Polymer Bulletin 34, 621–625 (1995)

Polymer Bulletin

Scanning electron microscopy of styrene-divinylbenzene copolymers

II. Surface and bulk morphology

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Received: 30 October 1994/Revised version: 1 January 1995/Accepted: 6 February 1995

SUMMARY

Styrene-divinylbenzene copolymers were synthesized by suspension polymerization in presence of di(2-ethytlhexyl) phosphoric acid and methyl ethyl ketone as diluents. The surface and bulk morphology of the beads were investigated through scanning electron microscopy. The influence of diluent-copolymer interaction, dilution degree and interfacial tension on the porous structure formation are discussed.

INTRODUCTION

In a previous paper (1) we have presented a scanning electron microscopy study of surface beads of styrene-divinylbenzene (Sty-DVB) copolymers synthesized by suspension polymerization. At fixed DVB content, when the dilution degree increased the sizes of macropores and polymer agglomerates on the bead surface increased. It was suggested that the same effects could be expected for the bulk morphology of the copolymer what is in accord with results presented elsewhere (2). However, some data in literature have shown that surface morphology can be very different of the bulk structure so that some care should be taken when we relate inner and outer features of the copolymer beads (3). The main difference is the formation of a surface shell less porous than the bulk. The formation or not of a less porous surface shell on macroporous resins obtained by suspension polymerization can by attributed to the thermodynamic affinity of the diluent by the polymer chains. In presence of precipitating diluents, the polymer chains become more entangled and less expanded forming rigid networks which show little tendency to shrink on drying. When a solvating diluent is used, the polymer chains become disentangled and expanded so that the network tends to shrink on drying to form a compact and smooth surface shell (1-4).

Another theory explains the shell formation by considering the effect of interfacial tension between aqueous and organic phases during usual suspension polymerization. The interfacial tension, which is relatively high because the aqueous phase contains only steric stabilizers, compresses the surface layers of microspheres which become more compact forming a less porous shell (5,6). This influence of interfacial tension is supported by a study of surface morphology of monodispense beads of glycidyl methacrylate-ethyleneglycol dimethacrylate copolymers synthesized by seed suspension polymerization. In the seed polymerization consisting of two-step swelling, the aqueous phase contains a real

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surfactant and the interfacial tension is much weaker. Then the compressive force is not strong enough to compact the globules forming a less porous surface shell.

This paper deals with surface and bulk morphology of Sty-DVB copolymers prepared by suspension polymerization in presence of di(2-ethylhexyl) phosphoric acid (DEHPA) and methyl ethyl ketone (MEK). The effect, of interfacial tension on inner and outer featues of resin beads will be discussed.

EXPERIMENTAL

Sty-DVB copolymers were synthesized by usual suspension polymerization in presence of DEHPA/MEK mixtures and purified as previously described (8). The dilution degree and the DEHPA/MEK ratios were expressed as percentages of the total volume of monomers. The DVB content was kept constant at 30 mol % of styrene.

Porous characteristics as pore volume (V_p), surface area (S) and average pore diameter ($\bar{D}$) were determined as in ref. 2. The morphological aspects of the copolymer beads were observed on a SEM Jeol JXA 840A.

RESULTS AND DISCUSSION

DEHPA is a precipitating diluent while MEK is a solvating one for Sty-DVB copolymers (8,9). Table 1 shows the porous characteristics of the copolymers observed by SEM.

At fixed dilution, the macropores and polymer agglomerates on the bead surface became bigger when the diluent solvating power decreased (Figs. 1a and 1c). In presence of MEK, the michospheres tended to compact and form a less porous surface shell (Figs. 1a and 1b). The differences between surface and bulk morphology diminished with the increase of the precipitating effects (Figs 1c and 1d). It is clear that the sizes of the macropores, microspheres and their agglomerates in the bulk structure followed the same trends of the surface, i.e., they increased as the solvating power decreased (Figs. 1b and 1d).

In general, the increase of dilution degree promotes the phase separation (1,2,10). The sizes of the macropores, microspheres and their agglomerates on both outer and inner surfaces became bigger with the dilution increase (Figs. 1c and 1e, 1d and 1f). The low dilution degree as a less precipitating condition promoted the formation of bead, with a less porous surface shell.

Table 1 - Porous Characteristics of Styrene-Divinylbenzene Copolymers

Sample	Total Dilution (Vol %)	DEHPA/MEK Ratio	VP (cm^2/g)	S (cm^2/g)	$\bar{D}$ (Å)
01	100	50/50	0.57	68	335
02	100	100/0	0.82	57	575
03	50	50/0	0.41	51	322
04	75	50/25	0.53	66	321
05	100	75/25	0.76	86	353
06	175	75/100	1.00	106	377

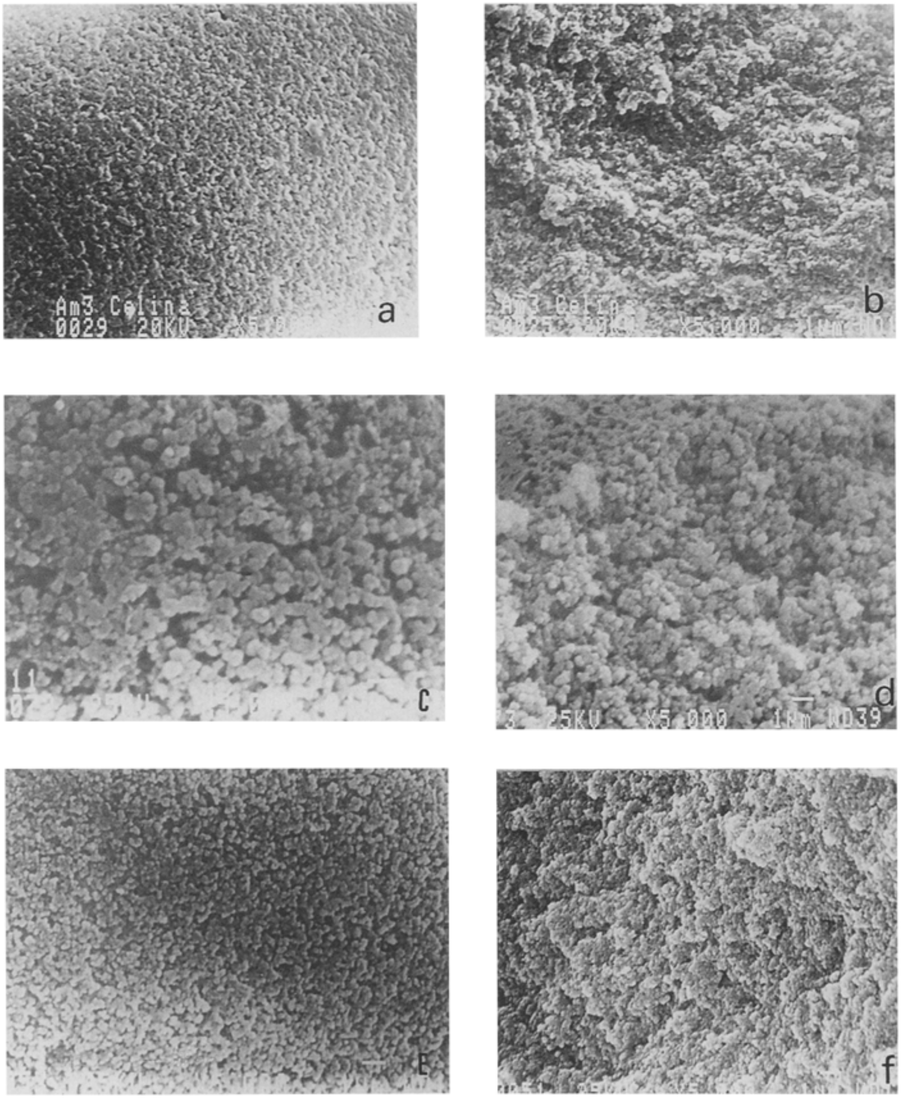
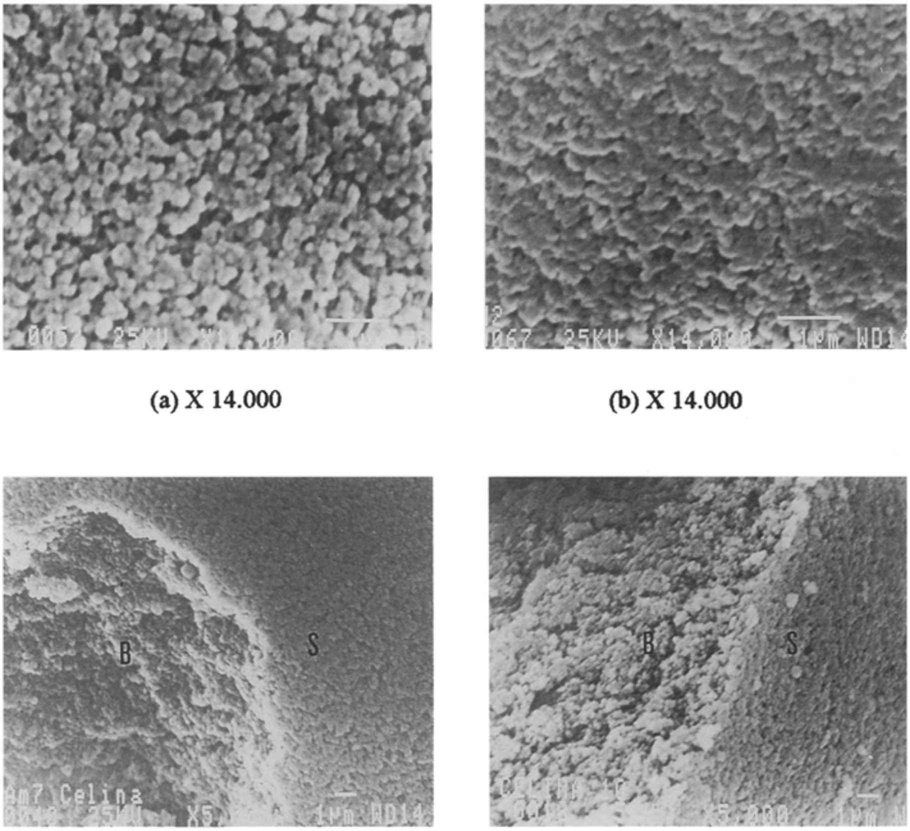


Figure 1 - SEM micrographs of Sty-DVB copolymers prepared with 100% dil-DEHPA/MEK = 50/50. (a) surface and (b) bulk; 100% dil-DEHPA/MEK = 100/0 (c) surface and (d) bulk; 50% dil-DEHPA/MEK = 50/0 (e) surface and (f) bulk. Magnification: X 5000.

Figures 2a and 2b show that the copolymer prepared with DEHPA/MEK = 50/0 presented bigger macropores on the bead surface than the copolymer prepared with DEHPA/MEK = 50/25. Since MEK is a component considerably more water soluble than the other components of the organic phase, the increase of MEK content produces a reduction of the interfacial tension. It seems that MEK solvated the polymer chains producing a flexible network so that the microglobules on the surface layers tended to collapsate even with a reduction of interfacial tension. Then, we can say that the diluent-copolymer interaction is a decisive factor on the formation of a less porous surface shell.



(a) X 14.000

(b) X 14.000

(c) X 5.000

d) X 5.000

Figure 2 - SEM micrographs of Sty-DVB copolymers: (a) 50% dil - DEHPA/MEK = 50/0 - surface; (b) 75% dil - DEHPA/MEK = 50/25 - surface; (c) 100% dil -DEHPA/MEK = 75/25 - Surface [S] and Bulk [B]; (d) 175% dil - DEHPA/MEK = 75/100 Surface [S] and Bulk [B].

Figure 2c and 2d show details of surface and bulk morphology of copolymer beads prepared with DEHPA/MEK = 75/25 and 75/100 respectively. The increase of MEK content affected more intensively the bead surface than the inner structure. The surface shell also became more compact and less porous when MEK content increased from 25 to 75 Vol %. In another hand, the sizes of macropores, microspheres and their agglomerates in the bulk practically did not change. At fixed DEHPA content, when the MEK proportion increases, there is an improvement of diluent solvating power and a dilution increase. As it was seen before, the solvating power increase induces the formation of smaller macropores and microspheres, while the dilution increase promotes opposite effects. Probably, these opposite effects compensated each other so that the average pore diameter ($\bar{D}$) and microsphere size had small changes in the bulk structure (Table 1).

CONCLUSIONS

The sizes of macropores, microspheres and their agglomerates on the bead surface and in the bulk increased when only the solvating power decreased or the dilution degree increased. When the solvating power and the dilution degree increased at the same time, the size of macropores and globules in the bulk almost did not change. In general, the diluent-copolymer interaction was a decisive factor on the formation of a less porous surface shell.

ACKOWLEDGEMENTS

The authors are very grateful to DIGER/CENPES/PETROBRÁS for the SEM analysis. We also thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Conselho de Ensino para Graduados e Pesquisa (CEPG/UFRJ), and Nitriflex S/A for financial support.

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