Reactive Polymers. XXXII. Effect of Composition of Polymerization Feed on Morphology and Some Physical Properties of Macroporous Suspension Copolymers Glycidyl Methacrylate–Ethylene Dimethacrylate*

D. HORÁK, Z. PELZBAUER, M. BLEHA, M. ILAVSKÝ, F. ŠVEC, and J. KÁLAL, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia*

Synopsis

The effects of inert solvent concentration of crosslinking agent and initiator and polymerization temperature on specific surface area, porosity, penetration modulus, stress at break, and inner and surface morphology of the copolymer glycidyl methacrylate–ethylene dimethacrylate were investigated. There is a direct influence of interfacial tension between the continuous and dispersed phases in suspension at the beginning of polymerization on the morphology of the bead, and hence on the resulting physical characteristics of the structure.

INTRODUCTION

Preparation of polymeric sorbents requires obtainment of an optimal morphology for the given type of application, e.g., catalytic, chromatographic, biomedical, etc. Particle size, specific surface area, porosity, and the mean pore size must be regulated. Satisfactory mechanical stability is also important.

In addition to inner morphology, compactness of the surface shell of the bead also plays an important part in the sorbent efficiency. The existence of a shell in sorbents based on glycidyl methacrylate was reported in an earlier article, and it was assumed that interfacial tension in suspension polymerization was involved in the formation of the shell.[1] The composition of the polymerization mixture affects both the inner and outer layer morphology differently. While the inner porosity is determined predominantly by the content of inert solvents in the dispersed phase, the specific surface area depends more on the concentration of the crosslinking agent. The content of these components determines the interfacial tension, which determines the morphology of the surface shell of particles. The objective of this study is to examine the effects of interfacial tension before polymerization and polymerization temperature on the morphology of the sorbent.

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EXPERIMENTAL

Preparation of Copolymers

The sorbents were prepared by radical suspension copolymerization of glycidyl methacrylate with ethylene dimethacrylate in the presence of a mixture of dodecanol and cyclohexanol and 2,2'-azobisisobutyronitrile as initiator. The composition of dispersed phases is given in Table I. A 1 wt % aqueous solution of the suspension stabilizer poly(vinylpyrrolidone), K 90 (Fluka A.G., Switzerland), was used as the continuous phase in all cases. The polymerization was conducted by a standard procedure at 70°C in a 250-ml reactor using an anchor-type stirrer (400 rpm). The polymerization procedure, separation, and fractionation with respect to particle size have been described.[2]

Determination of Interfacial Tension

The interfacial tension of the dispersed and continuous phases before the onset of polymerization was measured by the Harkins–Brown method. The liquid drop is squeezed in the modified apparatus (in our case this liquid is the dispersed phase because of good wetting, although it is lighter than the continuous phase) through a capillary with a highly polished orifice and with specific diameter. The pressure is developed by a mercury column, which is squeezed out by a syringe in a linear dosing device. The dispersed phase (20 to 40 drops) is slowly dropped at constant rate into the continuous phase thermostated at 25°C; the number of drops is recorded with a counter by means of a photocell. The volume of the added liquid is measured with an accuracy of 1% in a graduated buret.

The interfacial tension γ (in N/m) was calculated from[3]

$$\gamma = \frac{l^2 \Delta d g}{2 v^2}$$

where l is the radius of the capillary (m), Δd is the density difference (kg/m^3) between the dispersed and continuous phases (measured with a vibrational densitometer DNA 02 C, A. Paar, Austria), g is the acceleration of gravity (m/sec^2), and v is the ratio of the capillary radius and capillary constant (determined from tables[3]).

Electron Microscopy

Sorbent was fixed using an adhesive with colloid silver onto aluminum supports and cut with a blade. After coating with gold in a Balzers sputtering device, the grains were photographed with a JSM 35 scanning electron microscope (JEOL, Japan) at 20 kV in the mode of secondary electrons.

Determination of Specific Surface Area, Porosity, and Mechanical Characteristics

The specific surface area (S_{BET}) was determined by the nitrogen dynamic desorption method and calculation according to the BET equation using a Quantasorb apparatus.[4] Porosity (ϵ_{WR}) was determined from water regain in spherical particles by the centrifugation technique.[5]

TABLE I
Composition and Properties of Suspension Polymers[a]

Sample No.	x_1	x_2	x_3	x_4	S_{BET}, m²/g	ϵ_{WR}, %	σ_b, MPa	A, MPa	ϵ_b
1	20	75	2.2	15	0	0	244.39	289.69	0.50
2	60	75	0.2	15	157.5	63	21.38	32.27	0.31
3	67	85	4	10	304.0	69	10.26	17.35	0.41
4	77	85	4	10	266.4	79	2.27	3.25	0.41
5	77	95	4	10	338.3	79	2.30	3.80	0.37
6	60	25	2.2	15	40.4	60	10.63	15.29	0.41
7	60	75	2.2	0	232.5	65	—	—	—
8	60	75	2.2	30	161.8	68	—	—	—
9	60	85	2	10	311.7	66	16.81	32.92	0.30
10	60	85	2	20	281.1	66	12.42	24.15	0.26
11[b]	60	25	0.2	15	35.0	49	28.01	73.12	0.16
12	60	75	2.2	5	240.5	64	16.80	27.82	0.35
13[b]	60	75	0.2	5	161.1	64	19.99	29.59	0.39

[a] x_1 = Concentration of inert components in the dispersed phase in vol %; x_2 = concentration of ethylene dimethacrylate in the monomeric mixture in vol %; x_3 = concentration of initiator in the monomeric mixture in wt %; x_4 = concentration of dodecanol in the inert solvents mixture in vol %.
[b] Polymerization temperature 90°C.

The deformational characteristics of the individual beads in the dry state were measured at 20°C;[6] the planes compressing the bead were made of steel. The force transducer had a maximal range of 10 kg, and the deformation indicator operated with the accuracy ±0.0005 mm. The bead was deformed to a compression y_1, and the respective force F_1 was determined after 2 min of relaxation; the compression was then increased and the whole procedure repeated until the bead failed. The dependences thus obtained are shown in Figure 1. The penetration modulus A was determined from the dependence of F_i on y_i using the expression[6]

$$A = \frac{3(2S)^{3/2}}{16r^{1/2}}$$

where r is the bead radius and S is the slope of the dependence of $F_i^{2/3}$ on y_i (Fig. 1). The stress at break, σ_b, was related to the deformed bead surface area and calculated from

$$\sigma_b = \frac{F^m}{\pi \Delta^m (r - \Delta^m/4)}$$

where F^m is the breaking force and $\Delta^m = y^m - y_0$ (y^m and y_0 are, respectively, the y values at break of the bead and at the beginning, cf. Fig. 1). The relative compression (strain) of the bead at break, ϵ_b, was also determined, using the expression $\epsilon_b = \Delta^m/2r$. Measurements performed with beads of various radii showed that in the range $r \geq 0.25$ mm the deformational characteristics are independent of the bead size, and samples with $r > 0.25$ mm were used in further measurements.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of interfacial tension between the dispersed and continuous phases γ on the composition of the dispersed phase in a concentration range suited for practical applications. While steeply decreasing with
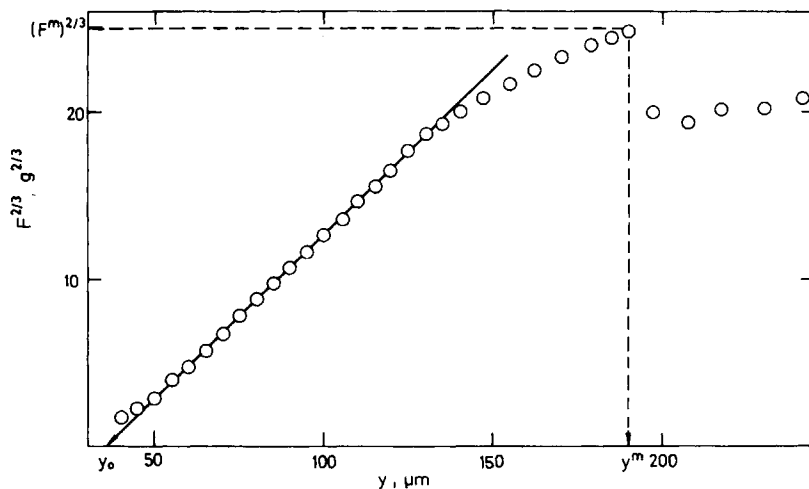

Fig. 1. Dependence of force F on compression y.
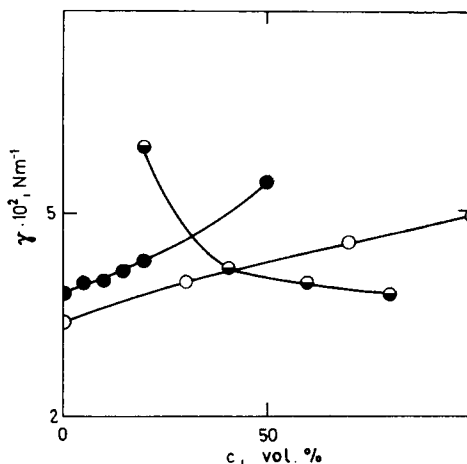
Fig. 2. Effect of composition of the dispersed phase c on interfacial tension between the dispersed and continuous phases γ: (O) c volume concentration of crosslinking agent. Polymerization mixture: monomeric mixture:inert solvents mixture 2:3, dodecanol:cyclohexanol 1:9; (◓) c volume concentration of inert solvents mixture. Polymerization mixture: glycidyl methacrylate:ethylene dimethacrylate 7:3, dodecanol:cyclohexanol 1:9; (●) c volume concentration of dodecanol in the inert solvents mixture. Polymerization mixture: monomeric mixture:inert solvents mixture 2:3, glycidyl methacrylate:ethylene dimethacrylate 7:3.

increasing content of the mixture of inert solvents, γ increases with decreasing content of the crosslinking agent or dodecanol in the mixture. Hence, by changing the composition of the polymerization mixture, it is possible to affect γ and thus also the resulting structure of the polymer.

Effect of Concentration of the Mixture of Inert Solvents and Crosslinking Agent

With decreasing content of inert solvents, not only the outer shell of the bead but the whole inner structure of the polymer become much more compact (Fig. 3), in agreement with the increasing interfacial tension γ (Fig. 2). In all cases, the inner structure of the macroporous beads consists of submicroscopic particles (globules), (Figs. 3–7) and also sugggests the dependence of force F on compression y (Fig. 1). The destruction of the bead brings about only a partial drop in force (~30–50%). The compact surface (shell) and inner structure are observed with sample 1 [Fig. 3(a)], as nonporous and in the glassy state. For pairs of samples with the same content of crosslinking agent, 75 vol % (samples 1 and 2) and 85 vol % (samples 3 and 4), the higher content of inert solvents is reflected in a higher porosity ϵ_{WR} (Table I) and in a higher zoning of the shell and of the inner structure of the polymer. This can be distinctly seen for the second pair, where the shell of the sample with the higher content of inert solvent [sample 4, Fig. 3(d)] exhibits larger surface pores, indicating a smaller compression of the product during polymerization due to the lower contraction of the monomeric drop compared with sample 3, Figure 3(c). In addition to the correlation between morphology and porosity, one can also see the correlation between morphology and mechanical characteristics (Table I). If the content of inert solvents and, consequently, the porosity are higher, the surface shell is less compact and the
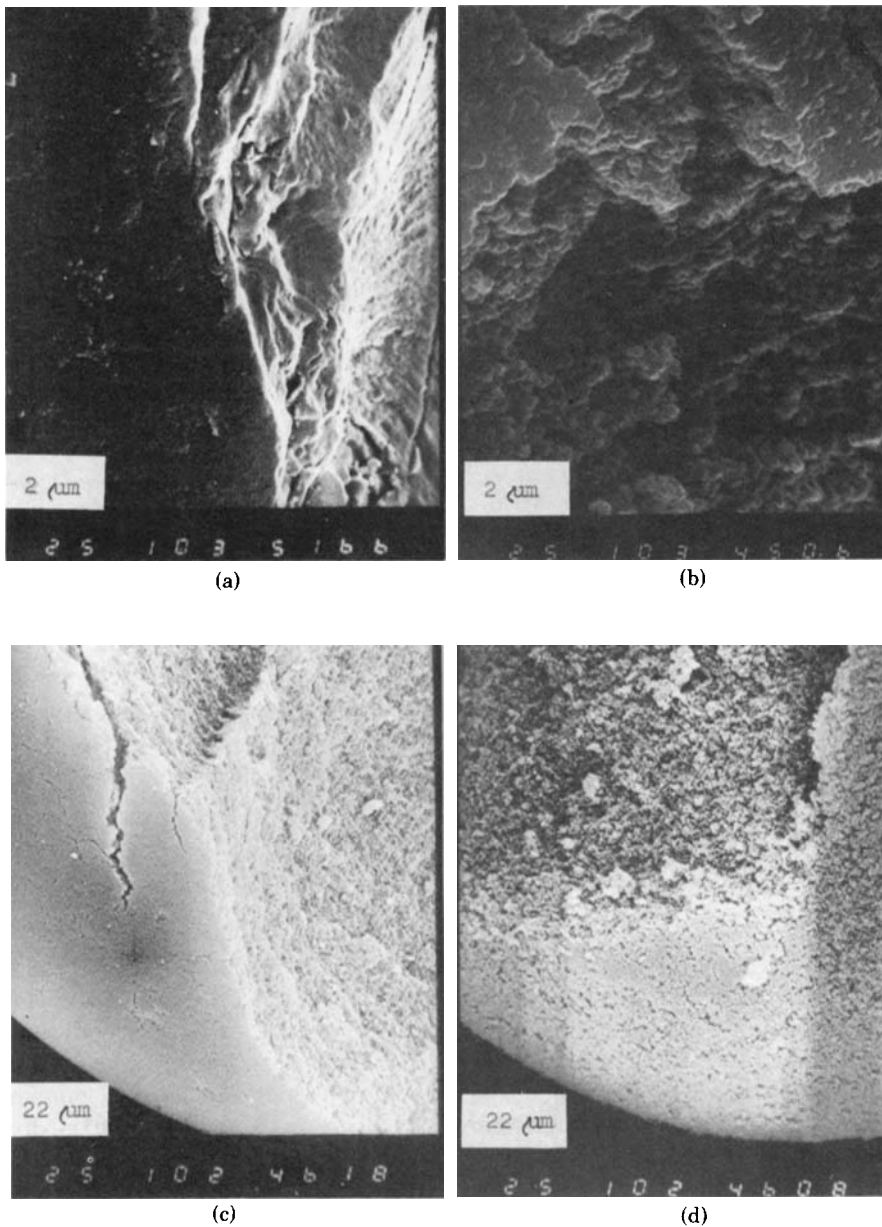
Fig. 3. Effect of content of inert solvents mixture on morphology of sorbents.   At 75% of cross-linking agent: (a) 20% of inert components (sample 1), (b) 60% of inert components (sample 2).   At 85% of crosslinking agent: (c) 67% of inert components (sample 3), (d) 77% of inert components (sample 4).

penetration modulus A and the stress at break σ_b are lower than those observed with less porous samples.   The strain at break ϵ_b does not depend on the content of the inert solvents to any considerable extent.   Extreme values for modulus A and stress at break σ_b and an unusually compact submicroscopic structure can be observed in sample 1 prepared at low concentration of the inert mixture and high interfacial tension.   The effect of the inert solvents becomes more
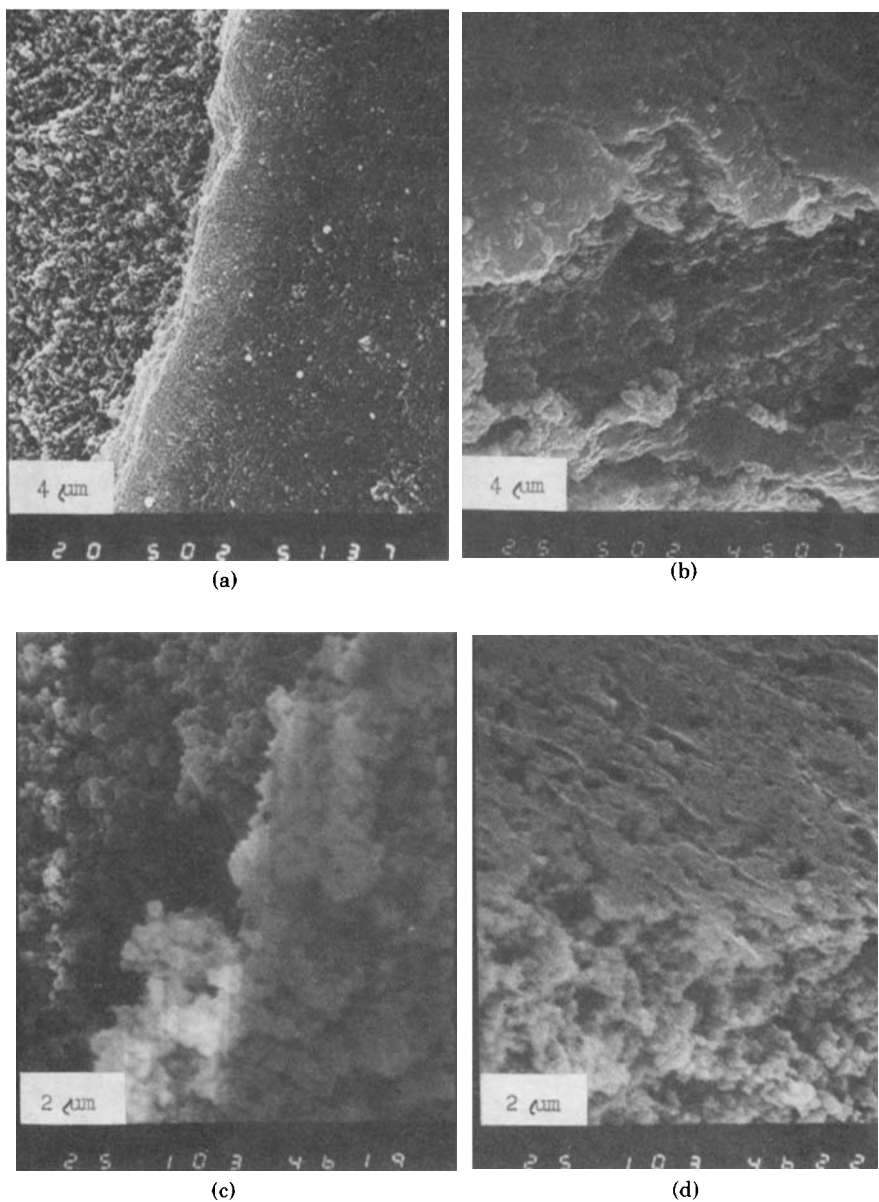
Fig. 4. Effect of content of crosslinking agent on morphology of sorbents. At 60% of inert components: (a) 25% of crosslinking agent (sample 6), (b) 75% of crosslinking agent (sample 2). At 77% of inert components: (c) 85% of crosslinking agent (sample 4), (d) 95% of crosslinking agent (sample 5).

pronounced at lower crosslinking (75 vol % crosslinking agent) than at higher crosslinking (85 vol %), where the system is more rigid.

An increase in crosslinking agent results in a finer globular structure of heterogeneous polymers and in a larger specific surface area.[7] The effect of the crosslinking agent on morphology is documented for the pair of samples 6 and 2 with 60 vol % and for the pair of samples 4 and 5 with 77 vol % of inert solvents
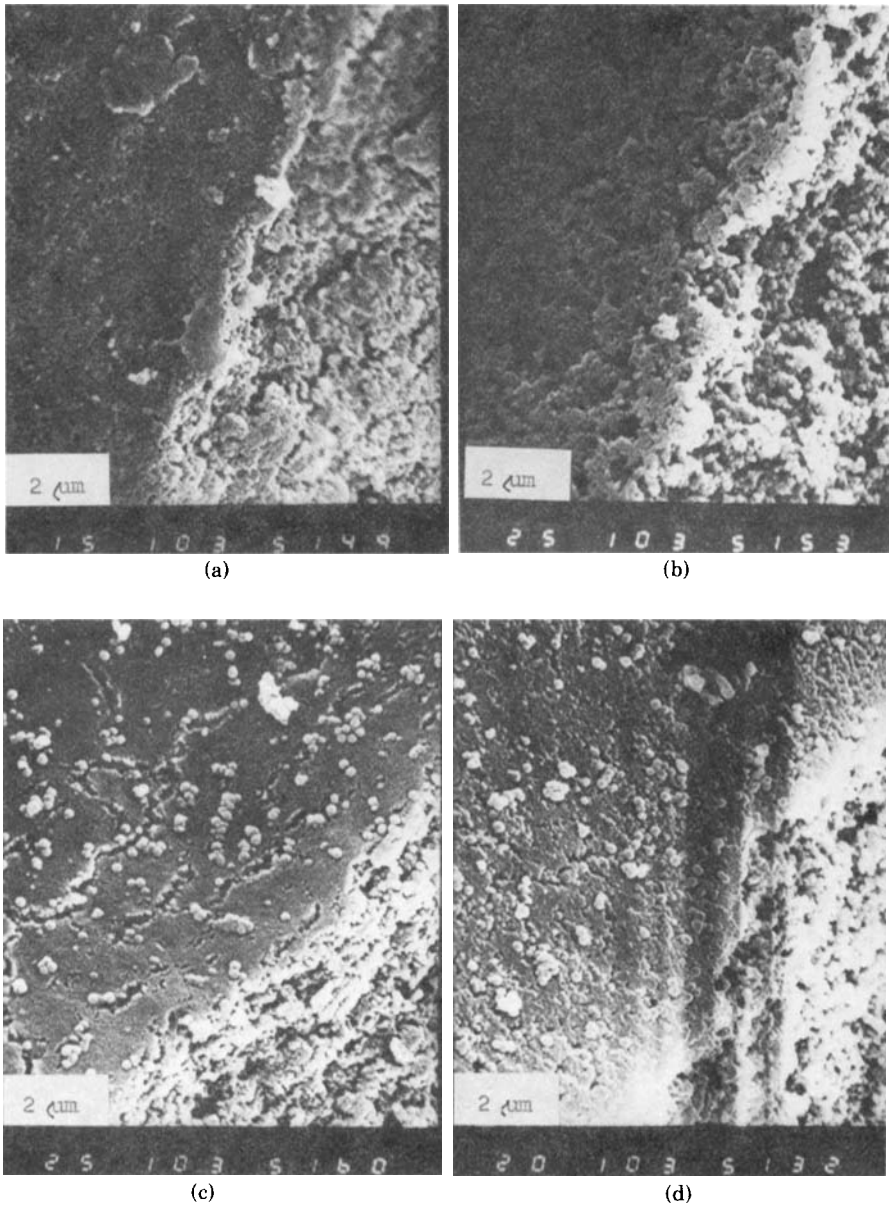
Fig. 5. Effect of content of dodecanol on morphology of sorbents at 60% of inert components. At 75% of crosslinking agent: (a) 0% of dodecanol (sample 7), (b) 30% of dodecanol (sample 8). At 85% of crosslinking agent: (c) 10% of dodecanol (sample 9), (d) 20% of dodecanol (sample 10).

(Fig. 4). With increasing concentration of ethylene dimethacrylate, the interfacial tension of the dispersed and continuous phases increases slightly (Fig. 2). The specific surface area also increases (Table I). The surface shell of the particle is more compact, as demonstrated by the increase in the modulus A. At low crosslinking the system is less rigid, the globules are large and "soft," and they are more compressed by external pressure. The increase in the surface area results from the decreasing size of the globules.[1] Porosity increases only in low
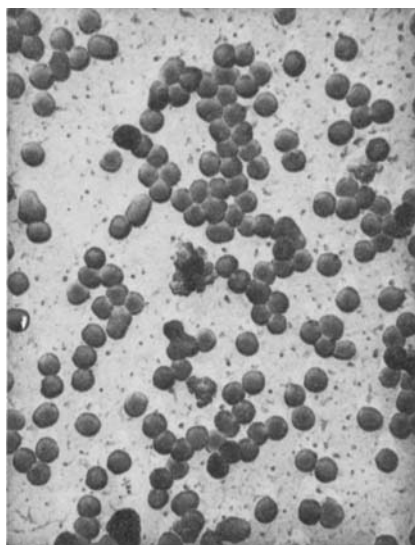
Fig. 6. Micrograph of an extraction replica of sample 10 taken with a transmission electron microscope; magnified 22000×.

crosslinking, while it remains unchanged at the higher levels (Table I). This is due to the higher compressibility during formation of the particle by interfacial tension in the less crosslinked samples. Although samples 1 and 2 and 2 and 6 differ in the initiator concentration, the conclusions presented above are valid. Within the given range of changes of initiator concentration, the latter has no effect on the morphology of the sorbent.

Effect of Thermodynamic Quality of the Inert Solvents and of Polymerization Temperature

A mixture of dodecanol and cyclohexanol was used as the inert component controlling the macroporous structure. In this mixture the former compound is a thermodynamically poorer solvent.[8] At its higher concentration (samples 7–10, Table I), the products formed have a smaller specific surface area and are more porous. Contrary to expectation, the compactness of the shell increases with decreasing dodecanol content (Fig. 5), although the interfacial tension decreases (Fig. 2). The increasing compactness of the shell with decreasing dodecanol content is also suggested by an increase in the modulus A and in the stress at break σ_b (samples 9 and 10, Table I). A factor counteracting interfacial tension exists at a higher concentration of the thermodynamically poorer solvent (dodecanol); larger globules are formed[7] [compare Figs. 5(c) and 5(d)—0.17 μm vs. 0.19 μm], whose adhesive properties are weaker. This is due to the lower stationary concentration of globules at higher dodecanol concentration.[7] The growing macromolecular radicals are more likely to become adsorbed on the globules already separated than to produce new globules. At the same time, larger globules have more difficulty in entering the shell than the small ones [Figs. 5(c) and 5(d)] and are, therefore, individually located on the bead surface. The globules are also less adhesive (in a poorer solvent they behave as if they were more crosslinked), and the compactness of the shell is thus weaker. This is
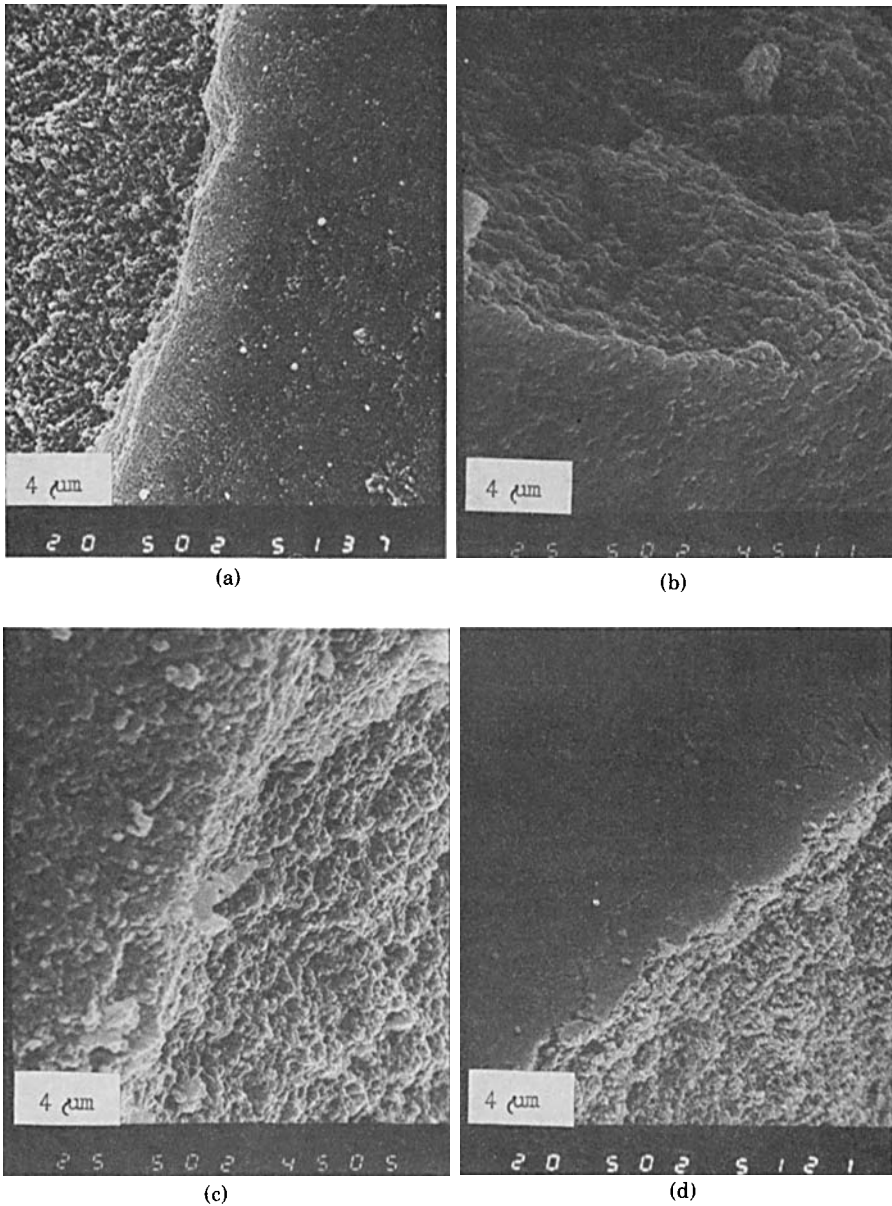
(a)   (b)

(c)   (d)

Fig. 7. Effect of polymerization temperature on morphology of polymers at 60% of inert compo-
nents. At 25% of crosslinking agent: (a) 70°C (sample 6), (b) 90°C (sample 11). At 75% of cross-
linking agent: (c) 70°C (sample 12), (d) 90°C (sample 13).

corroborated by the finding that these large globules may be readily extracted
by the polystyrene/carbon replica (cf. Fig. 6).

At higher polymerization temperature, the particles of the suspension polymer
have a more compact shell due to annealing of globules (Fig. 7). Samples ob-
tained at the higher polymerization temperature also have a higher modulus A
and stress at break σ_b (Table I); the temperature effect is stronger at low con-
centrations of the crosslinking agent (samples 11 and 6) than at higher ones

(samples 13 and 12). This again corroborates the finding that porosity is lower at lower crosslinking.

Finally, any change in the composition of the dispersed phase which brings about a change in the interfacial tension in suspension polymerization affects the morphology of the polymeric product. The decisive role is played by the inert solvents. Their decrease causes the interfacial tension to rise, leading to an increase in the compression of the dispersed polymerizing phase during particle formation. In the case of a higher concentration of the crosslinking agent, the polymer formed is more rigid; compression cannot be reflected in a change in structure as with a low ethylene dimethacrylate concentration.

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