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Refined Synthesis and Characterization of Controlled Diameter, Narrow Size Distribution Microparticles for Aerospace Research Applications

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Abstract

Flow visualization using polystyrene microspheres (PSL)s has enabled researchers to learn a tremendous amount of information via particle based diagnostic techniques. To better accommodate wind tunnel researchers' needs, PSL synthesis via dispersion polymerization has been carried out at NASA Langley Research Center since the late 1980s. When utilizing seed material for flow visualization, size and size distribution are of paramount importance. Therefore, the work described here focused on further refinement of PSL synthesis and characterization. Through controlled variation of synthetic conditions (chemical concentrations, solution stirring speed, temperature, etc.) a robust, controllable procedure was developed. The relationship between particle size and salt concentration, $MgSO_4$, was identified enabling the determination of PSL diameters *a priori*. Suggestions of future topics related to PSL synthesis, stability, and size variation are also described.

Keywords: dispersion polymerization, PSLs, particle image velocimetry,

Introduction

Seed Materials for Wind Tunnel Testing and PSL Advantages

In spite of the significant advances in computing power and computational fluid dynamics (CFD), wind tunnel testing remains a critical aspect of aeronautics development. Experimentally determining the impact of the airflow on wind tunnel models can be performed in two ways, either using sensors embedded in the structure itself or sensing the properties of the flow field directly. Pressure sensitive paints, shear stress sensors, and pressure taps are among the on-body approaches that can be used to ascertain the impact of airflow on the test article as well as to make inferences regarding the impact the structure has on the flow field. Off-body techniques make measurements of various parameters, such as velocity, pressure and temperature, in the flow field and can be divided into three categories. Intrusive probes such as Hot-wire anemometers and Pitot probes are inserted into the flow to make measurements. Molecular diagnostics such as laser-induced fluorescence (LIF), Rayleigh and Raman scattering, are examples of nonintrusive molecular techniques that can measure off-body flow parameters with minimal disturbance to the flow. Laser Doppler Velocimetry (LDV) and Particle Image Velocimetry (PIV) are examples of Particle based laser diagnostics that form the third category of off-body techniques, which represent the primary application for the seed particles described in the current study.

Throughout the history of wind tunnel measurements that utilized seeded airflows, a variety of seed materials have been investigated each with advantages and disadvantages. (For a review of several seed materials, see Ref. 1)¹ For example, kerosene and olive oil have both been used as seed materials with one of the primary advantages being availability of seed material. However, a major drawback for both systems is the broad size distribution of microdroplets generated by the nebulizing systems, not to mention flammability issues associated with kerosene and olive oil. Smoke has also been utilized as a seed material but issues regarding uniform dispersion of the smoke particulates have limited applications. Sand and other inorganic small particles have been demonstrated to be far too abrasive for use in wind tunnel testing, and the dense nature of these materials presents a severe drawback for obtaining reliable, truly representative data concerning the characteristics of the flow field. Plastic particles overcome many of these challenges due to the: relatively low density and hardness, capability to obtain and use significant volumes with narrow size distributions, ability to characterize the particles prior to use in the wind tunnel, and reduced risk to facility, model, and personnel, compared to some other seed materials.

Historically, the huge drawback for using plastic microparticles for seed material has been cost and availability. Researchers at NASA Langley investigated potential ways to reduce the cost of Polystyrene Latex (PSL) particles and improve the availability of these seed materials. Exploring synthetic

approaches available at the time for PSL generation, Cecil Nichols developed a dispersion polymerization technique to generate polystyrene PSLs.² This approach utilized basic chemical components and a straightforward reaction procedure to generate PSLs in a range of 0.5 – 3 micrometers. PSLs were generated in a temperature-controlled reaction kettle using mechanical stirring. Although this approach was effective, there were a number of areas that could be improved to enable improved PSL synthesis with more control over particle diameter and particle size distribution. Additionally, the work conducted by Cecil Nichols did not permit researchers to interpolate required chemical compositions for target particle sizes not specifically outlined in the original Nichols TM.

In this technical memorandum, improved processes for producing batches of polystyrene microspheres with controllable diameters are discussed in detail. Concentration/size relationships are described to enable generation of size-targeted PSLs over a broad range of diameters. Characterization techniques are also described.

Light Scattering and Signal Detection of PSLs

The seed particles required for LDV measurements must have both predictable laser scattering performance as well as consistent dynamic response to flow fluctuations. (For a review of the fundamental mathematics for LDV measurements the reader is referred to Ref 3.)³ Seed materials have a relaxation time constant, τ_p , indicative of the delay in particle velocity change from fluid velocity change.⁴ The τ_p depends on the particle's drag coefficient which is influenced by shear force and skin friction changes. Spherical particle response times in a fluid flow scale linearly to particle density, ρ , and as the square to the particle diameter, d :

$$\tau_p = \frac{4\rho d^2}{3C_d Re_r \mu} \quad (1)$$

where C_d , Re_r , and μ are the drag coefficient, Reynolds number, and dynamic viscosity, respectively. Seed particles are detected in the airflow as a result of Mie scattering incident laser light. Mie scattering is nonuniform with regions of enhanced and minimized scattered light intensity dependent on the direction of laser incidence. The intensity of the scattered light depends on the differential cross-section of the particle, among other variables. Thus, increasing the particle size increases the scattered light intensity. Concomitant to the increase in signal strength, the particle relaxation constant also increases. The balance between particle detection and particle behavior has resulted in use of a finite size regime of particle. Fortunately, polystyrene PSLs have a density close to water enabling use of these materials in wind tunnels over a much broader range than is capable with higher density, inorganic materials.

To quantify the accuracy of the LDV measurements of the flow field, the researcher has to know the scattering particle characteristics. In order to obtain optimum LDV measurements, the researcher is striving to achieve control of the particle characteristics and to verify those characteristics at the measurement point. The most desirable seeding characteristics are particles which are spherical, monodisperse (uniform size and shape), and have the ability to be sized according to a given wind tunnel and laser system. The ultimate objective of the particle formulation and fabrication process described is to achieve efficient operation of the particle based laser diagnostics during wind tunnel tests and, most importantly, to ensure accurate measurements with various particle based techniques. The accuracy of particle based measurement systems depends on the ability of the scattering particle to faithfully track the local flow field. A complex relationship exists between the particle motion and the local flow field, dependent upon particle size, size distribution, shape, and density. It should be noted that detection of scattered light from particles in the flow is often complicated by issues with light reflected from the model itself, this is especially true for near-wall measurements.

Polystyrene as a seeding substrate in microsphere form meets the challenges described above on nearly all accounts. In addition to its high performance as a seeding substance, polystyrene microspheres are relatively inexpensive and easily produced in large quantities in a short period of time.

Synthesis of PSL Particles using Dispersion Polymerization

PSL microparticles have been synthesized predominantly using emulsion polymerization.^{5,6} In this approach, styrene monomer is added to an aqueous solution containing a surfactant which stabilizes the emulsion. Introduction of an initiator molecule, typically a radical species, results in generation of the PSL microparticles. One major drawback to this approach is difficulty in controlling particle size and size distribution. Instead, greater success has been realized using dispersion polymerization which replaces the surfactants with alternative stabilizing molecules.⁷ Two categories of stabilizers are commonly used; electrostatic^{2,8} (salts) and steric^{9,10} (polymeric) stabilizers, each with advantages and disadvantages. For the work described here, MgSO₄ was utilized as an electrostatic dispersion stabilizing agent. In dispersion polymerization using electrostatic stabilizers, the ionic salt species stabilize the droplets of styrene in water, as an oil in water mixture, by migrating to the interface. Since dispersion stabilization using ionic salt species is realized using mechanical stirring, the stir speed has been demonstrated to be of significant importance with regards to generating monodisperse PSLs.¹¹ The requirement of stirring can be circumvented in mixed-solvent systems, typically water/acetone, due to a reduction in the solution surface tension.¹² This reduced surface tension enables the styrene microdroplets to be stabilized without the need of an ionic salt stabilizer. Once the oil-in-water dispersion has been generated, a polymerization initiator is added to the mixture. The initiator migrates to the oil (styrene) droplets and initiates polymerization that is propagated within the oil droplet. The size of the oil droplet, and thus the size of the resultant PSL particle, is controlled by the concentration of the dispersion stabilizing agent.

For the work described here, the radical initiator chosen was potassium persulfate (K₂S₂O₈, KPS) which decomposes, resulting in generation of an oxygen-centered radical.^{13,14} Although more stable radical polymerization initiators have been used in the past,¹⁵ such as TEMPO,¹⁶ issues with controlling particle size, size distribution, and the range of available particle sizes accessible with these initiators has detracted from their use. 2,2'-Azobisisobutyronitrile (AIBN) has also been successfully used as an initiator to generate monodisperse PSL;¹⁷ however, flammability and acute toxicity are strong detractors from using this material as a radical initiator. One drawback of using KPS, and many other radical chain polymerization initiators, is sensitivity to oxygen dissolved in the reaction mixture. Therefore, sparging the reaction mixture prior to addition of KPS is paramount to successfully generating PSLs with a narrow size distribution. For this work, this was achieved by sparging the mixture with N₂ to ensure displacement of all of the dissolved O₂.

In this technical report, the materials utilized to synthesize PSLs as well as the protocol developed to conduct the synthesis are described in detail. Next, characterization of the PSLs using light scattering and microscopy techniques is described. Size variation of PSLs with respect to MgSO₄ concentration and a statistical analysis of the concentration-size relationship are discussed in the following section.

Materials and Methods

Equipment-for PSL Synthesis

As this TM is being prepared with the idea that future researchers will be able to replicate the experimental set-up and procedures, the details given below should serve as an inventory of required equipment for PSL synthesis and characterization. The items listed below are those used in our work. Other suitable configurations are, of course, possible. Several of these items are also highlighted in Figures 1 and 2.

- (1) Chiller, NESLAB- RTE-111 set to approximately 20°C.
- (2) Stirring motor assembly. IKA Eurostar Power Control-visc 6000 with a conical non-push through shaft. The impeller purchased from Ace Glass was adapted to fit.

- (3) Teflon adaptor gasket, home-made, to fit on the stirring rod and over the center neck of the reactor lid.
- (4) Heating mantle. 3000 mL, Glas Col from Ace Glass order code 12058-22.
- (5) Reaction kettle assembly. Pyrex, 3000mL, 4-neck, from Fisher Scientific, catalog number 11-847D.
- (6) Clamp for reaction kettle assembly, above. Ace Glass order code 6508-11.
- (7) Two gaskets for reaction kettle clamp. Gaskets were cut in-house from a sheet of Teflon.
- (8) Beaker, Griffin, 4000 mL, heavy-duty. Fisher Scientific catalog number 02-555-25K. This beaker is used to hold filtered product until it is cool enough to pour into jugs for storage.
- (9) Adaptor tube, Pyrex, with parallel side arm, 24/40 joints. Fisher Scientific catalog number 15-326A
- (10) Graduated cylinder, 2000 mL, Class A. Fisher Scientific catalog number 08-553H.
- (11) Gas dispersion tube (sparge tube) Ace Glass order code 7198-06, lengthened by special order to 320 mm.
- (12) Condenser, cold finger, 24/40 joint, 215 mm length below joint.
- (13) Graham condenser, 24/40 joint, 200 mm jacket length. Ace Glass order code 5977-12
- (14) Agitator, 316 stainless, 75 mm. Ace Glass order code 8095-31.
- (15) RTD Sensor probe, PFA coated, detachable lead. Ace Glass order code 12139-35.
- (16) Temperature readout/controller, 120V, for temperature sensor probe above. Ace Glass order code 12107-20. Temperature set to 70 °C throughout the run.
- (17) Adaptor for temperature probe, "Mini", #7 Ace thread, 24/40 joint. Ace Glass order code 5272-15
- (18) Flowmeter/controller, Teledyne Hasting-Raydist 0-500 sccm (air).
- (19) 1-gallon plastic "milk" jugs with screw tops, available from U.S. Plastics, among other vendors.
- (20) Miscellaneous lab supplies: Tygon tubing, cheesecloth, sieve, large funnel, Swagelok valves, 50 or 100 mL beakers, glass syringe pipet, laboratory oven, milligram balance, wipes/paper towels.

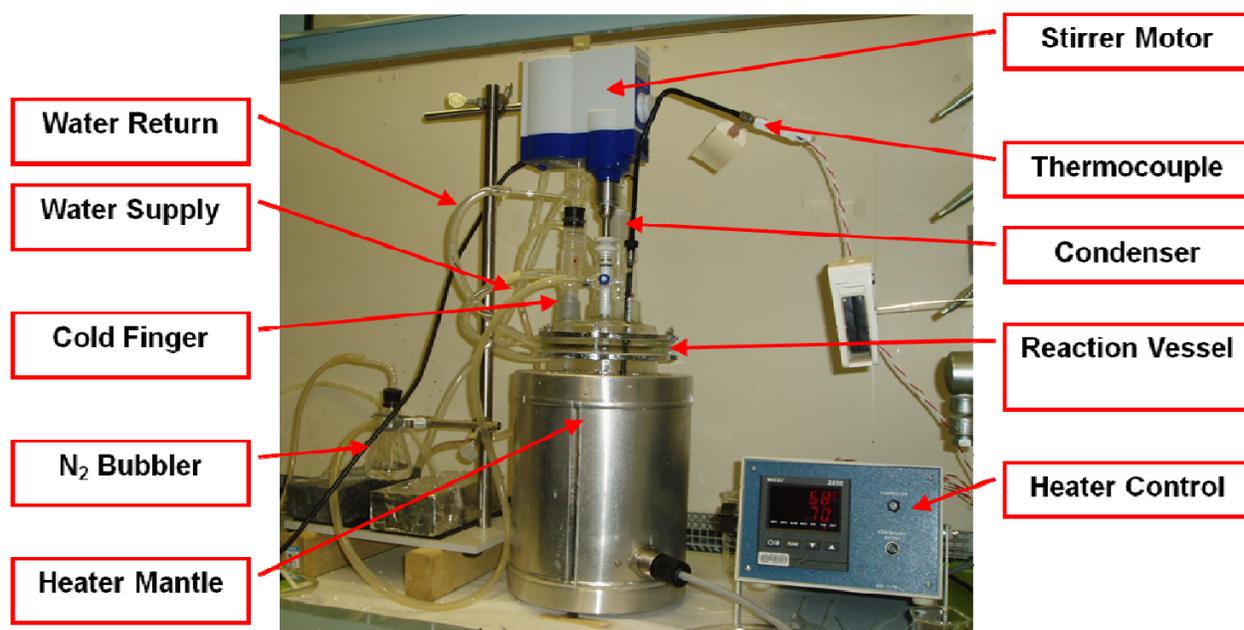


Figure 1. PSL reaction kettle and experimental setup.

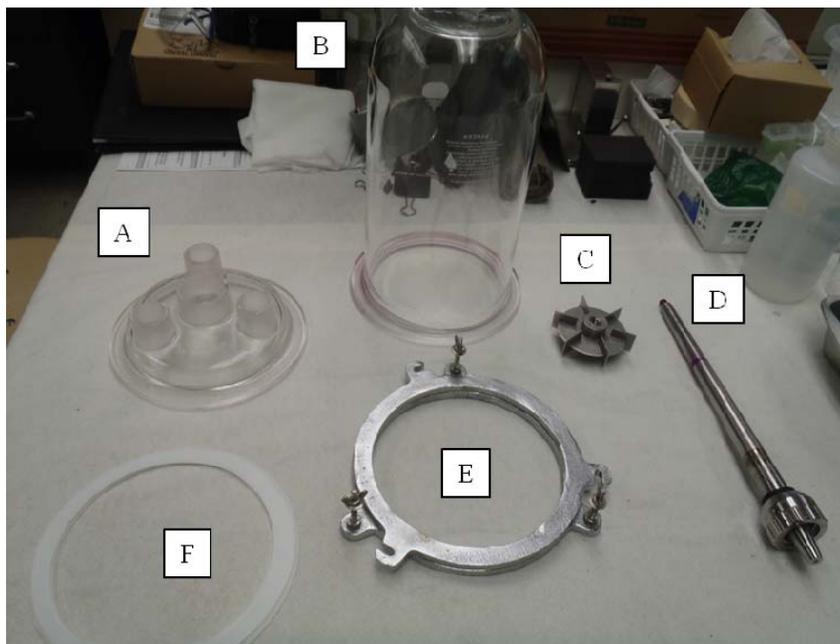


Figure 2. Photograph of the individual components of the PSL reaction kettle: (A) reaction kettle lid, (B) reaction kettle, (C) stir paddle, (D) stir rod, (E) reaction kettle clamp, (F) 2 Teflon[®] washers nested between the reaction kettle and the lid.

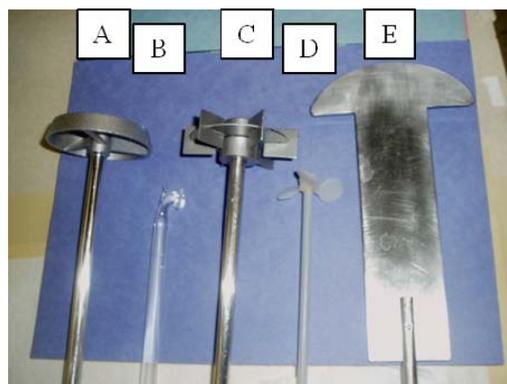


Figure 3. Several different stir paddle geometries were evaluated. The most reliable results were those obtained with paddle “C.” This is possibly due to an increased ability to agitate the solution creating the most homogenous styrene droplet sizes.

Equipment-for PSL Characterization

The synthesized PSLs were characterized using light scattering measurements and various microscopies. For light scattering, a NECOM -PSS Particle Sizing Systems light scattering instrument was used. To make the measurement, 1 drop of the PSL dispersion is placed in 40 mL of deionized water. This solution is stirred and 1 drop of this solution is transferred to the analysis container using a

pipette. Prior to PSL measurements, background scans were collected on deionized water to ensure the analysis chamber was properly flushed of particulates from previous measurements. If the total particle count of the background scan was greater than 500 at 0.5 μm , the reading was repeated. If the count exceeded this minimum value twice, the analysis chamber was drained and refilled with new deionized water. Once the data was collected, the number count size distribution was analyzed to determine the dispersity and modality of the PSLs. Microscopic characterization of the PSLs was performed using a NECOM-PSS Particle Sizing Systems and Hitachi S-3700 scanning electron microscope and a Zeiss LSM 5 Exciter confocal microscope operated in scattering mode with excitation at 543 nm.

Process Monitoring Software and Instrumentation

It was recognized that in order to ensure repeatability of the process and to facilitate the analysis of unexpected results it was necessary to accurately record all the variables of the process. Gathering this continuous data stream would alert us to abnormal behavior such as if the motor bogged down due to unusual viscosity changes or if the sparge gas flow rate changed because of a nitrogen supply problem. These variables included the temperature of the reactor, stirring motor speed, chiller temperature, ambient temperature and sparge gas flow rate. These parameters were measured using an Agilent 34970A data acquisition\switch unit. This is a self contained unit and is essentially a 20 channel scanner\multiplexer connected to a high precision voltmeter. All signals were connected to the multiplexer card which is inserted into the back of the unit. All channels are configurable for its respective input type. The temperatures were measured with thermocouples. It was determined that type "T" thermocouples would be most suitable for the expected temperature range. The reactor temperature thermocouple was dipped into the process solution through an access hole in the reactor. The ambient temperature thermocouple was mounted in room air in the general vicinity of the process equipment and the chiller thermocouple was dipped into the chiller reservoir.

The stirring motor has a built in analog output voltage that is available on a Sub "D" connector that is proportional to the speed of the motor. This voltage was 1 volt at 2000 revolutions per minute (RPM). The 34970A unit has the ability to enter scaling parameters for each channel. Using this function, the voltage as read by the unit was scaled to read out directly in engineering units, in this case RPM. The flow meter has a full scale output of 5 volts for a flow of 500 SCCM (standard cubic centimeters per minute). This was similarly scaled to read out in engineering units.

Synthesis of Polystyrene Microparticles

In order that other researchers could more easily produce their own particles, both a general description and a detailed description of the PSL synthesis procedure is included here.

General procedure: A 2 L reaction kettle was fitted with 2 Teflon[®] gaskets to ensure an airtight fit followed by the reaction kettle lid, mechanical stirrer, temperature probe, and a cold finger. The reactor was charged with deionized 18 MOhm water, MgSO_4 , and styrene in appropriate quantities. The chiller was turned on to 20°C which fed the condenser and cold finger. The cold finger was removed and replaced with a gas dispersion tube. N_2 was introduced to the reaction mixture through the dispersion tube at approximately 100 cc/m. The reaction mixture was stirred at 150 RPM and heated to 70°C. After 40 minutes, the gas dispersion tube was removed and replaced with the cold finger. $\text{K}_2\text{S}_2\text{O}_8$ was added to deionized 18 MOhm water held at 70°C. Once dissolved, this was added to the reaction kettle. The reaction mixture was stirred for 20 h at 250 RPM and 70°C under N_2 flowing at 450 cc/m. The solution was allowed to cool slightly and filtered through four layers of cheese cloth for analysis. The glassware will likely have plastic deposits on it and can be readily cleaned by wiping with xylenes or toluene. The stir paddle and reaction kettle may need to be soaked in these solvents overnight.

Detailed Procedure:

1. Assemble the reactor as shown in Figure 1. Turn the stirring paddle by hand to make certain that it is not binding or striking anything in the vessel.
2. Charge the reactor with 2000 ml water.
3. Using a 50 ml glass syringe and needle, remove 40 ml water from the reactor and discharge it into a 100 ml beaker. This water will be heated to 70 C and used to dissolve the $K_2S_2O_8$.
4. Use the formulation equation or Table 1 to determine the weight of magnesium sulfate ($MgSO_4$) based on the desired particle size. Add the $MgSO_4$ to the reactor water.
5. Add 200 g (265 ml) styrene to the reactor.
6. Close the stopcock in the line for padding the system with nitrogen (on the fitting for the thermocouple).
7. Start the cold water flowing through the condenser and cold finger. With the water flowing, invert the cold finger to remove the air. Do not place the cold finger into the reaction mixture at this time.
8. Insert the gas dispersion tube into the reaction vessel. Clamp off the nitrogen padding line, open the clamp on the dispersion tube line, and adjust the flow of nitrogen.
9. Start the stirrer (150 rpm) and begin heating to 70 C.
10. Bubble nitrogen through the reaction mixture for 40 minutes (approx. 100 cc/min).
11. Remove the nitrogen bubble tube from the reactor after 40 minutes. Do not allow the tube to hit the stirrer.
12. Insert the cold finger in place of the nitrogen bubble tube. Do not allow the cold finger to hit the stirrer.
13. Using the appropriate tubing clamps, divert the flow of nitrogen to the gas inlet on the thermocouple fitting. Open the stopcock. Maintain nitrogen flow into the reaction vessel during the entire reaction time (approx. 450 cc/min).
14. Using a mortar and pestle, grind 1.61 g $K_2S_2O_8$ until it is a fine powder.
15. Remove the 40 ml of water from the oven and dissolve the ground $K_2S_2O_8$ in the warm water. When the salt has completely dissolved transfer the solution to the reactor using the 50 ml syringe.
16. After 20 hours turn the temperature controller off, and stop the stirrer. After cooling for a few minutes, carefully remove the stirrer motor. Turn off the water, and remove the condenser and the cold finger. Remove the thermocouple. Remove the top of the reaction vessel.
17. Filter the reaction product through four layers of cheese cloth into a large beaker. Use a large, wire mesh filter to support the cheese cloth.
18. Clean the glassware with either xylenes (more preferable) or toluene. Soak the stir paddle in a xylene or toluene solution overnight with a parafilm covering to prevent evaporation of solvent.
19. Store the filtered product in a 1 gallon container.
20. Determine the weight percent solids by evaporation at 65-70 C.

Generation of PSL Samples for Microscopic Analysis

Microscope slides were coated with PSLs in order to determine their diameter microscopically. The slides were first submerged in a basic solution (potassium hydroxide aqueous solution, approximately 2 M) to remove the thin oil layer and improve slide wettability. Next, the slide was rinsed with deionized water and a droplet of the PSL suspension was deposited on the slide using a pipette. The side of the

narrow portion of the pipette stem was used to spread the droplet to all areas of the slide that had been submerged in the KOH solution. Since the best resolution of particle profiles can be obtained by observing a monolayer of particles, a minimal amount of solution was applied to the slide and spread over a maximum surface area. The slide was next placed in an oven at approximately 70 °C and allowed to dry. A good indication of adequate surface coverage of a glass slide was observed by tilting the slide. If the slide was somewhat transparent when viewed at a normal incidence and became very hazy upon tilting, a good monolayer of PSLs was often present on the surface. An example picture of good and bad PSL microscopy samples is shown below.



Figure 4. PSL microscopy slides exhibiting good (left) and poor (right) PSL depositions.

Results and Discussion

PSL Sphericity and Size Distribution

Building upon the work of Cecil Nichols,² PSLs were generated using dispersion polymerization with MgSO_4 as a dispersion stabilizing agent and $\text{K}_2\text{S}_2\text{O}_8$ as a radical polymerization initiator. Although the reaction progress was not quantitatively monitored, the transformation of the reaction mixture from transparent to opaque was a good indicator that the PSL synthesis was proceeding. (See region of the reaction kettle below the kettle clamp in Figure 5) Once the allotted time for the reaction to progress was complete, the solution was allowed to cool slightly and subsequently filtered through cheese cloth. Approximately 50% of the time, there were large deposits of amorphous polymerized styrene on the stir paddle and the sides of the reaction kettle.



Figure 5. PSL reaction vessel during PSL synthesis.

Once the particles were generated, they were analyzed using a light scattering particle analyzer and several microscopic techniques. Shown below is an example of the analysis results obtained from a batch of PSLs (Table 1). As can be seen, there are a number of different statistics calculated from the particle analyzer that are of utility when discussing the PSL batch. Although the volume-weighted averages are important for synthesis concerns, they are not as relevant as the number-weighted averages for wind tunnel uses and therefore are not considered for the remainder of this discussion. The number-weighted mean was calculated to be 1.2 mm for this batch, yet there were a significant number of particles that were greater in diameter. If this “tail” of larger particles was of concern for PSL users, they could readily be removed from the PSL dispersion by standard filtration techniques. Histograms of the particle counts and number-weighted cumulative particle counts were often of utility when a batch of PSLs was evaluated for a particular application. An example histogram with this information is provided below for the PSL batch analyzed in Table 1 (Figure 6).

Table 1. Analytical results from the Particle Sizing System light scattering particle analyzer for a batch of PSLs.

Particle Sizing Systems, Inc.						
Santa Barbara, Calif., USA						
Model 780 AccuSizer						
Caption: POLYSTYRENE PARTICLES, Final						
File Name = 021308.s						
LE400-0.5						
Sensor Model:	SUM	S/N:	409904	Cal.	File:	0409904s.sns
Elapsed Time of Data Collection =		120	Sec.			
Background File = 021308.bkg						
Total # Part. Sized (>=Thres. 0.50 um) =		296414				
Calculated Total No. of Particles in Sample =		16167930				
Dilution Factor, DF =		54.55	2nd-stage DF2=	1		
Fluid Volume		No. of				
Sampled =		120	ml	Channels =		128
NUM-WT Mean =	1.2	um	Mode =	1.29	um	Median = 1.29
VOL-WT Mean =	89.74	um	Mode =	133.28	um	Median = 133.28
Summary of Detailed Distribution, Weightings						
Diameter (microns)	# Part. Sized	Cum Num >=Diam.	Num %	Vol %	Cum Num % >=Diam.	Vol Num % >=Diam.
0.51	9947	296414	3.356	0.031	100	100
0.54	12849	286467	4.335	0.048	96.644	99.969
0.57	11023	273618	3.719	0.048	92.309	99.921
0.6	6112	262595	2.062	0.031	88.591	99.872
0.64	2479	256483	0.836	0.015	86.529	99.841
0.67	1022	254004	0.345	0.007	85.692	99.826
0.71	448	252982	0.151	0.004	85.348	99.819
0.75	442	252534	0.149	0.004	85.196	99.815
0.79	685	252092	0.231	0.008	85.047	99.811
0.83	771	251407	0.26	0.01	84.816	99.803
0.88	1032	250636	0.348	0.016	84.556	99.792
0.93	1369	249604	0.462	0.026	84.208	99.776
0.98	2012	248235	0.679	0.044	83.746	99.75
1.04	2624	246223	0.885	0.068	83.067	99.706
1.09	4372	243599	1.475	0.134	82.182	99.637
1.15	9918	239227	3.346	0.356	80.707	99.504
1.22	32283	229309	10.891	1.363	77.361	99.148
1.29	106296	197026	35.861	5.277	66.47	97.785
1.36	62821	90730	21.194	3.667	30.609	92.508
1.43	6780	27909	2.287	0.465	9.416	88.841
1.51	6070	21129	2.048	0.49	7.128	88.376
1.6	6887	15059	2.323	0.653	5.08	87.886
1.68	4730	8172	1.596	0.528	2.757	87.232
1.78	1503	3442	0.507	0.197	1.161	86.705
1.88	809	1939	0.273	0.125	0.654	86.508
1.98	496	1130	0.167	0.09	0.381	86.383
2.09	200	634	0.067	0.043	0.214	86.293
2.21	100	434	0.034	0.025	0.146	86.251
2.33	69	334	0.023	0.02	0.113	86.225
2.46	47	265	0.016	0.016	0.089	86.205
2.59	27	218	0.009	0.011	0.074	86.189
2.74	24	191	0.008	0.011	0.064	86.178
2.89	19	167	0.006	0.011	0.056	86.166
3.05	16	148	0.005	0.011	0.05	86.156
3.22	19	132	0.006	0.015	0.045	86.145
3.4	10	113	0.003	0.009	0.038	86.13
3.58	8	103	0.003	0.009	0.035	86.121
3.78	8	95	0.003	0.01	0.032	86.113
3.99	9	87	0.003	0.013	0.029	86.102
4.21	8	78	0.003	0.014	0.026	86.089
4.45	5	70	0.002	0.01	0.024	86.075
4.69	7	65	0.002	0.017	0.022	86.065
4.96	7	58	0.002	0.02	0.02	86.048
5.23	6	51	0.002	0.02	0.017	86.028
5.52	4	45	0.001	0.016	0.015	86.008
5.83	2	41	0.001	0.009	0.014	85.992
6.15	2	39	0.001	0.011	0.013	85.983
6.49	3	37	0.001	0.019	0.012	85.972
6.85	0	34	0	0	0.011	85.953

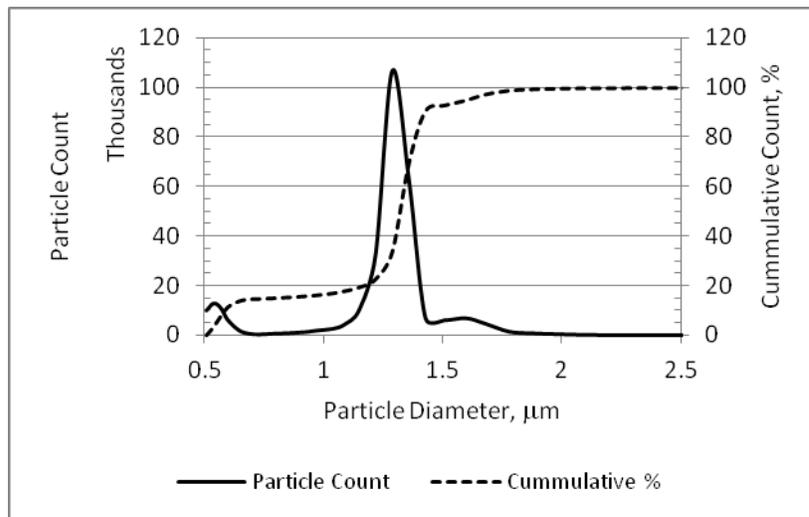


Figure 6. Example histogram of PSL particles.

Scanning electron, optical, and confocal microscopies were also used to characterize the PSLs. The analysis for each technique was similar with glass slides being prepared as described above. The diameter of the particles was then determined from the images collected on the sample slides. Several examples are shown below (Figures 7 and 8).

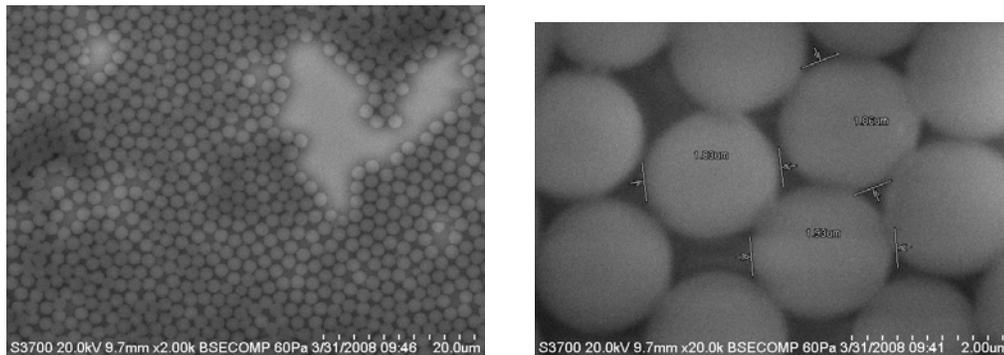


Figure 7. Scanning electron micrograph of PSL particles at low (left) and high (right) magnification.

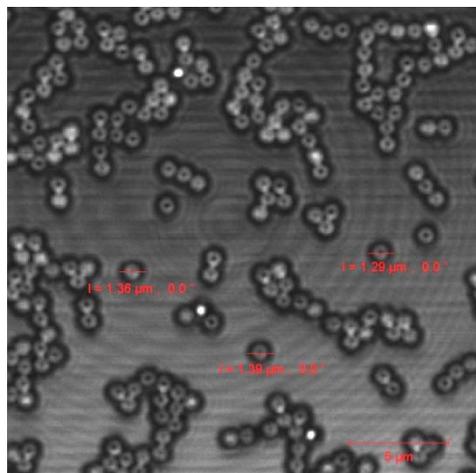


Figure 8. Micrographs of PSLs collected using the optical mode on the confocal microscope.

PSL Size Dependence on MgSO₄ Concentration

Initial results of PSL generation experiments revealed a repeatable trend regarding MgSO₄ concentration and PSL diameter. Therefore, a series of experiments were performed to assess the reliability of this trend. Several batches of PSLs were synthesized with the same concentration of each reactant in as rapid of a fashion as possible. Since the reaction runs for approximately 21 h, this required approximately 1.5 weeks to complete. This approach was taken to minimize unforeseen or unknown environmental variables that may impact particle size. PSL diameters from 0.5 μm to 2 μm were targeted as this is the range of diameters of utility for most wind tunnel experiments. The resultant mean particle size and standard deviation for each batch is presented in Table 1. As can be seen, increasing the MgSO₄ concentration resulted in an increase in PSL diameter. Similar results have been observed for PSLs generated using NaCl¹⁸ and CaSO₃¹⁹ as electrostatic stabilizers. In this work, production of larger particles was much less predictable than smaller ones, which could be the result of the MgSO₄ interfering with the radical reaction itself.

Table 2. PSL synthesis repeatability and reliability experimental results.

MgSO ₄ concentration, mM ^a	Batch	Mean Diameter, μm	Average Diameter, μm	Standard Deviation, μm
0.00	1	0.55 ^b		
	2	0.55		
	3	0.55	0.55	N/A
	4	0.55		
	5	0.55		
0.457	1	1.20		
	2	1.28		
	3	1.36	1.25	0.09
	4	1.28		
	5	1.12		
0.914	1	1.63		
	2	1.57	1.61	0.03
	3	1.62		
1.591	1	1.85		
	2	0.94		
	3	1.06	1.33	0.48
	4	0.94		
	5	1.85		

^aThis is the calculated concentration of Mg SO₄ in the aqueous solution.

^bThe minimum resolvable diameter for the light scattering detector is 0.5 μm. Therefore, these numbers are likely an artifact of the detector limitations.

The mean particle diameter was plotted against the MgSO₄ concentration and it was determined that the relationship between these two parameters was nonlinear and a reasonable correlation was calculated using Eq. 2. Similar nonlinear relationships between particle diameter and electrolyte concentration have been reported previously.¹⁸

$$d = d_M - Ae^{-B[M]} \quad (2)$$

d = particle diameter, μm

d_M = maximum particle diameter attainable with this technique, $1.99 \mu\text{m}$

A = pre-exponential coefficient, 1

B = multiplier, 1.44191 mM^{-1}

[M] = MgSO_4 concentration, mM

Although these results indicated that this synthetic approach was very robust for the PSL size range desired for wind tunnel uses, it is important to note that they are very specific to the setup used to generate the PSLs. Changing to a different stir paddle, using a different stir speed, even starting a new bottle of a reactant may impact the coefficients defined in Eq. 2. Therefore, Eq. 2 should be considered as a starting point towards development of a calibration curve for the specific setup and protocol to be utilized for PSL synthesis.

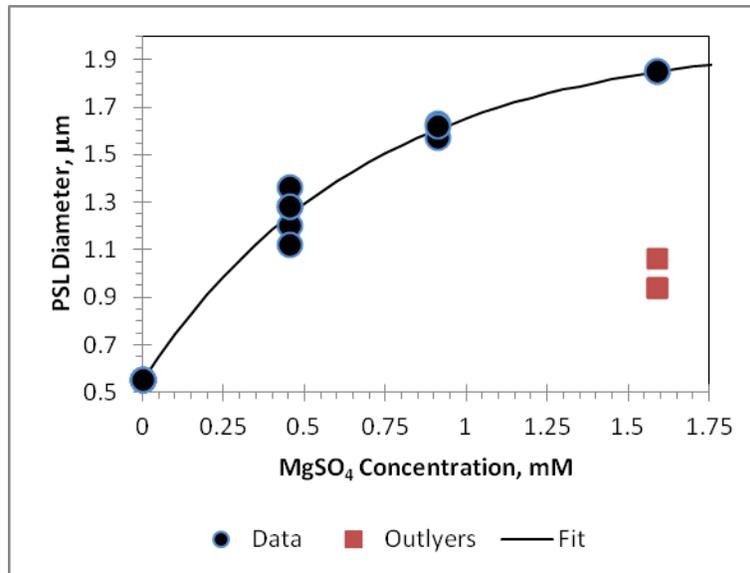


Figure 9. Particle diameter increases with MgSO_4 concentration. The correlation coefficient for the exponential fit was 0.9899.

Future PSL Synthesis Opportunities

PSL synthesis research has resulted in generation of an inventory of PSLs of various particle sizes and size distributions that are available in ASOMB for a variety of fluid characterization experiments (Figure 10). These particles have been used to successfully determine velocity in the flow field during testing in ground test facilities. Currently, research is being conducted to generate multifunctional particles that would provide additional information including temperature, pressure, and other parameters in the flow by evaluating excited state relaxation processes of fluorescent particles.



Figure 10. Inventory of PSLs synthesized in ASOMB.

Similarly, according to the results of fitting the particle diameter data to Eq. 2, the available range of particle diameters is limited. Although it is not clear what d_M depends on, one possibility is that there is a dependence on the ionic radius of the dispersion stabilizer, MgSO_4 . Thus, by changing the dispersion stabilizer, it is conceivable that the constants in Eq. 2 would be different and would enable a new size regime of particle to be synthesized due to differences in the ionic radius (Table 3). One way to examine this would be to change the cation of the sulfate salt. As an example, a schematic is presented in Figure 11 that shows the area of a styrene droplet that could be stabilized using the same number of Mg^{2+} and Ca^{2+} cations. As can be seen, the larger ionic radius of Ca^{2+} encompasses a larger styrene droplet area and may result in generation of larger PSLs. A preliminary investigation has indicated that changing to Na_2SO_4 resulted in generation of slightly larger particles (data not shown). It is unclear how changing from a divalent to monovalent cation would impact the PSL diameter.

Table 3. Ionic radii of select cations.²⁰

Cation	Ionic Radius, pm
Mg^{+2}	86
Cu^{+2}	87
Zn^{+2}	88
Ca^{+2}	114
Na^{+}	116
NH_4^{+}	143
K^{+}	152

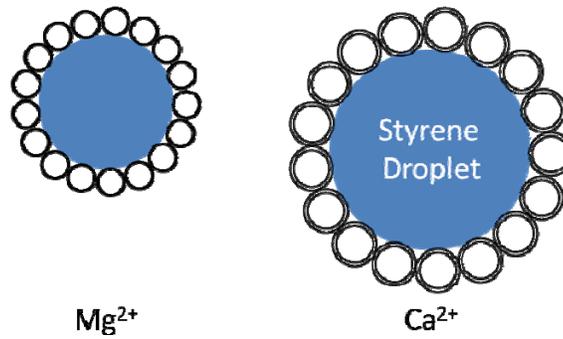


Figure 11. Schematic of the potential influence of ionic radius on maximum particle diameter attainable using dispersion polymerization.

Conclusion

The use of dispersion polymerization techniques to make PSLs for use in wind tunnel testing has been demonstrated to be an effective way to provide seed material for particle based laser diagnostics utilized by flow physics researchers and others involved with wind tunnel testing. Beyond being able to provide large quantities of narrow size dispersion particles at a fraction of what they would cost from commercial sources, the capability of being able to tune the properties of the seed material, namely the particle diameter, for specific applications is truly advantageous. Based on the described protocols, several gallons of PSLs of a specific size can be generated in a few weeks which is a much shorter lead time than would be required from a commercial entity that would have to ramp up to provide particles due to the niche nature of this requirement. Additionally, experimentation has begun on synthesis of multifunctional PSLs to further expand the capabilities for wind tunnel experiments that incorporate seed material to potentially include detection of temperature and pressure in the flow field using fluorescent particles.

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14. ABSTRACT Flow visualization using polystyrene microspheres (PSL)s has enabled researchers to learn a tremendous amount of information via particle based diagnostic techniques. To better accommodate wind tunnel researchers' needs, PSL synthesis via dispersion polymerization has been carried out at NASA Langley Research Center since the late 1980s. When utilizing seed material for flow visualization, size and size distribution are of paramount importance. Therefore, the work described here focused on further refinement of PSL synthesis and characterization. Through controlled variation of synthetic conditions (chemical concentrations, solution stirring speed, temperature, etc.) a robust, controllable procedure was developed. The relationship between particle size and salt concentration, MgSO ₄ , was identified enabling the determination of PSL diameters a priori. Suggestions of future topics related to PSL synthesis, stability, and size variation are also described.					
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