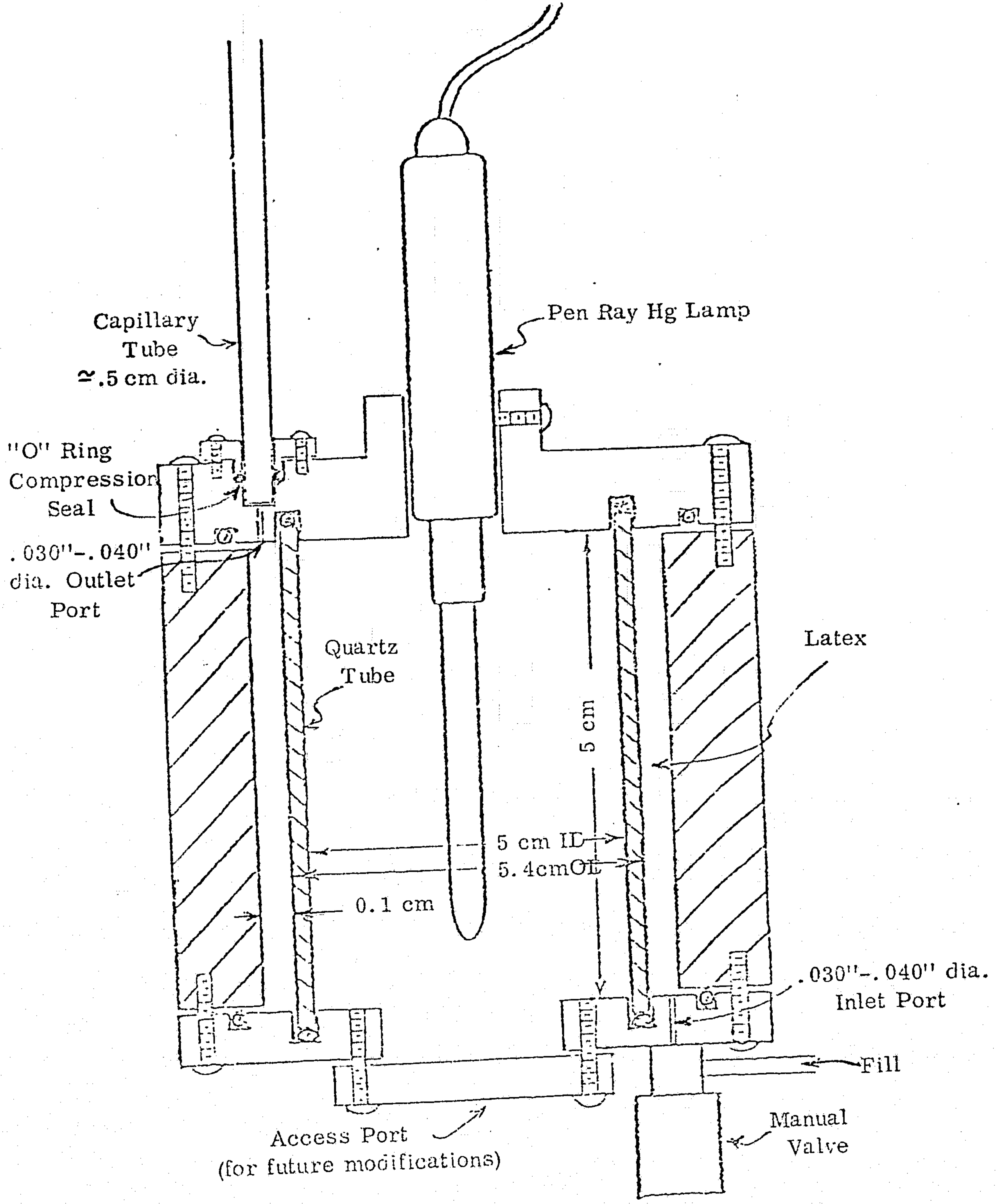

Figure 3. GE Laboratory Prototype of Reaction Vessel for SPAR Experiment.

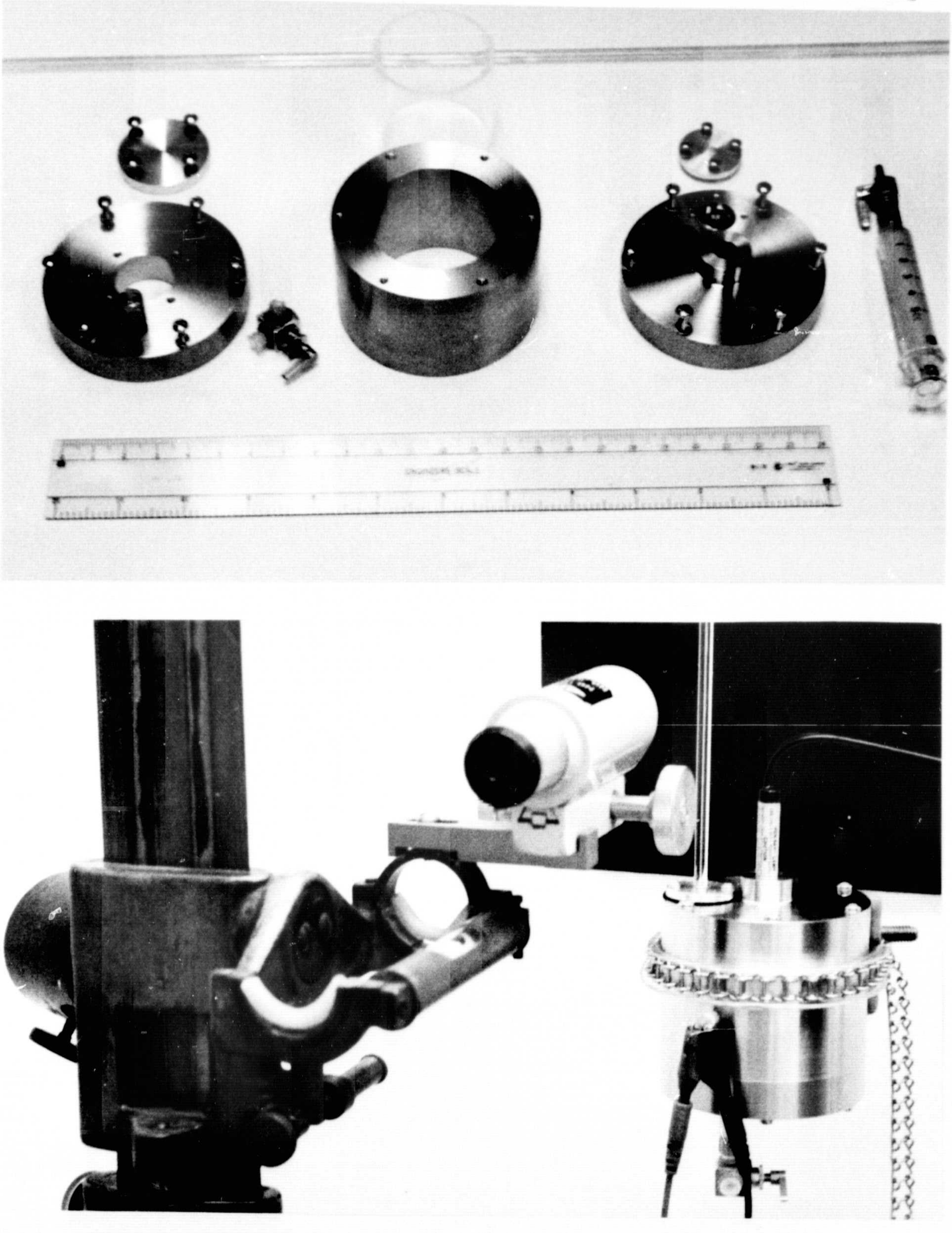

Figure 4. General Electric Laboratory Prototype Polymerization Vessel, unassembled (top) and operational (bottom).

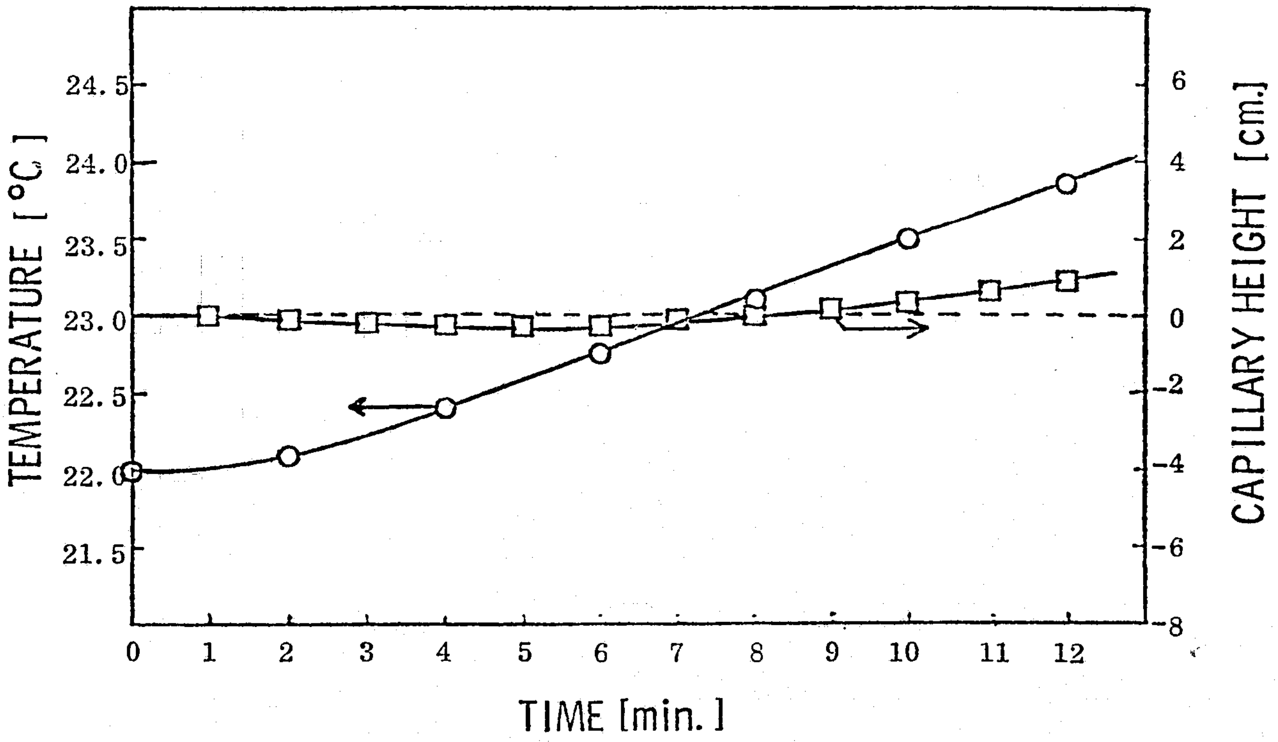

Figure 5. Temperature-time and the corresponding capillary change for water used as a control (GE cell).

This dark polymerization may be due to the initial exposure to ambient UV radiation and thermal generation of radicals in the sample. If necessary, this could possibly be reduced by more careful preparation, limiting exposure to light.

IV. RESULTS AND DISCUSSION

A. Conventional Emulsion Polymerizations

The variables in the polymerization recipe are the amount of surfactant, both SLS and a co-emulsifier, and the amount of photoinitiator (DEAP) based on the monomer. The amount of monomer was fixed at 3% by weight, higher concentrations having given poorer results. Table I shows the results for a series of experiments using the LU cell. Twenty-minute conversions determined gravimetrically are given together with the conversion at 7 minutes determined from the dilatometric conversion-time curves, which were calibrated using the 20-minute gravimetric conversion results. Figure 6 shows polymerization rate-time and conversion-time curves for two of the samples. The only variable is the emulsifier concentration where Sample 'A' has half the amount of emulsifier used in Sample 'B'. The initial rate of polymerization in Sample B is much faster than that of Sample A; moreover, the maximum rate of polymerization in Sample B takes place at approximately 3.5 minutes from the start of the polymerization whereas in Sample A the maximum polymerization rate is achieved at about 6.5 minutes. It is obvious that since the time allowed for the experiment is only 5 minutes, Sample A is inferior compared to that of Sample B.

The minimum conversions were calculated assuming all of the photoinitiator fragments were incorporated into the polymer mass, while the maximum conversions were calculated assuming no initiator was incorporated. The actual conversions are intermediate between these values. The 7-minute conversions are significant in that 7 minutes represents the amount of time of the experiment in the SPAR rocket flight: 5 minutes of microgravity; 1 minute warm-up period for the light; and 1 minute for the exponential decay of the polymerization rate after the light is turned off.

TABLE I

Photoinitiated Emulsion Polymerization of Styrene as a Function of Recipe Parameters

(3% styrene monomer)

Sample	Percent Sodium Lauryl Sulfate	Percent Co-Emulsifier	Percent Photoinitiator*	Percent Conversion 20 minutes ** minimum	Percent Conversion 20 minutes ** maximum	Percent Conversion 7 minutes *** minimum
10	3.0	0.0	1	31	32	16
13	3.0	0.0	10	50	60	34
13-2	3.0	0.0	10	54	64	35
14	3.0	0.0	15	27	42	18
14-2	3.0	0.0	15	51	66	32
15	3.0	0.05	10	55	65	34
16	1.5	0.05	10	42	52	16
19	3.0	1.5	10	58	68	29
27	3.0	1.5	15	60	75	28
22	3.0	1.5	20	75	95	31
22-2	3.0	1.5	20	49	69	28
23	3.0	1.5	30	40	70	21

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* diethyoxyacetophenone (DEAP), based on styrene

** determined gravimetrically

*** determined from the dilatometric conversion-time curves

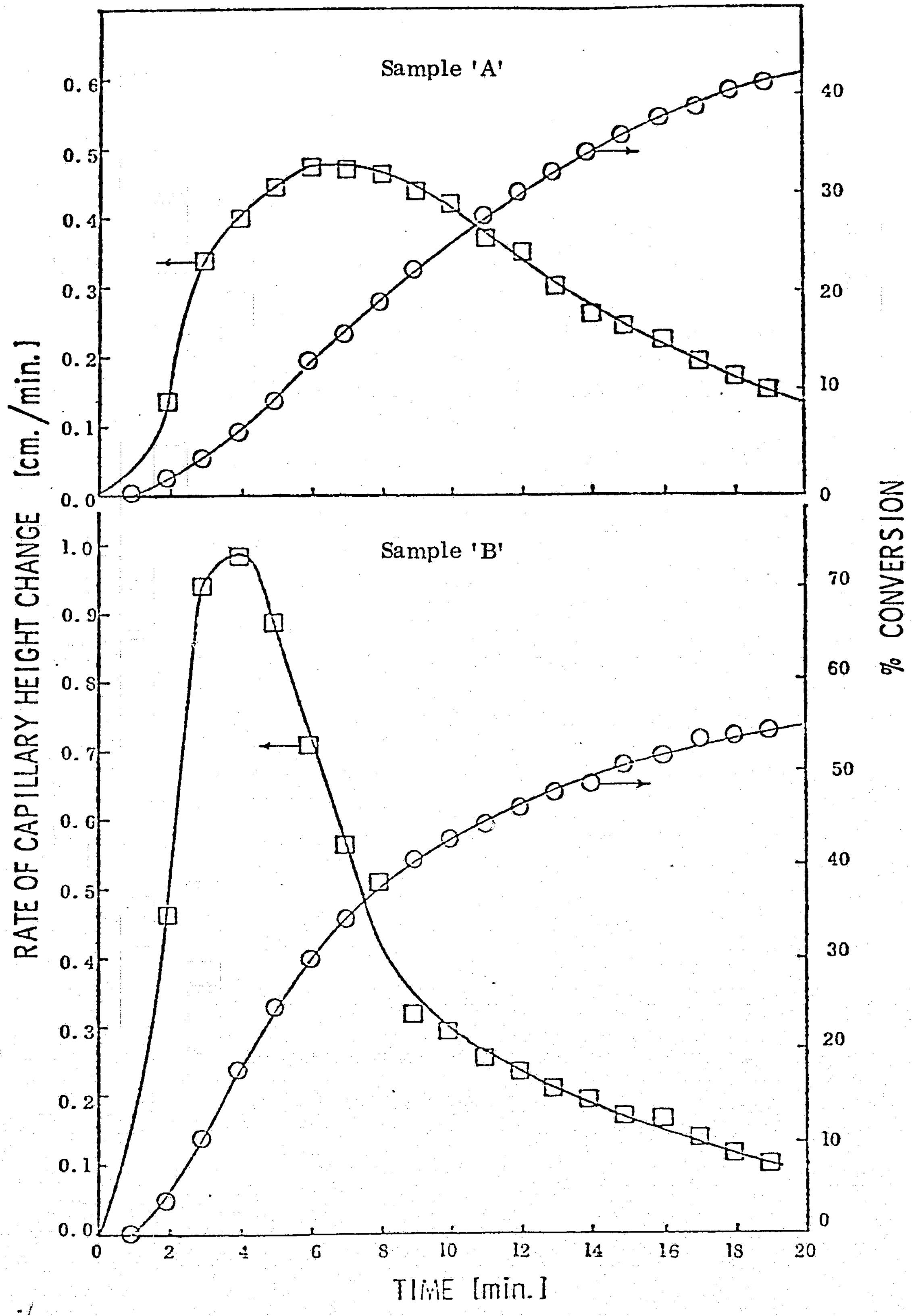

Figure 6. Conversion-time and Rate-time curves for samples 16 (top) and 22 (bottom) run in the LU cell.

The samples described in Table I did not satisfactorily fulfill the two requirements of good stability and high conversion which had been established. The conversions were generally satisfactory, but the emulsion stability prior to polymerization was too poor for insertion into the rocket some time before the launch. Improved stability was obtained with a co-emulsifier, but not to a sufficient degree.

An attempt was made to increase the conversion and stability of the system by increasing the concentration of surfactant to equal molar amounts of SLS and styrene with no co-emulsifier. This type of system produces a semi-transparent fluid more readily transmitting UV radiation as opposed to the opaque, white emulsions produced previously. At this time in the investigation, the GE laboratory prototype polymerization vessel became available. Initial experiments were carried out in order to determine whether the change in cell configuration would affect the rate of conversion of styrene to polystyrene and also to check possible time restrictions that may prove to be the actual conditions for the proposed project. These results are summarized in Table II. The conversions were again determined gravimetrically after 20 minutes and dilatometrically after 7 minutes of sample exposure to UV radiation. Samples 28 and 22 were run in the LU cell and serve as comparisons to the GE cell results. Samples 28 and the 32 series are the micellized system, which show good stability and give considerably higher conversions. Experiments in which the cell was charged 48 hours prior to polymerization gave significantly higher conversions as compared to freshly charged samples (e.g., 32-2 and 32-3 are the same composition, the former being charged 48 hours after preparation while the latter was freshly charged into the cell immediately following preparation).

Electron micrographs were obtained for many of the latexes to obtain an estimate of the resulting particle size. Figure 7 shows the electron micrographs for Sample 19 (Table I) and Sample 32 (Table II). The particles produced are quite small (< 500Å), particularly for the micellized system represented by the recipe of Sample 32.

Since the recipes which contain a 1:1 molar concentration of SLS to styrene, i. e., 8.3% SLS, show the highest possibility of fulfilling our requirements, a more intensive

TABLE II

Photoinitiated emulsion polymerization of styrene as a function of conditions and recipe parameters (3% styrene monomer)

Sample	Percent Sodium Lauryl Sulfate	Percent Co-Emulsifier	Percent Initiator*	Percent Conversion** 20 min. minimum	Percent Conversion** 20 min. maximum	Percent Conversion *** 7 min. minimum	Percent Conversion *** 7 min. maximum
28	8.3[1]	0.0	20	50	70	36	48
32[2]	8.3	0.0	20	49	69	37	51
32-2[3]	8.3	0.0	20	87	100	77	87
32-3	8.3	0.0	20	75	95	59	76
32-4	8.3	0.0	18	--	--	44	62
32-5[3]	8.3	0.0	18	--	--	58	76
22	3.0	1.5	20	75	95	31	36
33	3.0	1.5	20	61	81	22	30
33-2[4]	3.0	1.5	20	39	59	12	17

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* diethoxyacetophenone (DEAP) based on styrene

** determined gravimetrically

*** determined from dilatometric conversion-time curves

[1] 1:1 mole ratio sodium lauryl sulfate to styrene

[2] 4 days old sample

[3] cell charged 48 hours prior to experiment

[4] 2 days old sample

Figure 7. Electron micrographs of styrene particles produced by UV initiated polymerization, sample 19 (top) and 32-4 (bottom)

study was made to optimize the photoinitiator concentration and to check out capillary accuracy. The results are summarized in Table III. The time for UV exposure was set at 7 minutes. The conversions determined gravimetrically and dilatometrically are in good agreement and all were found to be above 40% as a minimum. These conversions are quite respectable for the 7-minute experimental restriction. Figure 8 shows the polymerization rate-time curves for this series of experiments. Two trends can be noted. First, the maxima of the curves increase with increasing DEAP and then decrease, giving an optimum value of 25% DEAP based on styrene. An optimum DEAP concentration is not unexpected. Two low a concentration gives too few radicals, and too high a concentration absorbs too much of the UV radiation. Second, the maxima shift to shorter times with increasing DEAP, from 3 minutes at 5% DEAP to 2 minutes at 25% DEAP. Also note that the lamp could possibly be shut off as early as 4-5 minutes with little change in the results because the exponential decay of the rate is already in progress and does not depend on irradiation of the reacting fluid. Figure 9 gives the corresponding conversion-time curves determined from capillary data.

B. Seeded Emulsion Polymerizations

Preliminary seeded emulsion polymerization experiments were carried out using the LU cell. The composition of the emulsion polymerization recipes were: Dow monodisperse polystyrene latex particles (880Å, 3750Å, and 7940Å), distilled styrene monomer, 2,2-diethoxyacetophenone, and an amount of water dependent upon the initial concentration of seed latex desired. The equations used for preparing the recipes and calculating the rate of conversions are (14):

a. Latex seed weight, L

$$L = \left(\frac{1.00}{D^3}\right) \cdot W \cdot \left(\frac{f}{S_i}\right)$$

b. Monomer weight, M

$$M = \left(\frac{D^3 - 1}{D^3}\right) \cdot W \cdot \left(S_f\right)$$

TABLE III

Photoinitiated polymerization of styrene as a function of initiator concentration (3% styrene monomer)

Sample	Percent Sodium Lauryl Sulfate	Percent Photoinitiator *	Percent Conversion ** 7 min. minimum	Percent Conversion ** 7 min. maximum	Percent Conversion 7 min. by Dilatometry
42	8.36	0.0	2.3		1.2
37	8.33[1]	4.6	40.7	45.3	48.2
34	8.19	9.7	61.0	70.7	63.6
40	8.33	12.1	42.2	54.3	55.2
35	8.16	15.00	41.2	56.2	48.7
41	8.32	17.6	50.9	68.5	69.5
39	8.31	20.5	43.1	63.6	57.4
38	8.30	25.2	46.9	72.2	75.4
36	8.30	30.0	39.8	69.8	68.0

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* diethoxyacetophenone (DEAP), based on styrene

** determined gravimetrically

[1] 1:1 mole ratio sodium lauryl sulfate to styrene

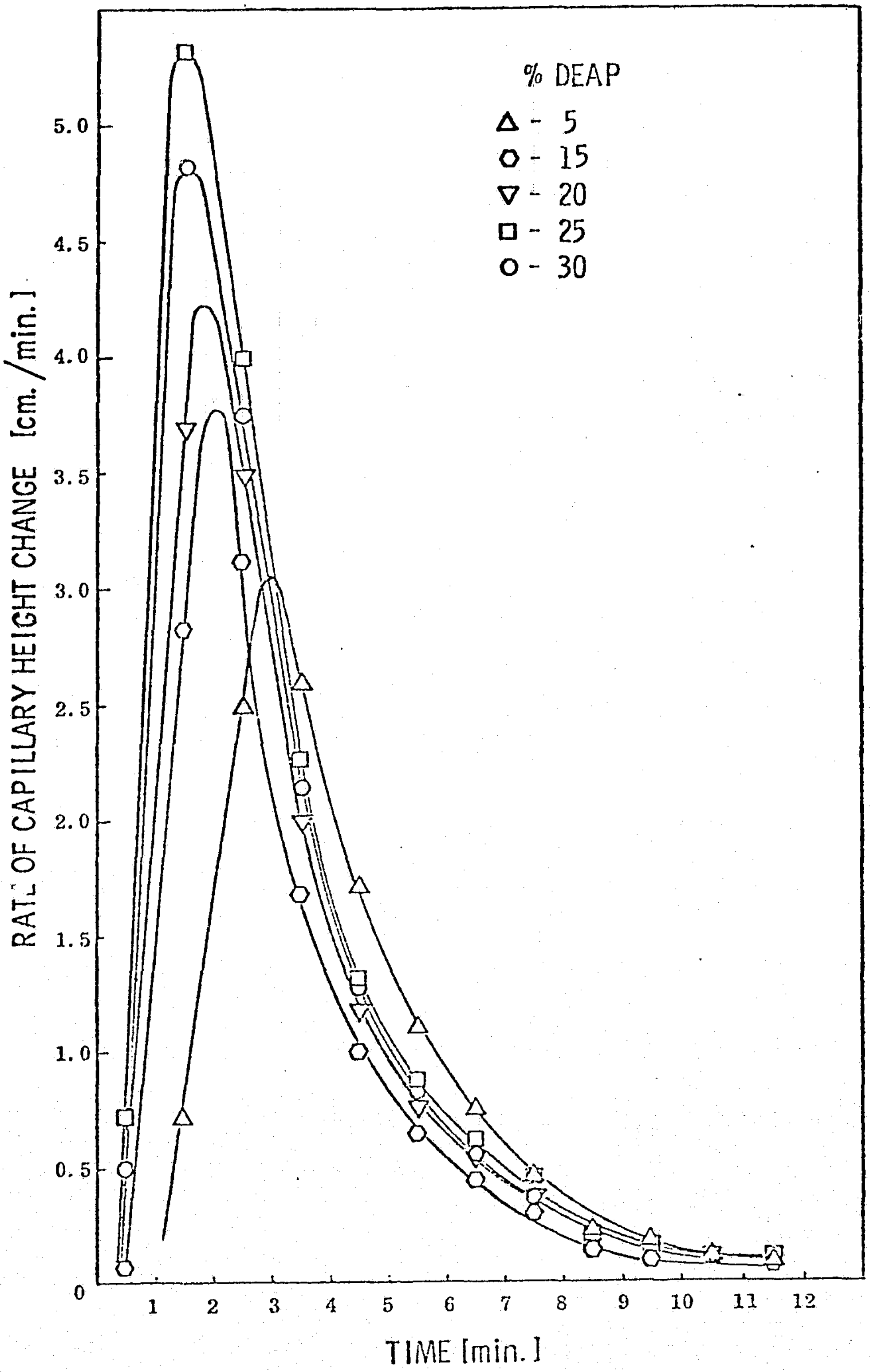

Figure 8.Rate-time curves as a function of percent photoinitiator (DEAP) with respect to styrene (GE cell).

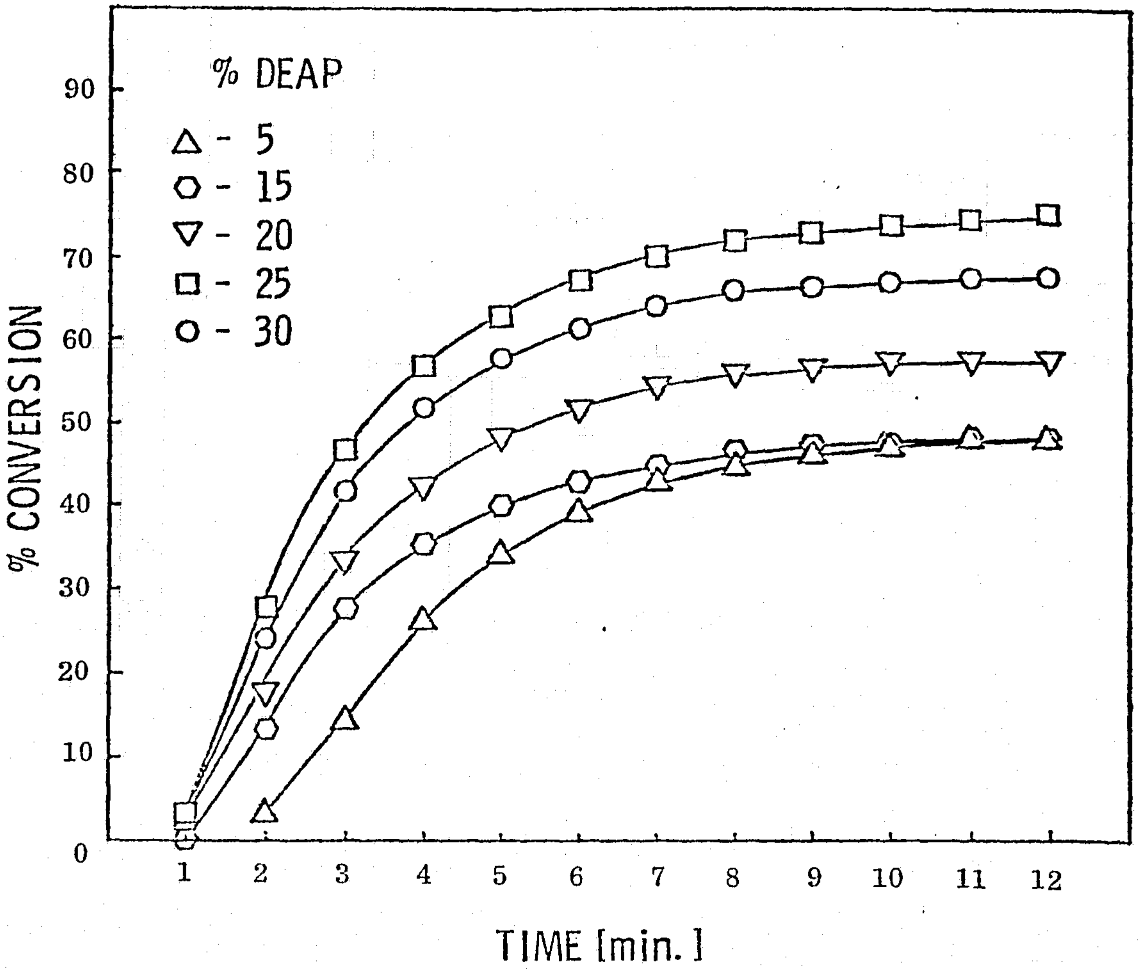

Figure 9. Conversion-time curves as a function of percent photoinitiator (DEAP) with respect to styrene (GE cell).

where W = final latex weight

S_i = seed latex total solids

S_f = final latex total solids

$D = \dfrac{\text{final particle diameter}}{\text{initial particle diameter}}$

The reactions were carried out according to the following procedures. First, a stock solution of vacuum-distilled monomer and 20% (by weight) DEAP was added to the seed latex (at a particular dilution), and exact weight measurements made on the Mettler Balance. The emulsion was then placed into the reaction cell using a syringe, and the 4.6 watt UV lamp turned on for a period of 15 minutes.

Following polymerization, the emulsion was removed from the cell using a syringe, and a 0.3% solution of hydroquinone in isopropanol was added to terminate the reaction. The final solids content was determined, and electron microscope grids were prepared. The final particle size was then determined by electron microscopy and the theoretical particle size (100%) was calculated using equations 1 and 2, solving for D. It was then possible to determine the actual conversion of the UV-photopolymerization using the following relation:

$$\%\ \text{conversion} = \frac{\text{final particle volume} - \text{seed volume}}{\text{theoretical particle volume} - \text{seed volume}} \times 100$$

In the initial polymerizations, seed latexes of about 3% solids were swelled with monomer and polymerized. The conversion was checked gravimetrically. None of these runs gave any evidence of conversion. Two factors seemed to be complicating the results in these experiments:

1. inaccuracy in the gravimetric measurements (dependent upon four weight measurements);
2. an insufficient intensity of UV light passing through the reaction cell.

It was then felt that, if meaningful results were to be obtained, the amount of UV light transmitted through the cell must be determined as a function of seed latex particle size and solids content. The relative (to pure water) transmittance through the cell was measured as a function of these two parameters. Figure 10 presents the results of these experiments and gives an insight into the amount of UV light actually being transmitted and why 880Å,3% solids seed latexes were not polymerizing to an appreciable extent.

Since the larger particle latex transmits a higher percentage of radiation, the 7,940Å seed latex was used for further experiments at 2.5 to 0.03% solids content. Conversion calculations were changed from the gravimetric method to electron microscopy. This change was imperative at these dilutions despite the slowness of the calculation method because of the potential increase in sensitivity.

The preliminary polymerizations run in the LU cell showed two important results:

1. conversions of 13-71% were calculated (based on 100% theoretical swelling) for 3.5-0.037% solid latexes, respectively;
2. the conversion appeared increased with decreasing solids content.

The results of these experiments could not be considered definitive, however, because the magnification of the electron microscope (used to calculate final particle size) is generally accurate to within 5-10%. Also, these calculations were based on an unrealistic 100% theoretical swelling of all the monomer uniformly into the particles. This assumption would tend to give a value for the calculated conversion lower than the actual conversion.

The error in the electron microscope magnification was resolved by placing a drop of seed latex on the microscope sample substrate to provide internal calibration of the sample. This method was used with the same recipe in the GE cell with a seven-minute UV irradiation. In this experiment, a 0.034% solid latex (7940Å) swelled to 10,120Å with monomer (theoretically assuming 100% swelling of particle with monomer) plus 20% DEAP was irradiated and terminated using solid hydroquinone crystals. The final particle size was determined by preparing an electron microscope grid of the final latex and shadowing the particles with approximately 10Å of platinum. Following this procedure, a drop of the original seed latex was placed on the grid, and shadowed with platinum at an angle of 90 degrees from the initial shadowing. Thus, the seed latex would have one

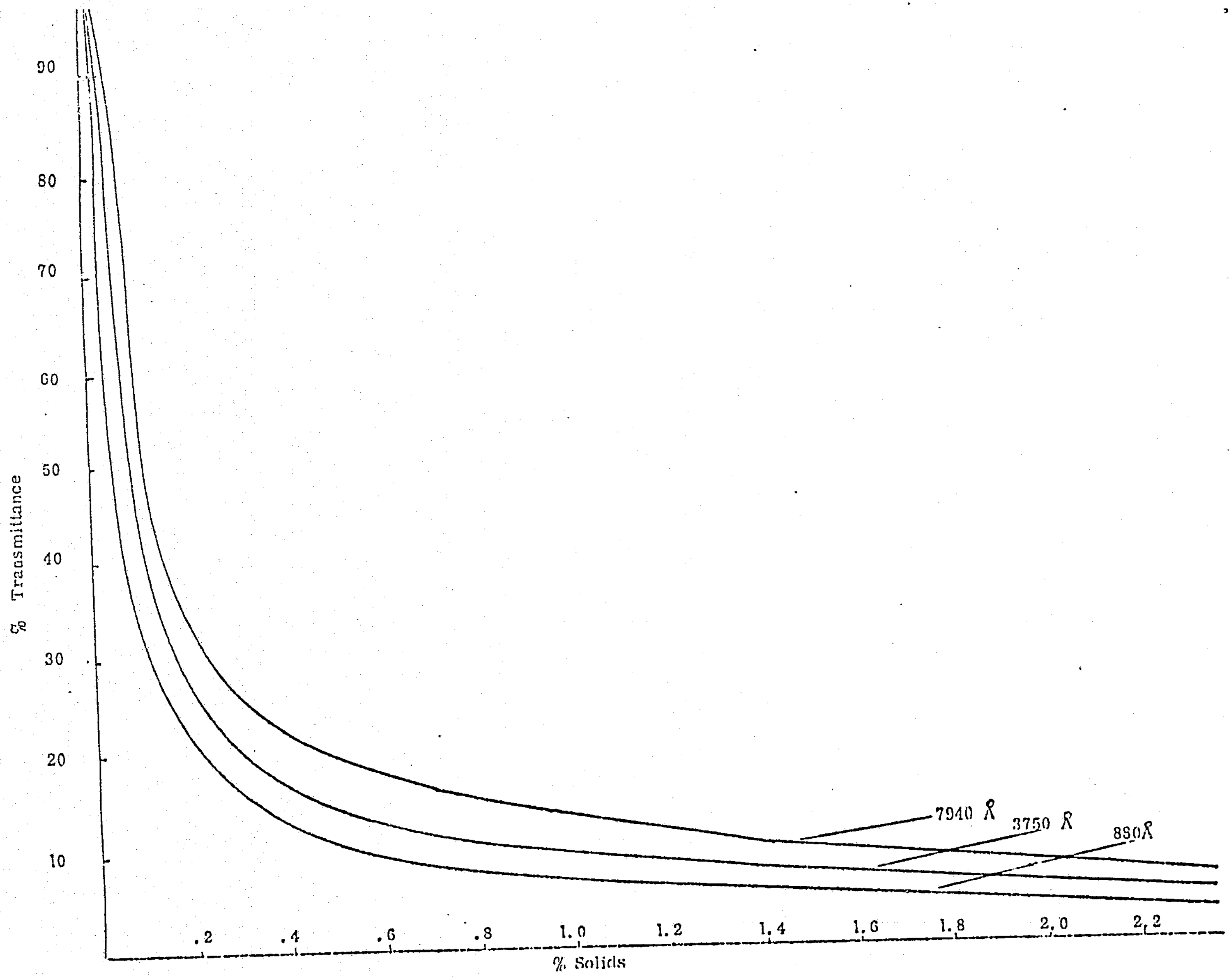

Figure 10. UV Light Transmittance vs. % Solid Content

shadow and the polymerized latex would have two shadows. This was done to provide internal calibration of the electron microscope's magnification, something which had been lacking in the preliminary experiments run in the LU cell.

Figure 11 is an electron micrograph of the final latex obtained from the G. E. reaction cell run. The seed latex particles (labeled a - d) are 7,940Å (one shadow). The rest of the particles, which had been seeded and irradiated (two shadows) have a number average diameter of 8,225Å, and a dispersity of 1.002. Based on 100% theoretical swelling of the monomer, this would give a calculated conversion of 15%. As mentioned before, however, this assumption is unrealistic and leads to low calculated values, and will be resolved in future experiments by obtaining the swelled particle diameter using cryogenic stage electron microscopy with internal calibration. This will allow actual conversions to be measured accurately.

V. CONCLUSIONS

The feasibility study described in this report leads to the following conclusions concerning the polymerization of monodisperse latexes within a six-minute period in the GE laboratory prototype of the SPAR rocket polymerization vessel.

1. Emulsion polymerizations can be carried out to conversions as high as 75%, using a stable micellized styrene-SLS system plus photoinitiator.
2. Dilatometry can be used to accurately determine both the rate and conversion of polymerization.
3. Thermal expansion due to the light source and heat of reaction is small and can be corrected for if necessary.
4. Although seeded emulsion polymerizations are unfavorable in photoinitiation, as opposed to chemical initiation, polymerizations can be carried out to at least 15% conversion using 7940Å seed particles, with 0.05% solids.
5. Photoinitiation should be used to initiate polymerization in the SPAR rocket experiments because of the mechanical simplicity of the experiment.

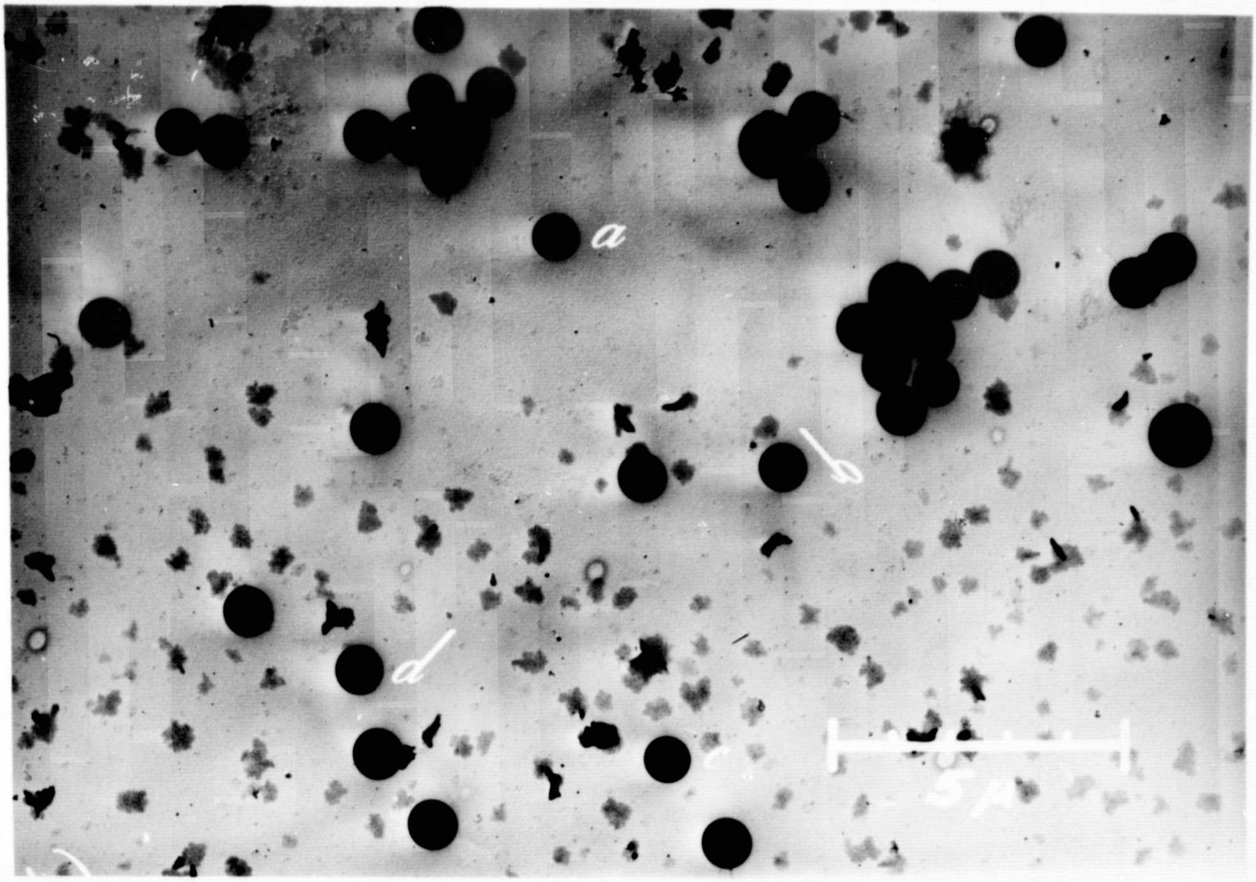

Figure 11. Transmission electron micrograph of monodisperse polystyrene latex particles (two shadows) prepared by photoinitiation of 0.7940μm diameter seed particles (a, b, c and d - single shadow)

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FINANCIAL STATEMENT

Contract value	$24,965.00
Expenditure for month of May, 1977 [a]	8,556.17
Expenditures to date	25,904.74
Estimated funds to completion	- 939.74
Anticipated overrun [b]	5,000.00

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[a] Latest month for which account status reports are available

[b] Financial overrun will be discussed with contracting office representative as soon as he returns from Europe.

APPENDIX A

Letters from The Dow Chemical Company and Polysciences, Inc.