# Resins Containing Extractants: Morphology of Polymers Prepared by Polymerization of Vinyl Monomers in the Presence of Uranium-Selective Extractants

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## Synopsis

The effect of a selective organophosphorus extractant on the structure and properties of crosslinked polymers was studied. The extractant, incorporated in the polymerization mixture, affected the formation of the polymer. The uranium capacity of the resin was directly proportional to the amount of extractant. The use of scanning electron microscopy showed that the polymers are macroporous and that the porosity depends on the amounts of extractant and crosslinking agent.

## INTRODUCTION

Macroporous polymer sorbents are most frequently prepared by cross-linking polymerization in suspension.[1-4] Macroporosity of vinyl and polyvinyl copolymers is induced by a nonsolvating diluent, which, by causing phase separation during the polymerization process, is responsible for the formation of macropores.[5-6]

The porosity of styrene–divinylbenzene (St–DVB) copolymers has been intensively studied during the past 15 years. It was established that the pores represent spaces between agglomerated microglobules and that the porous polymer consists of a system of globules arranged so that the spaces between them form communicating channels.[7-10]

The porosity, which is an important structural characteristic of polymer sorbents, may be directly evaluated by electron microscopy. In contrast with indirect methods for characterization of porosity (determination of apparent density, measurement of surface area by BET, and mercury porosimetry), this method "makes visible the porous structure and gives a good notion not only of the size but also of the shape and arrangement of the pores and aggregated globular particles," as Pelzbauer showed in his pioneering work.[9-11]

Knowledge of the structure of a macroporous copolymer and of mechanism of its formation is necessary for making the proper choice of conditions for the synthesis of polymers to be used as a basis for the preparation of polymer-supported catalysts and reagents or of "polymer-immobilized extractants." The latter is the name we use to designate polymeric sorbents prepared by polymerization of vinyl and polyvinyl monomers in the pres-

ence of an extractant. Using this method, Kanczor and Meyer[12,13] first prepared macroporous St–DVB copolymer sorbents containing bis-2-diethylhexylphosphoric acid (DEHPA) and tributylphosphate (TBP).

We are developing the above-mentioned method in our laboratory for the production of a selective sorbent for the recovery of uranium from wet-process phosphoric acid.[14-16] For this purpose, a synergistic mixture of two extractants, DEHPA and trioctylphosphinoxide (TOPO), was immobilized in a polymer matrix during the process of crosslinking polymerization. Having no vinyl groups, DEHPA and TOPO do not participate in the process of polymerization directly but may serve as nonsolvating diluents. In this case, the structure of the resultant copolymer and its properties may be strongly influenced by the extractant(s).

In the present work we studied the morphology and mechanical strength of polymer sorbents prepared in the presence of a mixture of DEHPA and TOPO. The sorption characteristics of the sorbent with respect to uranium were also studied.

## MATERIALS AND METHODS

**Preparation of Sorbents.** The monomers [St, methylmethacrylate (MMA), and DVB] were washed free of polymerization inhibitor with 10% sodium hydroxide followed by several water washes. The extractant mixture was prepared by dissolving TOPO in DEHPA. The polymerization mixture was prepared by mixing together the monomers, benzoyl peroxide, and the extractants. A 2% aqueous solution of starch was used as the continuous phase. The polymerization was done by a standard procedure at 80°C in a 100-mL reactor with an anchor stirrer. The speed of agitation was regulated according to the size of the drops that were created during mixing of the two phases. After completion of the reaction, the beads were filtered, washed with hot water, subjected to steam distillation, and dried.

**Electron Microscopy.** Samples of the beads were extracted with acetone in a Soxhlet apparatus in order to remove the extractant, which filled the pores, adhering closely to the polymer skeleton. (The extracted beads cannot be used for uranium sorption; they served only for demonstration of the morphology and structure of the polymer.) The beads were dried, fixed by an adhesive onto a support, cut with a blade, and vacuum-coated with gold. The fractured beads were photographed with a scanning electron microscope.

**Determination of Uranium Sorption.** Uranium sorption was determined in a batch experiment by equilibrating 0.2 g of the sorbent with 10 mL of $4.5M$ $H_3PO_4$ containing 140 ppm of uranium. The concentration of uranium in the acid before and after 24 h of contact with the resin was determined spectrophotometrically. The uranium dissolved in the phosphoric acid was reduced to uranium (IV) by adding a small amount of zinc powder. The zinc was dissolved in the acid for 10 min, and a 0.5-mL sample was removed and placed in a 10-mL calibrated cylinder. A solution of Arsenazo III (BDH) indicator was added to the sample to bring the volume to 10 mL. The adsorption of the resultant complex was measured at 618 nm in a Beckman DB Spectrometer immediately after mixing. The uranium

TABLE I
Composition of the Polymerization Mixtures Used and Uranium Capacity and Mechanical Strength of the Resultant Sorbents

| Sample no. | DVB (% in monomer mixture) | Monomer | $D_d^a$ | DEHPA/TOPO (molar proportions) | $U$ capacity | Mechanical strength (kg) | Illustrated in figure |
|---|---|---|---|---|---|---|---|
| 1 | 30 | Styrene | 0.34 | 0.1/0.012 | 46 | 20 | 2 |
| 2 | 30 | Styrene | 0.43 | 0.1/0.012 | 56 | 10 | 3 |
| 3 | 30 | Styrene | 0.51 | 0.1/0.012 | 70 | 3 | 4 |
| 4 | 15 | Styrene | 0.34 | 0.1/0.026 | 42 | — | — |
| 5 | 15 | Styrene | 0.43 | 0.1/0.012 | 56 | — | — |
| 6 | 15 | Styrene | 0.51 | 0.1/0.012 | 66 | — | — |
| 7 | 15 | Styrene | 0.34 | 0.1/0 | 19 | — | — |
| 8 | 15 | Styrene | 0.34 | 0.1/0.012 | 48 | 20 | 5 |
| 9 | 15 | MMA | 0.21 | 0.1/0.023 | 40 | 32 | 6(a), 7 |
| 10 | 15 | MMA | 0.30 | 0.1/0.012 | 28 | — | 6(b), 7 |

a $D_d$ = concentration of diluent (consisting of solvent and extractant) in the dispersed phase. $D_d = V_d/(V_m + V_d)$, $V$ = volume, $d$ = diluent, $m$ = monomer.

b $U$ = % uranium sorbed by 0.2 g sorbent from 10 mL of 4.5M phosphoric acid.
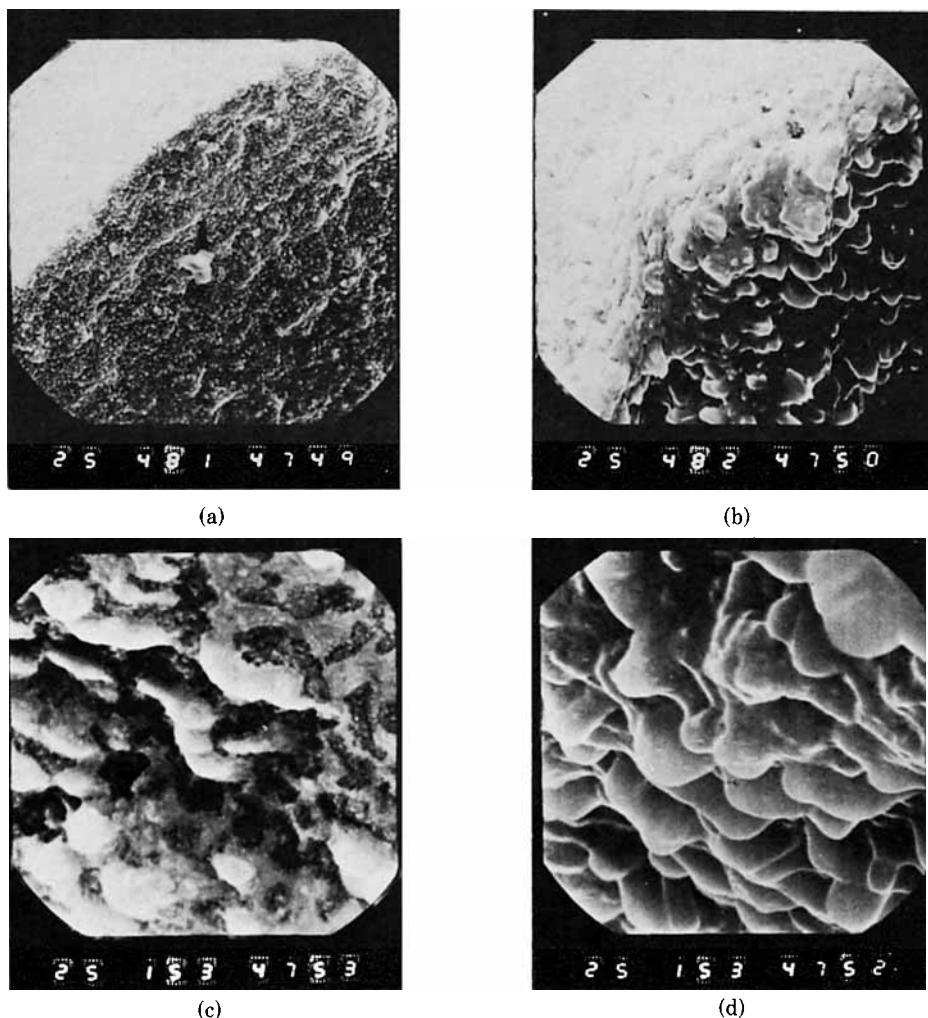
Fig. 1. Cross section of an unextracted styrene-based bead (filled with 50% of the extractant mixture). (a,b) Surface and interior; (c) surface; (d) interior. (a) $\times$ 480; (b) $\times$ 4800; (c) and (d) $\times$ 15,000.

sorption, or uranium capacity of the resin, was calculated from the difference between the concentrations of uranium measured in the acid before and after contact with the sorbent.

**Mechanical Strength.** The mechanical strength of individual beads in the dry state was measured by using an Instron instrument in which the bead is deformed by a constant force until it fails. For each sample, the procedure was repeated with 10 beads having a radius equal to the average radius. The mechanical strength was characterized by the magnitude of the force required to start breaking the beads. As a result of the threshold force, the bead was either broken completely, or it was gradually deformed, retaining its rounded shape under additional force. It should be noted that this test supplies only a partial indication of the mechanical resistance of the polymer sorbent when it is used in a column process. However, the method is regarded as a useful tool for preliminary information on the mechanical properties of ion-exchange resin.[17,18]
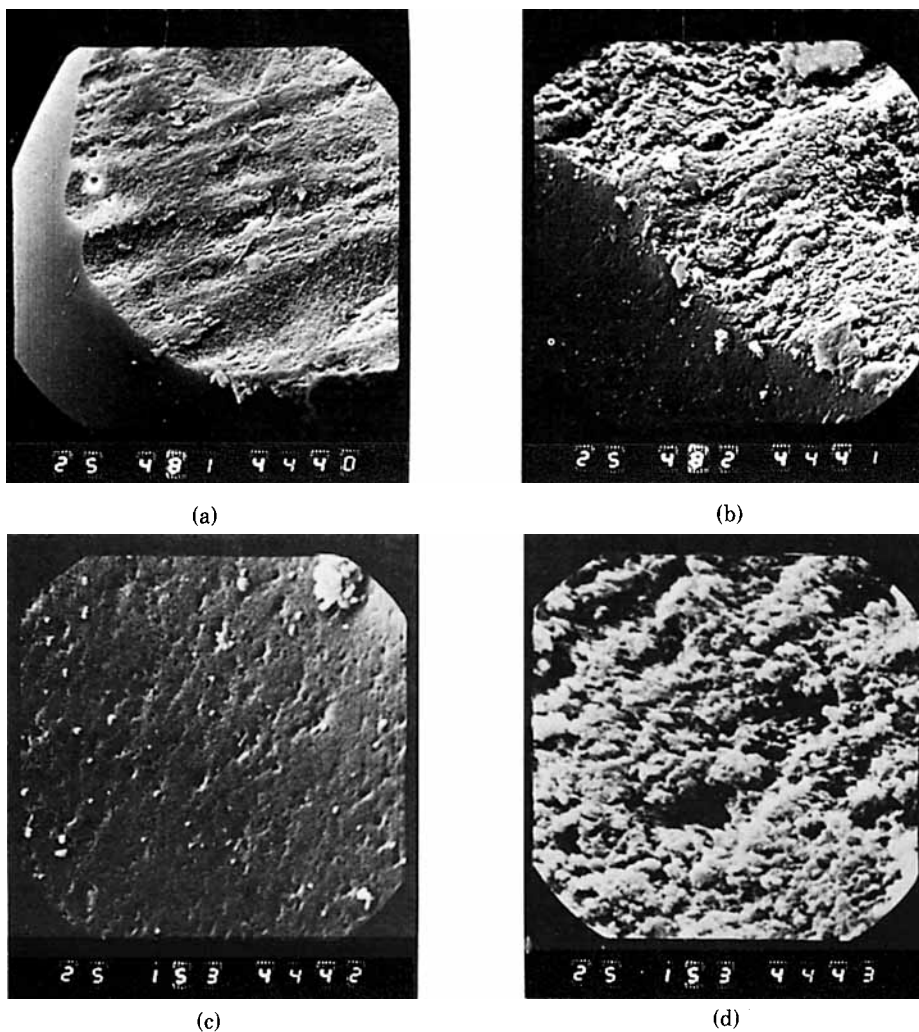
(a)

(b)

(c)

(d)

Fig. 2.   Cross section of a bead of styrene-based resin (34% DEHPA/TOPO). The DEMPA/TOPO was removed during preparation of the sample for electron microscopy as described under Materials and Methods. (a,b) Surface and interior; (c) surface; (d) interior. Magnifications same as in Figure 1.

## RESULTS

The effect of the components constituting the polymerization mixture on the properties of the resulting sorbents was studied by varying their proportions. The composition of the polymerization mixtures used in the various experiments, as well as the uranium capacity and mechanical strength of the resultant sorbents, are presented in Table I.

Figure 1 presents the results of an SEM examination of an extractant-containing bead (except for this instance, all the samples for SEM study were treated as described under Materials and Methods). The cross section of the bead clearly shows its structure: its surface is covered by extractant, which also fills the inner spaces (compare Fig. 1 with Fig. 4, which shows the same type of head after removal of the extractant mixture.)
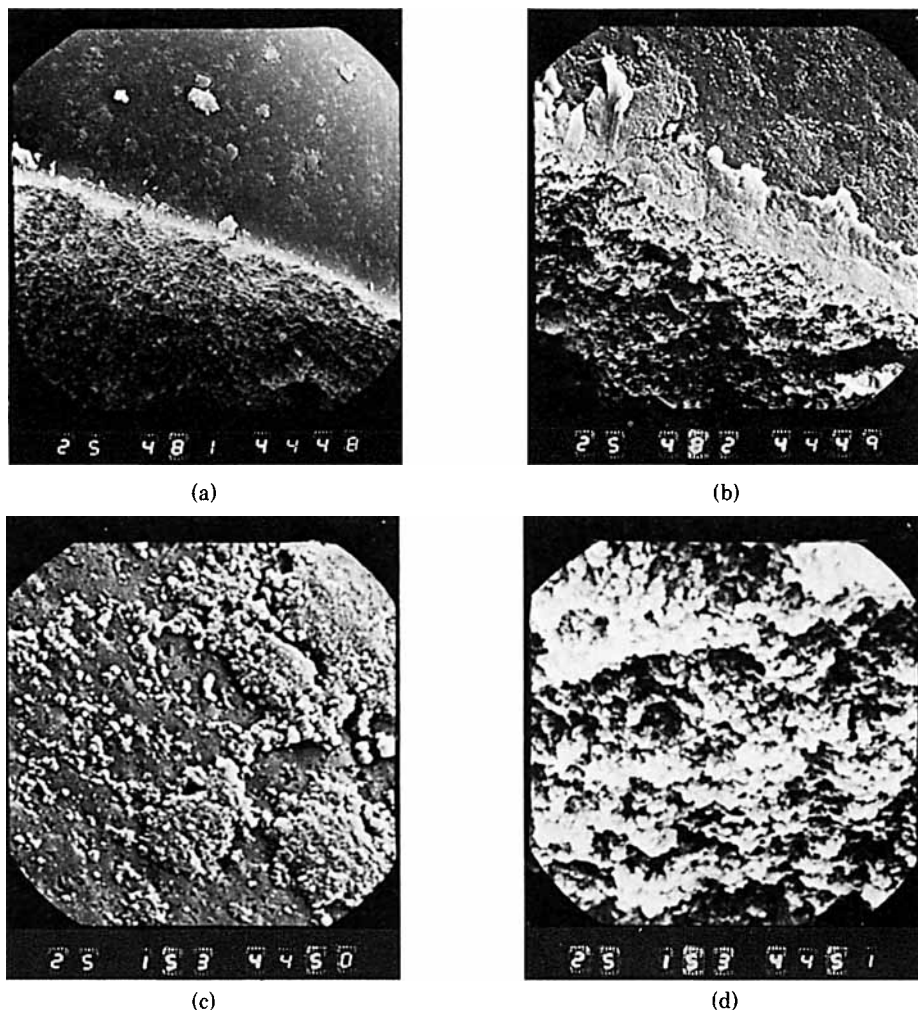
Fig. 3. Cross section of a bead of styrene-based resin (43% DEHPA/TOPO). Sample was prepared as described under Materials and Methods. (a,b) Surface and interior; (c) surface; (d) interior. Magnifications same as in Figure 1.

## Effect of the Diluent

In the first three samples (Table I), the volume fraction of the extractant DEHPA–TOPO in the reaction mixture was varied. As expected, the higher the percentage of the extractant mixture in the polymer mixture, the higher the uranium capacity. The mechanical strength was, however, inversely related to the extractant content; i.e., a force of 20 kg was needed to break the beads formed from a mixture containing 34% extractant mixture as compared with only 3 kg for those formed from a mixture containing 51% extractant mixture. In all samples, the beads were broken completely at the starting point of breakage.

SEM examination (Figs. 2–4) clearly revealed differences in the surface morphology of beads from the three samples. Those from sample no. 1 had
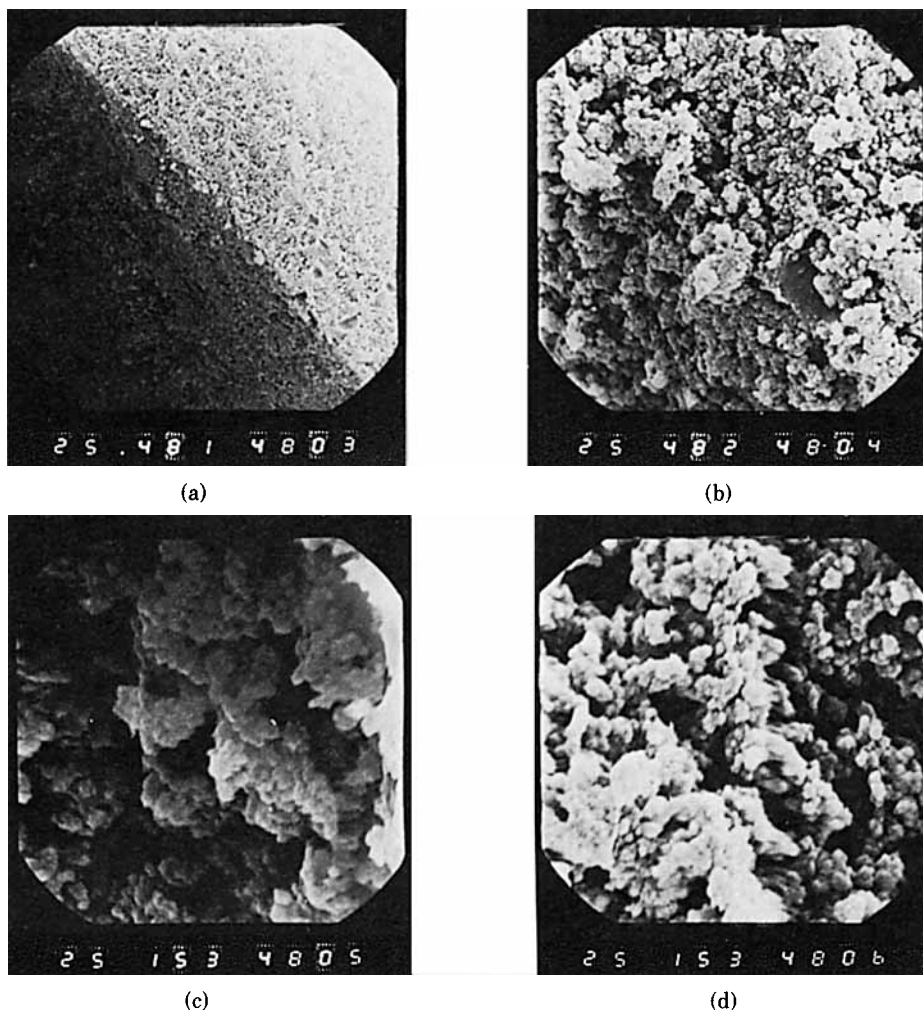
Fig. 4. Cross section of a bead of macroporous styrene-based resin (50% DEHPA/TOPO). Sample was prepared as described under Materials and Methods. (a,b) Surface and interior; (c) surface; (d) interior. Magnifications same as in Figure 1.

a rather smooth surface [Fig. 2(a)–(c)], the beads of sample no. 2 and a moderately porous surface [Fig. 3(a)–(c)], while the surface of beads from sample no. 3 isplayed a highly developed, open porous structure [Fig. 4(a)–(c)]. The beads of all three samples had a typical globular internal structure [Figs. 2(d), 3(d), and 4(d)]. However, the size and arrangement of these globules differed with the change in the content of diluent (the DEHPA–TOPO mixture). The higher the percentage of diluent, the globules and the less compactly they were packed. As a result of the differences between the surface and the interior, the beads of samples no. 1 and 2 were characterized by a sharp boundary between the two zones (Figs. 2(a), (b) and 3(a), (b), respectively). In contrast, the porous structure of the beads of sample no. 3 was more uniform along the diameter of the cross section [Fig. 4(a)], representing a continuous system of globules and voids forming communicating channels between the external layer and the interior [Fig. 4(b)].
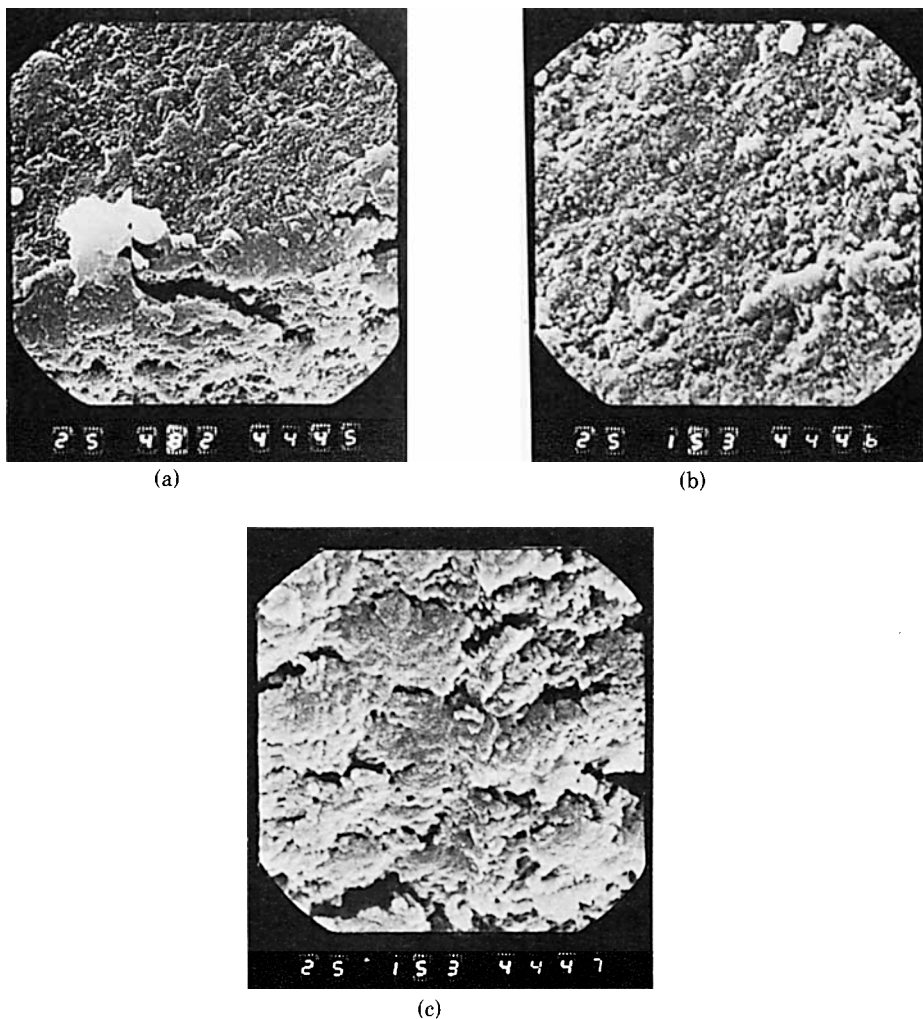
(a)



(b)



(c)

Fig. 5. Cross section of a styrene-based bead (15% DVB; 34% DEMPA/TOPO). Sample was prepared as described under Materials and Methods. (a) Surface and interior ($\times$ 4800); (b) surface ($\times$ 15,000); (c) interior ($\times$ 15,000).

## Effect of DVB

In the next three samples the amount of DVB was reduced to 15%. This reduction did not change the ability of the sorbent to sorb uranium. The capacity was influenced by the amount of extractant mixture. Sample no. 7 exhibited the lowest capacity because only DEHPA was used. Comparing samples no. 1 and 8, we can see that the force required to start breaking the beads was also unchanged, 20 kg being required for both these samples. However, unlike the beads of sample no. 1, those of sample no. 8 were gradually deformed and maintained their characteristic rounded shape during the process of deformation.

Figure 5 shows the surface and internal morphology of a bead from sample no. 8 at 15,000$\times$ magnification. The surface shell of the beads is rather

smooth [Fig. 5(a), (b)]. Their interior differed significantly from that of samples nos. 1–3, in that no clear globular structure could be discerned at 15,000× magnification. Instead, large structural blocks with free spaces between them could be seen [Fig. 5(c)]. No sharp boundary zone was evident between the exterior and interior of the beads [Fig. 5(a)].

### Effect of the Monomer

The polar MMA was used instead of the apolar styrene for the preparation of the last two samples, which differed from each other in the proportion of the extractant mixture to the monomer and in the DEHPA/TOPO ratio. The polymers based on MMA were superior to those based on styrene both in their higher uranium capacity [i.e., a smaller amount of extractant was required for obtaining the same uranium capacity (Table I, sample no. 10 vs. sample no. 2)] and in their higher mechanical strength (Table I). As was the case with styrene, the uranium capacity of the MMA-based beads also increased as the amount of DEHPA–TOPO mixture was increased.

The SEM photographs of the two samples [Fig. 6(a), (b)] illustrate the effect of the monomer on the morphology of the bead. Under the same conditions (contents of DVB and diluent), the beads based on MMA were much more porous than those based on styrene [compare Fig. 6(b) with Fig. 5]. There is again a direct relation between the concentration of extractant and the structural uniformity of the beads, as was also shown for the polymers based on styrene. The surface of beads from sample no. 9 was smooth [Fig. 7(a)] relatively to their rough interior [Fig. 7(b)] with a boundary line dividing them [Fig. 7(a)]. On the other hand, both the surface and interior [Fig. 7(e), (d)] of beads from sample no. 10 were uniformly macroporous.



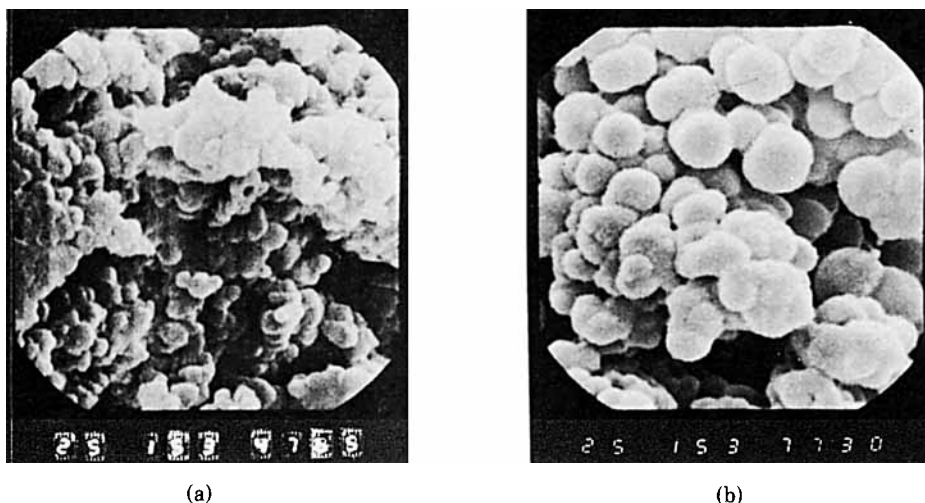(a)                                        (b)

Fig. 6. Interior of a bead of an MMA-based resin. Samples were prepared as described under Materials and Methods. (a) 20% DEMPA/TOPO; (b) 34% DEMPA/TOPO. (a) and (b) × 15,000.
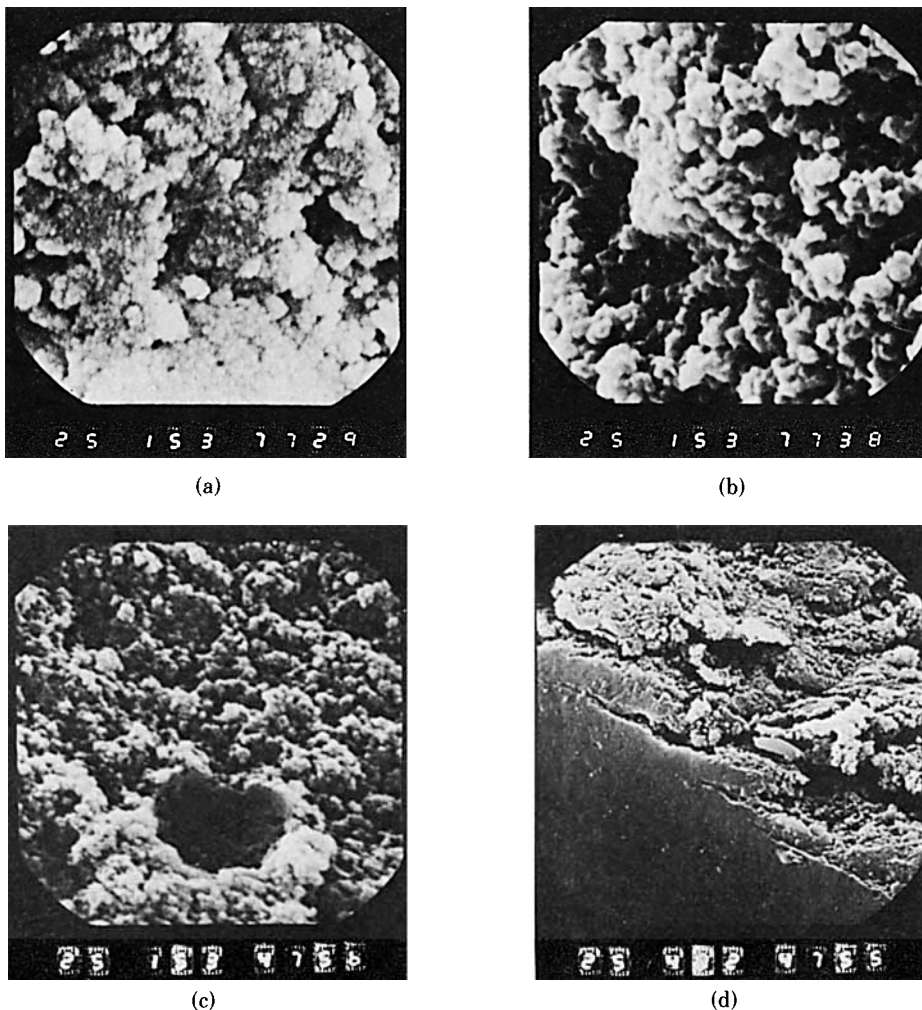
(a)

(b)

(c)

(d)

Fig. 7. Surface area of a bead of an MMA-based resin. Samples were prepared as described under Materials and Methods. (a) × 4800; (b)–(d) × 15,000.

## DISCUSSION

The two extractants, DEHPA and TOPO, which were used for the preparation of selective sorbents, are nonsolvents for the St–DVB copolymer. Therefore, the mechanism of formation of the porous structure in the St–DVB copolymer is most likely the same as that described by Millar and Dusek.[1,5,6] That is, nonsolvent leads to polymer precipitation very early in the reaction, prior to the gel point. This precipitating polymer forms a nucleus of microglobules, which aggregate to form larger particles. The size of these microglobules depends on the amount of the diluent and on its thermodynamic activity. When the DEHPA–TOPO content is low, the early precipitating polymer becomes relatively swollen in the monomeric mixture; the polymer nuclei formed later are in close proximity to those first

formed, resulting in a densely packed structure. This morphological feature is confirmed by the SEM photographs (Figs. 2 and 3). A remarkable feature here is the formation of a skin, i.e., a surface layer that is less porous than the interior of the bead (Figs. 2 and 3).

The mechanism of skin formation during the synthesis of macroporous ion-exchange resins has not been the subject of much attention. Skin formation was noted by Howard and Knutton[19] in their polymerization of vinylidene chloride and ethylenglycoldimethacrylate. Pelzbauer and co-workers[20] described the formation of a skin in the case of glycol–dimethacrylate copolymerization, as did Swatling and colleagues in the formation of membranes from St–DVB.[21] They attributed skin formation to a compressive effect of the interfacial tension that operates between the dispersed monomeric mixture and the aqueous phase.

In our work, skin formation was clearly evident at 30% DVB when the amount of DEHPA–TOPO mixture was lower than 50%. Evidently, under such conditions the polymer formed first is not sufficiently rigid to withstand the compression effect, probably as a result of good swelling in the monomer mixture. When the amount of this solvating monomer mixture is decreased by increasing the content of the nonsolvating DEHPA–TOPO, the polymer is not swollen, and is therefore rigid enough to resist. The structure of the surface and interior is then similar, with no skin formed (Fig. 4). The interior pores are thus open and in communication with the exterior.

The use of a large amount of crosslinkers results in the rapid formation of highly crosslinked polymer nuclei which trap and immobilize a significant amount of the extractant within the polymer skeleton. The rest of the extractant fills the spaces between the polymer particles and dissolves the remaining monomers. As polymerization progresses, newly formed polymer particles precipitate far from those precipitated earlier. Consequently, the porous structure of the completed bead will be uniform from the periphery to the core.

This explanation is supported by the formation of a relatively uniform porous structure with open pores when the polar MMA was used instead of styreme (Fig. 6). In this case, the fast precipitation of polymer nuclei is due to aggregation of the monomer molecules. Such aggregation is characteristic of polar monomers.[22-24] Therefore, with polar monomers a lower content of DVB is required for the formation of a highly porous polymer as compared with the amount needed for polymers based on apolar monomers.

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