

## Submicron Polymer Powder in Electrodeless Radio Frequency-Induced Plasma-Initiated Polymerization

R. LIEPINS and K. SAKAOKU,\* *Camille Dreyfus Laboratory,  
Research Triangle Institute, Research Triangle Park,  
North Carolina 27709*

### Synopsis

Of the 30 monomers and monomer combinations investigated, 11 were polymerized into essentially all powder, 17 into predominantly a film, and two could not be polymerized in an electrodeless rf plasma-initiated gas phase polymerization. Efficient powder formation was mainly determined by the type of the monomer, the monomer partial pressure, the type of inert gas used, and the design of the polymerization chamber. The powders examined consisted of spherical particles of submicron size and were almost completely or partially soluble; and in the case of polystyrene, the powders possess a very narrow particle-size distribution. In all cases, the soluble material was of a very low molecular weight. The best conversion to powder achieved was 18%.

### INTRODUCTION

In the past, electrodeless rf-induced plasma-initiated polymerization of organic monomers has been utilized in the formation of thin, pinhole-free coatings or films on different types of substrates. We find that, depending upon the experimental conditions used, it is possible also to form low molecular weight polymeric oils or fine polymeric powders by this technique. Plasma-initiated polymeric powder formation as a minor by-product in the film formation has been noticed before.<sup>1,2,3</sup> However, the generation of only the powder and its characterization have not been reported. In this paper we report our initial results on the generation and properties of various polymeric powders.

Of the 30 monomers and monomer combinations investigated, 11 were polymerized into essentially all powder, 17 formed mainly films, and two monomers could not be polymerized at the specific conditions used in this study. The four main variables for an efficient powder formation appear to be (1) the type of monomer, (2) the monomer partial pressure in the system, (3) the type of the inert gas used, and (4) the design of the polymerization chamber. Although powder formation may be observed in polymerization chambers of many different designs, we believe that certain designs may be more appropriate than others in generating large amounts of powder.

\* Present address: Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo, Japan.

All the powders that we have inspected appear to be of submicron size and, in the case of polystyrene, of a very narrow particle-size distribution. The powders formed in the initial 5–10 min are almost completely or partially soluble; however, longer polymerization time usually insolubilized them completely. In the initial stages, the powders appeared to be perfect spheres of very little coloration, and the soluble material of very low molecular weight. In our present reactor arrangement, the best conversion achieved was 18%. The amount of powder formed was determined by weighing the reactor before and after the polymerization.

## EXPERIMENTAL

### Materials

All of the monomers, except for 2,4,6-tri(diethylamino)borazine, were available commercially and were used as received. 2,4,6-tri(diethylamino)borazine was prepared according to the procedure of Niedenzu and Dawson<sup>4</sup> from 2,4,6-trichloroborazine and diethylamine. A tan-colored oil, bp 166°/10 mm (lit.<sup>4</sup> 164°/10 mm), was obtained in a 30% yield. Formaldehyde was generated by pyrolysis of a paraformaldehyde powder. Acetylene was passed through two Dry Ice/acetone traps before use to remove the acetone.

### Polymerization Procedure

**Low-Pressure Plasma Instruments.** Two instruments were utilized in the generation of the low-pressure plasma: (1) the LTA-600L low-temperature asher, manufactured by Tracerlab, a division of Laboratory for Electronics, Inc., and (2) an instrument of our design, constructed from Heathkit components and as described before.<sup>5</sup> For the polymerization chamber, three different chamber designs and system arrangements were investigated. One chamber design consisted of a modified low-temperature asher reaction chamber as depicted in Figure 1 and described earlier.<sup>3</sup> The chamber was filled vertically with 1.5-in.-long pieces of glass tubing of  $\frac{3}{8}$  to  $\frac{3}{4}$  in. in diameter. The LTA-600L asher was used to generate the plasma. The second chamber design consisted of a long-necked 500-ml round-bottom flask as depicted in Figure 2. Again, the LTA-600L was used to generate the low-pressure plasma. The third chamber design consisted of a double-walled standard bell jar as described before.<sup>5</sup> In this arrangement, the monomer entered the reactor through a glass tubing in the base plate of the bell jar. The instrument of our design was used to generate the plasma.

**Typical Procedure.** The polymerization chamber was evacuated to 0.10 torr or less pressure, and then helium (or argon, nitrogen, neon, air) was introduced at a flow rate of 10–20 cm<sup>3</sup>(S.T.P.)/min to achieve a pressure of 0.15–0.20 torr while the system was continuously pumped. The rf coil was then activated at power outputs from 40 to 200 watts to transfer the radio-frequency energy into the flowing helium. This resulted in a

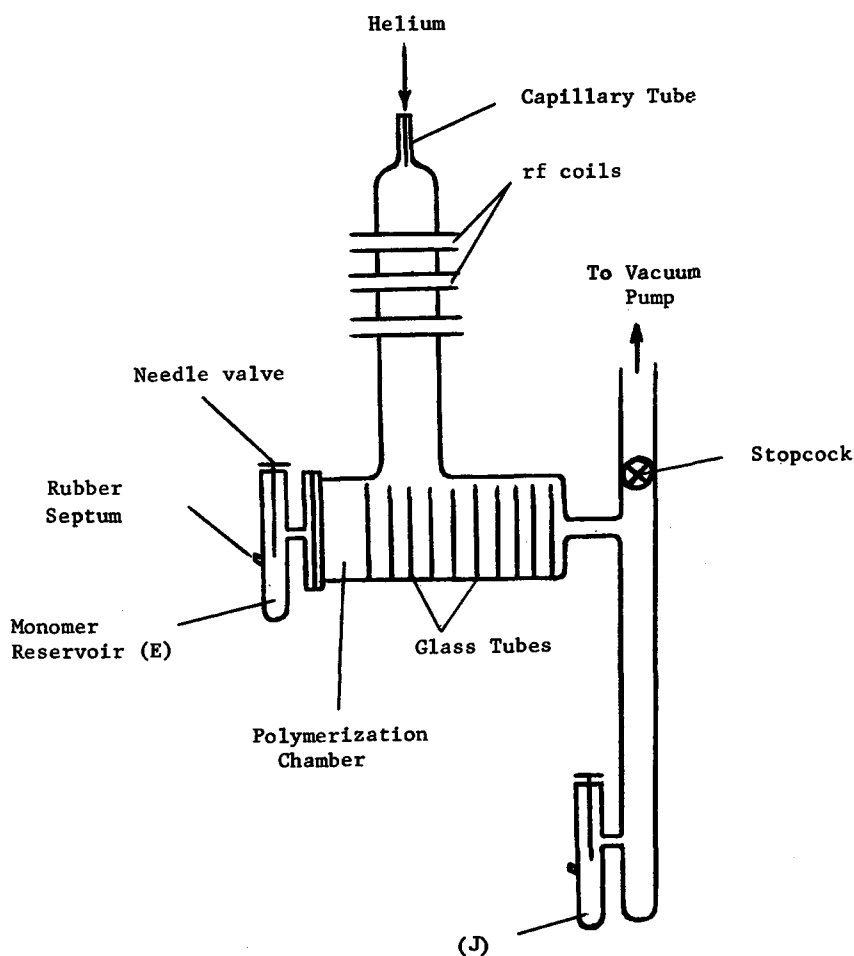


Fig. 1. Schematic system arrangement.

helium plasma that glowed and filled the entire polymerization chamber. With the stopcock partially closed, the monomer vapors were admitted through a needle valve into the reaction chamber at such a rate that the total pressure in the chamber was always maintained between 0.80 and 3.0 torr. The higher boiling monomers were heated by means of a water bath or a heat gun.

#### Characterization of the Powders

**Solubility.** All of the powders were tested for solubility in tetrahydrofuran at room temperature. A 0.1-g sample was combined with 10 ml tetrahydrofuran and was agitated for at least 1 hr before the suspension was filtered. The solution was evaporated in a vacuum oven and the residue was dried at 50°C for at least 6 hr before weighing.

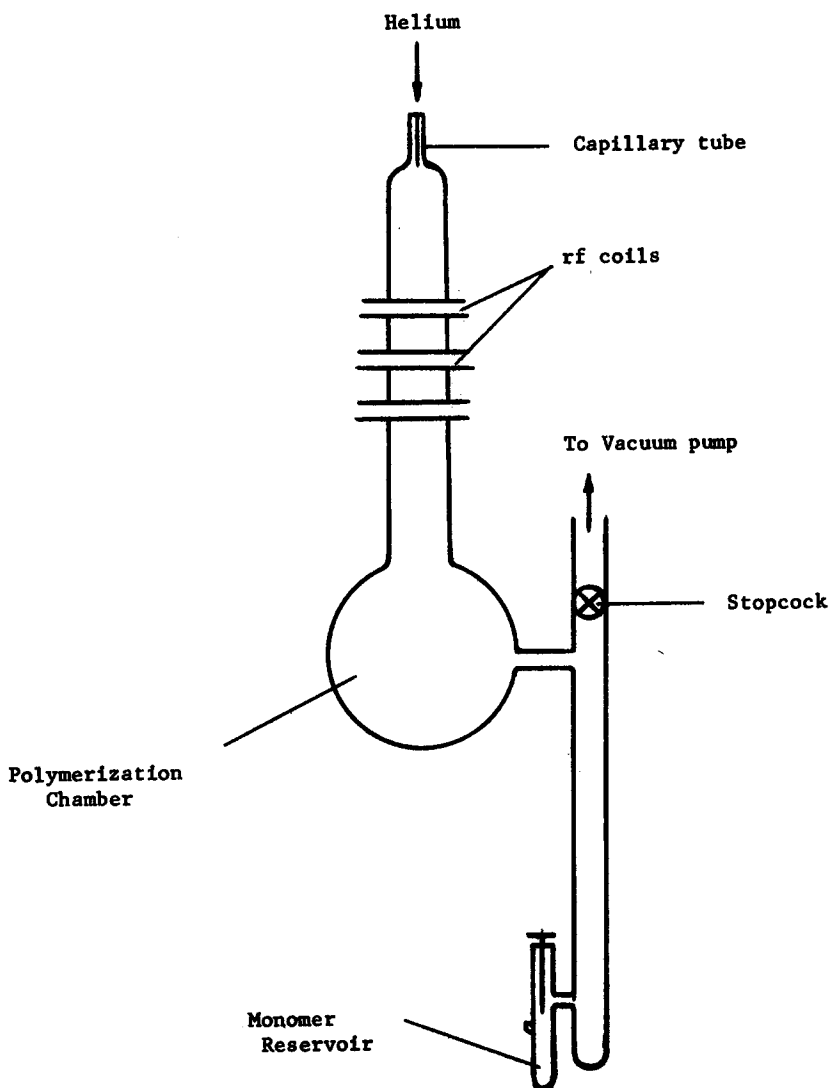


Fig. 2. Schematic system arrangement.

**Infrared Spectroscopy.** The data were obtained on KBr disks on a Perkin-Elmer spectrophotometer Model 237. The soluble materials were examined as films cast from the tetrahydrofuran solutions upon sodium chloride plates.

**Electron Microscopy—Sample Preparation.** A small amount of the powder was placed in a test tube containing distilled water. The sample was then subjected to high-energy sonication (Di-Son-Tegrator, Model T-40CL, Ultrasonic Industries, Inc.) from 5 to 30 min depending upon the material involved. After sonication, the test tube was allowed to stand

for about 15 min to permit the sedimentation of the larger particles. A drop of the suspension was then placed upon a collodion membrane-covered electron microscope screen and allowed to evaporate at room temperature. The sample was shadowed under high vacuum with platinum and carbon at an angle of about 30° and covered with a carbon film at 90°C.

**Instrument.** All of the work was done using a Japan Electron Optics electron microscope JEM-6A.

## RESULTS AND DISCUSSION

In gas-phase polymerizations by means of photochemical or free-radical initiation, only vinyl compounds can be polymerized; and unless the monomer contains polar groups, only low molecular weight products are obtained. Furthermore, such monomers as, for example, styrene, acrylonitrile, methylisopropenyl ketone, and vinyl chloride, do not polymerize in the gas phase unless they are photosensitized.<sup>6</sup> Usually, the monomer vapor pressures required in these polymerizations are of the order of 30 torr and more.

Such polymerizations may be contrasted with the rf plasma-initiated gas-phase polymerization as follows. The polymerization is not limited to only the vinyl class of monomers. Many different types of monomers can be polymerized (see Tables I and II), including those that are not polymerized by any of the conventional polymerization techniques. In general, insoluble materials are obtained; however, under certain conditions soluble materials, although of low molecular weight, may also be obtained. Of the many different types of functional groups investigated, only certain oxygen-containing groups would seem to have a polymerization inhibiting effect. This could well be due to the generation of active oxygen atoms in the breakup of such groups, thus resulting in further oxidative degradation of the monomer and any polymer formed. In the case of our plasma system, the optimum monomer-vapor partial pressure for powder formation was found to be 0.6–2.80 torr.

### Polymerization Studies

Some general observations regarding powder formation in the plasma system, utilizing the reactor design depicted in Figure 1, are as follows. Optimum conditions for powder formation required different vapor pressure–rf power input combinations for practically every monomer investigated. To form powder exclusively, a monomer vapor partial pressure above 0.6 torr was required. The upper vapor pressure was a point at which the plasma tended to be extinguished and thus is related to the capacity of our present instrument rather than any polymerization characteristics. To generate the powder at a high rate, we believe, the design of the polymerization chamber is very important.

**Polymerization Chamber Design.** Of the three polymerization chambers investigated, the design depicted in Figure 1 outperformed the other two

TABLE I  
Monomers Polymerized Into Powder

Monomer	Amt. monomer used, g	Amt. powder, g	Conversion, %	Polymeriz. time, min	$\eta_{inh}^a$	Solubility, <sup>b</sup> %	Color
Styrene	2.10	0.38	18	13	0.06	90	light tan
Toluene	2.60	0.39	15	16	0.05	80	light tan
Benzene	2.41	0.43	18	28	0.03	90	tan
<i>p</i> -Xylene	2.95	0.41	14	20	0.05	50	light tan
Hexane	5.20	0.17	3	35	0.03	60	light tan
Isoprene	2.30	0.31	13	25	—	insol.	tan
Acetonitrile	3.05	0.40	13	20	0.04	80	dark tan
Vinyl Chloride	—	0.21	—	30	0.04	80	dark brown
Tetrabutyltin	2.00	0.19	10	25	0.02	70	tan
Styrene/divinylbenzene <sup>c</sup>	3.10	0.36	12	20	—	insol.	light tan
Styrene/1,2-dibromoethane <sup>c</sup>	2.90	0.29	10	16	0.04	90	brown

<sup>a</sup> Determined on solutions from 0.123 to 0.315 g/100 ml of tetrahydrofuran at 30.0°C.

<sup>b</sup> In tetrahydrofuran; the data represent the highest solubility observed of material collected during the first 5–10 min of polymerization.

<sup>c</sup> A 1:1 mixture (by weight).

TABLE II  
Monomers Forming Predominantly Film<sup>a</sup>

Monomer	Type of product
Ethylene	film
Acetylene	film and powder
Propylene	film
Butadiene	film and powder
1,2-Dibromoethane	film
1,2-Dichloroethane	film
1,1,2,2-Tetrachloroethane	film
Tetrafluoroethylene	film and powder
Perfluoropropionitrile	film and powder
4-Vinylpyridine	film
Methyl methacrylate	film
Trimethyl borate	film and powder
Borazine	film and powder
Tris-B-diethylaminoborazine	film and powder
Diphenyldiethoxysilane	film and powder
Benzene/borazine <sup>b</sup>	film and powder
Trimethylborate/ethylenediamine <sup>b</sup>	film and powder

<sup>a</sup> Better than 50% by weight of the product is in the form of a coherent film.

<sup>b</sup> A 1:1 mixture (by weight).

in the rate of powder formation despite its much smaller total chamber volume. The rate of powder formation was further increased by vertically filling the chamber with pieces of glass tubing and thus introducing turbulence in the plasma flow through the chamber. We believe the increased powder formation in this situation can be attributed to increased plasma convection by the circulation cells that are formed in the glass tubings. The large amount of powder formed at the base of most of the tubings would seem to support this contention.

**The Effect of Inert Gas.** It has been suggested that electron-impact ionization is the major source for charged-species generation in a glow discharge.<sup>7</sup> However, another important ionization mechanisms is the direct ionization by collision with sufficiently energetic, metastable neutral species. This process is known as the Penning ionization and becomes the major mechanism whenever helium and neon are used as one of the gas components.<sup>7</sup> For helium, neon, and argon, the excitation energy of the lowest triplet state is 19.80, 16.62, and 11.55 eV, respectively. Although the lowest triplet state in "active nitrogen" does not exist because of the very efficient quenching of it by nitrogen atoms,<sup>8</sup> "active nitrogen" is unique because of its extensive vibrational excitations which persist for long times beyond the discharge zone and thus lead to extensive chemi-ionization.<sup>7</sup> The ionization potential for most neutral gases is in the neighborhood of 15 eV. In our powder generation experiments with styrene (Table III), the amount of powder formed at the same conditions but with different inert gas components decreased from helium to nitrogen to neon to argon to air. The data, except for nitrogen, are suggestive of a Penning

TABLE III  
Dependence of Yield of Styrene Powder on Type of Inert Gas

Inert gas	Yield, %
Helium	18
Nitrogen	16
Neon	15
Argon	7
Air	3

ionization mechanism operating in the initiation of this polymerization. The very poor results with the air are, no doubt, due to the oxygen component.

**The Effect of Monomer.** Monomer characteristics contributed to the ease of powder formation in several ways. The aromatic hydrocarbons (styrene, toluene, benzene, *p*-xylene) led all the others in the amount of powder formed. This was also true in the ease of film formation but at lower monomer partial pressure and total pressure conditions in the reactor. The only alkane (hexane) investigated was also the most difficult to convert into polymeric powder. Monomers containing oxygen were difficult even to convert into films, and vinyl acetate and formaldehyde could not be polymerized under the conditions used. Tetrabutyltin, because of its high boiling point ( $\sim 295^\circ\text{C}$ ), was passed into the reactor from monomer reservoir E rather than J (Fig. 1). With one exception (vinyl chloride), gaseous monomers formed predominantly films, although in the case of tetrafluoroethylene and acetylene considerable amount of powder was also obtained. With liquid monomers, the boiling point seemed to play little if any role in the ease of powder formation as the data on isoprene (bp  $34^\circ\text{C}$ ) and tetrabutyltin (bp  $295^\circ\text{C}$ ) would suggest.

#### Characterization of the Products

**Solubility.** The solubility of all the powders in tetrahydrofuran decreased with increasing polymerization time. Although in no case have we obtained a completely soluble powder, in many cases high solubility (90%) was realized. The solubility of the powder appears to be extremely sensitive to the exact experimental conditions existing in the reactor, as different batches of the same powder prepared under supposedly identical conditions had different solubility characteristics. For this reason, monomer structure-solubility correlations are meaningless.

**Color.** The presence of halogen (fluorine, chlorine, or bromine) or nitrogen seemed to be the single most important variable relating to the discoloration of the product (film or powder). Monomers containing any one of these elements invariably gave colored products. Two exceptions to the above generalization were tetrabutyltin and acetylene, which also gave dark-colored products. In the case of tetrabutyltin, the coloration of the product seemed to be related to the position in the reactor—the closer it was to the excitation tube the darker the coloration.



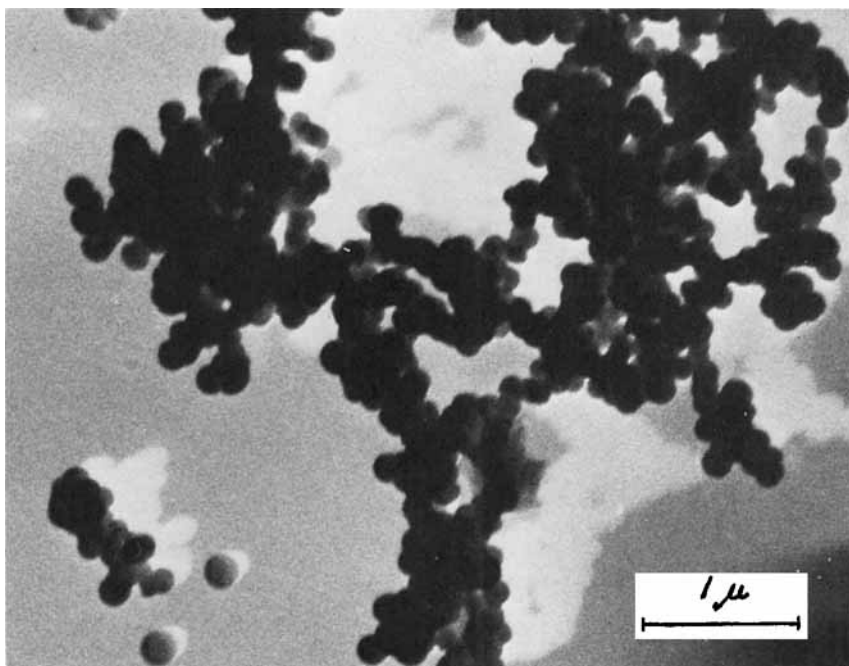


Fig. 3. As-prepared polystyrene powder.

**Viscosity.** Inherent viscosity was determined in tetrahydrofuran, and the data showed that regardless of the polymer involved, the soluble portion of it in all cases was of a very low molecular weight. Ways to minimize the crosslinking reactions are being explored.

**Infrared Spectroscopy.** *Polystyrene.* All of the absorptions of polystyrene present plus a new absorption as a shoulder at  $1700\text{--}1600\text{ cm}^{-1}$ . This could be due to aliphatic  $\text{C}=\text{C}$  stretching vibration, or saturated or  $\alpha,\beta$ -unsaturated ketone carbonyl stretching vibration.

*Polytoluene.* All of the absorptions of polystyrene present plus a new absorption at  $1700\text{ cm}^{-1}$  (see polystyrene).

*Polybenzene.* All of the absorptions of polystyrene present plus a new absorption at  $1720\text{--}1650\text{ cm}^{-1}$  (see polystyrene).

*Poly-p-xylene.* All of the absorptions of polystyrene present plus new absorptions at  $2230\text{--}2175\text{ cm}^{-1}$  (disubstituted  $\text{C}\equiv\text{C}$  stretching vibration) and  $1670\text{--}1600\text{ cm}^{-1}$  (CH out-of-plane deformation in  $\text{RRC}=\text{CHR}^9$ ).

*Polyhexane.* The following absorptions were present:  $3500\text{--}3300\text{ cm}^{-1}$  (moisture from KBr);  $3000\text{--}2900\text{ cm}^{-1}$  (CH stretching vibration in  $\text{CH}_3$ ,  $\text{CH}_2$ , and CH groups);  $2250\text{--}2150\text{ cm}^{-1}$  (disubstituted  $\text{C}\equiv\text{C}$  stretching vibration);  $1650\text{ cm}^{-1}$  (terminal  $\text{C}=\text{C}$  stretching vibration or internal  $\text{cis CH}=\text{CH}$ );  $1470$  and  $1385\text{ cm}^{-1}$  (CH deformation in  $\text{C}-\text{CH}_3$ ); the absorptions in the CH out-of-plane vibrations region were too weak for a definite assignment. The spectrum appeared similar to that of a paraffin oil (Nujol) except for the additional absorptions at  $2250\text{--}2150$  and  $1650\text{ cm}^{-1}$ .

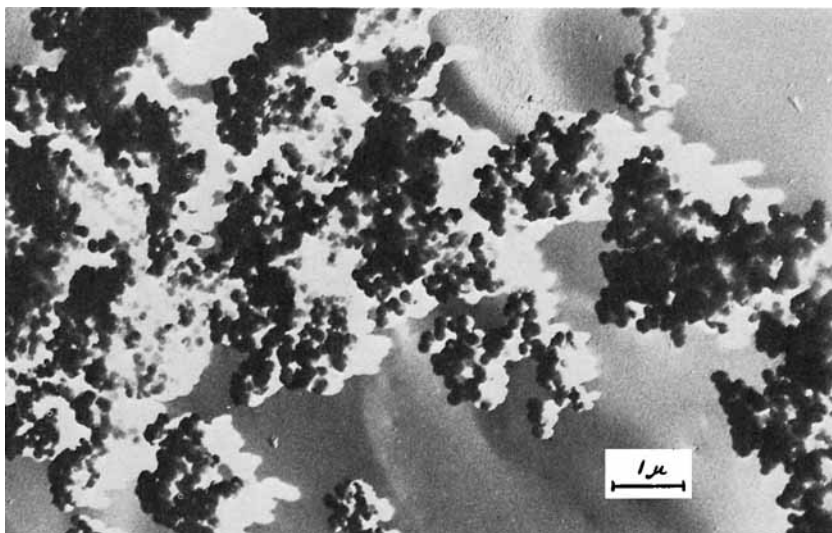


Fig. 4. As-prepared polytoluene powder.

*Polyisoprene.* The following absorptions were present: 3030–2900  $\text{cm}^{-1}$  (CH stretching vibration in  $\text{CH}_3$ ,  $\text{CH}_2$ , and CH groups); 2210–2170  $\text{cm}^{-1}$  (disubstituted  $\text{C}\equiv\text{C}$  stretching vibration); 1670–1610  $\text{cm}^{-1}$  (terminal  $\text{C}=\text{C}$  stretching vibration or internal cis  $\text{CH}=\text{CH}$ ); 1450 and 1375  $\text{cm}^{-1}$  (CH deformation in  $\text{C}-\text{CH}_3$ ); absorptions beyond 1100  $\text{cm}^{-1}$  too weak for a definite assignment.

*Polyacetonitrile.* Our powder contained all the absorptions listed by Deichert and Tobin<sup>10</sup> for their polyacetonitrile plus a weak absorption at 2250  $\text{cm}^{-1}$  (CN), very strong absorption at 2185  $\text{cm}^{-1}$  (conjugated  $\text{C}=\text{N}$ ), and strong absorption at 1115  $\text{cm}^{-1}$ . The assignment of these absorptions has been discussed before.<sup>11</sup>

*Poly(vinyl chloride).* All of the absorptions of poly(vinyl chloride) except for the absorption at 700  $\text{cm}^{-1}$  are present. Two new absorptions at 800  $\text{cm}^{-1}$  and 750  $\text{cm}^{-1}$  are present. The 750  $\text{cm}^{-1}$  absorption is present in poly(vinylidene chloride), and both the 800 and 750  $\text{cm}^{-1}$  absorptions are present in a rubber hydrochloride.<sup>12</sup>

*Poly(tetrabutyltin).* The following absorptions were present: 3000–2800  $\text{cm}^{-1}$  (CH stretching vibration in  $\text{CH}_3$ ,  $\text{CH}_2$  and CH groups); 1600  $\text{cm}^{-1}$  (absent in monomer; conjugated  $\text{C}=\text{C}$  or  $\text{C}=\text{O}$  stretching vibration); 1450 and 1385  $\text{cm}^{-1}$  (CH deformation in  $\text{C}-\text{CH}_3$ ); absorptions beyond 1100  $\text{cm}^{-1}$  too weak for a definite assignment.

*Poly(styrene/Divinylbenzene)* and *Poly(styrene/1,2-Dibromoethane).* Both materials contained the absorptions of polystyrene plus additional absorptions due to divinylbenzene or 1,2-dibromoethane.

*Some Film- and Powder-Forming Materials.* Some of the film- and powder-forming materials were examined in more detail. Thus, for example,

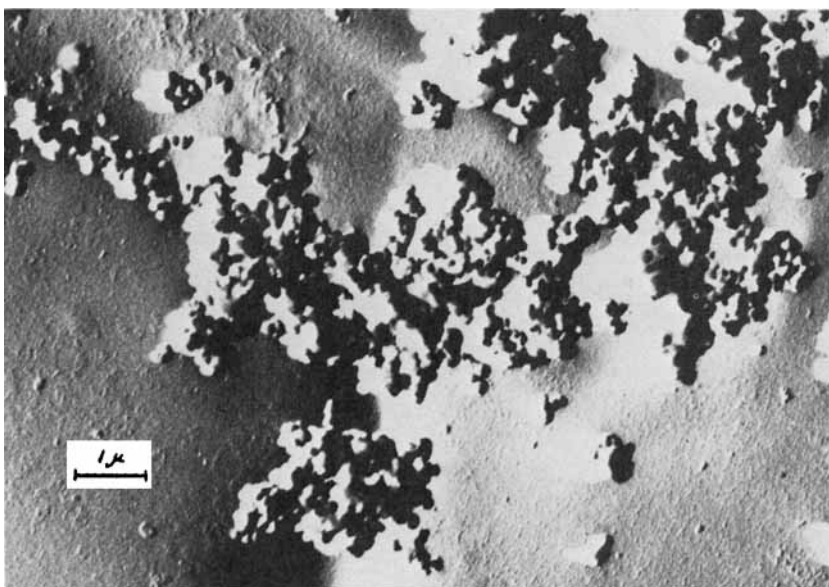


Fig. 5. As-prepared polybenzene powder.

the boron-containing monomers and monomer mixtures (borazine, trimethylborate, and benzene/borazine), except for tris-B-diethylaminoborazine, were the only materials that gave completely white powder or clear films. The diethylaminoborazine gave a dark, tan-colored product.

Although acetylene gave both dark-colored film and powder, the two products had some major differences in their infrared spectra: (1) the powder possessed a  $2250\text{--}2180\text{ cm}^{-1}$  absorption due to disubstituted  $\text{C}\equiv\text{C}$  group which the film material did not possess, and (2) the powder had a very strong absorption at  $1700\text{--}1610\text{ cm}^{-1}$  due to  $\text{C}=\text{C}$  and/or  $\text{C}=\text{O}$  groups which the film material did not possess. Minor differences in the infrared spectra between the film and powder materials were often noticed, however, those for polyacetylene products were the most unusual.

The two perfluoromonomers (tetrafluoroethylene and perfluoropropionitrile) yielded both a film and a powder. The poly(tetrafluoroethylene) powder formed had an infrared spectrum identical to that of commercial Teflon #6 powder in KBr with the absorptions at  $1260\text{--}1210$  and  $1180\text{ cm}^{-1}$ . The absorption at  $980\text{ cm}^{-1}$  that had been observed in photopolymerized fusible poly(tetrafluoroethylene) "floc" was absent in our powder.<sup>13</sup> The powder as well as the film that we obtained were dark, tan-colored, and not fusible.

**Electron Microscopy.** Electron photomicrographs were taken on the as-prepared polystyrene (Fig. 3), polytoluene (Fig. 4), and polybenzene (Fig. 5) powders. Initially, the materials examined were all in an agglomerated state. Effective breaking up of the agglomerate into individual

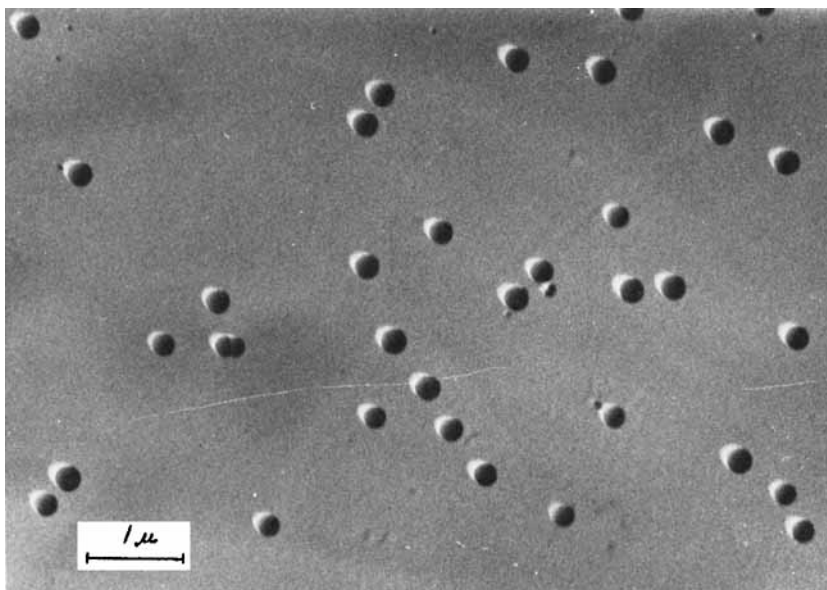


Fig. 6. Dispersed polystyrene powder.

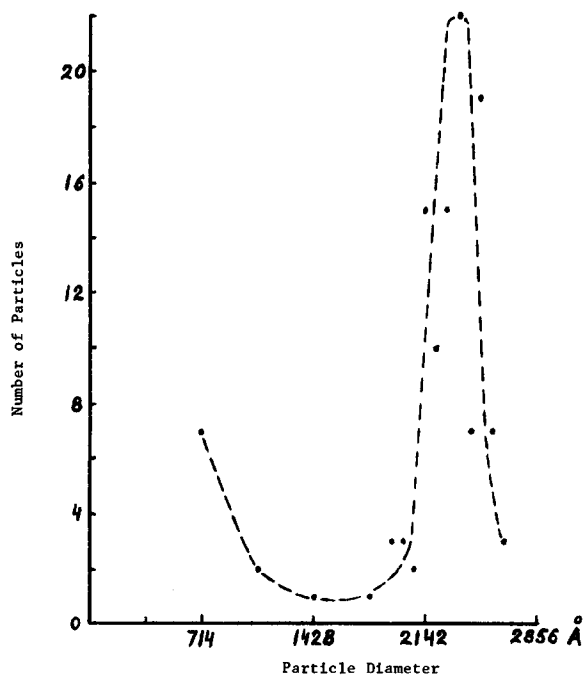


Fig. 7. Particle size distribution.

particles was accomplished in water by sonication. Because of the ease of polystyrene powder formation, it was examined in more detail. In Figure 6 are shown the individual polystyrene spheres from a 14-min preparation. In one of the higher concentration preparations, 117 particles were counted on the photomicrograph and their diameters measured. The particle-size distribution is plotted in Figure 7, giving 2357 Å as the most common particle-size diameter in this preparation. It is realized that a few photomicrographs cannot give a statistically valid picture of the size distribution of a bulk sample, and therefore no quantitative claims are made. In other polystyrene preparations the particle-size distribution was found to be much wider and increased with increasing polymerization time. To what extent particle initiation and growth can be regulated remains to be explored.

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