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Model Filled Polymers VIII. Synthesis of Crosslinked Polymeric Beads by Seed Polymerization

by

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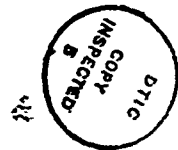
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<p>Monodisperse crosslinked polystyrene (PS) and polymethacrylate (PMA) beads of sizes greater than 1 <math>\mu</math>m in diameter are prepared by particle nucleation onto pre-existing polymer seeds in a multistage emulsion polymerization, in the absence of emulsifier. An adequate seed concentration, which decreases with increasing seed size, is necessary to achieve monodisperse beads. Monodisperse multicomposition beads are prepared by polymerizing styrene onto PMA seeds, but not by polymerizing methyl methacrylate onto PS seeds. Free radical capture by growing seed particles with surface polymerization may lead to the formation of asymmetric shaped particles.</p>			
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gradient: high, in the central region of the particle and dropping to a low value, in the peripheral region. At saturation, the swollen seed particles are encapsulated by a sheath of nearly pure monomer. Chung-li, Goodwin and Ottewill [5] found that the rate of swelling, of preformed latex particles by monomer, is too slow to account for the rate of particle growth. Therefore, a hetero-coagulation mechanism was proposed, in which coagulation of polymer particles freshly formed in solution onto seed particles, plays an important role in particle growth. New particles swollen with monomer would appear to transport monomer to pre-existing seed particles.

A free radical capture mechanism has been developed by Fitch and Shih [8] and Kao, Gundlach and Nelson [9], based on the classic mechanism of Smith and Ewart [10, 11]. In this model, sulfate free radicals, generated by the decomposition of persulfate initiator, react with styrene monomer dissolved in the aqueous phase to form oligomeric free radicals. These free radicals either enter latex particles, to initiate emulsion polymerization, eventually terminating inside the particle, or terminate in the aqueous phase.

Okubo *et al.* [13-15] prepared composite polymer particles, consisting of two different polymers, by seed polymerization, in the absence of emulsifier. They obtained anomalous particles with "raspberry-like" or "confetti-like" shapes and beads including voids. Dhingra [16] prepared seeded crosslinked resin beads with good fracture resistance by increasing crosslink densities.

By examining bead morphology, following successive stages of seed polymerization, we hope to adduce information relevant to the mechanism of particle growth.

## EXPERIMENTAL DETAILS

### Materials

Styrene monomer of 99% purity from Aldrich Chemical Co., is inhibited with 10-15 ppm 4-tert-butylcatechol (4-TBC). Divinylbenzene (DVB) is inhibited by  $\leq 1500$  ppm 4-TBC and

# **Model Filled Polymers. VIII. Synthesis of Crosslinked Polymeric Beads by Seed Polymerization**

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## **INTRODUCTION**

Recently, we reported on the preparation of crosslinked monodisperse polystyrene (PS) and polymethacrylate (PMA) beads in emulsifier-free emulsion polymerization [1, 2] and the rheological behavior of model filled polymers consisting of polymer beads in a PS matrix [3, 4]. It was found that PS beads with a diameter greater than 1  $\mu\text{m}$  could not be obtained in a single stage reaction [5]. In order to investigate the effect of bead size and surface composition on the rheology of filled polymers, seed polymerization, in the absence of emulsifier, was conducted in order to prepare crosslinked monodisperse PS beads exceeding 1  $\mu\text{m}$  diameter and, also, composite beads with layers of different compositions.

Seeded polymerizations have been conducted for several decades and various mechanisms proposed for the growth of latex particles. Uncrosslinked PS beads, of particle size greater than 1 $\mu\text{m}$ , were prepared by the seed polymerization of styrene without emulsifier [5]. Grancio and Williams [6] suggested that the growing particle consists of an expanding polymer-rich core surrounded by a monomer-rich shell, with the outer shell providing the major locus of polymerization. Keusch and Williams [7] proposed the existence of a polymer segment density

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contains 55% meta and para isomers, 42% ethyl vinyl benzene and 3% diethylbenzene. Styrene and DVB are washed with an equal volume of an aqueous solution of sodium hydroxide for 4 times, followed by deionized water for 4 times to remove the inhibitor before polymerization [1].

Methyl methacrylate [MMA] monomer, with an assay 98% and inhibited with  $25 \pm 5$  ppm hydroquinone (HQ), is a product of Fisher Scientific Co. Ethyl methacrylate [EMA] and n-butyl methacrylate [BMA] monomers, both 99% purity, are inhibited with 15 ppm and 10 ppm hydroquinone monomethyl ether (MEHQ), respectively, and are produced by Aldrich Chemical Co. Crosslinking agents, allyl methacrylate [AMA] and ethylene glycol dimethacrylate [EGDMA], both 98% purity, are inhibited with 50-185 ppm HQ and 100 ppm MEHQ, respectively, and are purchased from Aldrich Chemical Co. The initiator, potassium persulfate [ $K_2S_2O_8$ ], is a certified Fisher Scientific product; the water used for polymerization and washing is deionized water from Sparkletts; methanol is analytical reagent grade from Mallinckrodt Co.; and nitrogen is purchased from MG Industries Gas Products.

## Polymerization

Polymerizations were conducted in 1-liter or 3-liter resin reaction flasks with internal stirring. Flasks were immersed in a thermostated water bath to maintain constant temperature. A water-cooled condenser, connected to the atmosphere via a wash-bottle containing water, to prevent back-diffusion of oxygen into the reaction system, is fixed to the reactor. Nitrogen is continuously bubbled through a thin teflon tube into the reactor.

### (1) Continuous polymerization

140 g prewashed styrene and DVB monomers (double that of typical batch reactions [1, 2]) were continuously added dropwise into a stirred reactor containing water and initiator at 80°C for 16 hours. Stirring and bubbling were continued at 80°C for another 8 hours, until the polymerization was complete.

## **(2) Seed preparation**

The preparation of crosslinked PS, polymethylmethacrylate (PMMA), polyethylmethacrylate (PEMA) and polybutyl methacrylate (PBMA) beads, which are used as seed latices, was described in previous publications [1, 2]. Seed latices obtained were either left (partially) in the reactor for seeded polymerization in a "continuous" particle growth process, or removed from the reactor and stored at 5°C, for subsequent use in "discontinuous" seeded polymerization.

## **(3) Continuous particle growth process**

After batch polymerization proceeds for several hours and the initial monomer is almost exhausted, a fraction of the latex formed is removed from the reactor. A desired amount of latex remaining in the reactor is used for a subsequent stage of reaction. Hot water, preheated to the reaction temperature, and subjected to nitrogen flow for at least 15 minutes, and styrene monomer and DVB crosslinking agent, which had been previously washed with an aqueous solution of sodium hydroxide and water, are added to the reactor, containing preformed seed latex. Stirring is resumed, while nitrogen bubbling has been continuous. 30 minutes later, additional initiator is added, and the reactants kept for specified hours at the selected temperature. For methacrylate monomers, prewashing was not necessary [2], and methacrylate monomers are added to the reaction, directly.

This procedure is repeated for successive stages of seed polymerization. 2 g samples were taken at the end of each stage to examine bead morphology and conversion.

## **(4) Discontinuous seed polymerization**

In this procedure, we utilize an empty reactor for each stage. Preformed seed latex, water and monomer are added into a reactor, stirred and bubbled with nitrogen for 30 minutes. Initiator, dissolved in a small amount of water, is added to start seed polymerization. Stirring and nitrogen

bubbling are continued, at the desired temperature, until the reaction is complete. The latex formed was used both as final product or as the seed for further growth. In this way, 4-stage reactions were completed stepwise.

### Scanning Electron Microscopy

For morphology studies, bead size and shape are determined with a scanning electron microscope (Cambridge Stereoscan model 360). Details were reported in a previous publication [1].

## RESULTS

In a continuous polymerization at 80°C, by adding a styrene and DVB mixture dropwise for 16 hours and using 140 g monomers, we obtained spherical PS beads, 391 nm in diameter.

Fig. 1 shows bead morphologies obtained from successive stages of a 4-stage seeded polymerization, involving a "continuous" process of copolymerizing styrene and 1% DVB by weight. Reaction conditions and results are listed in Table 1. Since free radicals persist in the seed latex, a reduced amount of  $K_2S_2O_8$  initiator was added. The overall conversion increased after each step. Conversions were determined by gravimetry and calculated according to the following equations:

For the first stage of reaction, e.g., the seed preparation stage,

$$\text{Conversion} = \frac{W_{ds}}{[W_{mo} / (W_{wa} + W_{mo})] \times W_{sa}} \quad (1)$$

For successive polymerizations,

$$\text{Conversion} = \frac{W_{ds} - [(C_{se} W_{se}) / (W_{wa} + W_{se} + W_{mo})] \times W_{sa}}{[(W_{mo}) / (W_{wa} + W_{se} + W_{mo})] \times W_{sa}} \quad (2)$$

where  $W_{ds}$ ,  $W_{mo}$ ,  $W_{wa}$ ,  $W_{se}$ , and  $W_{sa}$  are the weights of the dried polymer sample, "fresh" monomer, water, seed latex and sample latex, respectively;  $C_{se}$ , is the weight fraction of PS seed particles in the latex.

As can be seen from Fig. 1, crosslinked PS beads obtained from each of the 4 stages were monodisperse in size. In general, we have observed that, if the seed particle concentration is high enough, monodisperse sized seeded beads can be obtained. If a lower seed concentration were used, new small particles are initiated, yielding a polymodal size distribution (Fig. 3D).

A continuous polymerization of styrene was carried out in a 3-stage reaction at 60°C with 1 weight% DVB, without additional initiator added after the first stage. In order to sustain the reaction, as long as possible, more initiator (640 mg) was added at the beginning of the reaction. Details of this reaction are shown in Table 2. Although the reaction continued without additional initiator, the conversion, calculated using Equations (1) and (2), decreased in each stage, because of free radical depletion, and was only 9% in the 3rd stage, after 24 hours reaction. Beads obtained by this technique are shown in Fig. 2.

Often, as shown in Fig. 1, seeded beads are nonspherical, especially after the 3rd and 4th stages. Using similar reaction conditions as those in Table 1, but with a higher DVB content, 5 weight% (Fig. 3), or without DVB (Fig. 4), beads obtained after each successive stage are perfectly spherical. A reaction carried out at 80°C, with the same reactant concentrations as shown in Table 1, produced spherical particles (Fig. 5). Fig. 6 shows bead morphologies of crosslinked PS from stages of a typical discontinuous seed polymerization in a 3-liter resin reaction flask at 60°C. In general, in the copolymerization of styrene and DVB, seeded beads are extremely spherical after the 2nd and 3rd stage of reaction (Figs. 6B, C). Beads formed after a 4th stage of growth were mostly spherical if the DVB content was higher than the 3rd stage, but were

not spherical if the DVB content was equal to the 3rd stage (Fig. 6D). Other experiments show that even with equal DVB content (1 weight%) in the 1st, 2nd and 3rd stages of the reaction, the beads obtained from each stage were also spherical.

Fig. 7 shows the second and third stages of uncrosslinked PEMA beads prepared by continuous particle growth.

Fig. 8B shows composite beads with a PS core crosslinked with 1 mol% DVB (Fig. 8A) and a PMMA shell crosslinked with 5 mol% EGDMA. These composite beads were not monodisperse.

Fig. 9 shows composite beads with a crosslinked PMMA core (Fig. 9A) and crosslinked PS shell. Such seeded beads are extremely monodisperse in size (Fig. 9B).

Fig. 10 shows PBMA beads crosslinked with 1 mol% AMA (A) and core/shell beads consisting of A (as the core) and crosslinked PS shell (B), which are also monodisperse.

Corresponding reaction conditions for composite beads are listed in Table 3.

## DISCUSSION

In order to increase the size of polymeric beads from emulsion polymerization in the absence of emulsifier [1, 2], alternative reaction routes have been examined in our laboratory. Spherical PS beads obtained from *continuous* polymerization with 140 g of monomer, were only 391 nm in diameter, and monodisperse in size, compared to 450 nm for typical batch reaction at 80°C, with 70 g of monomer [1]. In the beginning of continuous polymerization, styrene monomer did not saturate the aqueous phase before the addition of initiator. Since initiator was added *before* monomer, and the aqueous solubility of the monomer was increased by the attachment of polar sulfate groups after reaction with initiating radicals, it is possible that an

increased amount of monomer polymerizes from the aqueous phase, reducing the monomer concentration in water. Fresh monomer added dropwise dissolves in the aqueous phase and particle nucleation [17] occurs continuously as polymerization occurs. Therefore, more particles form and a smaller particle size is obtained. Another possibility, is that a larger amount of surface active oligomeric PS chains are produced leading to an increased concentration of micelles [18], more growing particles and a smaller final particle size.

Apparently, the best way to obtain larger size polymer beads is by seed polymerization with a preformed polymer latex, with a controllable seed particle concentration, either by a "continuous" or "discontinuous" particle growth process [Figures 1 and 6]. In this way, not only can single polymer beads of larger size be made, but composite beads, with a different polymer composition in successive layers, can be prepared, as well. The main difference, between "continuous" and "discontinuous" particle growth processes, is that many free radicals are left in a "continuous" process, from the previous stage. Ordinarily, even though no additional initiator is added to the seeds, particle growth proceeds after the addition of fresh monomer and water to a suspension of beads. However, without added initiator, polymer yields were low [Table 2], but resulting beads are almost spherical [Figure 2].

The monodispersity in size of the final beads strongly depends on the seed concentration in the reaction. Perhaps, there is a critical value of the seed particle concentration for a specific polymer. If the seed particle concentration exceeds this critical value, resultant particles are monodisperse in size. Otherwise, small particles are formed in a later stage of polymerization, producing a polymodal size distribution [Figure 3D]. Here, in stage four, the seed particle concentration was reduced sufficiently for new particle initiation to compete with seed growth, allowing the formation of new (small) particles. In order to obtain monodisperse beads after the second stage [Figure 1], we used about 45% of the original latex as seeds. The critical seed particle concentration, also, appears to be related to particle size. In order to obtain monodisperse sized seeded beads, a higher concentration of seed particles of smaller size are needed than for

particles with a larger size. For example, in the continuous reaction listed in Table 1, the growing particle number was decreased in each stage of reaction. In the fourth stage, the number of growing particles was less than one fourth of that in the second stage, but monodisperse seeded beads were obtained after the fourth stage of reaction [Figure 1]. However, if we used such a small seed particle number in the *second* stage of reaction, where seed particles are much smaller, monodisperse seed particles are *not* obtained. Mostly monodisperse uncrosslinked PEMA beads were also prepared in a multistage process [Figure 7].

For multicomposition beads, it was very difficult to get monodisperse sized seeded particles, if seed latex particles were composed of a monomer of lower water solubility than the monomer used for the shell. For example, composite seeded beads with PS as the core and PMMA as the shell are not monodisperse [Figure 8]. However, if we use PMMA or PBMA seed particle latex, with higher monomer water solubility, as the cores, and PS, with lower monomer water solubility, as the shell, it was easy to obtain monodisperse sized seeded polymer beads [Figures 9 and 10], even though a smaller volume of seed latex was used [Table 3]. The formation of monodisperse sized beads which are asymmetric in composition may be a result of differences in nucleation mechanism. For example, if the "shell" polymer is more water soluble and can undergo homogeneous nucleation from the aqueous phase [17], competition exists between seed nucleation and homogeneous nucleation and some homogeneous nucleation occurs, leading to bimodality of size. However, if the "shell" polymer undergoes a micellization mechanism of nucleation [18], the adsorption of surface active PS oligomers onto preformed beads, precludes further particle nucleation.

In some cases of seed polymerization, subsequent particle growth occurred at one point of the seed particle surface [Figure 1: C, D; and Figure 6: D]. This may be evidence for a free radical capture mechanism for seed polymerization. In accord with Smith and Ewart [10, 11], growing polymer particles in emulsion polymerization undergo alternating periods of "activity" and "inactivity", as free radicals enter and, alternately, initiate or terminate polymerization. As a

result, the average number of free radicals per particle,  $\bar{n}$ , equals 0.5. Recent studies on emulsion polymerization, in the absence of added emulsifier, indicate that  $\bar{n}$  is not constant, but increases, from 0.5 in stage 1, almost linearly with conversion during stage 2 of batch emulsion polymerization [19, 20]. The exact value of  $\bar{n}$  depends on monomer and initiator concentrations and may approximate the order of 100. The direct observation and measurement of the concentration of propagating free radicals in the emulsion polymerization of MMA by electron spin resonance spectroscopy has been reported [21-23]. For particle sizes of about 500 nm, the average number of propagating radicals approximated 700 at a polymerization temperature of 60°C [24]. By analogy to ordinary emulsion polymerization, the growth of seed particles, in the continued polymerization of pre-existing seed particles in emulsion, also involves free radical capture. Such radicals are probably oligomeric radicals from the reaction of free radical initiator fragments with monomer dissolved in the aqueous phase.

Perhaps, as the seed particle grows in size, the number of free radicals captured per particle also increases [18, 24]. As a result, the conversion increases in each stage in seed polymerization in the "continuous" process [Table 1]. However, it would be necessary that an adequate supply of free radicals be available. The half-life of  $K_2S_2O_8$  at 60°C is 61 hours [25], so that added persulfate is needed at each stage of seeded polymerization to sustain a rapid polymerization. If additional initiator is not added in successive stages of "continuous" seed polymerization, the conversion decreases [Table 2].

We suggest that, in successive stages of seed polymerization, secondary nucleation on pre-existing seed particles competes with primary nucleation by the generation of *new* growing particles. For monomers, such as styrene, with extremely low water solubility [26, 27], primary nucleation by a micellization mechanism [18] is *not* favored compared to nucleation on seeds. Perhaps, oligomeric free radicals are captured by large seed particles, rather than form micelles and initiate new particle growth. As a result, a unimodal distribution of large particles often results [Figures 1, 4, 5, 7, 9, 10].

When a seed particle captures an oligomeric free radical, ordinarily, this surface active species aligns itself with the sulfate ion, from the initiator fragment, on the seed surface and the growing free radical in the interior of the bead. Continued polymerization inside the bead, but near the surface, leads to spherical particles. However, if the free radical is located on the bead surface, then subsequent polymerization may lead to protrusions and asymmetric beads. Occasionally, double particles were observed in "discontinuous" seed polymerization [Figure 6: D, particle  $\mathcal{K}$ ]. In a count of 376 particles in the scanning electron micrograph, 13 double particles, about 3%, were found. We suggest that termination of polymeric radicals on the surfaces of growing particles, by combination, lead to such double particles. It has been proposed that emulsion polymerization occurs on the bead surface for these systems [28]. With increasing particle size, monomer diffusion into growing particles becomes polymerization rate determining and a concentration gradient is established with a decreasing monomer concentration toward the particle center, leading to inhomogeneous polymerization for large particle sizes [24]. Small-angle neutron scattering analyses of PS latex particles establish that the particles have a core-shell structure, with the locus of polymerization at the particle surface [29-31]. A study of the seeded emulsion polymerization of styrene onto PMMA seeds, indicates composite particles characterized by a heterogeneous morphology of three types of PS domains [32].

We have identified two frequent deviations from monodisperse spherical beads: asymmetric beads containing protrusions [Figure 1: C and D] or bimodal size distributions [Figure 3: D]. The formation of protrusions was sensitive to the concentration of DVB and to temperature [Figures 1, 3-6]. In the continuous growth process, particles with protrusions formed only in successive stages of seed polymerization of PS with 1 weight% DVB at 60°C [Figure 1]. However, spherical beads were obtained with 5% DVB or no DVB at 60°C and, even with 1% DVB at 80°C. In "discontinuous" seed polymerization [Figure 6], DVB content does not appear to affect the bead shape of crosslinked PS beads after the first three stages of reaction [Figure 6: A, B, C]. After the fourth stage of reaction, with DVB content higher than the third stage, mostly spherical seeded particles form. If the DVB content were equal to the third stage, protrusions form

on seeded particles and double beads are observed [Figure 6: D].

We have suggested that asymmetric beads result from reactions of surface free radicals. It is reasonable that the concentration of surface free radicals depends on DVB concentration and temperature. Also, in repeated seed polymerization, the ultimate concentration of beads becomes very low. As a result, competition between bead growth, by the absorption of oligomeric free radicals onto pre-existing beads, and the formation of new particles, by micellization of oligomeric free radicals in the aqueous medium, allows some formation of new particles.

## CONCLUSIONS

Monodisperse crosslinked PS and PMA beads of sizes exceeding 1  $\mu\text{m}$  in diameter may be prepared in a multistage emulsion polymerization, in the absence of emulsifier, by particle nucleation onto pre-existing polymer seeds. In addition to control of bead size, specific crosslinking and compositional gradients can be selected. Monodispersity of final bead size requires an adequate seed concentration at the beginning of polymerization; otherwise, a polymodal size distribution results. In order to obtain monodisperse PS beads in a *second* stage, using PS seeds approximately 500 nm in diameter, a critical seed concentration of about 16.9 grams/l was required. The critical concentration could be reduced by increasing the seed particle size.

Monodisperse sized seeded multicomposition beads were prepared by polymerizing styrene monomer onto PMA seeds, but not for the reverse process. In successive stages of seed polymerization, secondary nucleation on pre-existing seed particles competes with primary nucleation and the formation of new growing particles. For monomers of very low aqueous solubility, such as styrene, secondary nucleation predominates. On the other hand, MMA monomer undergoes primary nucleation, as well as polymerization onto pre-existing PS seeds, yielding a polymodal particle distribution.

Free radical capture by growing seed particles is a likely mechanism for seed polymerization. As the particle grows in size, the number of free radicals captured by growing particles increases and the rate of polymerization accelerates. Free radical capture with *surface* polymerization may lead to the formation of asymmetric shaped particles. The formation of protrusions on PS beads occurred at 1% DVB concentration in the later stages of seed polymerizations at 60°C.

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**TABLE 1.****Continuous Seed Polymerization of Crosslinked PS**

		1st Stage	2nd Stage	3rd Stage	4th Stage
Seed Latex Vol.	(ml.)		350	350	350
Styrene	(g.)	69.3	69.3	69.3	69.3
DVB	(g.)	0.7	0.7	0.7	0.7
Water	(ml.)	700	350	350	350
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	(mg.)	320	240	240	240
Temperature	(°C)	60	60	60	60
Reaction Time	(hrs.)	12	12	12	12
Conversion	(%)	41	63	89	100
Particle Size	(μm)	0.47	0.66	1.07	1.42

**TABLE 2.****Continuous Seed Polymerization of PS without Additional Initiator**

		1st Stage	2nd Stage	3rd Stage
Seed Latex Vol.	(ml.)		200	200
Styrene	(g.)	69.3	69.3	69.3
DVB	(g.)	0.7	0.7	0.7
Water	(ml.)	700	500	500
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	(mg.)	640	0	0
Temperature	(°C)	60	60	60
Reaction Time	(hrs.)	12	20	24
Conversion	(%)	71	52	9.2
Particle Size	(μm)	0.599	0.979	1.10

**TABLE 3.**

**Seed Polymerization to Prepare Composite Beads**

		PS core	PMMA shell	PMMA core	PS shell	PBMA core	PS shell
Seed latex vol.	(ml.)		350 <sup>(b)</sup>		150 <sup>(a)</sup>		250 <sup>(a)</sup>
Styrene	(ml.)	228.5 <sup>(a)</sup>			186.0		186.0
DVB	(ml.)	5.2			22.1		22.1
MMA	(ml.)		67.5	219.3 <sup>(a)</sup>			
BMA	(ml.)					232.8 <sup>(a)</sup>	
AMA	(ml.)					2.0	
EGDMA	(ml.)		6.25	3.91			
Water	(ml.)	2100	350	2100	1650	2100	1550
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	(mg.)	960	100	300	411	300	411
Temperature	(°C)	60	60	70	60	70	60
Bead diameter	(nm)	663	1030	315	927	410	924

(a) The reaction was conducted in a 3-liter resin reaction flask.

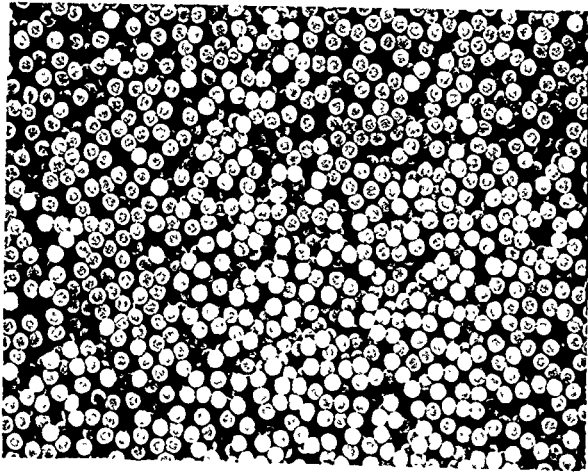
(b) The reaction was conducted in a 1-liter resin reaction flask.

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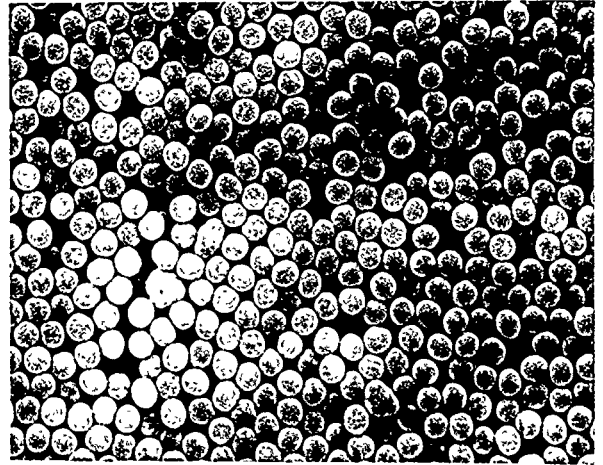
1. Monodisperse PS beads, crosslinked with 1 weight % DVB prepared by "continuous" seed polymerization at 60°C (experimental details in Table 1), scanning electron micrographs, magnification 5000x.
  - A. After the first stage of polymerization, bead diameter 473 nm;
  - B. After the 2nd stage of seeded polymerization; using the latex from A as the seed; bead diameter 663 nm;
  - C. After the 3rd stage of seeded polymerization, using the latex from B as the seed; bead diameter 1.07  $\mu\text{m}$ ;
  - D. After the 4th stage of seeded polymerization, using the latex from C as the seed; bead diameter 1.42  $\mu\text{m}$ .
  
2. PS beads, crosslinked with 1 weight % DVB, prepared by "continuous" seed polymerization at 60°C *without* additional initiator (experimental details in Table 2), scanning electron micrographs; magnification 5000x.
  - A. After the 1st stage of reaction, bead diameter 599 nm;
  - B. After the 2nd stage of reaction, bead diameter 979 nm;
  - C. After the 3rd stage of reaction, bead diameter 1.10  $\mu\text{m}$ .
  
3. PS beads, crosslinked with 5 weight % DVB, prepared by "continuous" seed polymerization at 60°C, scanning electron micrographs; magnification 5000x.
  - A. After the 1st stage of reaction, bead diameter 505 nm;
  - B. After the 2nd stage of reaction, using the latex from A as the seed, bead diameter 852 nm;
  - C. After the 3rd stage of reaction, using the latex from B as the seed, bead diameter 1.32  $\mu\text{m}$ .
  - D. After the 4th stage of reaction, using the latex from C as the seed, seeded bead diameter 2.08  $\mu\text{m}$ .
  
4. Uncrosslinked PS beads prepared by "continuous" seed polymerization at 60°C, scanning electron micrograph, magnification 10,000x.
  - A. After the 2nd stage of reaction, using latex from a 1st stage reaction (not shown) as the seed, bead diameter 643 nm;
  - B. After the 3rd stage of reaction, using the latex from A as the seed, bead diameter 1.29  $\mu\text{m}$ .

5. PS beads, crosslinked with 1 weight % DVB by "continuous" seed polymerization at 80°C, scanning electron micrographs, magnification 5000x.
  - A. After the first stage of reaction, bead diameter 441 nm;
  - B. After the 2nd stage of reaction; using the latex from A as the seed; bead diameter 631 nm;
  - C. After the 3rd stage of reaction, using the latex from B as the seed; bead diameter 820 nm.
  - D. After the 4th stage of reaction, using the latex from C as the seed; bead diameter 1.04  $\mu\text{m}$ .
  
6. Crosslinked PS beads after "discontinuous" seed polymerization at 60°C, scanning electron micrographs, magnification 5000x.
  - A. 1st stage latex particles of PS with 1 mol % DVB, bead diameter 663 nm;
  - B. Seeded beads, using the latex from A as the seed, the 2nd addition of PS contains 5 mol % DVB, bead diameter 947 nm;
  - C. Seeded beads using the latex from B as the seed, the 3rd addition of PS contains 10 mol% dVB , bead diameter 1.64  $\mu\text{m}$ ;
  - D. Seeded beads using the latex from C as the seed, the 4th addition of PS contains 10 mol % DVB, bead diameter 1.73  $\mu\text{m}$ . Bead  $\mathcal{R}$  is a "double" bead.
  
7. Uncrosslinked PEMA beads prepared by "continuous" seed polymerization, scanning electron micrographs.
  - A. After the 2nd stage of reaction, using the seed latex from the 1st stage reaction as the seed (not shown) magnification 5000x. Bead diameter 851 nm.
  - B. After the 3rd stage of reaction, using the seed latex from A as the seed, magnification 10,000x, bead diameter 1.40  $\mu\text{m}$ .
  
8. Composite beads: crosslinked PS core/crosslinked PMMA shell, prepared by seed polymerization (experimental details in Table 3), scanning electron micrographs, magnification 5000x.
  - A. PS (core) beads crosslinked with 1 mol % DVB, bead diameter 663 nm;
  - B. Seeded composite beads using PS latex from A as the seed, 5 mol % EGDMA-MMA as the shell.

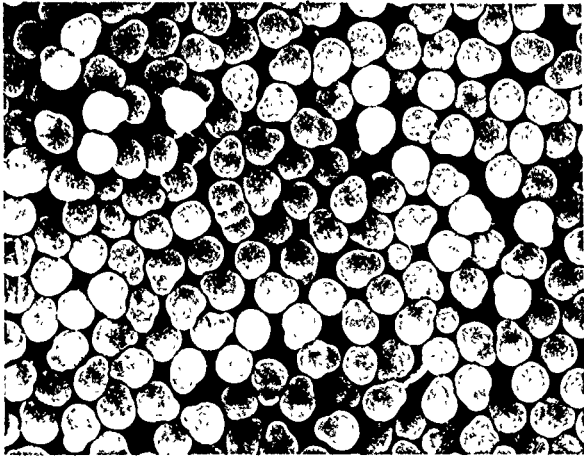
9. Composite beads: crosslinked PMMA core/crosslinked PS shell, prepared by seed polymerization (experimental details in Table 3), scanning electron micrographs.
  - A. PMMA core beads crosslinked with 1 mol % EGDMA, magnification 5000x, bead diameter 315 nm;
  - B. Seeded composite beads using A as the core, 5 mol % DVB-PS as the shell, magnification 10,000x, bead diameter 927 nm.
  
10. Composite beads; crosslinked PBMA core/crosslinked PS shell, prepared by seed polymerization (experimental details in Table 3), scanning electron micrographs.
  - A. PBMA (core) beads crosslinked with 1 mol % AMA, magnification 5000x, bead diameter 410 nm;
  - B. Seeded composite beads using A as the core, 5 mol % DVB-PS as the shell, magnification 10,000x, bead diameter 924 nm.



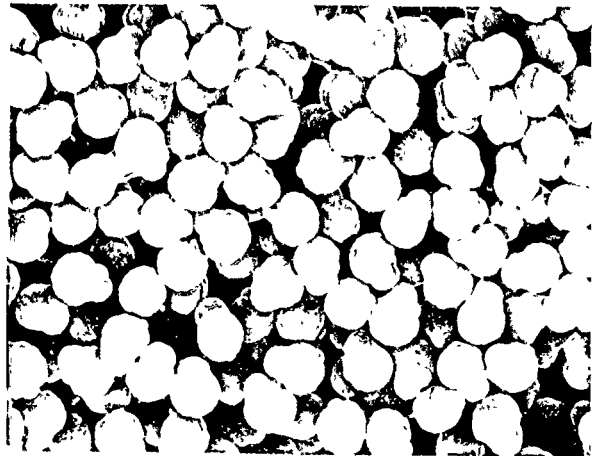
A



B

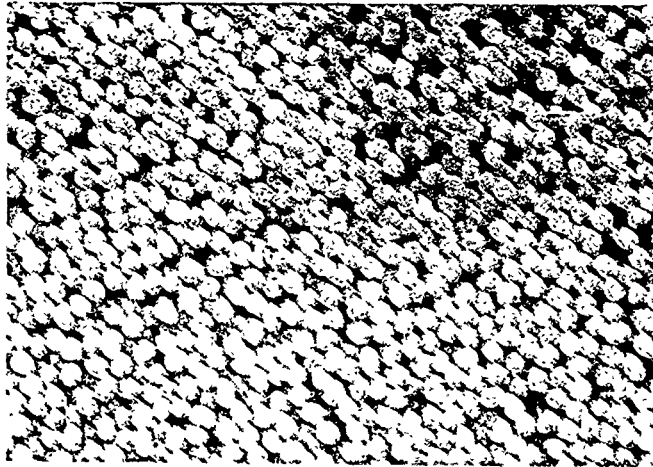


C

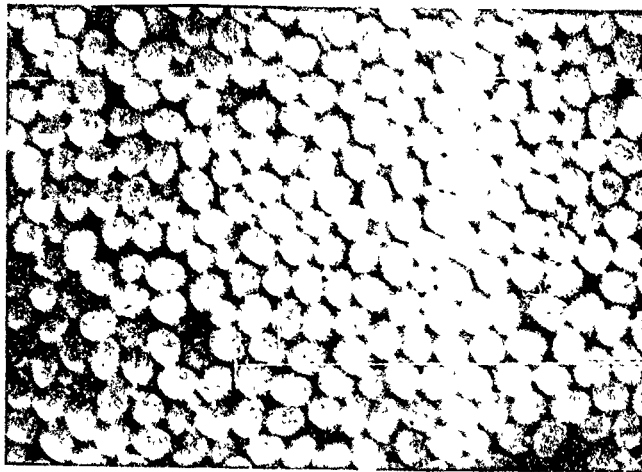


D

FIGURE 1



A

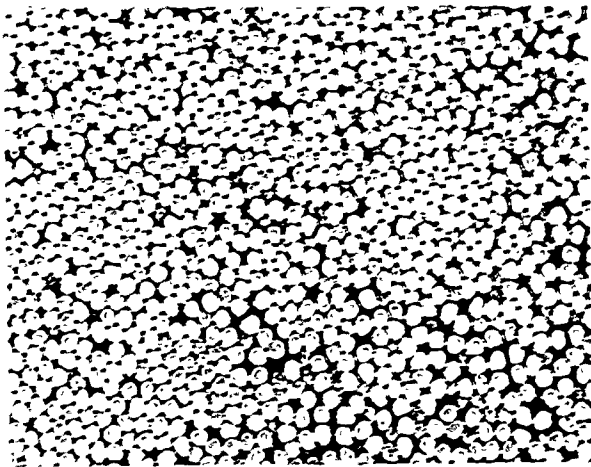


B

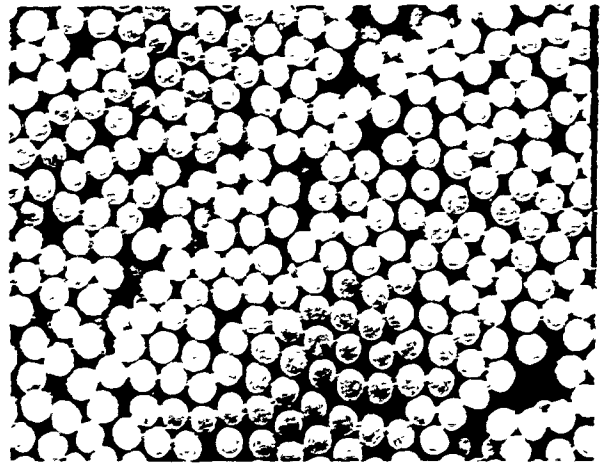


C

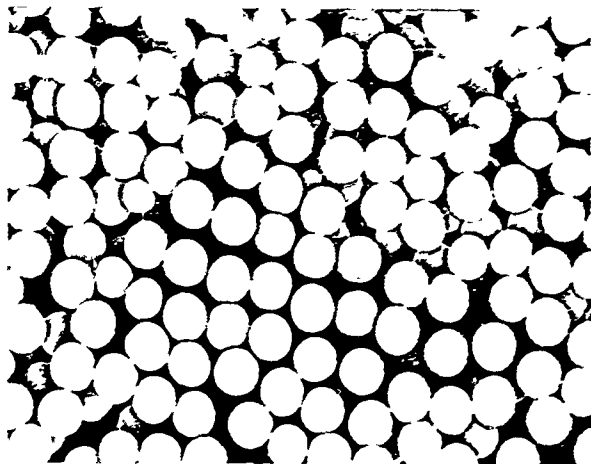
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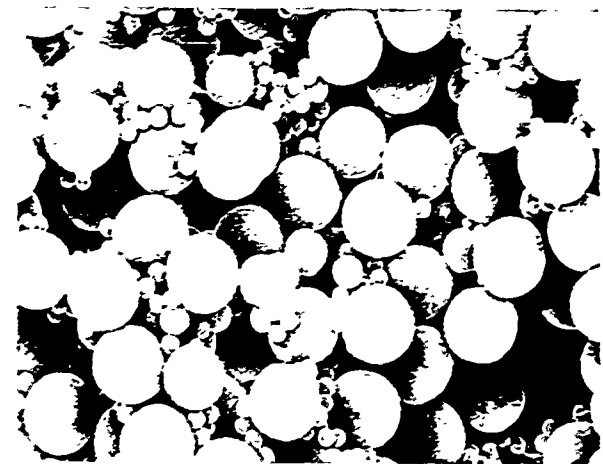
**A**



**B**

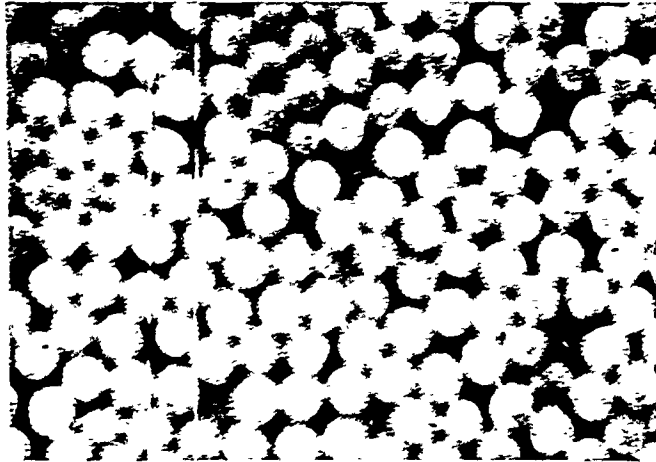


**C**

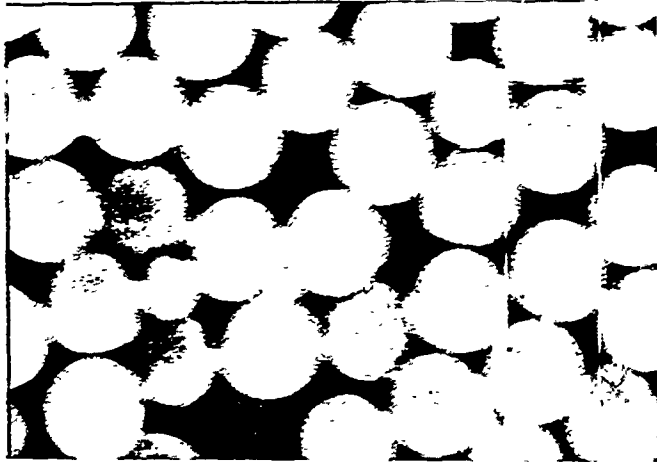


**D**

**FIGURE 3**

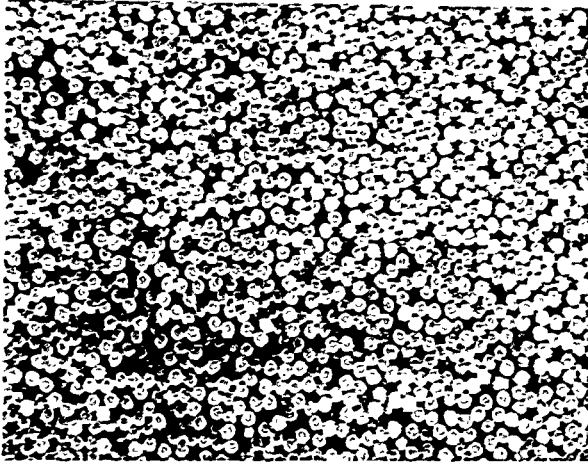


A

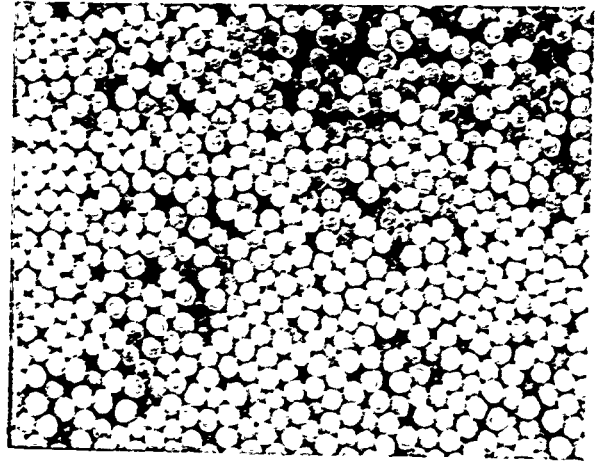


B

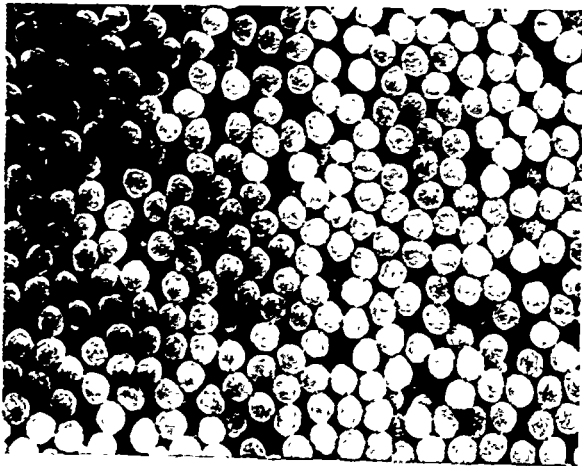
**FIGURE 4**



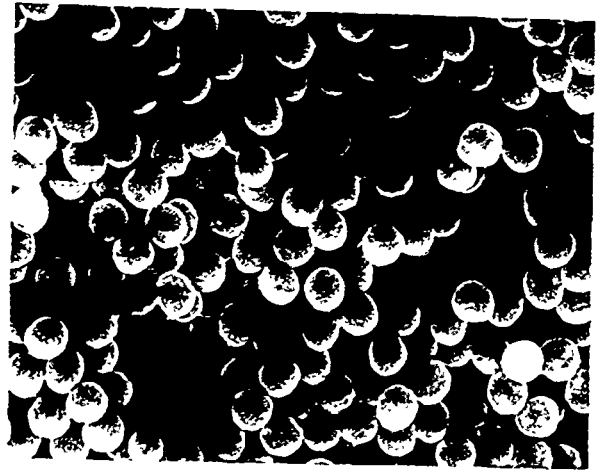
**A**



**B**

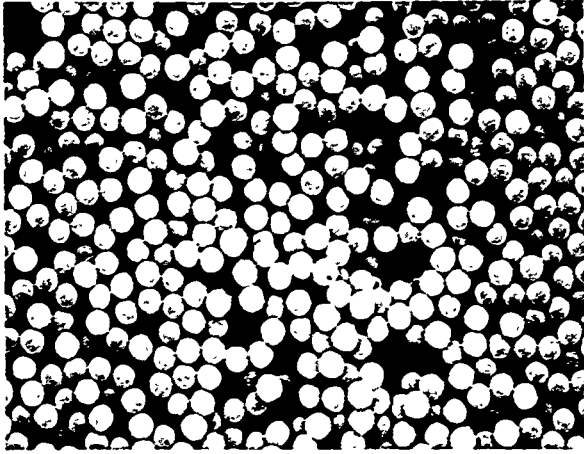


**C**

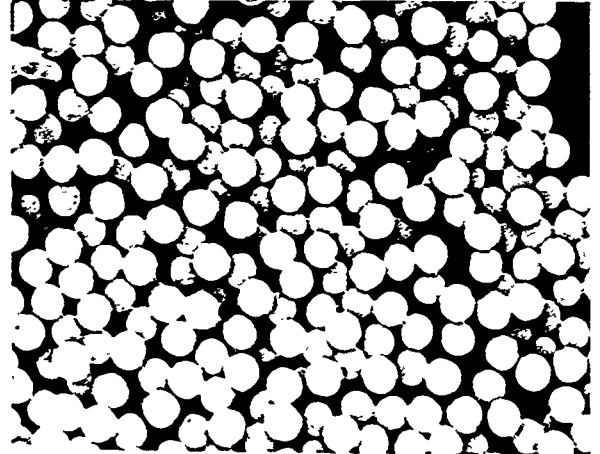


**D**

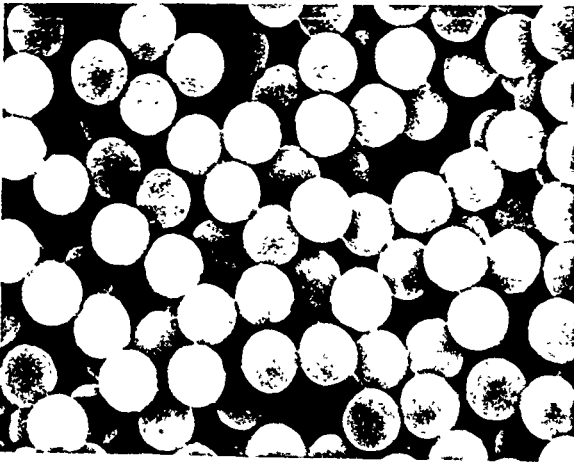
**FIGURE 5**



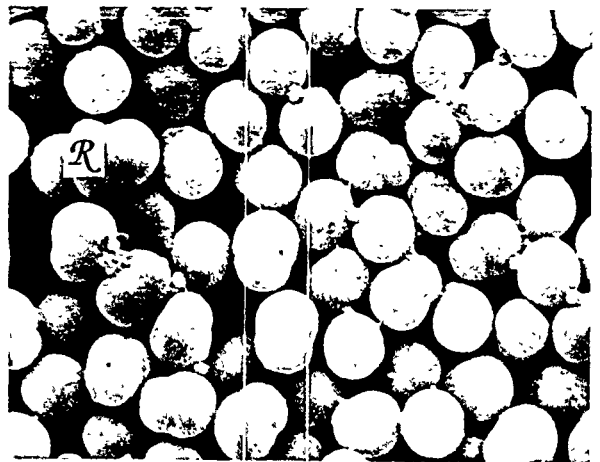
A



B

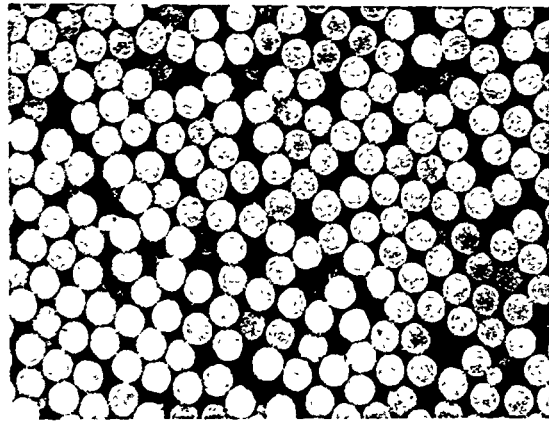


C

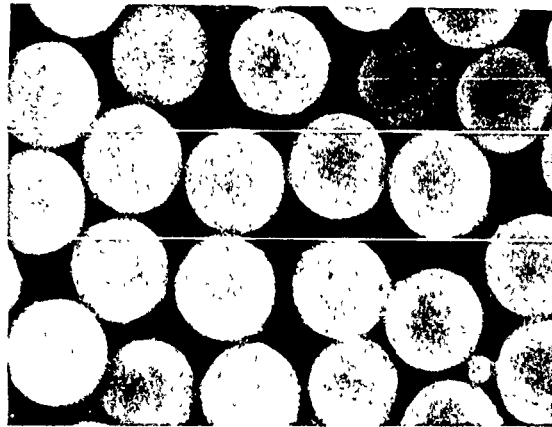


D

FIGURE 6

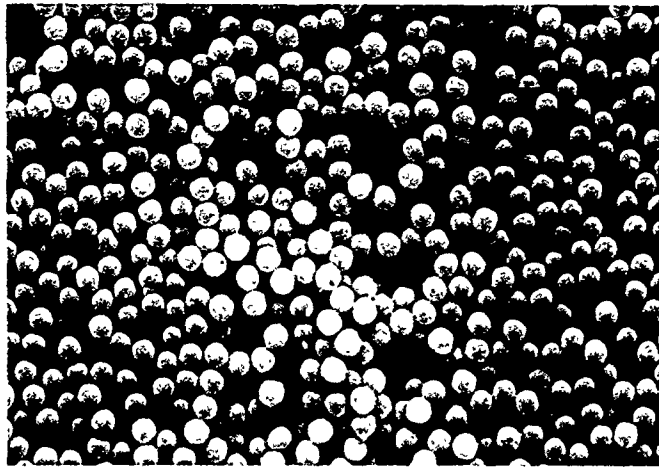


A

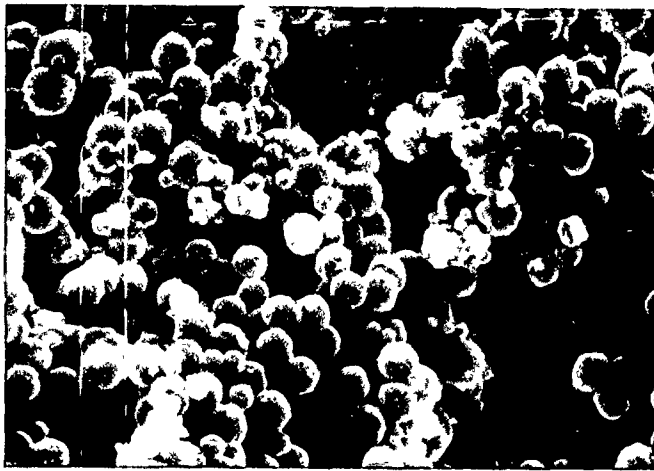


B

**FIGURE 7**

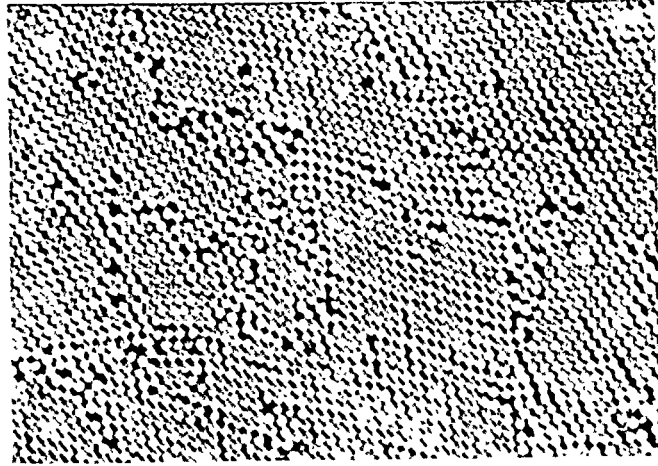


A

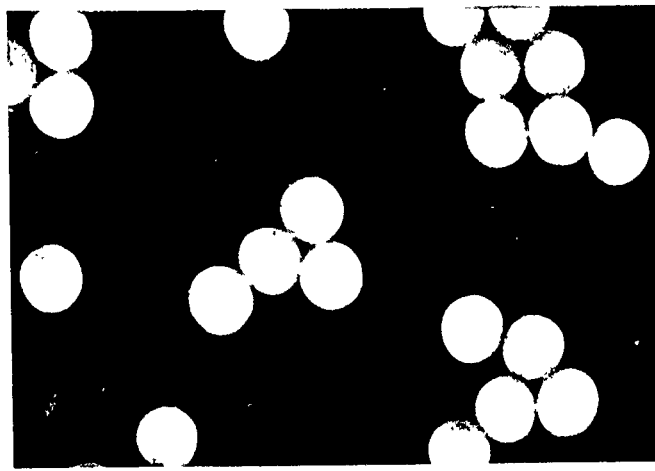


B

**FIGURE 8**

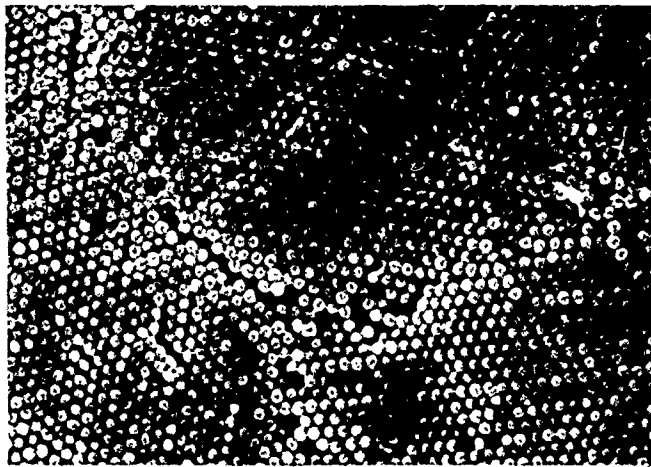


A

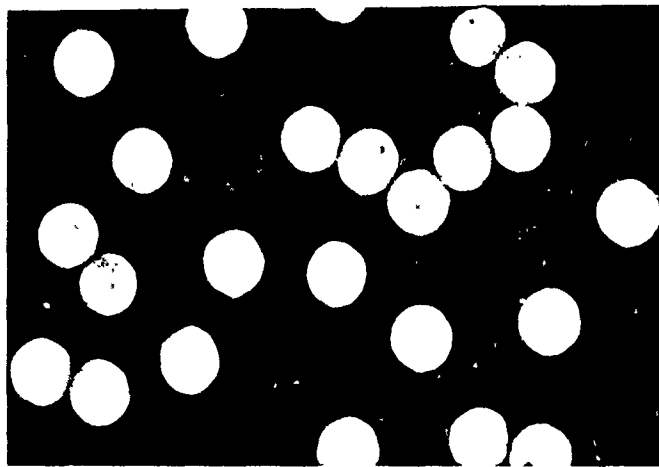


B

FIGURE 9



A



B

**FIGURE 10**

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