

Independent Control of Mechanical and Chemical Properties of Monodispersed Polystyrene–Divinyl Benzene Microspheres by Two-Step Polymerization

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SYNOPSIS

Monodispersed polystyrene (PS) latices of the particle size ranging between 4 and 10 μm were prepared by a conventional dispersion polymerization technique using poly(acrylamide) as a stabilizer. Styrene containing 2–20% of divinyl benzene (DVB) was subsequently polymerized on the surface of the latex by a seeded polymerization technique for the purpose of modifying the thermo-mechanical and chemical properties of the microspheres. The softening temperature during hot pressing and the resistance against the dissolution on swelling in toluene or methyl ethyl ketone increased with increasing amount of DVB. The state of seeded polymerized particles was revealed to depend more on the total amount than the composition of the monomer added. By using the present technique, it is possible to prepare chemically stable, monodispersed microspheres with their diameters and softening temperature varying from 4.5 to 12 μm and from 106 to 126°C, respectively, with a free combination by choosing the appropriate dispersion polymerization condition and the amount of DVB during subsequent seeded polymerization.

INTRODUCTION

Polymer latices with functional surfaces are attracting much interest from various fields, including toners for xerography, packed beds for chromatography, paint fillers, and cosmetics. Most latices are prepared by emulsion polymerization and hence their diameters are in the nanometer regime.

Monodispersed microspheres in a single-micron regime were prepared by seeded polymerization of those microspheres preliminarily prepared by emulsion polymerization.^{1–4} With the advent of dispersion polymerization,^{5–7} however, it became much easier to obtain such microspheres in a single step. Lok et al.^{8,9} studied these techniques in detail and reported that the solubility parameter plays an important role on the monodispersity of the products.

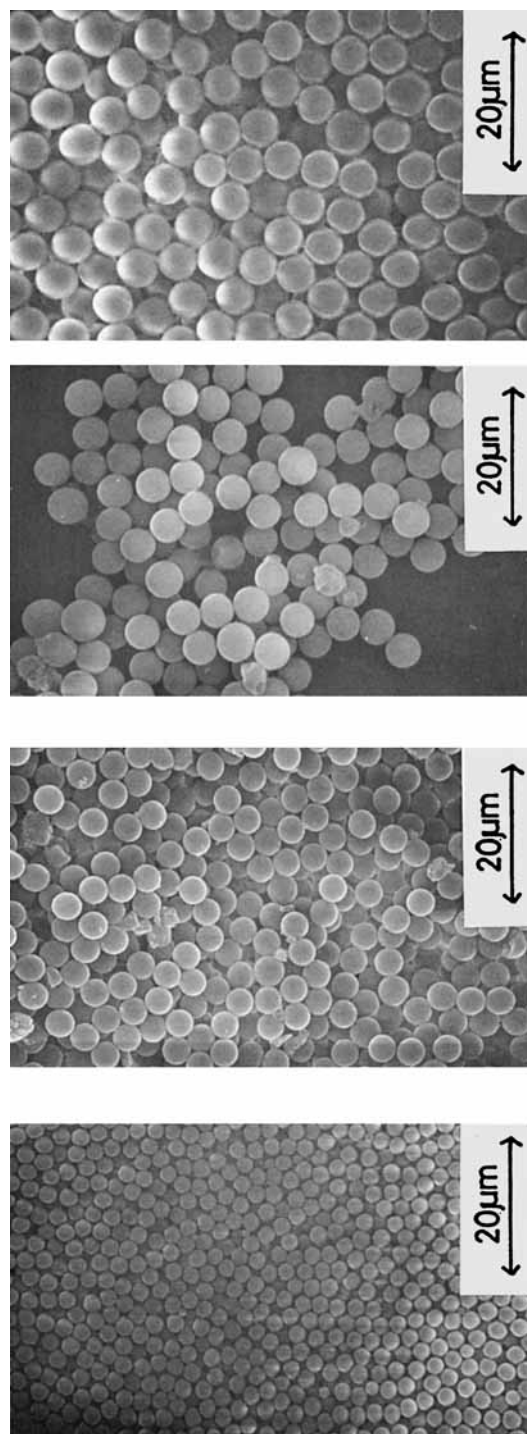
As far as poly(styrene) is concerned, the monodispersity of the product of dispersion polymerization is almost excellent. However, when the second phase, like divinyl benzene, is added for the purpose of crosslinking, the sphericity and the monodispersity of the microspheres prepared by conventional dispersion polymerization are seriously skewed.⁵ Some technical improvement is, therefore, still necessary to obtain well-monodispersed, perfectly spherical particles with appropriate crosslinking.

Starting from the microspheres prepared by dispersion polymerization is much easier to control the particle geometry, since the enlargement factors during the subsequent seeded polymerization are orders of magnitude smaller than those from emulsion polymerization. In addition, swelling of the microspheres obtained by dispersion polymerization can be carried out easily due to relatively low degree of polymerization.¹⁰

The purpose of the present study is to obtain monodispersed microspheres with controlled extent of crosslinking and particle size by using a two-step

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No.1 **No.2** **No.3** **No.4**

Figure 1 Scanning electron micrographs of seed microspheres, Nos. 1-4. Refer Table I for preparation condition.

Table I Preparation Condition and Properties of the Seed Particles Obtained by Dispersion Polymerization

| | | | | |
|-------------------|-------|-------|-------|-------|
| Specimen number | 1 | 2 | 3 | 4 |
| Ethanol/vol% | 85 | 45 | 40 | 35 |
| Mecell/vol% | 0 | 40 | 45 | 50 |
| $D_n/\mu\text{m}$ | 2.430 | 3.996 | 4.950 | 5.530 |
| D_s/D_n | 1.002 | 1.003 | 1.003 | 1.007 |

polymerization technique, i.e., dispersion polymerization and a subsequent seeded polymerization.

EXPERIMENTAL

Dispersion Polymerization

The synthesis consisted of two distinct steps, i.e., the dispersion polymerization to produce seed poly(styrene) microspheres and seeded polymerization to give a crosslinking on the seed particles.

Dispersion polymerization was carried out after the technique presented by Lok et al.^{8,9} To 250 cm³ of a mixed solution comprising ethanol and methoxyethanol (mecell) with its ratio varied, 16.8 g of 25% aqueous solution of poly(acrylamide) (av. molecular weight 25,000) was added. Dehydration of the monomer was carried out by adding 50 g molecular sieve 3A and letting stand overnight. Then 37.5 g styrene monomer and 1.5 g benzoyl peroxide as an initiator were added to the above-mentioned mixed medium. Dispersion polymerization was carried out at 68°C for 24 h in N₂ atmosphere under a mild stirring at 150 rpm.

When the dispersion polymerization was finished, the reaction mixture was cooled to room temperature, the excess medium solution was decanted, and the product was redispersed into 500 cm³ of ethanol with the aid of ultrasonication for 10 min to prevent undesired agglomeration. After changing the dispersing medium (ethanol), and repeating the dispersion process twice by ultrasonication, the product microspheres were obtained by centrifugation and drying at 50°C for 72 h.

Seeded Polymerization

Two grams of seed particles were dispersed into 100 cm³ deionized water containing 0.065 g of sodium lauryl sulfate under ultrasonication for 10 min. To a mixed monomer comprising divinyl benzene

(DVB) and styrene with varying proportion, 0.3 g benzoyl peroxide was added and then dispersed into 100 cm³ of deionized water containing 0.15 g sodium lauryl sulfate and 3 cm³ ethanol. With the aid of ultrasonic vibration, the mixed monomer was emulsified. The amount of the added monomer was varied from 6.4 to 51 cm³ per charge, and the volume percent of DVB in the monomer from 0 to 17.9%.

A suspension containing seed particles and an emulsion containing a mixed monomer were then mixed together. Seed particles were swollen by the mixed monomer for 4 h at 30°C under constant stirring at 400 rpm. To this dispersion, 43.5 cm³ deionized water and poly(vinylalcohol) (av. molecular weight 86,000, ca. 98.5% hydrolysis) was added. Seeded polymerization was then carried out by raising the temperature up to 70°C for 20 h. The separation, redispersion, and drying were carried out in a same manner as with the seed particles.

Characterization

Particle size was measured with an electron micrograph. The surface averaged particle size, D_s , was divided by the number-average particle size, D_n , to obtain an index for the monodispersity, D_s/D_n .

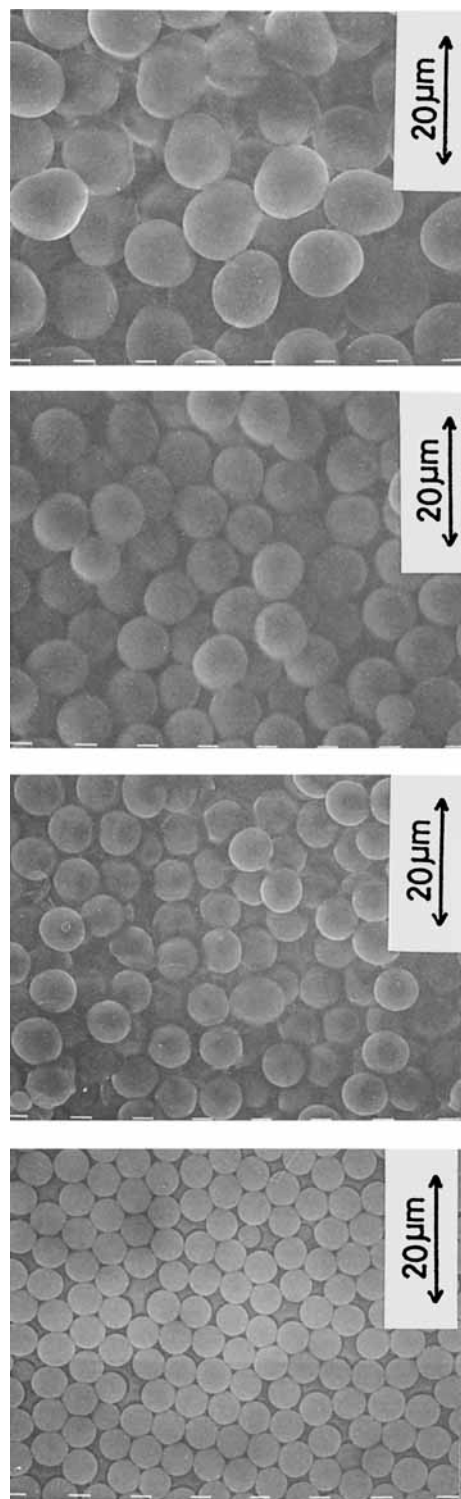
The softening temperature of the compact of the microspheres was determined by hot pressing 0.5 g of the specimen powders filled in a 10-mm diameter die cavity under the constant compressive stress of 2 MPa and constant rate of heating, 10 K min⁻¹, up to 230°C. The process of swelling in acetone or methyl ethyl ketone (MEK) was observed under the optical microscope. The extent of swelling was described as a specific volume change defined as V/V_0 , where V and V_0 are the average volume of particles after and before the swelling test, respectively.

Fine structure of the microsphere was observed by embedding the spheres into an epoxy resin and polishing the cross section. Observation was done with and without preliminary etching with MEK.

RESULTS AND DISCUSSION

Seed Particles

An example of the seed particles obtained by the dispersion polymerization, with styrene monomer concentration 15 vol % and the ethanol-mecell ratio varying from 85/0 to 35/50, is shown in Figure 1. The properties of the seed microspheres are summarized in Table I. By increasing the meccl content,



No.5 **No.6** **No.7** **No.8**

Figure 2 Scanning electron micrographs of subsequently seeded polymerized microspheres, Nos. 5-8 prepared from seed Nos. 1-4. Refer Table II for preparation condition.

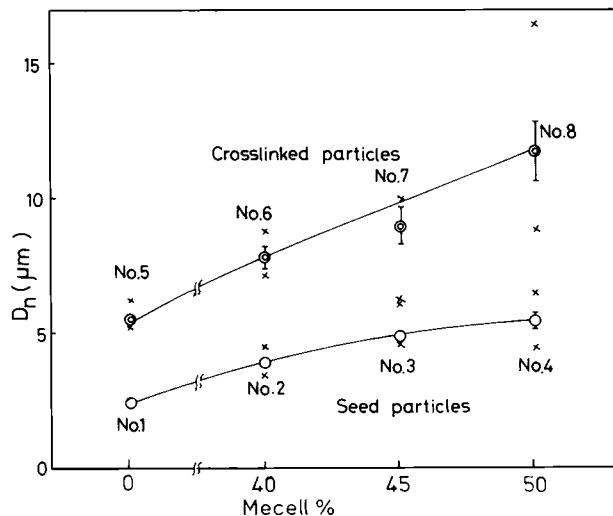


Figure 3 Change in the diameter of seed microspheres and subsequently seeded polymerized microspheres with mec cell concentration during dispersion polymerization.

the average particle size and the breadth of the particle size distribution, D_s/D_n , decreased.

Seeded Polymerization

The seeded polymerized particles, Nos. 5–8, are shown in Figure 2. They correspond to the seed particles Nos. 1–4, respectively. The amount and the composition of the monomer added during seeded polymerization were kept constant at 25.5 cm³ and 4.45 mol % DVB, respectively.

As shown in Figure 3, the diameter of the particles was almost doubled after seeded polymerization. Properties of these seeded polymerized particles are given in Table II. In Figure 3 the standard deviation of the particle diameter is indicated by vertical bars. The maximum and minimum particle sizes are indicated by crosses.

In order to elucidate the effect of the amount of added monomer, its volume was changed from 6.4 to 51 cm³ per charge. The concentration of DVB was kept constant at 8.9 mol %. Samples Nos. 9–12 shown in Figure 4 were obtained from seed particles No. 3. The number and extent of small bumps observed on the surface of the spheres increased with increasing amount of monomer, as shown in Figure 4. The average particle size increased slightly with increasing amount of monomer added, as shown in Table III and Figure 5. No regular change in the standard deviation of D_n was observed, however, as shown in Figure 5.

Effect of DVB on the Internal Texture

The particles were embedded in the epoxy resin, and the cross section of the particles was observed. As shown in Figure 6, no particular texture was found on the cross section of the particles before etching. However, some spotlike substructure appeared after etching by MEK. This indicates that the penetration of the mixed monomer during swelling, and hence the crosslinking after seeded polymerization, takes place not uniformly but within certain small blocks. The boundary of those blocks became clearer with increasing monomer volume. This kind of inhomogeneity is understood fairly well in terms of a modified lattice theory^{1,11} based on the theory of Flory and Huggins. This kind of inhomogeneity can also be used to control the morphology of the resulting microspherical particles.¹²

When the relative amount of DVB was varied during seeded polymerization, the surface roughness of the particles increased, as shown in Figure 7 with their diameters summarized in Table IV. For the series Nos. 13–17, the total amount of the monomer added during seeded polymerization was kept constant at 25.5 cm³. The particle size reduced and the particle size distribution became narrower with increasing amount of DVB.

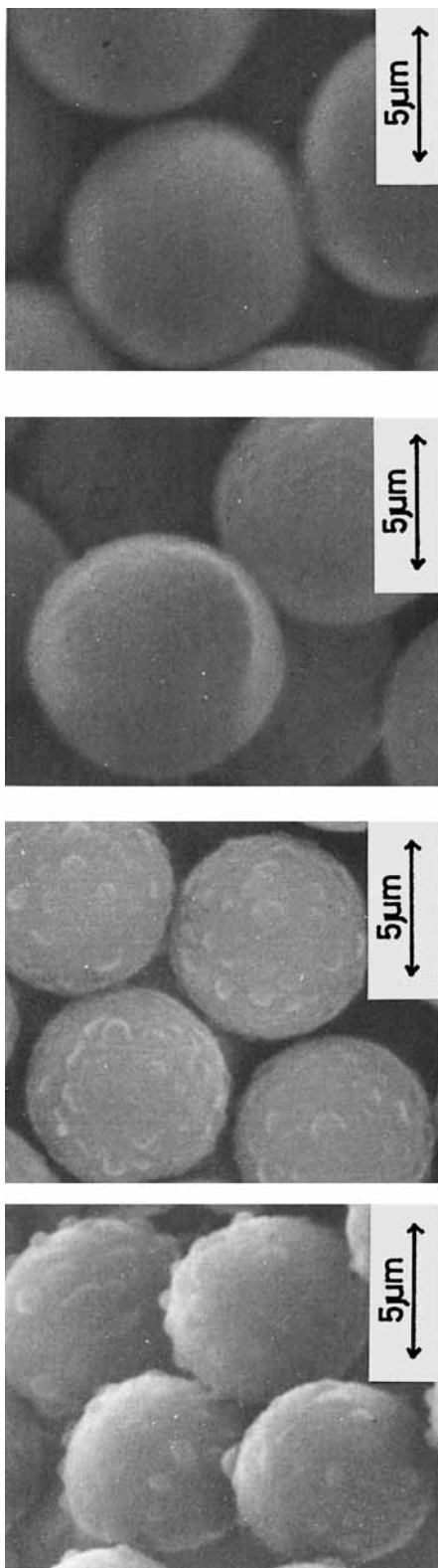
In Figure 8 the cross-sectional view of a series of samples before and after etching by MEK is shown. When the relative concentration of DVB was small, no substructure was detected even after etching by MEK. The development of such textural inhomogeneity by adding DVB to the monomer was already discussed above. Since, however, uniform microspheres with smooth surface is quite sufficient for the present purpose, we do not enter into further details in the inhomogeneous texture developed with increasing amount of DVB.

Dependence of Size Change during Seeded Polymerization on the Added Monomer

In order to examine the dependence of size change during seeded polymerization on the amount and

Table II Properties of the Seeded Polymerized Particles Nos. 5 to 8 Obtained from the Seed Particles Nos. 1 to 4

| Specimen number | 5 | 6 | 7 | 8 |
|-------------------|-------|-------|-------|--------|
| Seeds | 1 | 2 | 3 | 4 |
| $D_n/\mu\text{m}$ | 5.563 | 7.844 | 8.955 | 11.816 |
| D_s/D_n | 1.003 | 1.004 | 1.016 | 1.019 |



No.9 **No.10** **No.11** **No.12**

Figure 4 Scanning electron micrographs of subsequently seeded polymerized microspheres, Nos. 9–12. Refer Table III for preparation condition.

Table III Properties of the Seeded Polymerized Microspheres Nos. 9 to 12

| Specimen number | 9 | 10 | 11 | 12 |
|--------------------------------|-------|-------|-------|-------|
| Monomer volume/cm ³ | 51.0 | 25.5 | 12.8 | 6.4 |
| $D_n/\mu\text{m}$ | 9.530 | 8.902 | 7.840 | 7.297 |
| D_s/D_n | 1.004 | 1.009 | 1.006 | 1.004 |

composition of the added monomer, the size ratio, $R_D = D/D_0$, where D and D_0 are the particle diameter after and before seeded polymerization, was calculated and shown in Table V.

When the different seed particles are used (sample Nos. 5–8), the ratio R_D scattered considerably with its average and standard deviation values being 2.05 and 0.18, respectively. It is natural that R_D increased systematically with increasing total amount of the monomer (Nos. 9–12), starting from the common seed particle, No. 2. With increasing concentration of DVB, R_D decreased (Nos. 13–17), started from the common seed particle, No. 3.

It was further examined whether the added monomer merely contributes to the size increase by polymerizing to completion, by calculating the theoretical size ratio, R_C , based on the equation,

$$R_C = \left[\frac{W_M(\sigma_P/\sigma_M) + W_S}{W_S} \right]^{1/3} \quad (1)$$

where W_M and W_S are the weight of the added monomer and seed particles, and σ_P and σ_M are the

specific volumes of the polymer and monomer, respectively, used in the seeded polymerization. The density or the specific volume of the polymer, σ_P , was not available from the literature. An effort to obtain σ_P experimentally was not successful either because the dispersion polymerization of pure DVB was not possible. Therefore, an estimation was made by using 1.04 and 1.25 Mg m⁻³ for the density of polystyrene and poly(divinyl benzene). The above arbitrariness cannot disturb the relative comparison of R_C with the observed value R_D .

The average value of the ratio R_D/R_C of sample Nos. 5–8, where the same amount of the same monomer was added to the different seed particles, was 0.913 with its relative standard deviation being 8.9%. It is to be noted that the ratio R_D/R_C remained almost unchanged for sample Nos. 13–17 at 0.821 ± 0.027 , i.e., with its relative standard deviation 3.3%, i.e., being much smaller than that of sample Nos. 5–8, in spite of the wide variation of the DVB concentration in the added monomer. In contrast, the decrease in the ratio R_D/R_C with increasing amount of the monomer added was significant when compared within the group of sample Nos. 9–12, where the common seed particle, No. 2, was used.

No new small particles were observed throughout the seeded polymerization experiments. Not only because of that, the value of R_D/R_C smaller than unity does not directly mean the loss of the monomer during the second-stage polymerization. It should rather be interpreted as the deviation of the density or the specific volume from the additivity. The ab-

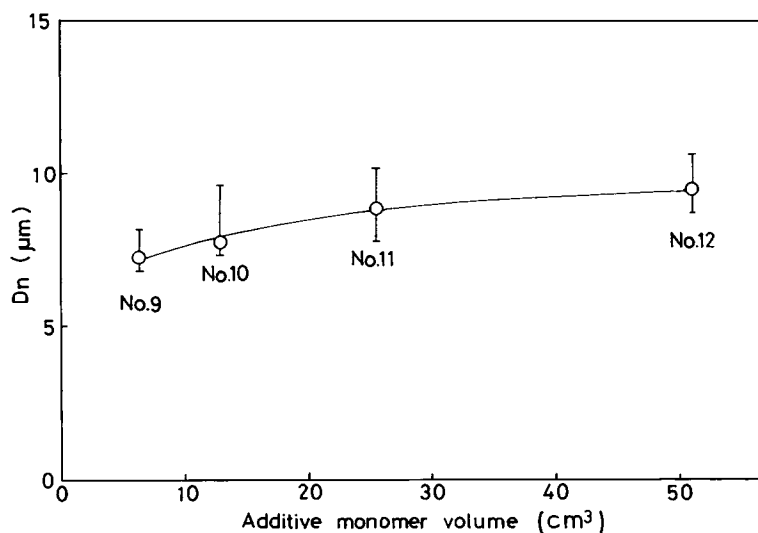
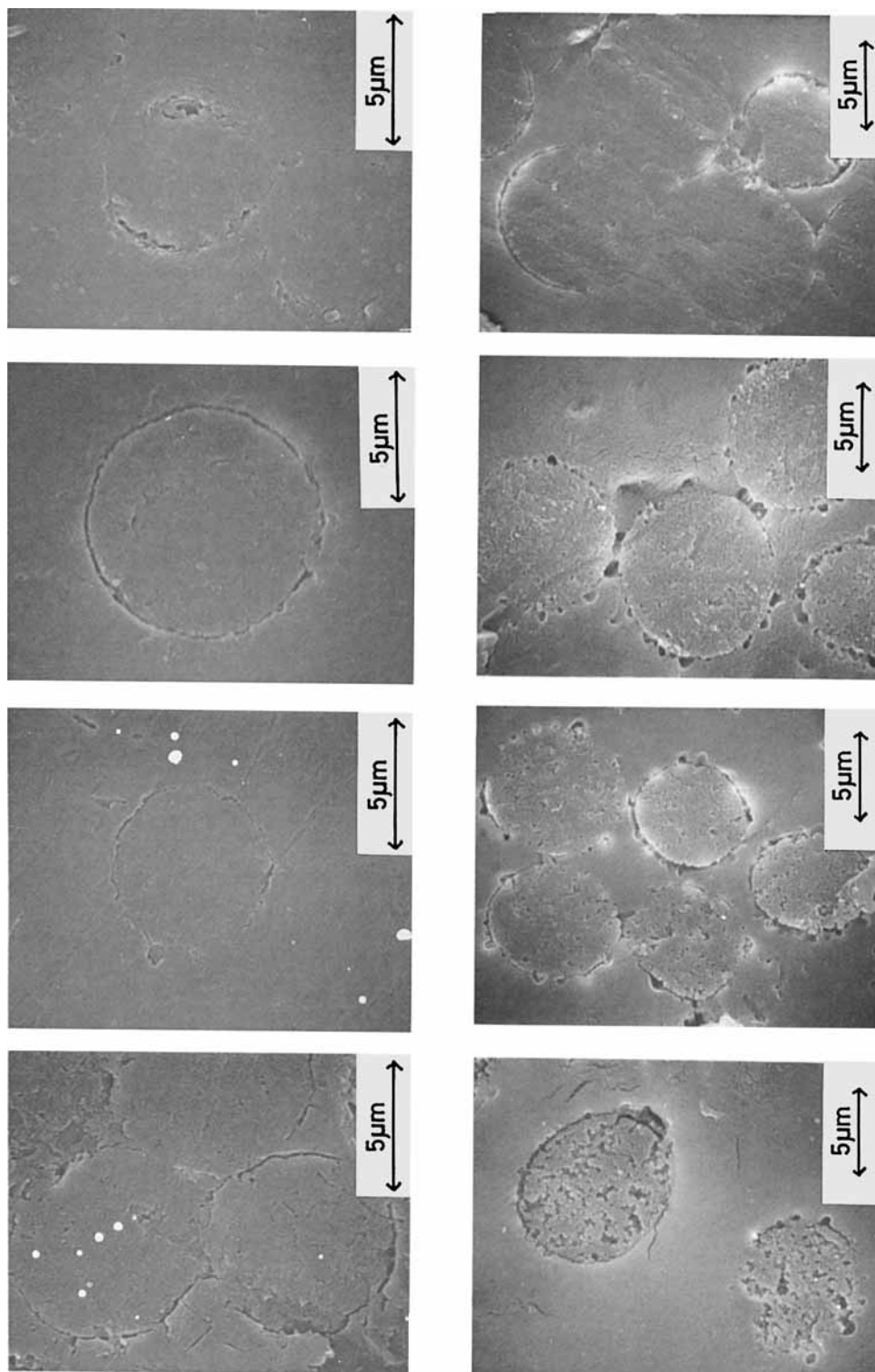


Figure 5 Change in the diameter of the microspheres of seed microspheres and subsequently seeded polymerized microspheres with total monomer volume added for seeded polymerization. DVB concentration in the monomer was kept constant at 8.9 mol %.



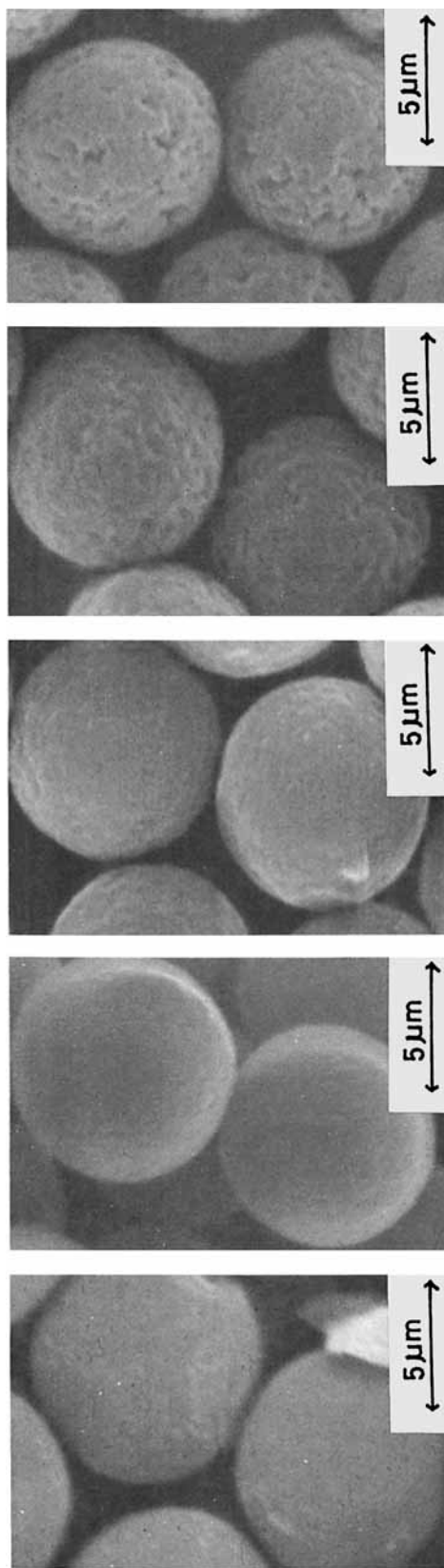
No.12

No.11

No.10

No.9

Figure 6 Cross-sectional view of the seeded polymerized microspheres, Nos. 9–12 before (upper row) and after (lower row) etching by MEK.



No.17

No.16

No.15

No.14

No.13

Figure 7 Scanning electron micrographs of subsequently seeded polymerized microspheres, Nos. 13–17. Refer Table IV for preparation condition.

Table IV Properties of the Seeded-Polymerized Microspheres Nos. 13 to 17

| | | | | | |
|-------------------------|-------|-------|-------|-------|-------|
| Specimen number | 13 | 14 | 15 | 16 | 17 |
| DVB concentration/mol % | 0 | 4.9 | 8.9 | 13.4 | 17.9 |
| $D_n/\mu\text{m}$ | 9.990 | 8.955 | 8.902 | 8.839 | 8.821 |
| D_s/D_n | 1.049 | 1.016 | 1.009 | 1.008 | 1.006 |

solute value of the ratio R_D/R_C is not very significant but only the relative value and its change, because of the arbitrariness of the value σ_p used, as mentioned previously.

It is therefore to be concluded that the average state of the seeded polymerized particles did not change so significantly as might be expected from its texture difference, whereas the manner and the extent of seed polymerization changes considerably, when the total amount of the monomer was changed.

Swelling Properties of Seeded Polymerized Particles

Seed particles comprising poly(styrene) with a small amount of poly(acrylamide) were dissolved completely in MEK. However, the particles containing DVB after seeded polymerization were insoluble in MEK. It is therefore obvious that the crosslinking due to DVB was accomplished during seeded polymerization. However, particles were swelled by the solvent and increased their volume, as shown in Figure 9. As the DVB monomer concentration increased, the specific volume of the particles, V/V_0 , where V and V_0 are the particle volume after and before swelling, respectively, was reduced, as shown in Figure 10. With DVB concentration 18%, the specific volume was unity, i.e., no dilation of the particles was observed after swelling test, showing that the amount of crosslinking was sufficient for the prevention of swelling.

Deformation of the Microspheres During Hot Pressing

The softening temperature during hot pressing of the compact bed of microspheres was defined as the temperature where the fast shrinkage step due to softening is completed just a half way, as shown in a model diagram in Figure 11. The difference between the initial and final thickness of the bed was defined as the specific displacement. The relationship between the softening temperature, specific

displacement, and DVB monomer concentration is shown in Figure 12.

With increasing DVB concentration in the added monomer during seeded polymerization, the softening temperature increased from 99 to 124°C. At the same time the specific displacement decreased from 0.37 to 0.22. This again must be the result of increased crosslinking density with increasing amount of DVB during seeded polymerization.

Figure 13 shows the upper surface of the hot-pressed tablet after softening. When DVB concentration was low, particles were deformed substantially and connected with the neighboring particles by a thick neck as in the case of an initial stage sintering. With increasing amount of DVB, the extent of interparticle connection decreased and well-developed interparticle necks were not observed, although the deformation of the individual particle was still recognized.

Control of Particle Size and Softening Point

The relationship between the softening temperature and the number-averaged particle size, D_n , is summarized in Figure 14 for the different series of experiments. By varying the diameter of the starting seed particles with the DVB concentration during

Table V Observed and Calculated Diameter Ratios, R_D and R_C and Its Ratio R_D/R_C

| | | | | | |
|-----------------|-------|-------|-------|-------|-------|
| Specimen number | 5 | 6 | 7 | 8 | |
| R_D | 2.29 | 1.96 | 1.81 | 2.14 | |
| R_C | 2.25 | 2.25 | 2.25 | 2.25 | |
| R_D/R_C | 1.020 | 0.873 | 0.806 | 0.953 | |
| Specimen number | 9 | 10 | 11 | 12 | |
| R_D | 2.38 | 2.23 | 1.96 | 1.83 | |
| R_C | 2.81 | 2.24 | 1.83 | 1.53 | |
| R_D/R_C | 0.847 | 0.995 | 1.070 | 1.198 | |
| Specimen number | 13 | 14 | 15 | 16 | 17 |
| R_D | 2.02 | 1.81 | 1.80 | 1.79 | 1.78 |
| R_C | 2.32 | 2.28 | 2.24 | 2.20 | 2.16 |
| R_D/R_C | 0.870 | 0.793 | 0.803 | 0.814 | 0.826 |

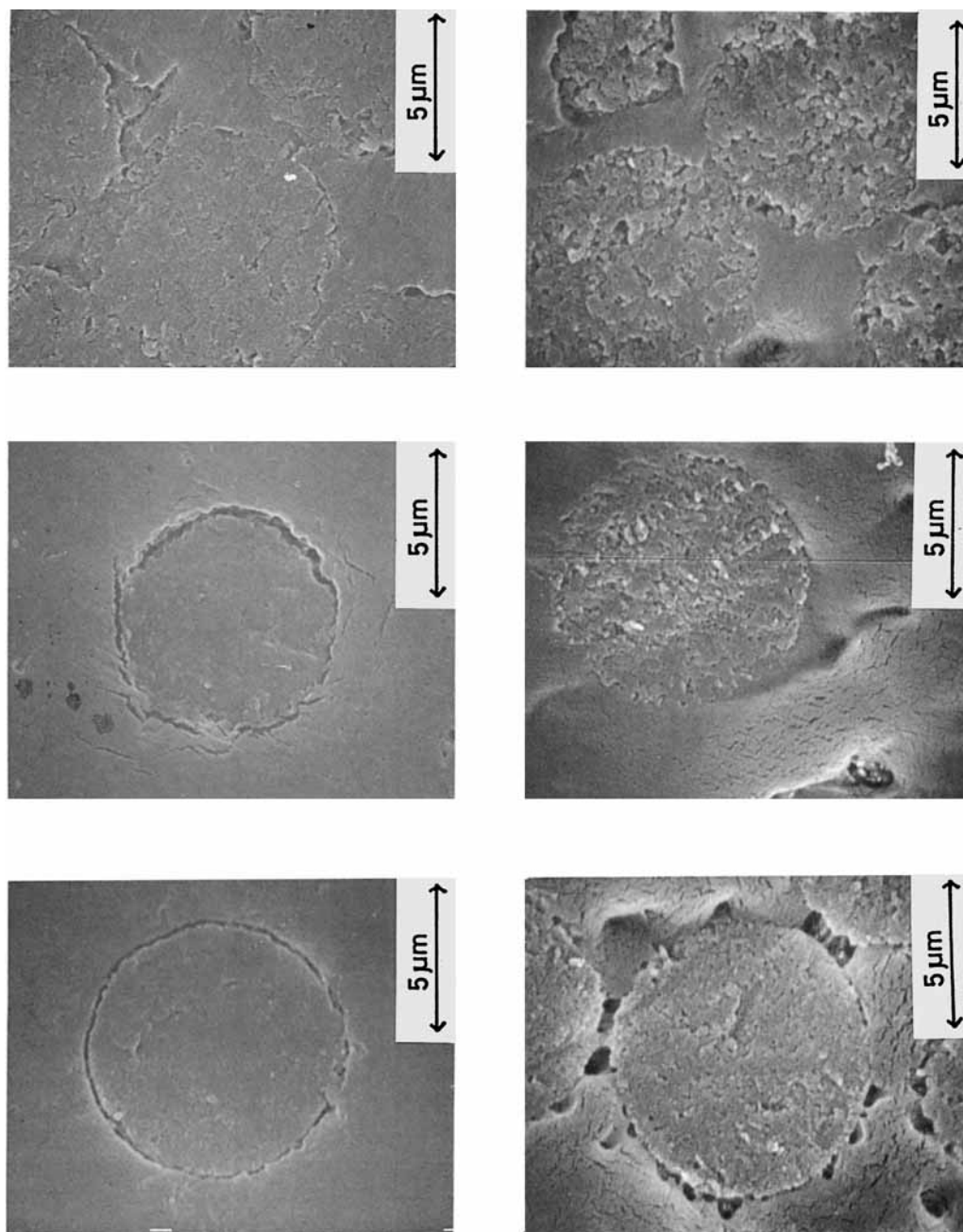
**No.15****No.16****No.17**

Figure 8 Cross-sectional view of the seeded polymerized microspheres, Nos. 15–17 before (upper row) and after (lower row) etching by MEK.

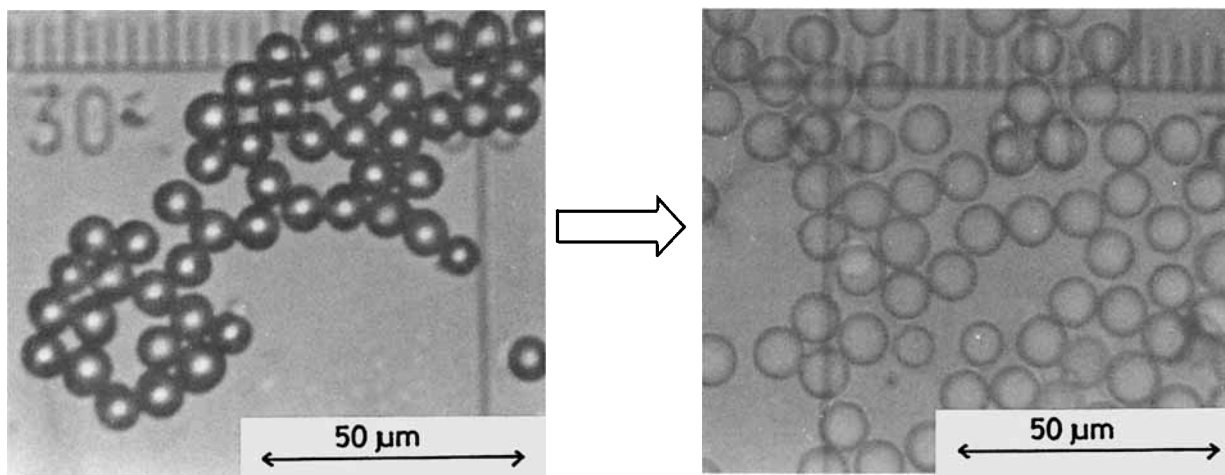


Figure 9 Optical micrographs showing the particles before (left) and after (right) swelling of the seeded polymerized particles of No. 14 (see Table IV) after soaking in MEK for 100 h.

subsequent seeded polymerization constant, microspheres with varying particle size with constant softening temperature are obtained. Instead, by increasing DVB concentration with all the other conditions kept constant, microspheres with almost the same particle size with varying softening temperature are available. It is thus obvious that, by choosing the appropriate concentration of DVB for the seeded polymerization starting from the seed microspheres of different particle size, the latter being controllable by varying the concentration of meccl during dispersion polymerization, we can prepare chemically

stable, monodispersed microspheres of the diameters varying from 4.5 to 12 μm and the softening temperature between 106 and 124°C with a free choice of their combination.

CONCLUSION

A two-step polymerization comprising the preparation of monodispersed polystyrene microspheres by dispersion polymerization and the subsequent seeded polymerization with the monomer containing divinyl benzene, crosslinked, chemically stable

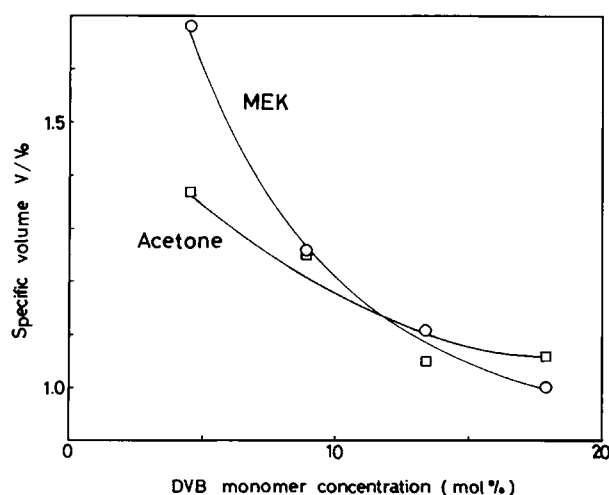


Figure 10 Change in the specific volume with DVB concentration during seeded polymerization. Volume change took place as a result of swelling after soaking in MEK or acetone for 100 h.

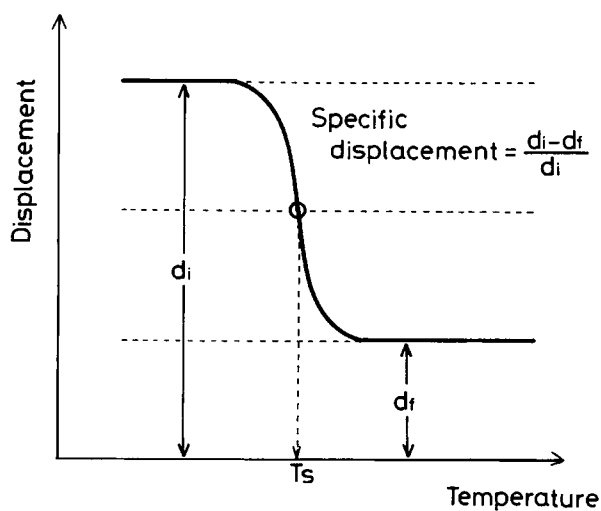


Figure 11 A scheme for the displacement-temperature diagram to determine the softening temperature, T_s , during hot pressing of the bed of microspheres.

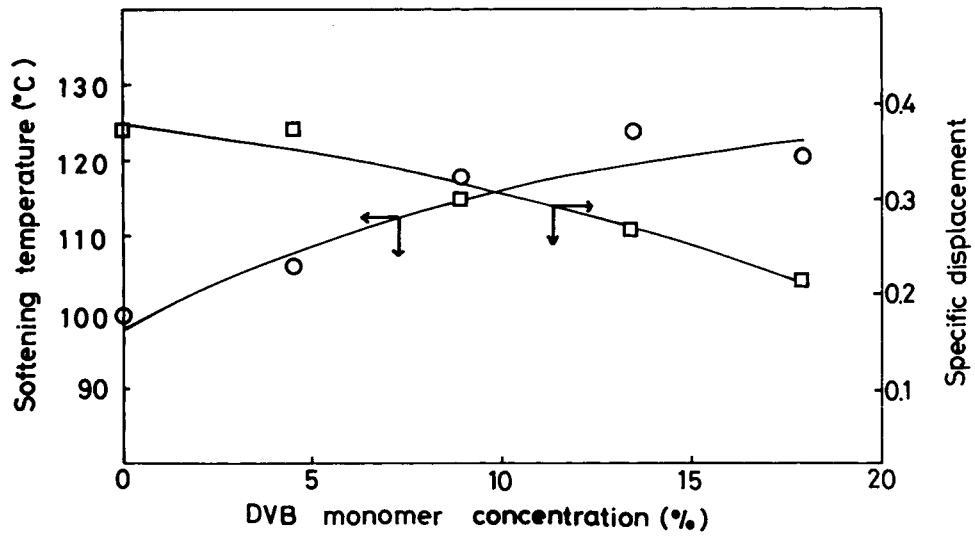
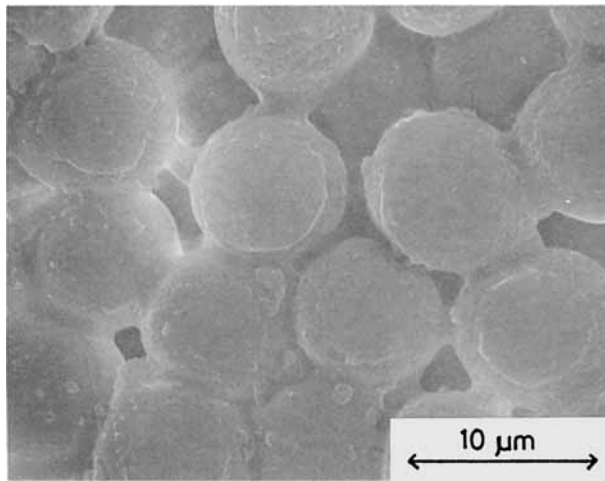
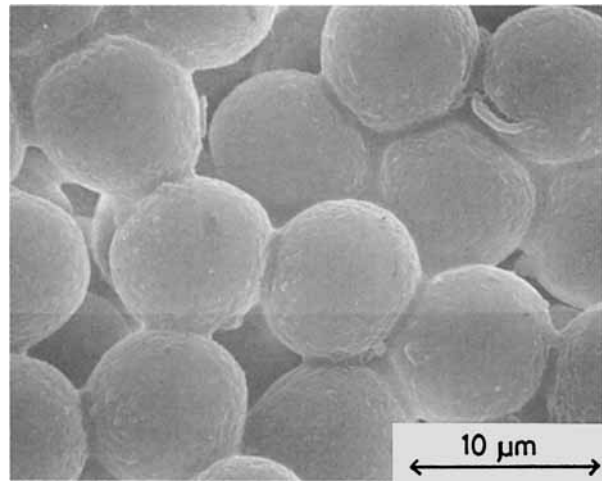


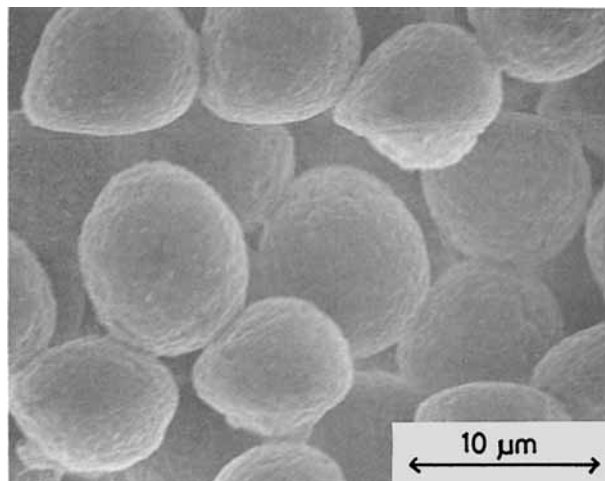
Figure 12 Change in the softening temperature and specific displacement with DVB concentration during seeded polymerization.



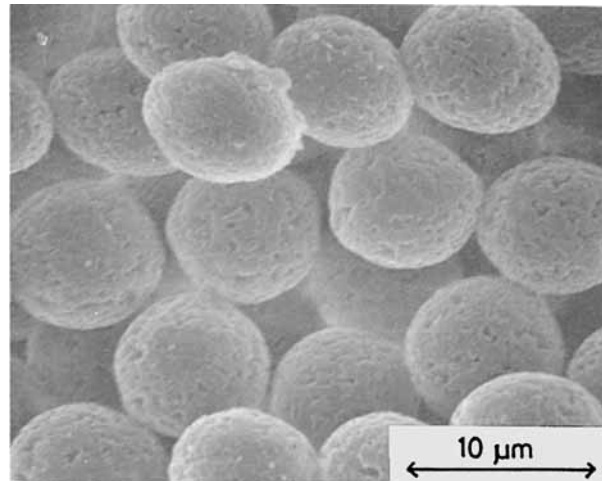
4.5%



8.9%



13.4%



17.9%

Figure 13 Scanning electron micrographs of the surface of the compacts obtained after hot pressing at 2 MPa up to 230°C. Percentage inscribed is that of DVB during seeded polymerization.

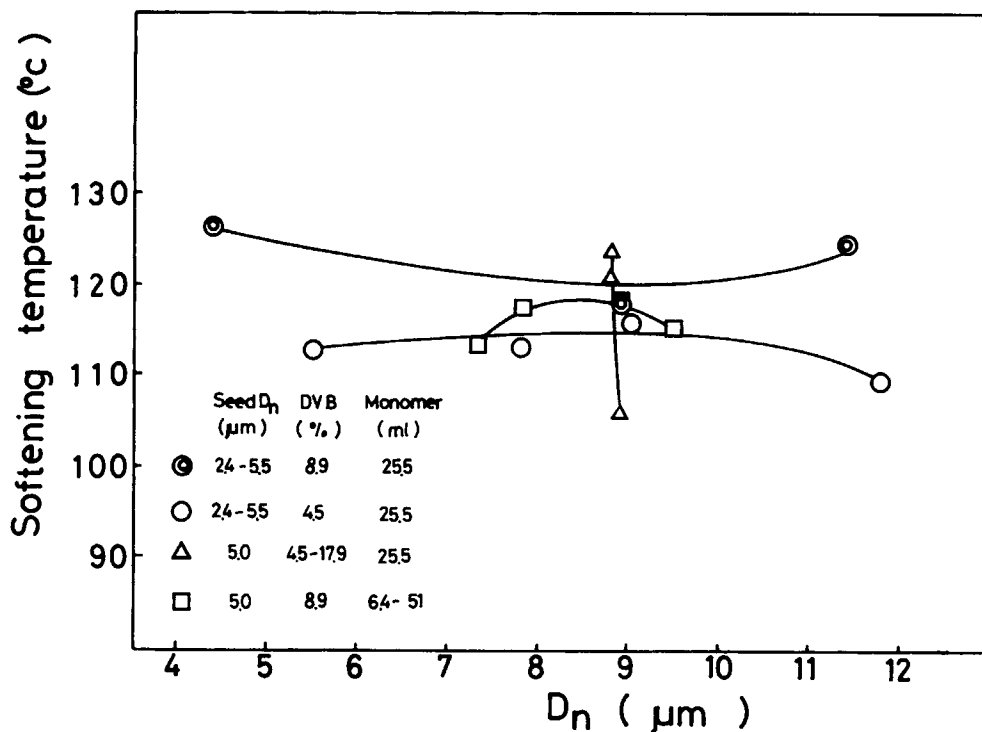


Figure 14 Relationship between the softening temperature, T_s , and the number-average diameter, D_n , of the seeded polymerized microspheres.

polystyrene microspheres containing divinyl benzene were prepared. State of seeded polymerized particle depends more on the total amount than on the composition of the monomer added. Monodispersed microspheres between 4.5 and 12 μm with desired softening temperatures ranging between 106 and 124°C are available with a free combination of these two properties.

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