

Polymer Bead Preparation from Bulk Polymers

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SYNOPSIS

A method of preparing polymer beads from chloroform solutions of bulk polymer was developed. The technique involved solvent removal while the polymer solution was stirred in an aqueous dispersing medium. Bead size could be varied by adjusting the concentration of the suspending medium and the method was found to be applicable to chloroform-soluble, water-insoluble polymers. Copolymers, low-tack rubbers, and polyblends were also converted to bead form and, in the latter case, phase separation occurred. Furthermore, it was possible to encapsulate finely divided inorganic fillers within the polymer beads.

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INTRODUCTION

Polymers prepared in spherical particulate form have a wide range of industrial applications. Various methods have been employed to produce polymer beads of various dimensions from monomers, including suspension polymerization,¹ dispersion polymerization,^{2,3} emulsion polymerization,⁴ or by colloidal coacervation techniques.^{5,6} All methods rely upon the preparation and stabilization of monomer droplets in an aqueous medium, followed by thermal polymerization of the dispersion producing polymer beads of various dimensions, depending upon the technique used; suspension polymerization produces polymer beads in the 100 μm range, dispersion polymerization produces beads in the range 100–5 μm , while emulsion techniques produce beads in the submicron range. Many polymers cannot be produced directly in this form and here we describe a simple method of converting bulk polymer into polymer beads with particle size in the range 5–500 μm .⁷

EXPERIMENTAL

A solution of polymer (5.0 g) in chloroform (20 mL) was stirred in an aqueous solution of gelatin (3.0 g)

and Sodium Dodecyl Sulphate (1.0 g) in water (100 mL) at 45°C. Chloroform was slowly removed under vacuum (water pump) or by passing a steady stream of air across the surface of the stirred suspension. When all the organic solvent had been removed, hot water (2 L) was added, the mixture poured into a tall vessel, and the polymer beads allowed to settle out. The polymer beads were washed repeatedly by suspending in hot water and decanting off the supernatant after the beads had settled out; finally the beads were filtered off and dried under vacuum.

Bead size was determined by direct measurement of photomicrographs; quantitative analysis of size distribution was not possible since the clean-up technique removed the finer material that remained suspended, hence the average bead size was weighted toward the larger particle size.

Scanning electron photomicrographs were obtained using a Cambridge stereoscan 600 scanning electron microscope. Transmission electron photomicrographs were obtained by first suspending the polymer beads in epoxy resin, curing the sample, and trimming the surface with an ultramicrotome. The sample was immersed in 2% osmium tetroxide for 14 days; finally the trimmed surface was sectioned and the ultra-thin sections were supported on copper grids and were viewed directly without further staining, using a Philips 400T electron microscope.

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RESULTS AND DISCUSSION

Suspension of a chloroform solution of polymer in water results in a dispersion, provided that the mixture is stirred vigorously. If the chloroform is slowly evaporated, the viscosity of the organic phase increases and a stage is reached when the shearing forces are insufficient to maintain the dispersion and the droplets of the organic phase coalesce. Addition of a colloidal dispersant to the aqueous phase prevents coalescence at this stage by providing a repulsive energy barrier between the droplets of the polymer solution, which are transformed smoothly to polymer beads as the organic solvent is removed.

Not all dispersants were found to be equally effective, 2% poly(acrylic acid), 10% gum acacia, or 2% soluble starch produced aggregates of fused beads: 3% gelatin gave discrete beads in the range 30–500 μm , while 3% sodium dodecyl sulphate produced aggregate lumps of very fine beads. A combination of gelatin and sodium dodecyl sulphate was found to produce polymer beads in the size range of 10–100 μm under the experimental conditions used.

Polymer bead size was related to the size of the droplets in the initial dispersion. An initial fine dispersion, achieved with high concentrations of gelatin, produced fine beads, whereas a lower concentration of gelatin, producing a larger droplet size, resulted in a coarser size range of polymer beads upon evaporation of the organic phase.

Control of the size of the dispersion is a complex process related to the geometry of the vessel, interfacial tension between the two phases, the volume fraction and density of the dispersed phase, stirrer speed, and design of the stirrer.⁸ Experimentally, it was found to be more convenient to control the bead size by varying the concentration of the gelatin solution, keeping the other parameters constant. The variation in bead size with different gelatin concentrations for the preparation of poly(methyl methacrylate) beads is tabulated below (Table I).

A variety of chloroform-soluble polymers were converted to bead form by this method including, poly(methyl methacrylate), poly(carbonate), poly(sulphone), poly(styrene), "Kraton 1001" (a poly(styrene)/poly(butadiene) tri-block copolymer), and the following polymer blends: 10% Kraton 1001 with 90% PMMA, 50% poly(carbonate) with 50% poly(sulphone), and 25% of a PMMA-Pb poly(acrylate) copolymer (90/10) with 75% PMMA. The previous three examples produced phase separated polymer beads.

Bead form and morphology are shown in a series

Table I PMMA Beads Prepared by Solvent Evaporation

Gelatin Concn. (%)	SDS Concn. (%)	Average Bead Size (Range)
1	1	Aggregates 2–5 mm
2	1	Aggregates 2–5 mm
3	1	55 μm (150–2 μm)
5	1	35 μm (50–2 μm)
6	1	29 μm (50–2 μm)
7	1	26 μm (50–2 μm)
8	1	13 μm (20–2 μm)
9	1	14 μm (20–2 μm)
10	1	11 μm (20–2 μm)
11	1	10 μm (20–2 μm)
12	1	5 μm (10–2 μm)
15	1	6 μm (10–2 μm)
3	0	380 μm (500–2 μm)

of photomicrographs. Figures 1 and 2 are photomicrographs of poly(methyl methacrylate) and "Kraton 1001" beads, respectively. The surface appearance of the polymer beads varies: poly(methyl methacrylate), poly(sulphone), and poly(styrene) produce clear beads, and observation by scanning electron microscopy showed the surface to be smooth, unlike beads prepared from "Kraton 1001" or poly(carbonate), which appeared more opaque and whose surfaces appeared textured when examined by SEM (Fig. 3).

Phase separation in blends of incompatible polymers was evident from scanning electron photomicrographs. Beads of a polymer blend, prepared from a solution of PMMA in chloroform containing 10% "Kraton 1001," exhibited small, nodular irregularities on the surface with dimensions on the order of 3 μm (Fig. 4). Transmission electron microscopy of the sectioned beads showed these nodules to consist of the poly(styrene)/poly(butadiene) rubber phase. Furthermore this phase is distributed throughout the bead as spherical domains of up to 3 μm (Fig. 5). Higher magnification (Fig. 6) of these domains revealed the characteristic phase separation of hexagonal arrays of poly(styrene) domains in a matrix of poly(butadiene), characteristic of styrene-butadiene block copolymers of similar composition.⁹

The beads produced from a blend of PMMA and the Pb salt of a 10% poly(acrylic acid)-PMMA copolymer were remarkably nodular (Fig. 7). Again, transmission electron microscopy of sectioned beads revealed the lead phase was distributed throughout the PMMA beads as discrete domains.

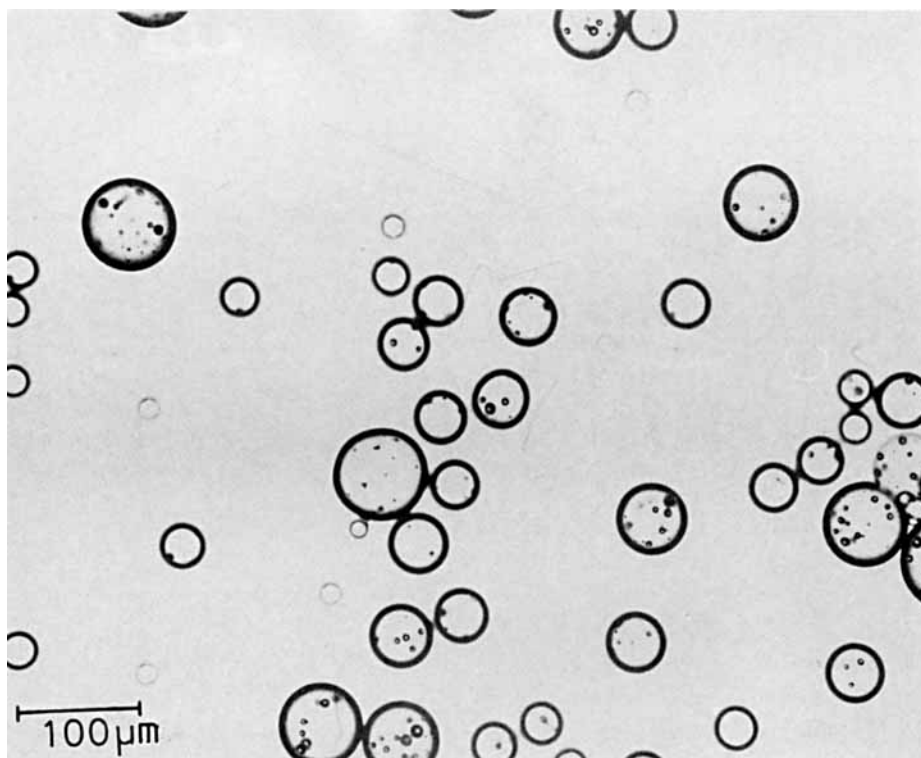


Figure 1 Poly(methyl methacrylate) beads.

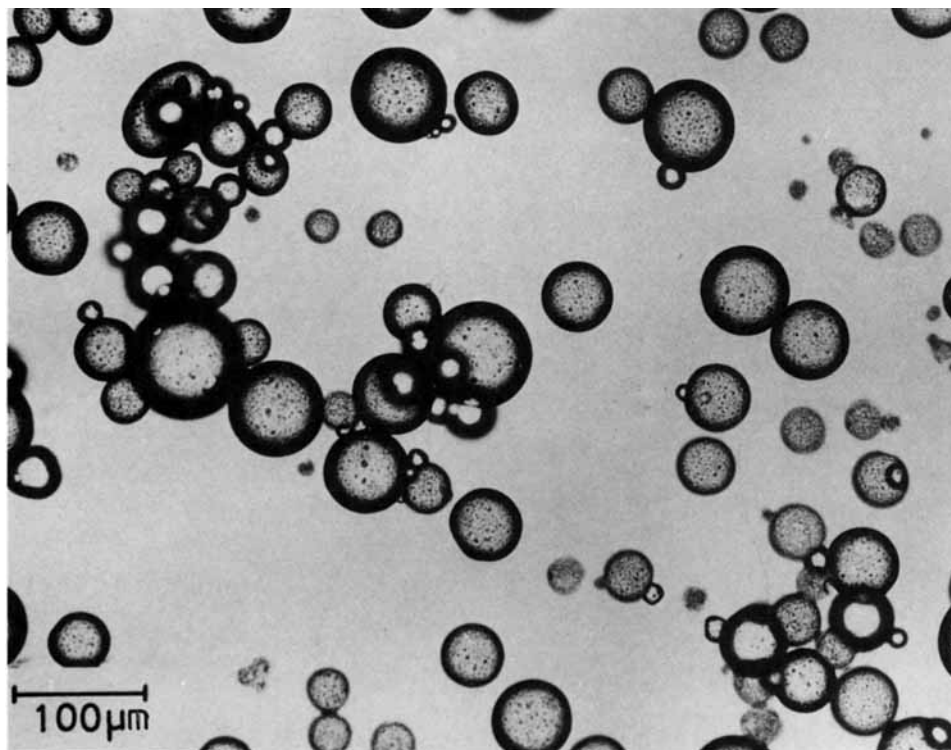


Figure 2 "Kraton 1001" beads.

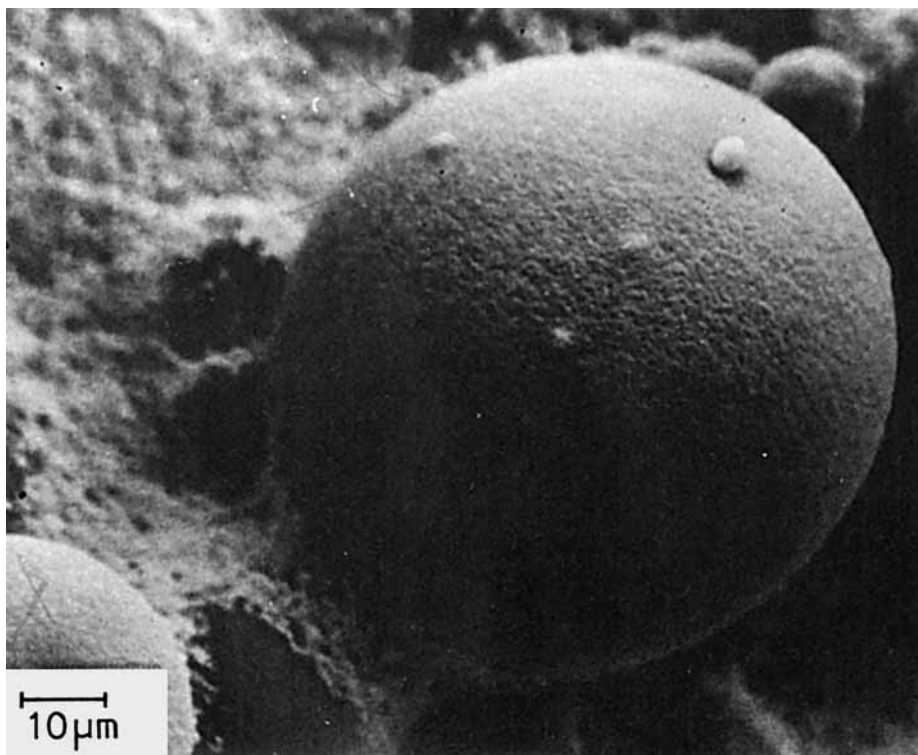


Figure 3 Scanning electron micrograph of poly(carbonate) beads.

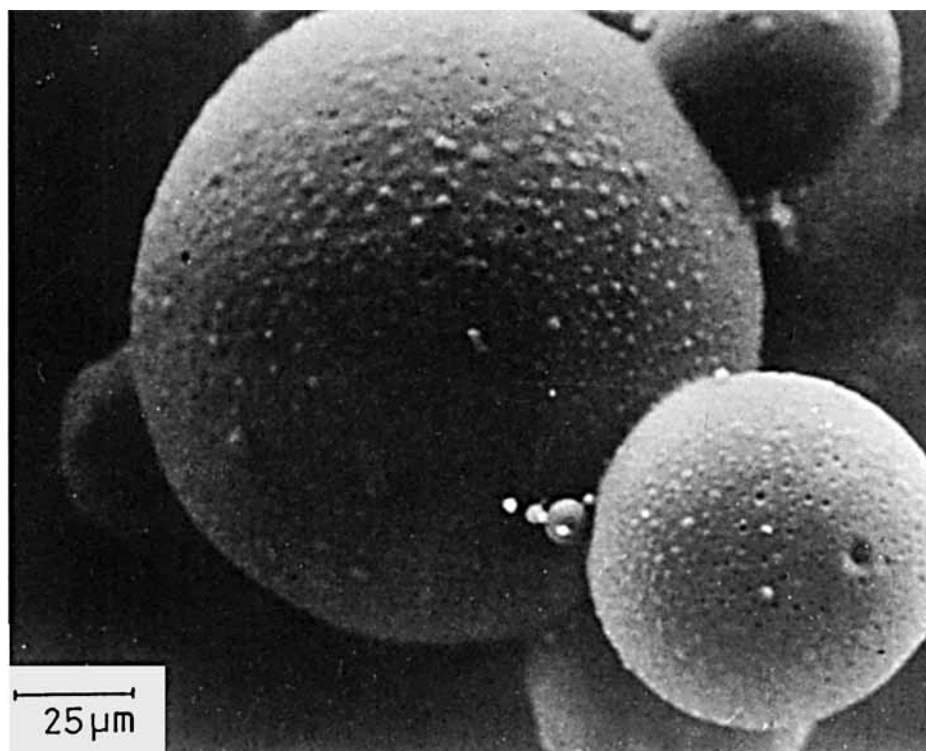


Figure 4 Scanning electron photomicrograph of polymer beads from a blend of 10% "Kraton 1001" and 90% PMMA.

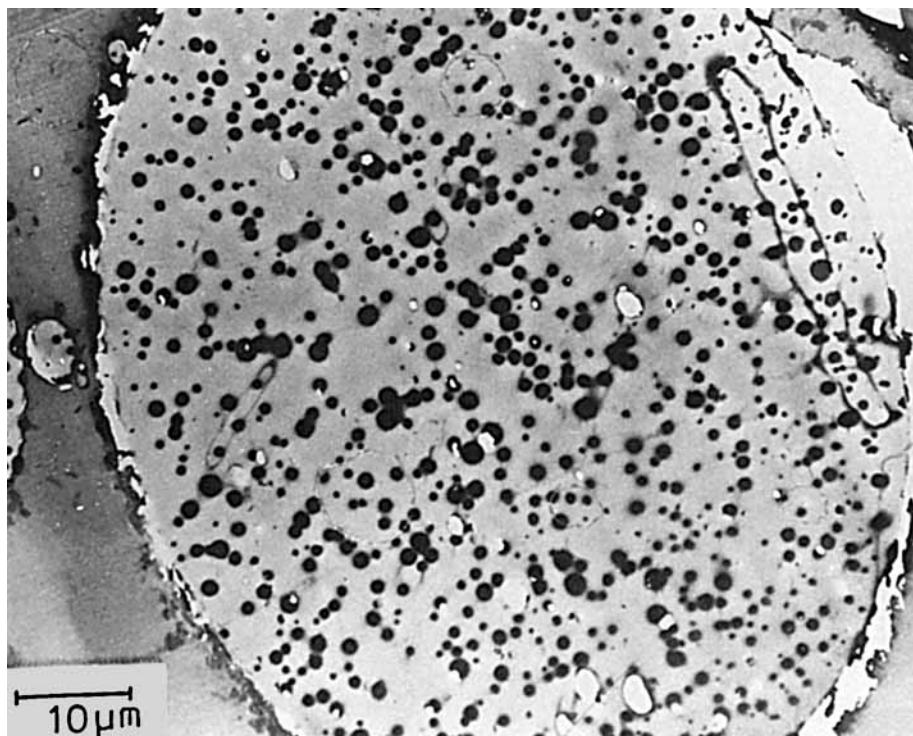


Figure 5 Transmission electron photomicrograph of a section through a single polymer bead of a 10% "Kraton 1001"/90% PMMA blend. (Note the fine dispersion of "Kraton" rubber domains throughout the bead.)

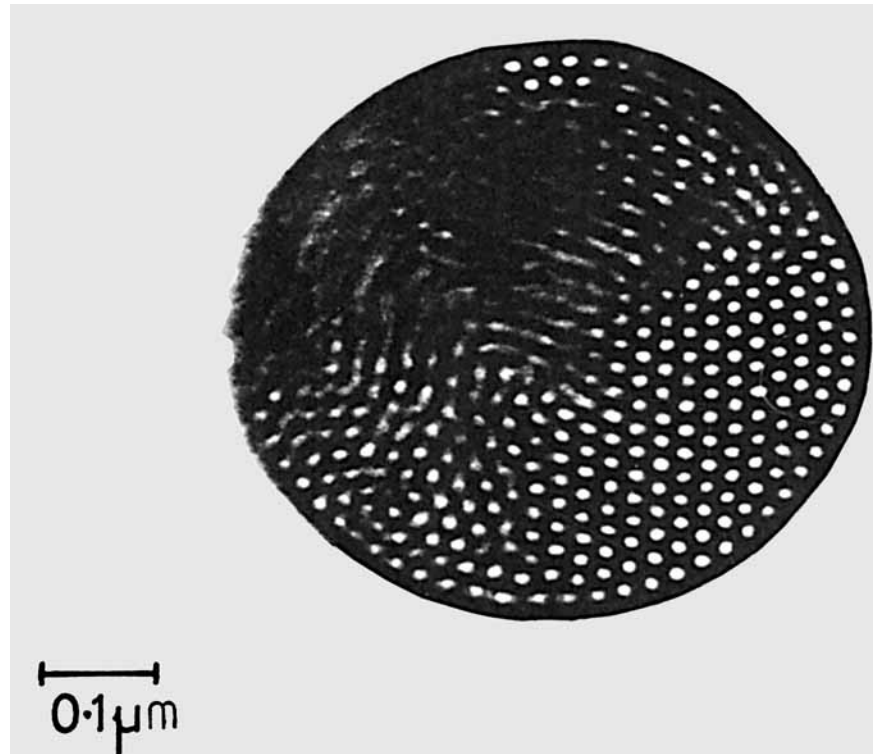


Figure 6 Higher magnification transmission electron photomicrograph of a single "Kraton" rubber domain shown in Figure 5.

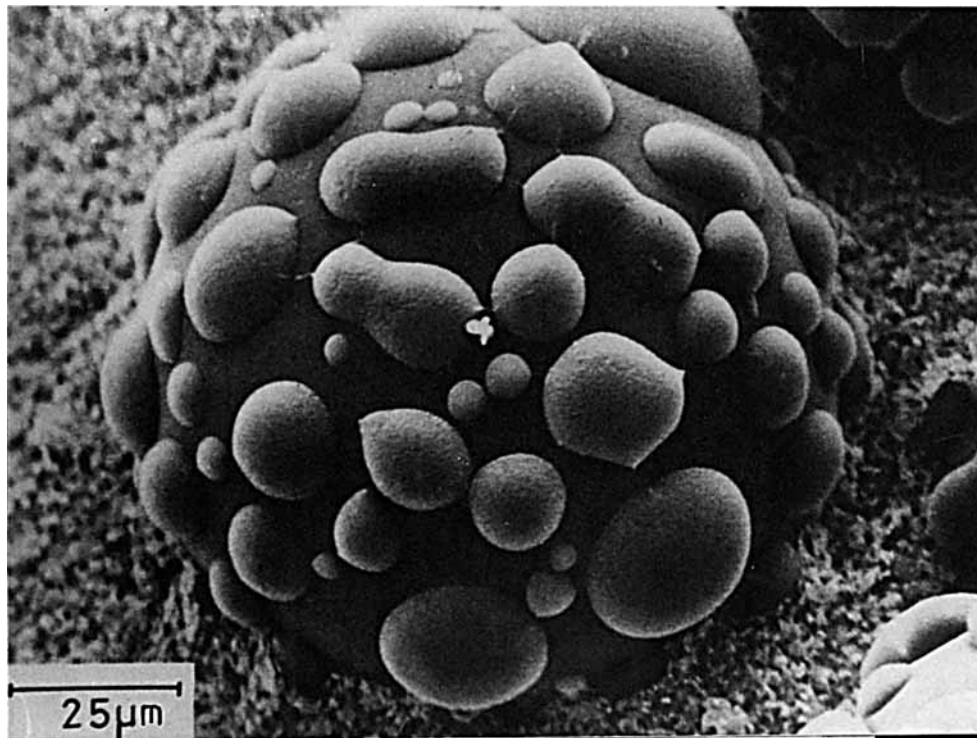


Figure 7 Scanning electron photomicrograph of beads prepared from a blend of 75% PMMA and the Pb salt of a 10% poly(acrylic acid)-PMMA copolymer.

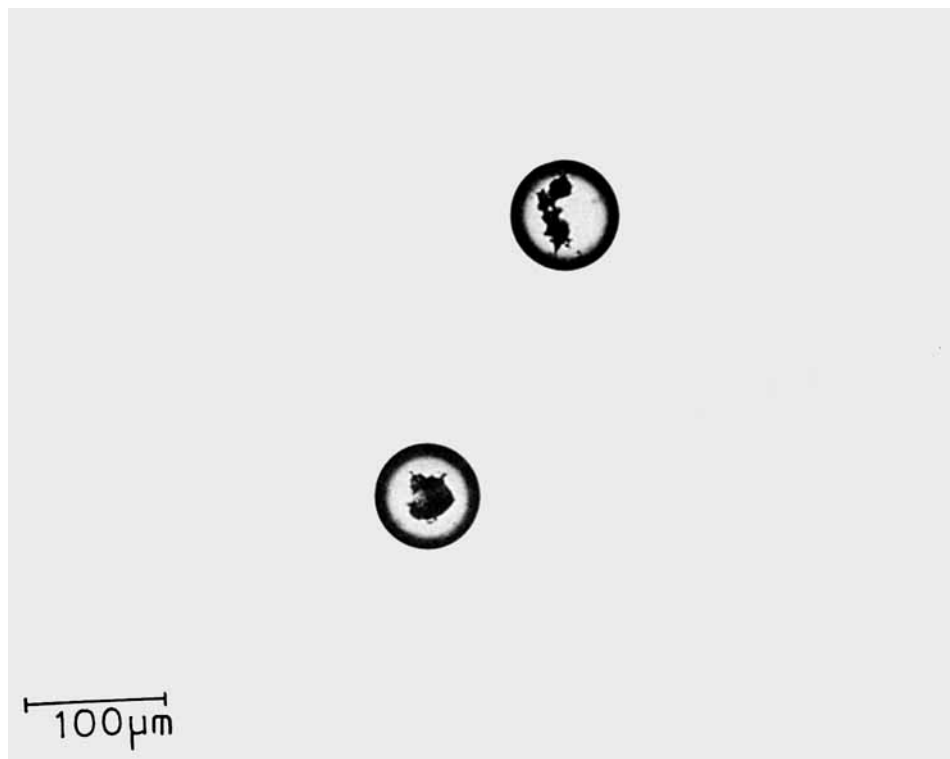


Figure 8 PMMA beads containing finely powdered Barium glass.

Finally, filled beads could be prepared by adding finely powdered filler to the chloroform solution of the polymer before the organic solution was suspended in the aqueous phase. Both powdered barium glass (Fig. 8) and pyrolytic silica could be encapsulated within PMMA beads by this technique.

CONCLUSIONS

A simple technique for producing polymer beads from bulk polymer has been developed. Applications include the preparation of filled polymer beads, while dispersions of one polymer within the bead matrix of a second polymer could be achieved when mixtures of solutions of incompatible polymers were converted to bead form by this method.

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