Preparation of Macroporous, Monodisperse, Functionalized Styrene–Divinylbenzene Copolymer Beads: Effect of the Nature of the Monomers and Total Porogen Volume on the Porous Properties

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ABSTRACT: The staged templated suspension polymerization method was used for the preparation of 5 μm beads from mixtures of styrene and several substituted styrene monomers, including 4-methylstyrene, 4-aminostyrene, 3-aminostyrene, 4-acetoxystyrene, and 4-*tert*-butoxycarbonyl oxystyrene, with divinylbenzene in the presence of various amounts of linear polystyrene and dibutyl phthalate as porogens. The nature of the monomer as well as the total percentage of porogenic compounds in the polymerization mixture have a large effect on the porous properties and surface morphology of the monodisperse beads. Beads with large pores can only be obtained once the percentage of porogen in the mixture exceeds a threshold value that varies with the type of monomers involved in the polymerization. The level of incompatibility of the functional polymer chains formed during the crosslinking polymerization with the linear polystyrene porogen that is present in the polymerization mixture is another variable that also affects both the porous properties and the morphology of the beads. Because better compatibility is achieved, this effect is less pronounced if unfunctionalized styrene is used as a monomer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 597–607, 1998

Key words: monodisperse macroporous beads; aminostyrene; 4-methylstyrene; 4-hydroxystyrene; staged templated suspension polymerization

INTRODUCTION

Macroporous poly(styrene-*co*-divinylbenzene) beads are very popular due to their good mechanical properties and stability in the entire range of pH. However, attachment of functionalities, required for a number of ion-exchange or chromatographic separation processes, or for solid phase

and combinatorial syntheses, necessitates additional steps.

The number of chemical modification reactions, such as lithiation[1,2] and chloromethylation,[2–4] which can be carried out to introduce functional groups onto polystyrene-based beads, is limited, and the reactions themselves may be difficult to control. In addition, some of these processes are not convenient to perform, and the lack of control over the specific sites where these reactions occur may lead to problems of reproducibility, additional crosslinking, and unequal reactivity of the functional groups introduced.

Some of the problems listed above can be avoided if a reactive styrene derivative is used in the polymerization. The use of functionalized

monomers allows for complete control over the introduction of the reactive centers in the polymeric beads, without an additional postpolymerization step. For example, commercially available chloromethylstyrene and protected 4-vinylphenol monomers, including 4-*tert*-butoxycarbonyloxystyrene and 4-acetoxystyrene, have been used to prepare macroporous polymers[5–8] using a classical suspension polymerization technique. However, the size polydispersity of the resulting beads limits their utility.

Therefore, several methods for the direct preparation of beads with reduced polydispersity that avoid the need for size fractionation have been designed recently.[9–17] We have developed the staged templated suspension polymerization of styrene and divinylbenzene, which involves the use of size monodisperse linear polystyrene particles as part of the porogenic system in the suspension polymerization process that leads to porous beads. This method allows for the fine tuning of the pore size distribution in uniformly sized porous beads.[13,18–22]

Our previous work has focused on the synthesis of poly(styrene-*co*-divinylbenzene) beads with well-controlled porous properties and surface morphologies and large pore volumes. Typically, the overall percentage of porogens in the polymerization mixture was constant and kept at relatively high values of 41–50%.[18–22] In contrast, there is little data available on the preparation of monodisperse, porous beads from functionalized styrene monomers. It is well known that the presence of a substituent on the monomer affects both the reactivity of the monomers and the solubility of polymer molecules within droplets of the organic phase during the polymerization. Therefore, specific polymerization conditions must be found for each substituted styrene monomer to obtain porous beads with desired properties. Changing the overall porogen content in the organic phase used for the polymerizations is one of the most useful methods to achieve control over the porous properties of the final, size monodisperse, macroporous beads.

This report describes the copolymerization of a variety of functionalized styrene monomers with divinylbenzene in the presence of different percentages of porogens consisting of linear polystyrene (polymeric porogen) and dibutyl phthalate. Although the total volume of porogen was changed throughout the experiments, the fraction of polystyrene in the porogen mixture was kept constant at 37 vol %. Our aim was to achieve pre-

cise control over the porous properties of the beads.

EXPERIMENTAL

Materials

Divinylbenzene (91%, Dow Chemical), styrene (99%, Aldrich), and 4-methylstyrene (96%, Aldrich) were extracted with 10% aqueous sodium hydroxide and water, dried over anhydrous magnesium sulfate, and distilled under vacuum. Azobisisobutyronitrile (AIBN) and 4-*tert*-butoxycarbonyloxystyrene were obtained from Eastman Kodak Fine Chemicals. 4-Aminostyrene was obtained from Lancaster Inc., and 4-acetoxystyrene from Hoechst Celanese Corporation. All other materials were purchased from Aldrich and used as obtained.

Preparation of 3-Aminostyrene

The synthesis of 3-aminostyrene was accomplished as shown in Scheme 1. A solution of 75.7 g (0.41 mol) of 4-toluenesulfonhydrazide in 100 mL of hot acetic acid was added quickly to a flask containing 50 g (0.37 mol) of 3′-aminoacetophenone dissolved in 100 mL of hot acetic acid. The solution was heated to 70°C until precipitation was observed, then the solution was cooled to 0°C. The precipitate was filtered, dried, and recrystallized from methanol to give 90.6 g (81%) of 3′-aminoacetophenonetosyl hydrazone (**1**); m.p. 158–160°C.

A solution of 50.0 g (0.17 mol) of (**1**) in 100 mL of dry THF was prepared in a 500-mL flask equipped with a mechanical stirrer and an addition funnel, and kept under N_2. After cooling to −70°C, a solution of *n*-butyllithium in hexanes (200 mL, 0.5 mol) was added dropwise to the reaction mixture over 1 h. The temperature of the solution was raised, and the mixture stirred for 4 h at 0°C, and 1 h at room temperature. The solid slowly dissolved as the reaction progressed to give
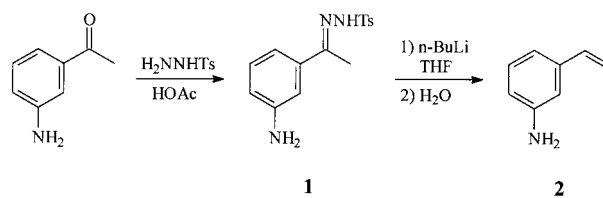
Scheme 1

a red solution, and the temperature of the reaction mixture was adjusted during the last hour so that a moderate evolution of gas from the reaction mixture was maintained. After cooling to −50°C, excess water was added. The crude reaction mixture was diluted with CH_2Cl_2, and extracted twice with 150 mL of 2 mol/L HCl. The aqueous fractions were brought to pH 8 with 10% aqueous NaOH, and extracted with CH_2Cl_2. The organic phase was washed with water, and dried over anhydrous $MgSO_4$. After removal of the solvent under vacuum, the crude oil was distilled in the presence of 4-*tert*-butylcatechol under reduced pressure. A yield of 14.5 g (74%) of a colorless oil (**2**) was obtained.

Elemental analysis: calculated for C_8H_9N (119.16): C, 80.6%, H, 7.6%, N, 11.7%, found: C, 79.5%, H, 7.5%, N, 11.6%; b.p. 52–54°C at 0.1 mmHg (lit.[23] b.p. 82–85°C at 6 mmHg); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.82 (s; 2H, —NH_2), 5.2–5.8 (dd; 2H, =CH_2), 6.5–7.1 ppm (m, 5H).

Preparation of Monodisperse Porous Beads

The preparation was carried out as described in ref. 21. In all of the experiments, AIBN was used as the initiator, and the polymerizations were performed in sealed, 500-mL Erlenmeyer flasks placed in an orbiting shaker bath (Lab-Line) at 240 rotations/min and 70°C for 24 h.

Beads produced in the absence of external porogen were prepared by swelling the polystyrene shape templates in 0.25% aqueous sodium dodecyl sulfate solution (30 mL) directly with the emulsified monomer and initiator mixture. Transfer of the monomer droplets into the templates was slow, typically lasting at least 15 h. Once the transfer was complete, sodium nitrite and 5% aqueous poly(vinyl alcohol) solution (PVA, 87–89% hydrolyzed, average M_w 85,000–146,000) were added, and the polymerization was carried out as described above.

Hydrolysis of Ester Groups in Poly(4-acetoxystyrene-*co*-divinylbenzene) Beads

A solution of KOH (3.0 g) in water (15 mL) and methanol (15 mL) was added dropwise to porous poly(4-acetoxystyrene-*co*-divinylbenzene) beads (3.0 g) suspended in methanol (30 mL). After stirring at room temperature for 24 h, the suspension was diluted with water and filtered through a 4–8 μm sintered glass filter. The beads were washed several times with water and methanol, then dried under vacuum. Monitoring by IR spectroscopy showed the loss of the strong ester carbonyl band near 1765 cm^{-1}, and the appearance of a broad hydroxyl band centered at about 3400 cm^{-1}.

Deprotection of Poly(4-*tert*-butoxycarbonyloxystyrene-*co*-divinylbenzene) Beads

Removal of the *tert*-butoxycarbonyloxy groups using thermal deprotection at a temperature of 230°C was performed as described elsewhere.[24]

Characterization of Porous Properties

The morphology and particle size of the beads were observed using a scanning electron microscope (Leica Stereoscan 440, Cambridge, UK). The specific surface area of the beads was calculated from the BET isotherm of nitrogen, and the pore size distribution in the dry state was determined by mercury porosimetry using an automated, custom-made combined BET-sorptometer and mercury porosimeter from Porous Materials Inc., Ithaca, NY.

Inverse Size-Exclusion Chromatography

A Waters HPLC system consisting of two 510 HPLC pumps, a 717 plus autosampler, and a 486 UV detector controlled by Millenium 2010 software were used for all of the chromatography. Particles were packed into 150 × 4.6 mm i.d. stainless steel columns from a THF suspension. Alkylbenzenes and 14 polystyrene standards with molecular weights ranging from 266 to 2,950,000 were injected to determine the SEC calibration curves.

RESULTS AND DISCUSSION

Poly(4-Methylstyrene-*co*-divinylbenzene) Beads

4-Methylstyrene has reactivity and solubility characteristics very similar to its parent monomer, styrene. The porous properties of the monodisperse poly(4-methylstyrene-*co*-divinylbenzene) beads are summarized in Table I. As expected, the data clearly documents the effect of increasing the volume of porogen in the organic phase used for the suspension polymerization. The pore volume remains relatively small when the volume of porogen in the organic phase is less

Table I Porous Properties of Monodisperse Beads Prepared from Styrene Derivatives and Divinylbenzene[a]

Comonomer	Porogen, %[b]							
	0	9	17	29	38	44	50	55
	Pore volume, mL/g[e]							
Styrene	0.32	0.33	0.37	0.54	0.65	0.89	0.92	—
4-Methylstyrene	0.31	0.33	0.32	0.37	0.40	0.63	0.62	0.92
3-Aminostyrene	—	0.50	0.43	0.52	0.78	—	—	1.07
4-Aminostyrene	—	0.36	0.40	0.49	0.51	—	0.75	0.61
4-Hydroxystyrene[c]	0.30	0.31	0.29	0.30	0.29	0.31	0.44	0.49
4-Hydroxystyrene[d]	0.40	0.36	0.40	0.39	0.40	0.43	0.46	—
	Specific surface area, m²/g[f]							
Styrene	<5	<5	<5	24	262	282	244	—
4-Methylstyrene	<5	<5	<5	<5	16	216	159	253
3-Aminostyrene	—	15	32	25	138	—	—	102
4-Aminostyrene	—	<5	9	15	28	—	132	149
4-Hydroxystyrene[c]	<5	<5	<5	<5	6	6	18	30
4-Hydroxystyrene[d]	<5	<5	<5	<5	<5	<5	11	—

[a] Reaction conditions: porogen particles (shape templates, 0.15 mL 22% dispersion); styrene; AIBN; 0.25% aqueous dodecyl sulfate solution, 30 mL); co-monomer, 2.5 mL; divinylbenzne, 2.5 mL; AIBN, 0.05 g; dibutylphthalate.
[b] Volume % of total porogens in the organic phase.
[c] Derived from 4-acetoxystyrene.
[d] Derived from 4-*tert*-butoxycarbonyloxystyrene.
[e] According to mercury intrusion porosimetery.
[f] According to BET.

than 38%. As the volume of porogen increases above this threshold value, the porosity increases and reaches a pore volume of 0.92 mL/g with 55% porogens. Our porosimetric measurements also indicate that this increase in the pore volume results from the increase in the volume of macropores larger than 50 nm. While their percentage in the beads prepared with 9% of porogen is 19%, their volume almost doubles at higher pore volumes. Simultaneously, the fraction of pores both smaller than 10 nm and in the range 10–50 nm decreases from 19 and 62% to 9 and 48%, respectively.

The pore size distribution curves for the beads prepared with 9, 38, and 50% of porogens (Fig. 1) show an increase in the total porosity, while the actual distributions of the pores remain similar over a size range from 6 to 100 nm. Unexpectedly, this indicates that the total pore volume can be controlled to produce monodisperse beads with a wide range of porosities, while keeping the pore size distribution constant. The large increase in
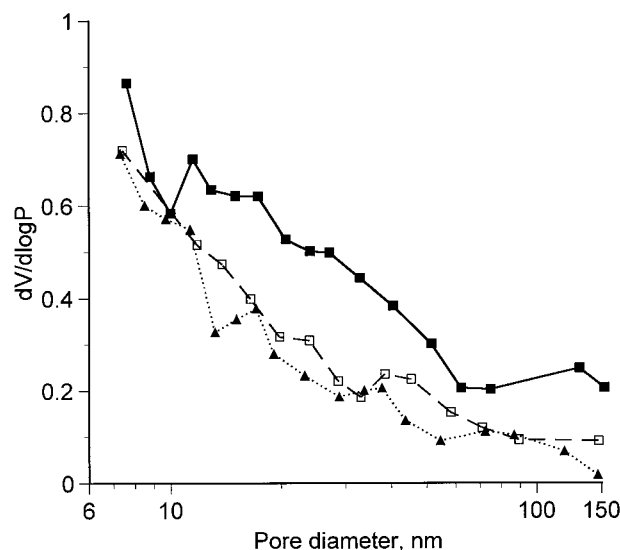

Figure 1 Differential pore size distribution curves of poly(4-methylstyrene-*co*-divinylbenzene) beads measured by mercury porosimetry; (■) 50% porogen, (□) 38% porogen, (▲) 9% porogen.
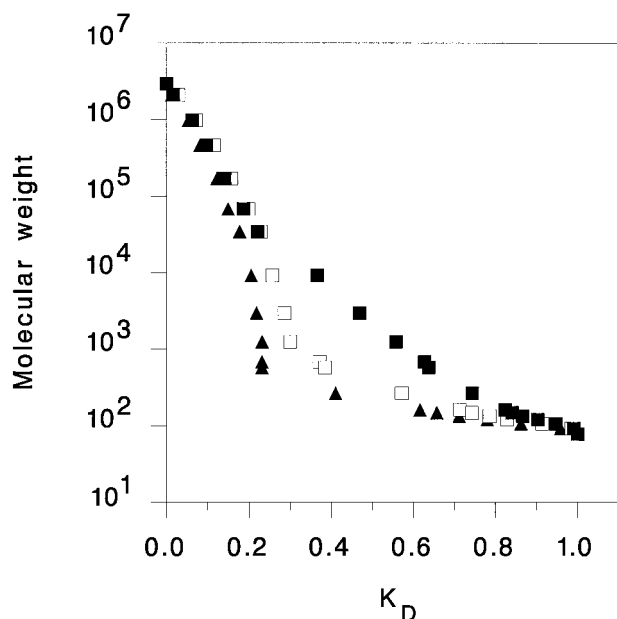
Figure 2 Size-exclusion calibration curves of poly(4-methylstyrene-*co*-divinylbenzene) beads with polystyrene standards and alkylbenzenes in tetrahydrofuran; beads, (■) 44% porogen, (□) 29% porogen, (▲) 9% porogen; conditions: column 150 × 4.6 mm i.d.; flow rate 1 mL/min; UV detection at 254 nm.

surface area, measured by nitrogen adsorption, for the beads using more than 38% of porogen can be attributed to an increase in the volume of the micropores that cannot be detected by mercury porosimetry.
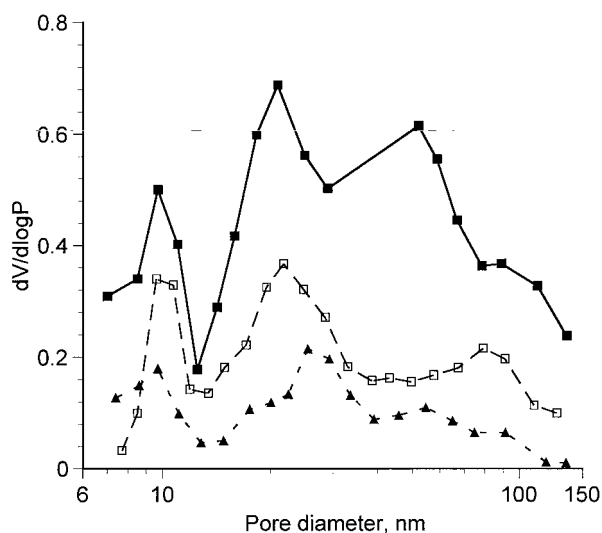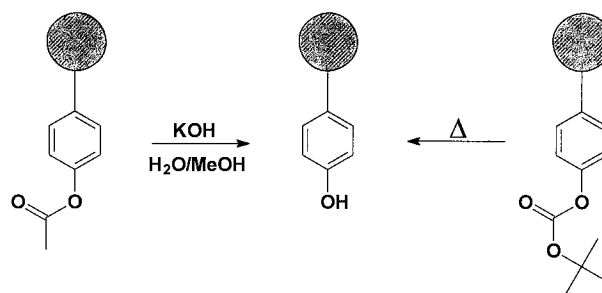

Scheme 2

Inverse size-exclusion chromatography (ISEC) is a useful tool for the analysis of the porous properties of the beads in an environment in which they are typically used.[25] ISEC calibration curves obtained for several poly(4-methylstyrene-*co*-divinylbenzene) beads (Fig. 2) confirm the changes in the pore volume of the polymer suggested by the mercury porosimetry data. Beads prepared with only 9% porogen have few macropores, as indicated by the almost complete lack of separation of polystyrene standards above 500 molecular weight. As the total pore volume becomes larger, the calibration curves become increasingly linear within a molecular weight extending to 10^5. This increase in selectivity for the higher molecular weight solutes can be attributed to the increase in volume of meso- and macropores larger than 10 nm in size, leading to a more balanced pore size distribution.
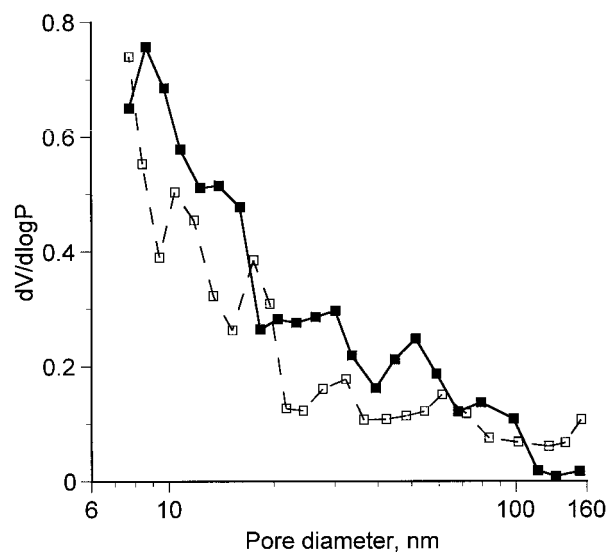

Figure 3 Differential pore size distribution curves of poly(styrene-*co*-divinylbenzene) beads measured by mercury porosimetry; (■) 44% porogen, (□) 29% porogen, (▲) 9% porogen.

Figure 4 Differential pore size distribution curves of poly(4-vinylphenol-*co*-divinylbenzene) beads derived from 4-*tert*-butoxycarbonyloxystyrene (■) and 4-acetoxystyrene (□).
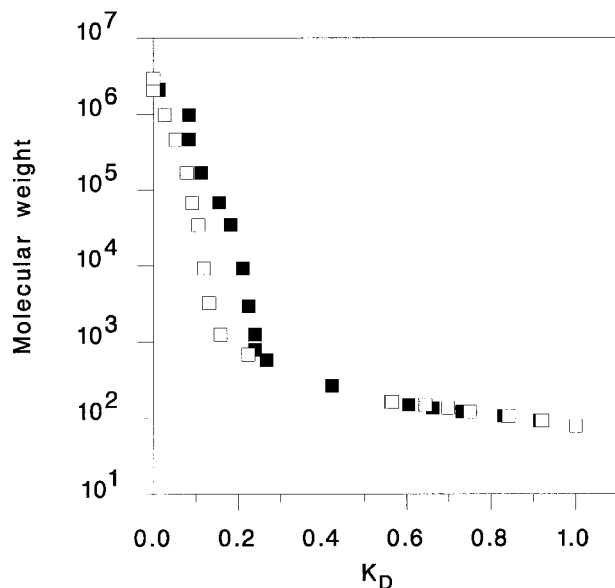
Figure 5 Size-exclusion calibration curves of poly(4-vinylphenol-*co*-divinylbenzene) beads derived from 4-*tert*-butoxycarbonyloxystyrene (■) and 4-acetoxystyrene (□) with polystyrene standards and alkylbenzenes in tetrahydrofuran; beads; conditions: column 150 × 4.6mm i.d.; flow rate 1 mL/min; UV detection at 254 nm.

In a simplified, macroscopic view, the pore volume in macroporous polymers can be assumed to be roughly equal to the volume of added porogen. Obviously, the lower the percentage of the porogen in the system, the lower the porosity. In practice, this assumption is not completely valid. The permanent porosity occurs only after the percentage of porogen in the system achieves a threshold value that depends on the type of porogen and percentage of crosslinking monomer.

Microscopically, the change in the overall porosity of the beads is a result of differences that occur in the pore formation process. With large volumes of porogen present, phase separation occurs very early in the polymerization, leading to a larger number of irregular voids (macropores) between the clusters of spherical globules that make up the bulk of the macroporous polymer and between the globules in individual clusters (mesopores). As the amount of porogen is decreased, phase separation occurs at later stages of the polymerization. Even after this phase separation, the polymerizing system still contains a large percentage of monomers that continue to polymerize either in the swollen monomer nuclei or in the solution. The latter leads to macromolecules that are captured by the nuclei and their

clusters. The chains polymerizing within the swollen units grow through neighboring microglobules and connect them at multiple sites. As a result, the microglobules are grown together, their individuality, which is normally typical of macroporous polymers prepared with a large volume of porogen, is almost lost, and the porosity is lower. Therefore, the beads are denser and their size is smaller.

For comparison, poly(styrene-*co*-divinylbenzene) beads were also prepared using identical polymerization conditions. As expected, the pore volume of the beads follow a pattern similar to the that observed for poly(4-methylstyrene-*co*-divinylbenzene) beads as the porogen volume is increased (Table I). However, the threshold percentage of porogen required for large pore volumes is lower.

The difference in porous properties of 4-methylstyrene and styrene beads can result from changes in the compatibility of the polystyrene co-porogen and the polymer molecules that are formed during the course of the suspension polymerization. The compatibility is better in the system that contains styrene as one of the monomers. The shapes of the pore size distribution curves for styrene-based beads are also different (Fig. 3). Although the actual distribution of pores remains similar as the overall pore volume is increased, BET isotherm data for these polymers indicates
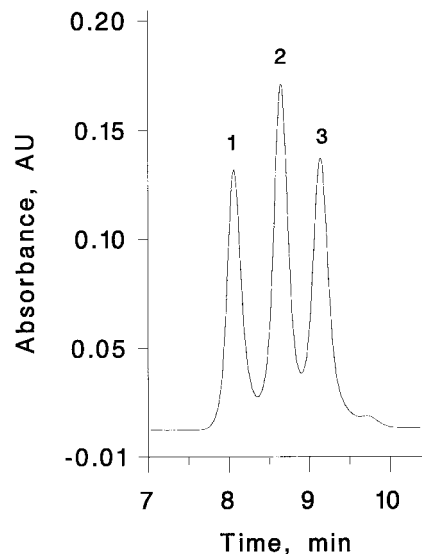

Figure 6 Separation of pentylbenzene (1), ethylbenzene (2), and benzene (3) by size-exclusion chromatography. Conditions: poly(4-vinylphenol-*co*-divinylbenzene) beads; column 300 × 7.8 mm i.d., flow rate 1 mL/min, solvent tetrahydrofuran.

a large increase in the surface area of the beads, presumably due to an increase in the number of micropores.

Aminostyrene

Two positional isomers of aminostyrene were copolymerized with divinylbenzene to observe the effect of location of substitution on the polymerization leading to functionalized beads. The pore volume of monodisperse poly(4-aminostyrene-*co*-divinylbenzene) beads (Table I) increases slowly as the amount of porogen in the organic phase is increased to 50%. Above this amount the pore volume and the size of the beads decreases significantly, and a dramatic change in the surface morphology is seen (*vide infra*).

The porous properties of beads containing 3-aminostyrene are different from beads obtained from 4-aminostyrene. A much larger increase in the pore volume is observed when a porogen content exceeds 29%. The reactivity ratios of the two aminostyrene monomers in the copolymerization with styrene are very similar,[26] which indicates that the reactivity of the vinyl groups in aminostyrene resulting from the relative positions of amino and vinyl groups has no significant effect on the porous properties of the products. Therefore, the variations in porous properties observed for beads obtained from the two aminostyrene isomers are assumed to reflect the difference in phase separation that results from the different compatibilities of the growing chains with the porogenic polymer in the system.

Protected 4-hydroxystyrene

Because 4-vinylphenol does not polymerize well,[24] the commercial availability of 4-acetoxystyrene and 4-*tert*-butoxycarbonyloxystyrene makes them
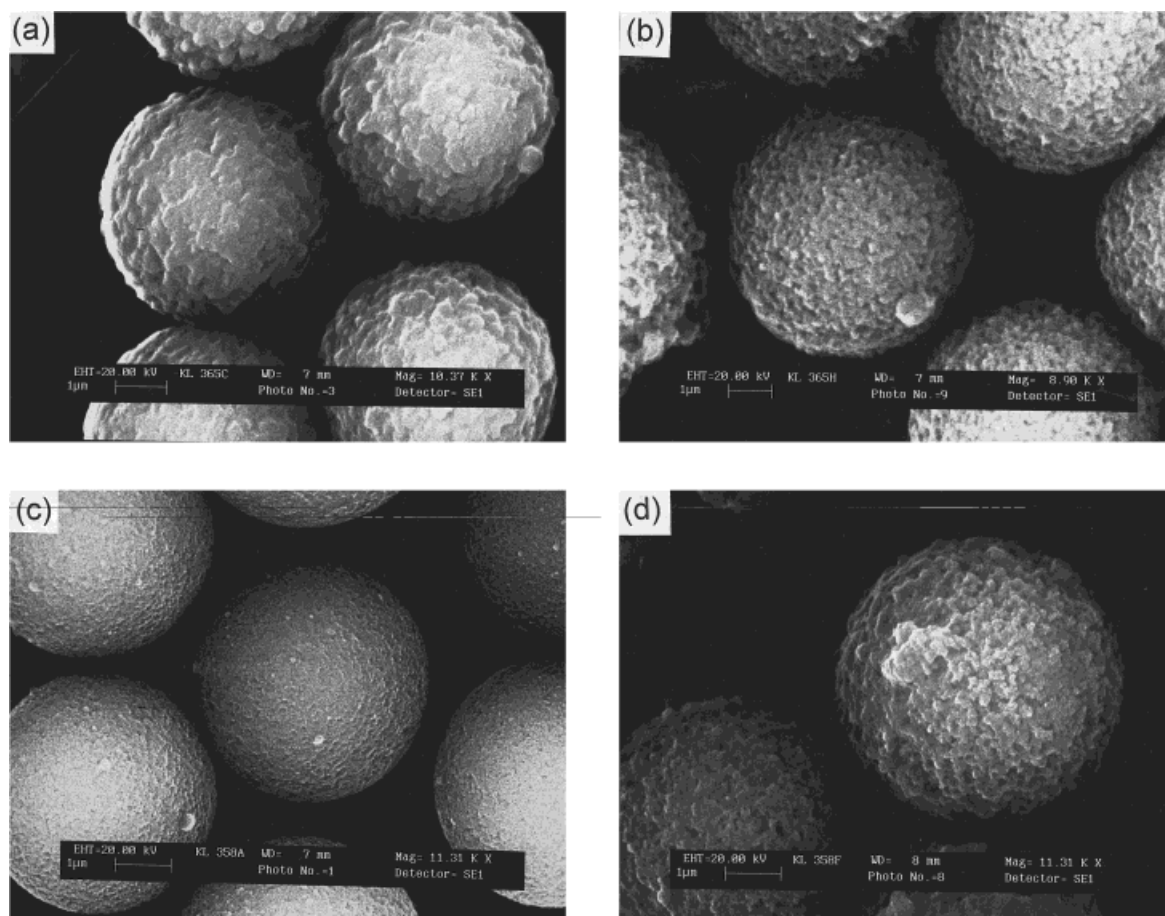

Figure 7 Scanning electron micrographs of poly(4-methylstyrene-*co*-divinylbenzene) beads: (a) 9% porogen, (b) 50% porogen and poly(styrene-*co*-divinylbenzene) beads, (c) 9% porogen, (d) 50% porogen.
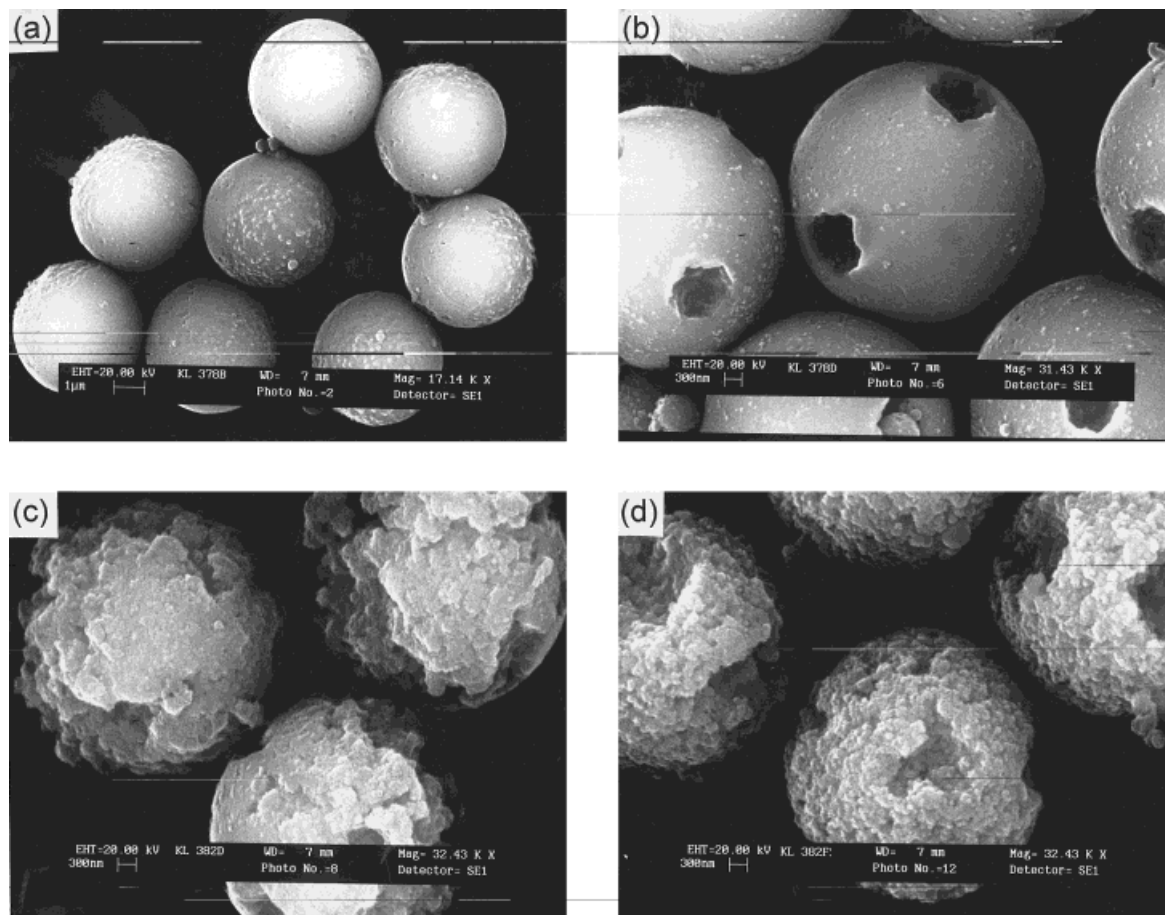
Figure 8 Scanning electron micrographs of poly(4-aminostyrene-*co*-divinylbenzene) beads: (a) 9% porogen, (b) 29% porogen, (c) 38% porogen, (d) 55% porogen.

very useful monomers for the production of beads containing aromatic hydroxyls. Therefore, the co-polymerization of protected 4-vinylphenol mono-mers with divinylbenzene, and the corresponding beads after deprotection of the phenolic hydroxyl group (Scheme 2), were investigated.

The porous properties of beads derived from 4-acetoxystyrene and 4-*tert*-butoxycarbonyloxysty-rene-divinylbenzene copolymers are shown in Table I. Generally, no large differences are observed for beads prepared from either functional mono-mer. The pore volume does not change signifi-cantly using porogen volumes ranging from 0–44%, and the beads contain mostly small pores less than 80 nm in diameter (Fig. 4). At higher volumes of porogen (over 44%), the monodisperse beads still have only a modest porosity of 0.44 and 0.46 mL/g, respectively. Obviously, it is not possible to prepare monodisperse beads con-taining large pore volumes using protected 4-hy-droxystyrenes by simply increasing the volume of

porogen in the organic phase of the suspension polymerization. At the same time, the very small surface areas determined by nitrogen adsorption/ desorption of dry beads indicate that only a few micropores are present. This suggests that phase separation during polymerization is incomplete and, therefore, the porous structure does not de-velop sufficiently. A similar observation has been made recently with copolymers of ethoxylated tri-methylolpropane triacrylate.[27]

In contrast to the polymers previously dis-cussed in this work, the beads prepared from the protected 4-vinylphenol monomers exhibit a re-markably different behavior when tested in in-verse size-exclusion chromatography. The ISEC calibration curves obtained for columns packed with beads prepared with 29% porogen (Fig. 5) show that more than 70% of the porosity is only available to molecules with a molecular weight of less than 1000. This makes the beads an excellent separation medium for small molecules.[28] Figure

6 shows the separation according to hydrodynamic size of three alkylbenzenes that differ only by 28 and 42 units of molecular weight.

Surface Morphology

Scanning electron micrographs (SEM) provide an excellent tool for investigating the relationship between surface structure and porous properties for the monodisperse beads. SEM micrographs of poly(4-methylstyrene-*co*-divinylbenzene) beads [Fig. 7(a) and (b)] reveal a porous, irregular surface. At low porogen volumes, the decreased porosity leads to a fairly smooth surface, but the surface becomes very rough as the pore volume increases. The morphologies of poly(styrene-*co*-divinylbenzene) beads [Fig. 7(c) and (d)] are similar to those of beads containing 4-methylstyrene and divinylbenzene.

In contrast to methylstyrene and styrene-based beads, the surface morphology of 4-aminostyrene beads is different. Although beads prepared in the presence of 9% porogen have a smooth surface [Fig. 8(a)], SEM micrographs of those prepared with a larger proportion of porogen (29%) reveal multiple large holes and deformations along the relatively smooth exterior of the beads. The surface morphology of beads with 50 and 55% of porogens [Fig. 8(c) and (d)] is no longer smooth, and crater-like holes that penetrate the surface can be seen. These large craters are no longer measurable by mercury porosimetry and, therefore, the total pore volume of these beads appears to decrease. The origin of these holes can most likely be attributed to the high degree of incompatibility of the polymeric porogen with the polymerizing monomers.

Scanning electron micrographs of poly(3-aminostyrene-*co*-divinylbenzene) beads are slightly different from those containing 4-aminostyrene. Figure 9 shows that there are holes in the surface of the beads, however these are smaller and more irregular in shape than those found in similar 4-aminostyrene beads. When a higher volume of porogen is used with aminostyrenes, relatively large, interconnected, and irregular microglobules can be observed on the surface. Although this loose agglomeration leads to a higher porosity, the highly globular structure of the beads causes a decrease in their mechanical stability.

SEM micrographs of beads derived from the protected 4-vinylphenol monomers (Fig. 10) show that in the presence of small amounts of porogen, the surface is relatively smooth and similar in appearance to the poly(styrene-*co*-divinylben-
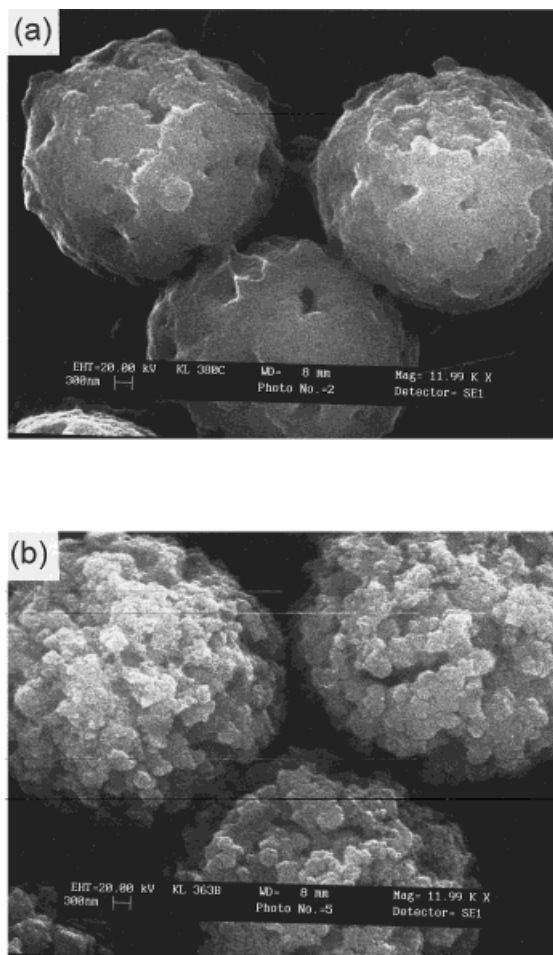

Figure 9 Scanning electron micrographs of poly(3-aminostyrene-*co*-divinylbenzene) beads: (a) 17% porogen, (b) 55% porogen.

zene) beads containing low pore volumes. When the volume of porogen is increased up to 50%, the surface becomes increasingly jagged and covered with small globules. This again results in decreased mechanical stability, even thought the total pore volume is relatively constant. The physical appearance of beads derived from both protected monomers is almost identical. Therefore, the use of 4-acetoxystyrene over 4-*tert*-butoxycarbonyloxystyrene is recommended due to the ready availability of the monomer and the fact both monomers lead to beads with similar physical and porous properties.

CONCLUSION

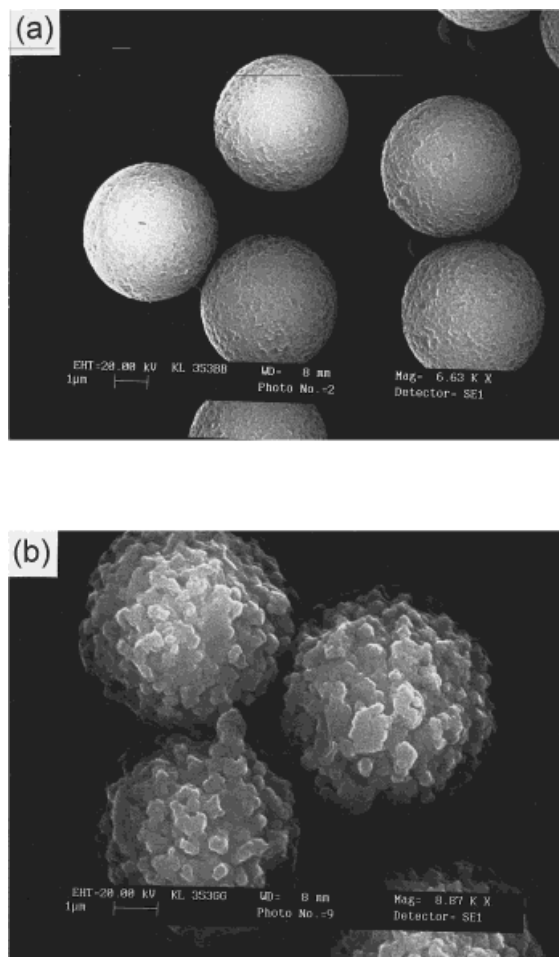Monodisperse porous beads prepared from functionalized styrene monomers, including 4-methyl-

Figure 10 Scanning electron micrographs of poly(4-hydroxystyrene-*co*-divinylbenzene) beads: (a) 9% porogen, (b) 55% porogen.

styrene, aminostyrene, and protected 4-vinylphenol, with divinylbenzene can be obtained using the staged templated suspension polymerization. The porous properties of the beads can be controlled within a broad range by the percentage of linear polystyrene-dibutylphthalate porogen used in the polymerization mixture. However, the porosity, pore size distribution, and surface morphology of beads obtained from each substituted styrene monomer differ considerably, and are not a simple function of the porogen volume.

In general, the porosity and pore sizes of products prepared in the presence of a constant volume of porogenic mixture are always smaller for all of the substituted monomers tested in this study than is the case for typical styrene-divinylbenzene beads. This is attributed to differences in the compatibility of the polystyrene porogen and the copolymers formed during the polymerization.

This compatibility issue is of prime importance, as it controls the phase separation during polymerization, and thus, the creation of pores.

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