

# Styrene Divinyl Benzene Copolymers. I. Texture of Macroporous Copolymers with Ethyl-2-Hexanoic Acid in Diluent

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## Synopsis

The texture and the pore size distribution of a set of styrene divinylbenzene copolymers, prepared by suspension polymerization with various compositions and various amounts of ethyl-2-hexanoic acid as diluent, have been studied using nitrogen adsorption-desorption isotherms, mercury porosimetry, and scanning-electron microscopy. It appears that pore volume and surface area may be well predicted in a large range of conditions (divinylbenzene contents between 20 and 60%, ethyl-2-hexanoic acid contents between 35% and 60%). In this range of conditions there are three structures: the elementary nuclei are spherical particles of about 100–200 Å in diameter. They are organized in microspheres of about 500–1000 Å, and the microspheres form aggregates (2500–5000 Å) more or less separated by large holes. The smaller pores (<40 Å) are in the microspheres, between the nuclei; they are present only if the amount of divinylbenzene is high enough. Intermediate pores (40–500 Å) are, in the aggregates, between the microspheres, although the larger pores between the aggregates range from about 500 Å to more than 10,000 Å, depending on the amount of diluent.

## INTRODUCTION

Macroporous styrene-divinylbenzene (DVB) copolymers, used as a base for ion-exchange resins, have been the subject of a large number of studies, very well reviewed by Seidl et al.<sup>1</sup> in 1967. Most of the more recent studies have been limited to the determination of pore volume and pore size distribution using mercury porosimetry. For instance, the effect of the combination of three types of diluents (polymer, precipitant, or solvent) have been described recently by Sederel and De Jong.<sup>2</sup> The pore size distribution of the small pores has been less thoroughly studied,<sup>3,4</sup> although the pollution control problems have renewed the interest in polymers with large surface areas and small pores. We assume that the use of ethyl-2-hexanoic acid, recently described in a French patent,<sup>5</sup> might be interesting in this connection. The present study deals with the texture of a set of styrene-DVB copolymers, prepared in suspension polymerization with various compositions of DVB from 5% to 60% of the monomer, and various amounts of ethyl-2-hexanoic acid (from 35% to 75% of the organic phase) as diluent. The technique used covered nitrogen adsorption-desorption isotherms, mercury porosimetry, swelling experiments with benzene, and, finally, scanning-electron microscopy.

## EXPERIMENTAL

### Materials

*Styrene* is a technical product (CdF Chimie) 99.2% pure, containing  $\alpha$ -methylstyrene (0.5%), ethylbenzene (0.07%), cumene (0.07%), toluene (0.06%) *o*-xylene (0.04%), benzene (0.02%), and vinyltoluene (0.02%). It is stabilized with 20–40 ppm *tert*butylcatechol.

*Divinylbenzene* (DVB) is also a technical product (CdF Chimie) with 61.3% DVB (29% *para* and 71% *meta*), ethylvinylbenzene (36.6%), diethylbenzene (0.95%), naphthalene (0.90%), triethylbenzene (0.21%), and vinyltoluene (0.01%). It is stabilized with 400–1000 ppm *tert*-butylcatechol. The *diluent* is 2-ethyl-1-hexanoic acid. Its content is expressed as weight percent of the total mixture of monomers and diluent.

Benzoylperoxide (BPO) is used as *initiator* (1% versus monomers). It is 82% pure and contains 18% water.

Lytron<sup>®</sup>, an ammoniacal salt of a copolymer of styrene and maleic anhydride, is used as a dispersive agent in a 2.5% concentration in water, although the protective agent is gum arabic (2% in water).

### Polymerization

The polymerization is carried out in water suspension at 88°C. A typical copolymerization is as follows. A volume of water corresponding to the volume of styrene plus DVB plus diluent is heated in the reaction vessel at 88°C. Gum arabic is then added as a protecting agent. The reaction mixture components are added rapidly at low stirring speed. The mixture contains 8% pure DVB (which means 13.1% commercial DVB), 86.9% pure styrene, 1% initiator, and 44% diluent added in the preceding sequence. The addition represents the zero time of the copolymerization. At this time the temperature is about 71°C. Then, the stirring speed is slowly increased (up to 200 rpm), and the dispersion agent is introduced when the first beads begin to “sparkle” (2–3 min after time zero). Within 10 min, the temperature is again at 88°C, remaining constant ( $\pm 0.5^\circ\text{C}$ ) until the end of the reaction. After about 26 min the “sticking point” occurs, at which time the beads give sticky filaments when pressed. The stirring speed is then increased in order to avoid coalescence. Three minutes later, the gel point appears (at about 20% conversion), where the beads are no longer sticky. The original stirring speed is resumed. Thirty minutes after the gel point, the “solidification” state is reached, and 3 hr later the conversion is 95%. The last 4 hr at 88°C correspond to the annealing time. During this last period, the beads harden and take their final mechanical properties. Heating is switched off 8 hr after the introduction of the reaction mixture. The beads are decanted, sieve-sized (0.15-mm diameter), and washed with water.

### Post-treatment

The diluent is extracted after polymerization with methylalcohol in a soxhlet and finally dried for 24 hr at 60°C under vacuum. Sieving is applied to separate the 0.315 to 1-mm-diameter fraction. The products result as white opaque spherical beads.

**Texture Determination**

The surface area is obtained from nitrogen adsorption measurements following the BET method.<sup>6</sup> From the adsorption-desorption isotherm, the pore size distribution (pore radii between 11 and 400 Å) is derived, according to Barrett et al.<sup>7</sup> The apparatus used is a pore volume analyzer (Micromeritics, Model 2100 D). Mercury porosimetry is used to determine the porous volume and the pore size distribution (pore radii larger than 75 Å) (apparatus Carlo Erba). Scanning-electron microscopy has been carried out for a few samples with a magnifications of 40,000 to 100,000 (apparatus JEOL JSM 35).

**RESULTS AND DISCUSSION**

The influence of two main parameters has been studied: the concentration of DVB and of diluent. The ranges of concentration have been limited because of technical reasons. For DVB, except for a few experiments at low DVB content, the range has been 8%–60% (styrene content from 8.7% to 1%). The 2-ethyl-1-hexanoic acid concentration has been varied between 35% and 75%, because below 35% the structure collapses on drying and no stable pores remain and above 75% the mechanical properties are too weak to withstand the porous volume.

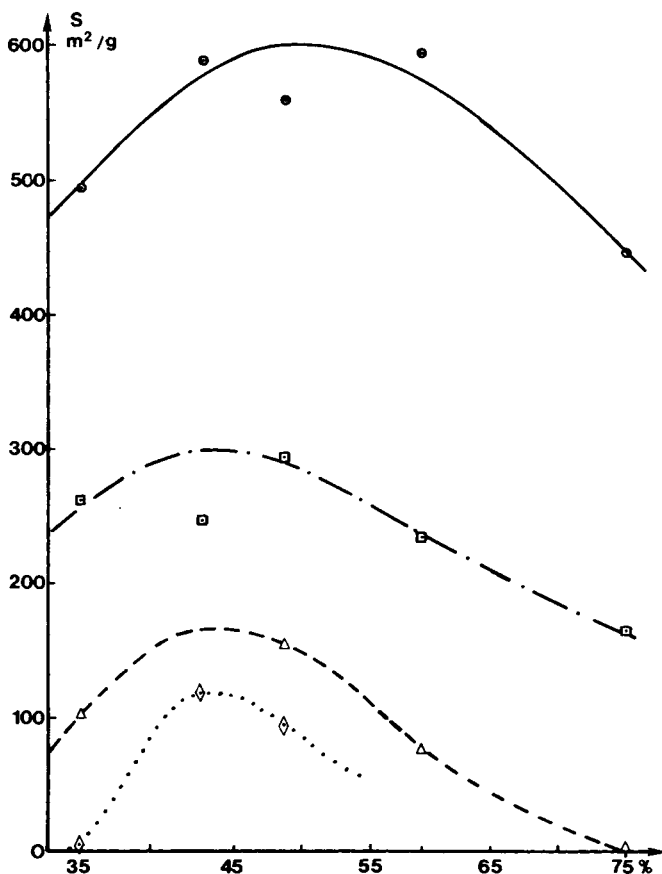


Fig. 1. Surface area (m<sup>2</sup>/g) vs the percent of diluent for various amounts of DVB: 8% (•-•-), 20% (- - Δ - -), 40% (-□-), and 60% (-○-).

Figure 1 shows the surface area plotted versus the diluent content for different amounts of DVB. A high percent of DVB is necessary to get high surface area. The surface area is not too dependent on the amount of diluent in a large range (40%–60%), where there is a flat maximum. Too large an excess of diluent causes the surface area to decrease, although not as much as hydrocarbons or alcohols.<sup>3,4</sup>

The behavior of the porous volume is illustrated in Figure 2. One can see that except for a very high diluent concentration, provided the DVB content is high enough, the porous volume depends only on the diluent concentration. It may also be seen that, using 2-ethyl-1-hexanoic acid as a diluent, it is possible to predict the porous volume as well as the surface area in a large range of DVB (20%–60%) or diluent concentrations (35%–60%).

Figures 3–5 illustrate pore size distributions as given by the nitrogen adsorption-desorption isotherm (a) in the differential mode and by mercury porosimetry in the integral mode (b). The differential curves are rather complex, showing a set of different size distribution. There is clearly a large number of very small pores, especially for high DVB contents. Experiments with low amounts of DVB show that this family is not yet present if the amount of DVB is lower than 20%.

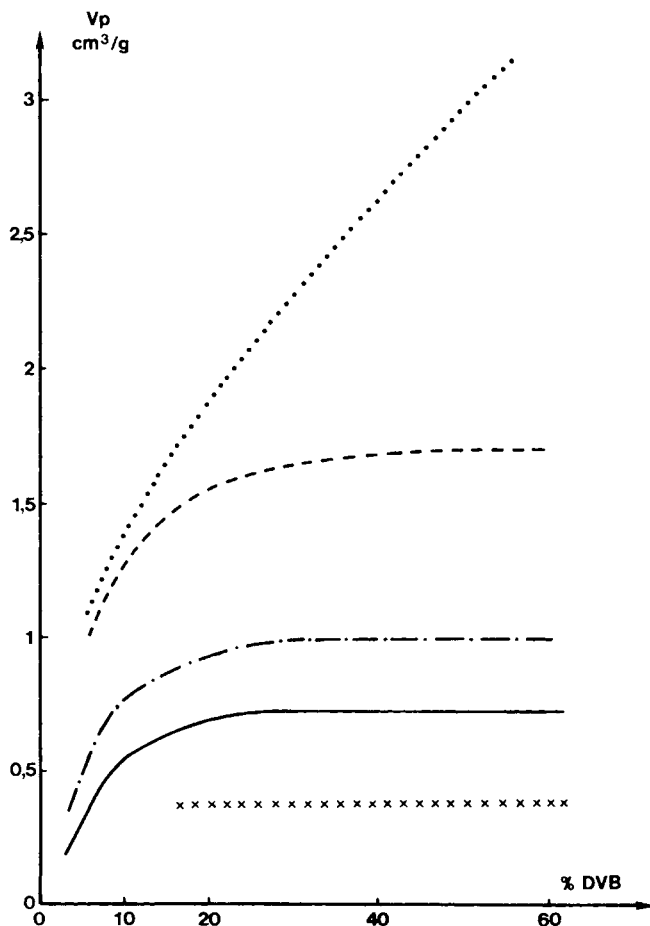
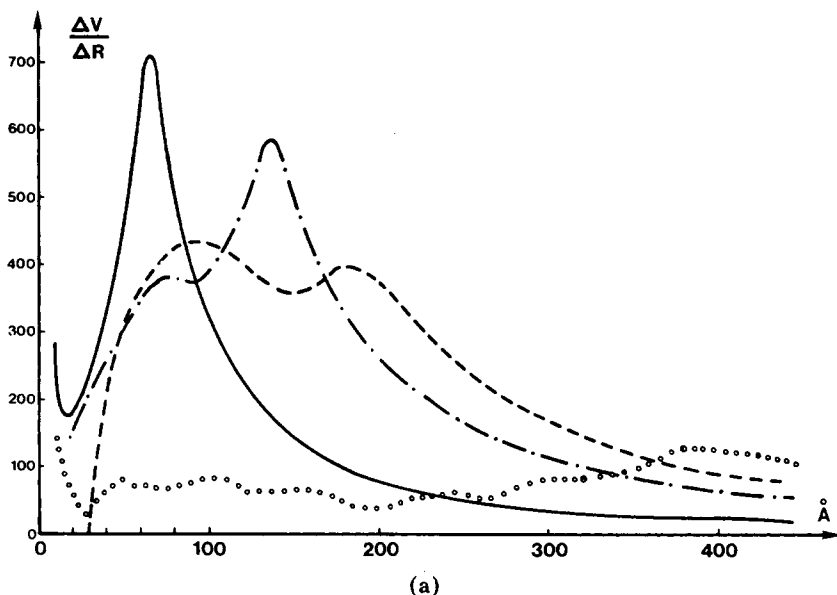
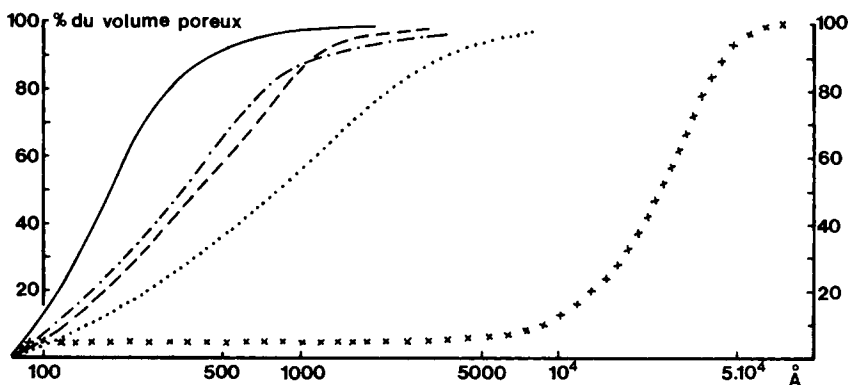


Fig. 2. Pore volume ( $\text{cm}^3/\text{g}$ ) vs the percent of DVB for various amounts of diluent: 35% (XXX), 44% (— · —), 50% (— — —), 60% (- - -), and 75% (—).



(a)



(b)

Fig. 3. Pore size distribution for copolymers prepared with 20% DVB and various amounts of diluent: 35% (—), 44% (---), 50% (- - -), 60% (···), and 75% (xxx). (a) Differential mode for small pores; (b) integral mode for large pores.

It seems that 40 Å is a reasonable upper limit for the radii of this family of micropores. They account for a rather large part of the surface area, chiefly when the amount of DVB is the higher. It is possible to calculate from the computer program handling the results of nitrogen adsorption-desorption experiments the surface area from intermediate pores (noted S inter in Table I for pores larger than 38 Å). Results in Table I show that these intermediate pores account for most of the surface area if the DVB content is less than 20%, but their contribution becomes smaller and smaller as the DVB contents increases. It is interesting to note the drop of their contribution for high percentages of diluent: 60% with 20% DVB or 75% with 40% or 60% DVB. Most probably, this fact is an indication of the proximity of the border line of the range of existence of macroporosity. The experiment with 8% DVB and 35% diluent is clearly on this borderline, because the surface area is limited and the value is not reproducible in the same polymerization batch.

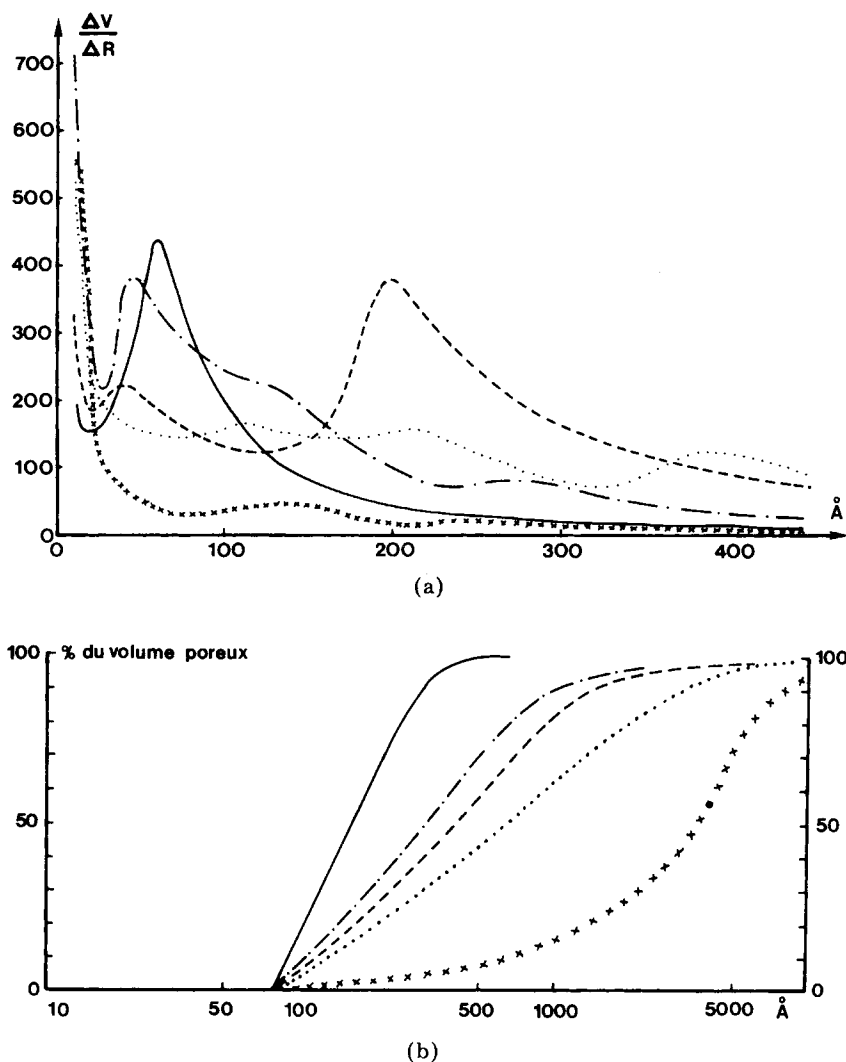


Fig. 4. Pore size distribution for copolymers prepared with 40% DVB and various amounts of diluent: 35% (—), 44% (---), 50% (- - -), 60% (· · ·), and 75% (xxx). (a) and (b) as in Figure 3.

Pores of intermediate size (40–400 Å) are distributed in more than one family in most cases. The shapes of the distribution strongly depend on the amount of diluent. With 35% diluent the distribution is clearly unimodal, with a maximum at about 80 Å that is independent of the amount of DVB (Fig. 6). More complex figures are observed for higher amounts of diluent; nonetheless, the position of the maximum corresponds to larger size. With 60% diluent the distribution is very wide and flat with badly defined maxima. With 75% diluent it seems that these intermediate pores mostly disappear.

The distribution of large pores (integral curves) also show interesting features: for each amount of DVB, the distribution is dependent on the amount of diluent, a regular unimodal distribution which appears to be broader and broader as the amount of diluent increases. Anomalous behavior is indicated for 75% diluent. The distribution is displaced towards very large pores and tends to be bimodal for high amounts DVB. Other details are shown in Figures 7–9. Figure 7 shows

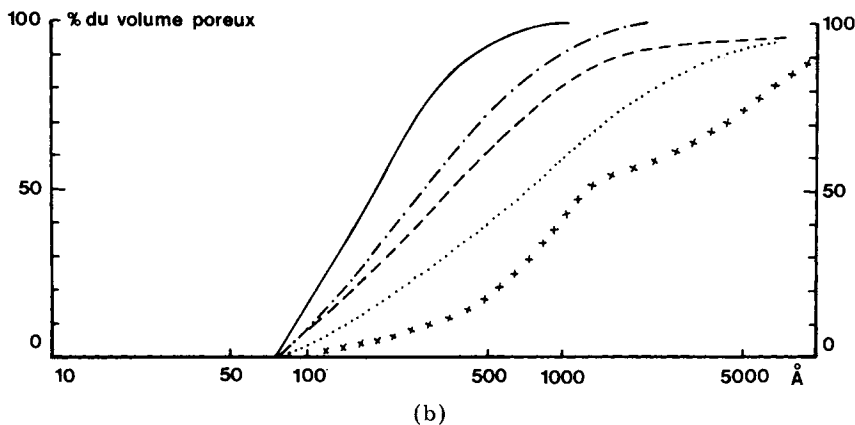
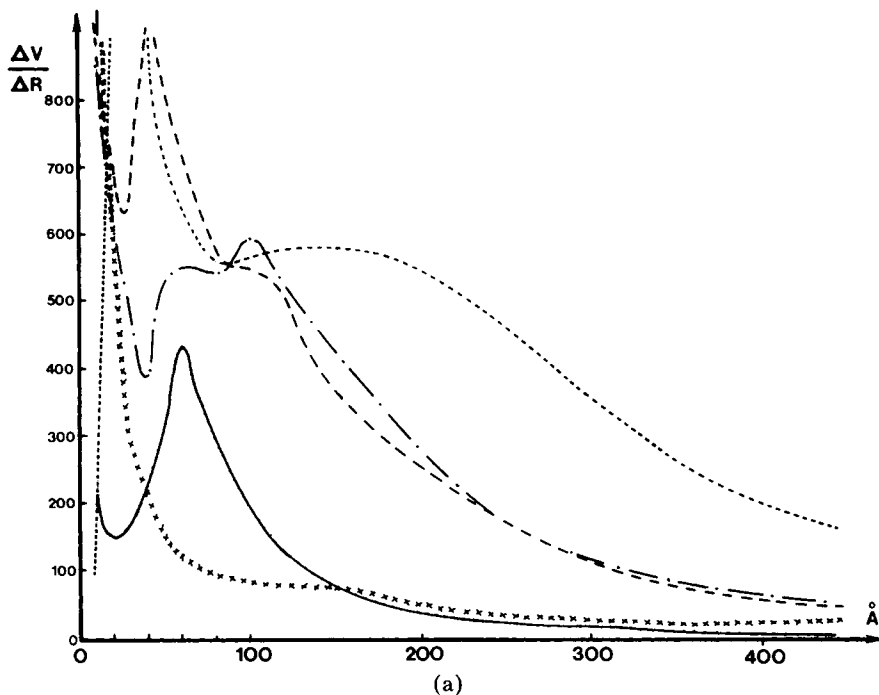


Fig. 5. Pore size distribution for copolymers prepared with 60% DVB and various amounts of diluent: 35% (—), 44% (---), 50% (- - -), 60% (···), and 75% (xxx). (a) and (b) as in Fig. 3.

that for low amounts of DVB the distribution seems to be dependent on the amount of DVB. A possible reason is that, if the amount of DVB is too low, the mechanical strength of the structure is weak, and it may be compressed by the mercury so that the large pores tend to be eliminated. Figure 8 shows that the distribution is not dependent on the amount of DVB when it is between 20 and 60%. This is also true for an amount of diluent varying between 35 and 60%. With 75% diluent, the distribution is again dependent on the amount of DVB (Fig. 9): with low amounts of DVB (20%), the intermediate pores are practically absent, and there are only very large pores around 30,000 Å. The same is true for 40% DVB, except that the average radius of the large pores is about 4000 Å. But for 60% DVB there are two distributions of large pores: the first one is in

TABLE I

% DVB	% Diluent	$S$ (m <sup>2</sup> /g)	$S$ inter (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	$\bar{r}$ (Å)	$r_{\max}$ (Å)
8	35	1-10	—	0.66	—	410
8	44	120	108	0.53	89	750
20	35	104	104	0.38	74	600
20	50	156.5	141	0.92	118	1500
20	60	77.5	38	1.56	404	5000
40	35	262	120	0.33	26	350
40	44	247.5	94	0.75	60	1500
40	50	294	90	0.97	66	2100
40	60	235	70	1.65	140	4500
40	75	166	15	2.64	317	12500
60	35	495	75	0.41	17	550
60	44	590	183	0.75	25	1250
60	50	560	215	0.93	34	4500
60	60	595	269	1.72	58	7000
60	75	447	43	3.26	146	23000

line with that expected for 60% DVB from the other amounts of diluent. The second distribution again corresponds to very large pores.

A typical SEM photograph of the inner part of a copolymer bead is shown in Figure 10. The high magnification ( $10^5$ ) allows visualization of the texture of the material: the smallest particles are rather spherical with diameters of about 100–200 Å. They correspond to the “nuclei” suggested by Sederel and De Jong.<sup>2</sup> They are aggregated in microspheres of about 500–1000 Å. The microspheres are aggregated in particles (2500–10,000 Å) more or less separated by large holes. The photograph in Fig. 10 corresponds to a copolymer prepared with 50% DVB and 44% diluent, that is, typical conditions of the macroporous field. The same

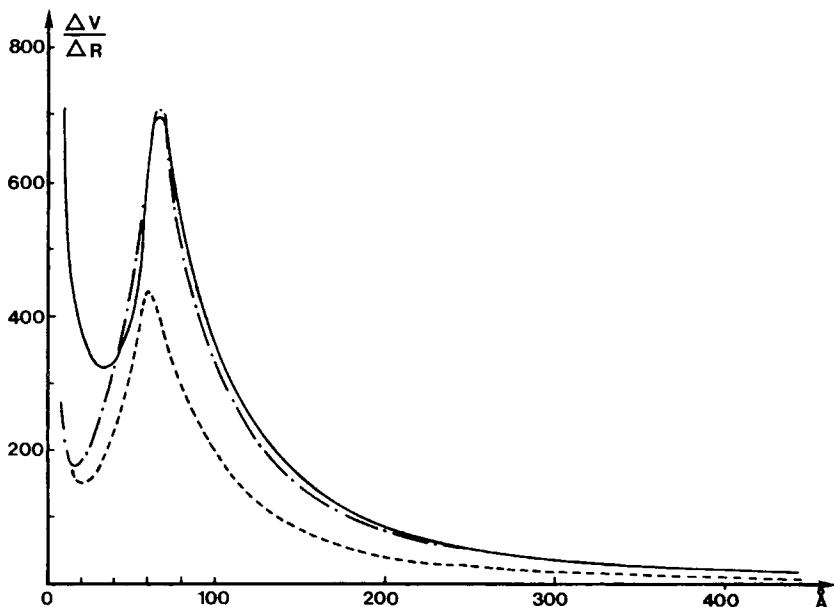


Fig. 6. Pore size distribution: differential mode for copolymers prepared with 35% diluent and 20% (- · -), 40% (---), or 60% (—) DVB.



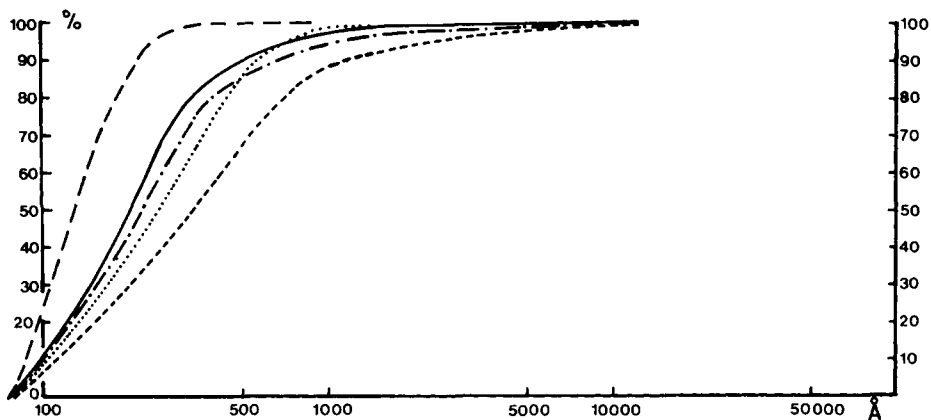


Fig. 7. Pore size distribution: integral mode for copolymers prepared with 44% diluent and 5% (---), 8% (—), 12% (-·-·-), 16% (·····), or 20% (- - -) DVB.

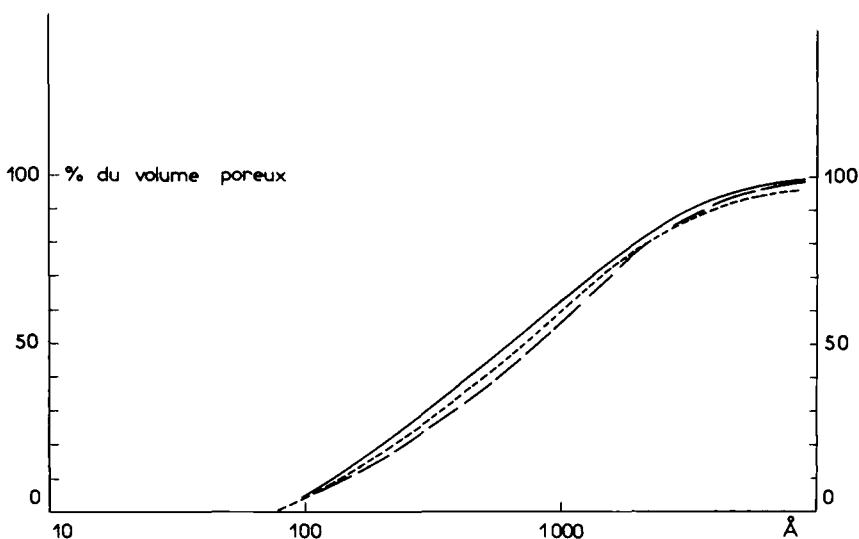


Fig. 8. Pore size distribution: integral mode for copolymers prepared with 60% diluent and 20% (-·-·-), 40% (—), or 60% (- - -) DVB.

kind of texture is observed throughout the macroporous field. For instance, Figure 11 shows two photographs of copolymers prepared with the same amount of diluent (44%), but lower amounts of DVB (8 and 16%). When the amount of DVB decreases, the size of the microsphere, along with that of the nuclei, decreases, and the microspheres tend to be slightly fused. As shown in Figure 12, decreasing the amount of diluent to 35% (DVB 40%) also causes the microspheres to be more fused. The same phenomenon appears at the other borderline of the macroporous field by increasing the amount of diluent to 75%. Figure 13 corresponds to such a copolymer, again with 40% DVB. Although the magnification is lower in Figures 12 and 13, the nuclei remain invisible in the microspheres. The texture of the surface of the polymer bead is not different from that of the inner part, except if the amount of DVB is low, in which case the surface shows fused spherical granules with a small number of holes.

The relation  $S = 6/\pi\rho d$  between the surface area  $S$ , the volumic mass  $\rho$ , and

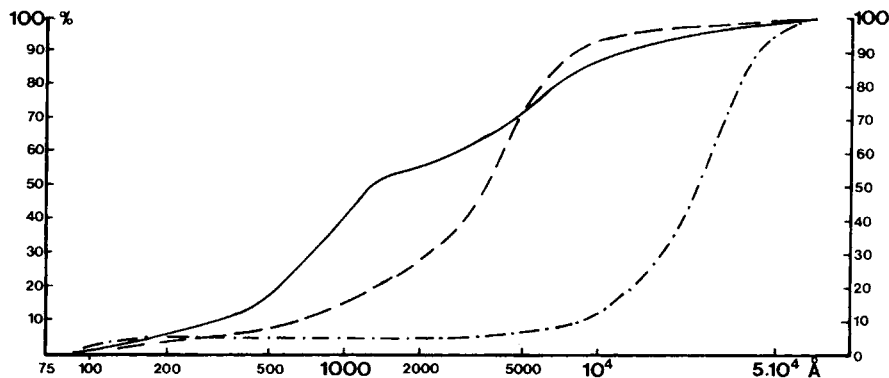


Fig. 9. Pore size distribution: integral mode for copolymers prepared with 75% diluent and 20% (---), 40% (-.-), or 60% (—) DVB.

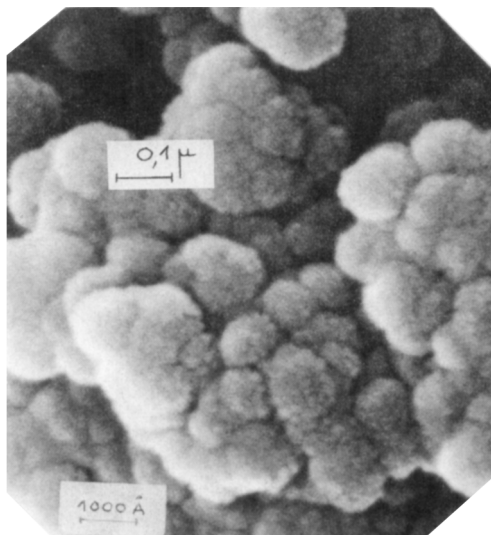
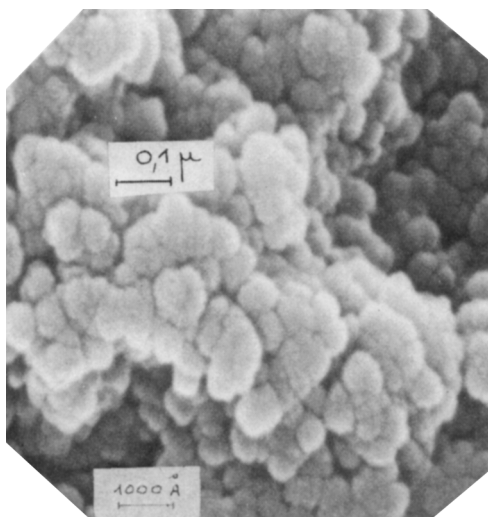


Fig. 10. SEM photograph of the inner part of a bead of copolymer prepared using 50% DVB and 44% diluent ( $\times 100,000$ ).

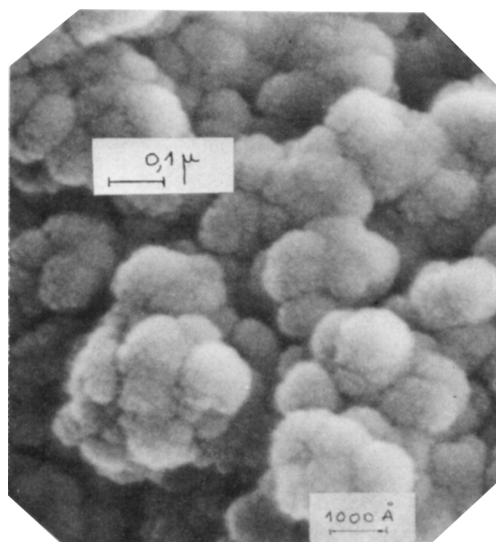
the diameter  $d$  of a nonporous sphere allows us to estimate the surface area of an aggregate of microspheres. Some data are reported in Table II for typical styrene divinylbenzene material ( $\rho = 1.25 \text{ g/cm}^3$ ). From these data, it may be estimated that the main part of the surface area can be accounted for by the surface of the nuclei. The micropores are interstices between these nuclei in the microspheres, and it may be concluded that the nuclei are probably nonporous. The intermediate pores are the interstices between the microspheres in the aggregates. When the microspheres tend to be fused, these intermediate pores tend to disappear and then the surface area "S inter" in Table I decreases

TABLE II

	Diameter ( $\text{\AA}$ )					
	50	80	100	200	500	4000
Surface area ( $\text{m}^2/\text{g}$ )	960	600	480	270	96	15



(a)



(b)

Fig. 11. SEM photographs of the inner part of beads of copolymers prepared with 44% diluent and either 8% (a) or 16% (b) DVB.

significantly. Such a situation arises at the borderline of the macroporous field.

It is interesting to compare the SEM photograph and the pore size distribution curves. In the macroporous field, the correspondence is very clear and direct. Such a correspondence suggests that the nuclei are fused in the microspheres if the amount of DVB is lower than about 20% and becomes individually separated, although aggregated in microspheres, for higher amount of crosslinking agent.

It may be suggested, too, that the size of the nuclei decreases when the amount of DVB increases. Their dependence on the amount of diluent is less clear, and the reason for a minimum size (maximum surface area) for a given amount of

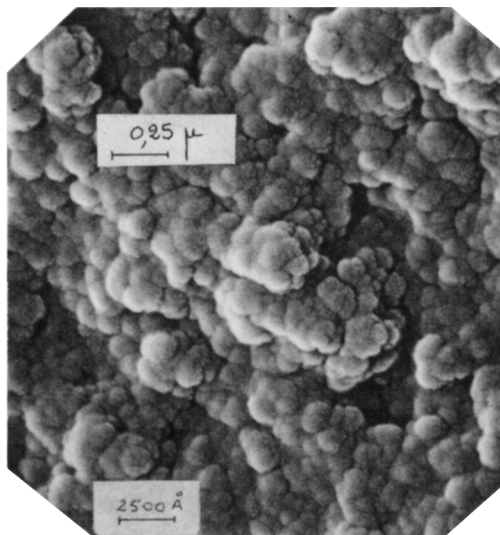


Fig. 12. SEM photograph of the inner part of a bead of copolymer prepared using 40% DVB and 35% diluent ( $\times 40,000$ ).

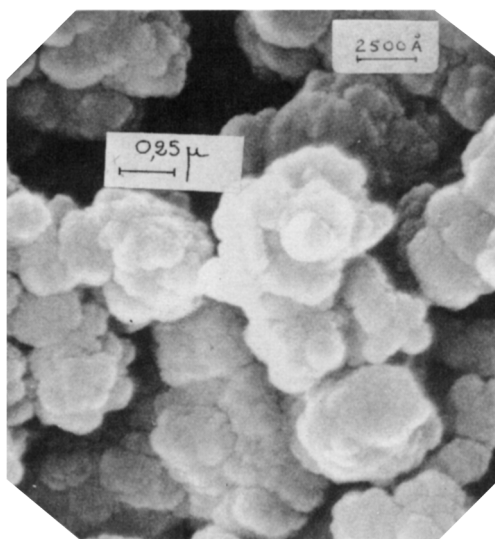


Fig. 13. SEM photograph of the inner part of a bead of copolymer prepared with 40% DVB and 75% diluent ( $\times 40,000$ ).

diluent remains to be fully explained. The comparison of the behavior of other kinds of diluent, which will be the purpose of a further paper, will be valuable in this respect.

The authors are indebted to Professor Per Flodin, of the Royal Institute of Technology in Stockholm for valuable discussions. The assistance of Mrs. Gary in the adsorption experiments, as well as the support of the DGRST research contract 73-7-0129, have been appreciated.

### References

1. J. Seidl, J. Malinsky, K. Dusek, and W. Heitz, *Adv. Polym. Sci.*, **5**, 113 (1967).
2. W. L. Sederel and G. J. de Jong, *J. Appl. Polym. Sci.*, **17**, 2835 (1973).
3. A. A. Tager, M. V. Tsilipotkina, E. B. Marovskaya, A. B. Phaskov, Y. I. Lyustgarten, and M. A. Pechenkina, *Vysokomol. Soedin.*, **A10**, 1065 (1968).
4. A. A. Tager, M. V. Tsilipotkina, E. B. Marovskaya, Y. I. Lyustgarten, A. B. Pashkov, and M. A. Lagunova, *Vysokomol. Soedin.*, **A13**, 2370 (1971).
5. French Patent 1,483,946 (to the DIA Prosim Co.).
6. S. Brunauer, Ph. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
7. E. P. Barrett, L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).

Received July 25, 1977

Revised May 30, 1978