

Surface Morphology Evaluation of Polymer Beads Based on Divinylbenzene by Atomic Force Microscopy

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ABSTRACT: Macroporous poly(styrene-*co*-divinylbenzene) and poly(divinylbenzene) beads were synthesized by modified suspension polymerization in the presence of different mixtures of toluene and heptane as porogen agent. Through atomic force microscopy, it was possible to identify the microspheres and the channels between them that constitute the bead pores. It was also possible to make a comparison with the results obtained by nitrogen desorption, a traditional technique used to determine the porosity of macroporous copolymers in the dry state. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 541–551, 2002; DOI 10.1002/app.10290

Key words: poly(styrene-*co*-divinylbenzene); poly(divinylbenzene); atomic force microscopy; pore structure; microspheres; nitrogen adsorption

INTRODUCTION

Macroporous poly(styrene-*co*-divinylbenzene) copolymers have been synthesized since the 1960s.^{1–3} These copolymers are produced by suspension polymerization in the presence of porogen agents. In suspension polymerization, the mixture of monomers, initiator, and porogen agents is dispersed by mechanical stirring as organic droplets suspended in a continuous second liquid phase in which initiator, monomers, and polymers are essentially insoluble. The monomer droplets are then polymerized while dispersion is maintained by continuous stirring.⁴ The most important factors which control the heterogeneity of

the macroporous network polymer are the type and amount of porogen agent as well as the amount of crosslinking agent. Three types of porogen agents, as pure compounds or as mixtures, were used to produce porous resins, namely, solvating diluents, nonsolvating diluents, and soluble polymers.^{5–6}

Kun and Kunin⁷ described the mechanism of pores formation as a three-stage process. In the first stage (i.e., the early stage of polymerization), a polymer is formed having linear chains with pendant vinyl groups. As the polymerization continues, the pendant vinyl groups react intramolecularly, forming the microgels and high-molecular-weight linear chains soluble in the diluent system. In the reaction system as the conversion increases, polymer-phase separation occurs and two phases are formed: one rich in copolymer and another one rich in diluent with low concentration of polymer, the monomers being distributed between the two phases. This phenomenon de-

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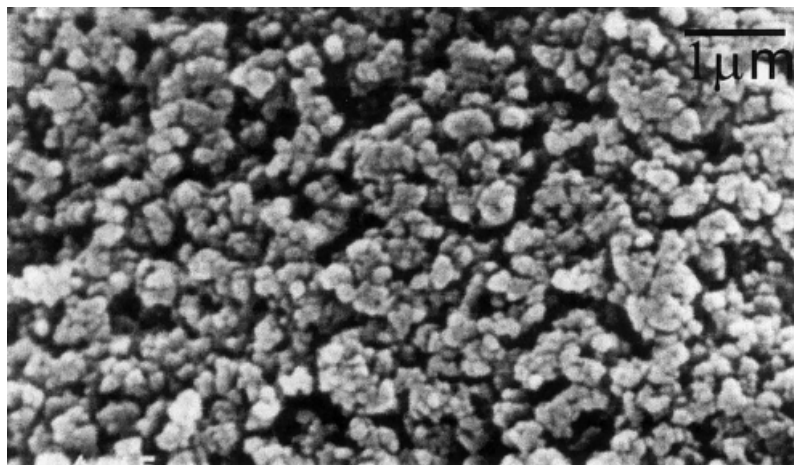


Figure 1 SEM micrograph of a poly(styrene-*co*-divinylbenzene) bead synthesized by conventional suspension polymerization (magnification, $\times 14,000$).¹⁰

pends mainly on the type and amount of porogen agent, and crosslinker proportion. At a determined value of conversion of monomer to polymer, an agglomeration of microgels occurs, resulting in the formation of microspheres. At the second stage of the porous structure formation, the microspheres aggregate. It is during that stage the macroreticular structure is actually formed. In the third stage, the porous structure is completed, the concentration of monomers in the system is low, and as a consequence, the rate of copolymerization decreases.

In the 1980s, macroporous poly(styrene-*co*-divinylbenzene) with particle size around $10\ \mu\text{m}$ was successfully produced by a modified suspension polymerization.⁸ In that method, the reaction mixture was submitted to a high-speed stirring at low temperature for a specified interval of time to obtain droplets in the desired size that by polymerizing will be converted into $10\text{-}\mu\text{m}$ beads. After the high-speed stirring stage, the polymerization was carried out as a conventional suspension polymerization. Thus, the mechanism of porous structure formation was similar to that of a conventional suspension polymerization.⁸⁻⁹

Until now, the main technique used to observe the resins porous structure was scanning electron microscopy.¹⁰⁻¹² For porous resins with particle diameters around $100\ \mu\text{m}$, which is the typical size of beads obtained by conventional suspension polymerization, it is possible to visualize clearly the microspheres and the channels between the microspheres' aggregates that constitute the resins pores (Fig. 1).¹⁰ For particles with a diameter around $10\ \mu\text{m}$, that is the size produced by modified suspension polymerization; the examination

of the pores by scanning electron microscopy needs high magnifications, and in that case, the resolution is poor. Thus, atomic force microscopy (AFM) that allows higher magnifications was tried to examine the porous structure of these particles.

Since its invention in 1986, AFM has evolved as a valuable imaging technique with resolution in the micrometer to subnanometer range. By using this technique, it is possible to produce 3 days' images of polymer surfaces in both air and liquid, and it is not necessary to pretreat any of the sample under examination.¹³⁻¹⁴

In this article, we show how AFM may be applied to characterize the porous structure of co-

Table I Reaction Conditions Employed to Produce Beads of Poly(styrene-*co*-divinylbenzene)^a

Sty-DVB ^b Copolymers Samples	tol/hep ^c v/v (%)	S ^d (m ² /g)	Vp ^e (cm ³ /g)	Dm ^f (nm)
MA-08	100/0	g	g	135
MA-10	70/30	g	g	53
MA-11	50/50	56	0.13	78
MA-12	30/70	102	0.31	97
MA-16	0/100	92	0.48	125

^a Aqueous phase/organic phase = 4/1 (v/v).

^b Commercial DVB = 60% (relative to styrene, mol).

^c Dilution degree = 100% (v/v) (relative to the total volume of monomers).

^d Surface area.

^e Fixed pore volume.

^f Average diameter of microspheres by AFM.

^g Nonmeasurable.

polymer beads on the basis of divinylbenzene with diameters around 10 μm . These copolymers with varied porosities were obtained by modified suspension polymerization by using different compositions of mixtures of toluene and heptane (porogen agents). By AFM, it is possible to visualize the size of microspheres formed during the polymerization. A comparison between the AFM images and statistical analysis of the AFM data and the results of nitrogen adsorption was carried out to evaluate the polymer bead morphology.

EXPERIMENTAL

Materials

Reagents' List

Reagent	Reagent's Short Name	Manufacturer/Donator	Location
Styrene	Sty	Nitriflex S.A.*	BR
Divinylbenzene	DVB	Nitriflex S.A.*	BR
2,2'-azobis(isobutyronitrile)	AIBN	Matacil S.A.*	BR
Methanol	MeOH	PROSINT S.A.*	BR
Toluene	Tol	VE TEC Química Fina Ltda	BR
Heptane	Hep	Rio-Lab Ltda	BR
Poly(vinylalcohol)	PVA	Kuraray Company	JP

* Donator.

Styrene (Sty) and commercial divinylbenzene (DVB) were distilled under reduced pressure. The initiator 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Toluene and heptane were used as received. Poly(vinyl alcohol) (degree of polymerization = 2400 and degree of hydrolysis = 88%) was used as steric stabilizer.

Copolymer Synthesis

Beads of poly(styrene-co-divinylbenzene) and poly(divinylbenzene) were obtained by modified suspension polymerization. Mixtures of toluene and heptane of varied compositions were used as porogen agents. The reaction mixture (organic phase) consisting of styrene, divinylbenzene, AIBN, and porogen agent was poured in a 1-L three-necked round-bottomed flask (polymerization reactor) containing the aqueous phase (water and steric stabilizer) at 10°C and submitted to a high-stirring speed (20,500 rpm) for 10 min. After this stage, the polymerization reactor was fitted with a mechanical stirrer, condenser, and Hg seal. Finally, the polymerization was carried out at 70°C, at 400 rpm during 24 h.⁹

Purification of the Copolymer Beads

After the polymerization period, the resulting beads were vacuum-filtered and washed repeatedly with hot water (60°C), by stirring each time for 30 min, until the water became transparent, and with acetone, until the filtrate did not cloud in water. Finally, the beads were filtered, washed with methanol, and dried at 60°C for 48 h.⁹

Characterization

Pore Size Determination by Nitrogen Adsorption

The specific surface area was obtained by N₂ adsorption following the Brumauer, Emmett, and Teller (BET) method. The pore size distribution and the fixed pore volume were obtained by nitrogen desorption measurements following the Barrett, Joyner, and Halenda (BJH) method. These analyses were carried out in an ASAP 2010 instrument (Micromeritics).

Atomic Force Microscopy

AFM analysis was carried out in a Topometrix Accurex IIL system in AC-Mode, with a Silicon 1660TM Topometrix probe. The cantilever was vibrated at the resonance frequency (around 200 MHz) at low amplitudes. All images were acquired in constant amplitude mode. The measurement parameters were chosen to ensure that no substantial modification of the sample surface occurred during scanning.

The beads of poly(styrene-co-divinylbenzene) were simply glued on silicon wafers with the aid of double-faced tape and the polymer bead excess was eliminated with nitrogen flux. Large areas of the samples (extensions around 20 μm) were ini-

Table II Reaction Conditions Employed to Produce Beads of Poly(divinylbenzene)^a

Copolymers Samples	DVB ^b Dilution Degree ^c (%)	S ^d (m ² /g)	V _p ^e (cm ³ /g)	D _m ^f (nm)
Gi-02	100	480	0.77	56
Gi-03	150	528	1.30	70
Gi-04	200	377	1.20	143

^a Aqueous phase/organic phase = 4/1 (v/v).

^b Commercial DVB.

^c tol/hep ratio = 30/70 (v/v).

^d Surface area.

^e Fixed pore volume.

^f Average diameter of microspheres by AFM.

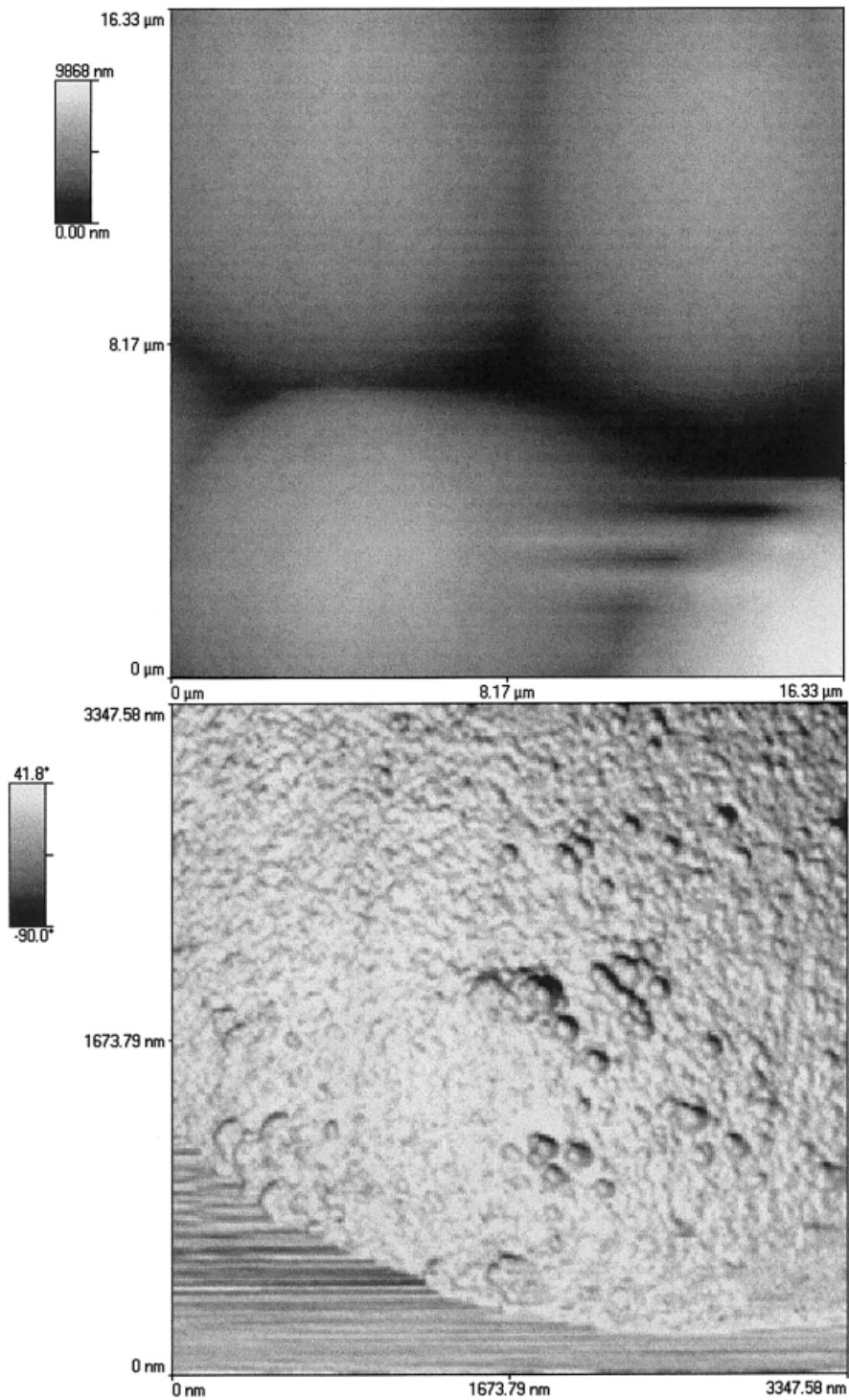


Figure 2 Atomic force image of poly(styrene-*co*-divinylbenzene) beads synthesized by modified suspension polymerization.

tially scanned to localize the spheres. All images presented were obtained by zooming on the central region of one bead.

Peak and valley analysis was the measurement technique chosen for quantifying the size of the microspheres by defining the lateral spac-

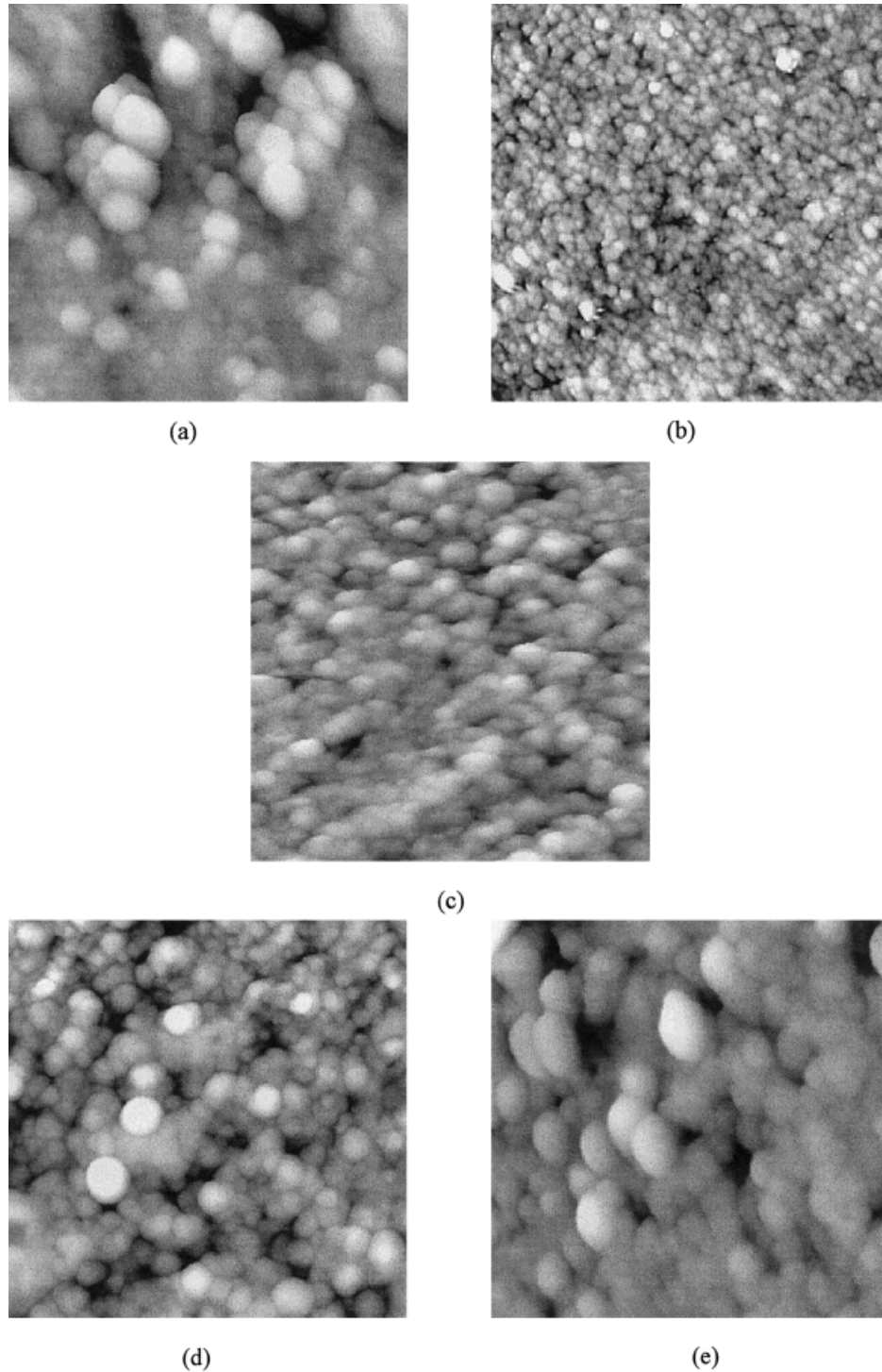


Figure 3 Atomic force image of poly(styrene-co-divinylbenzene) beads prepared at different tol/hep ratios: (a)100/0, (b)70/30, (c) 50/50, (d)30/70, (e) 0/100 (lateral dimensions, $1.4 \mu\text{m}$).

ing and the slope of the features. As opposed to other analysis techniques that focused primarily on the Z height component of the

sample topography, peak and valley analysis allows roughness analysis based on peak density (lateral spacing) and on peak slope. The

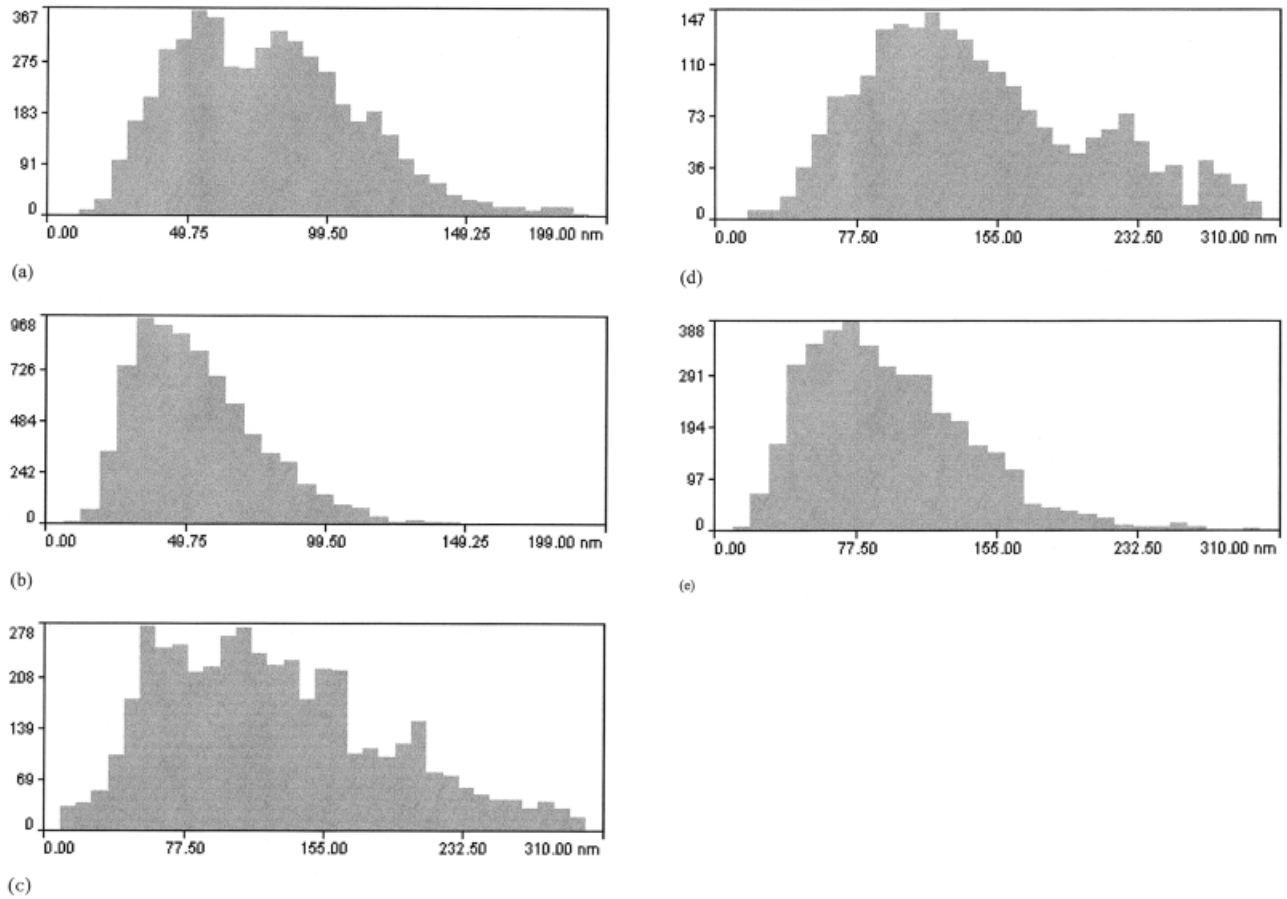


Figure 4 Peak spacing distribution of microspheres of poly(styrene-*co*-divinylbenzene) beads prepared at different tol/hep ratios: (a)100/0, (b)70/30, (c) 50/50, (d)30/70, (e) 0/100.

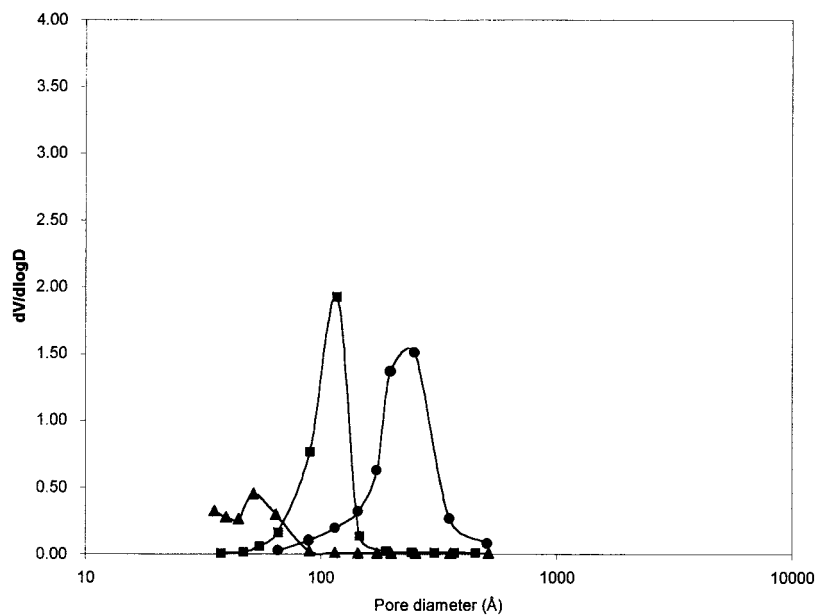


Figure 5 Differential pore size distribution curves of poly(styrene-*co*-divinylbenzene) beads measured by nitrogen desorption at different tol/hep ratios: (▲) 50/50, (■) 30/70, and (●) 0/100.

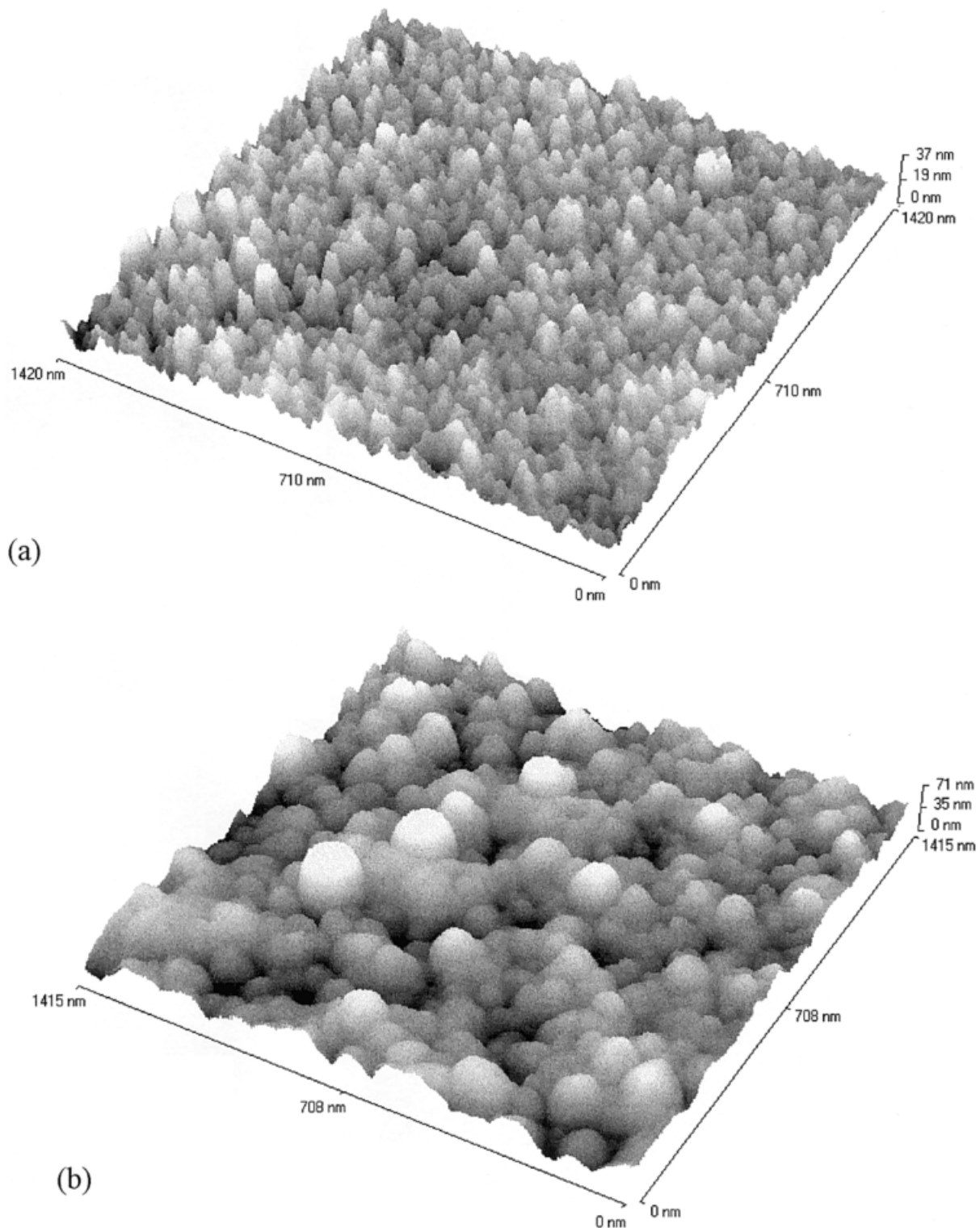


Figure 6 3D AFM images of poly(styrene-co-divinylbenzene) beads prepared at different tol/hep ratios: (a)70/30 and (b)30/70.

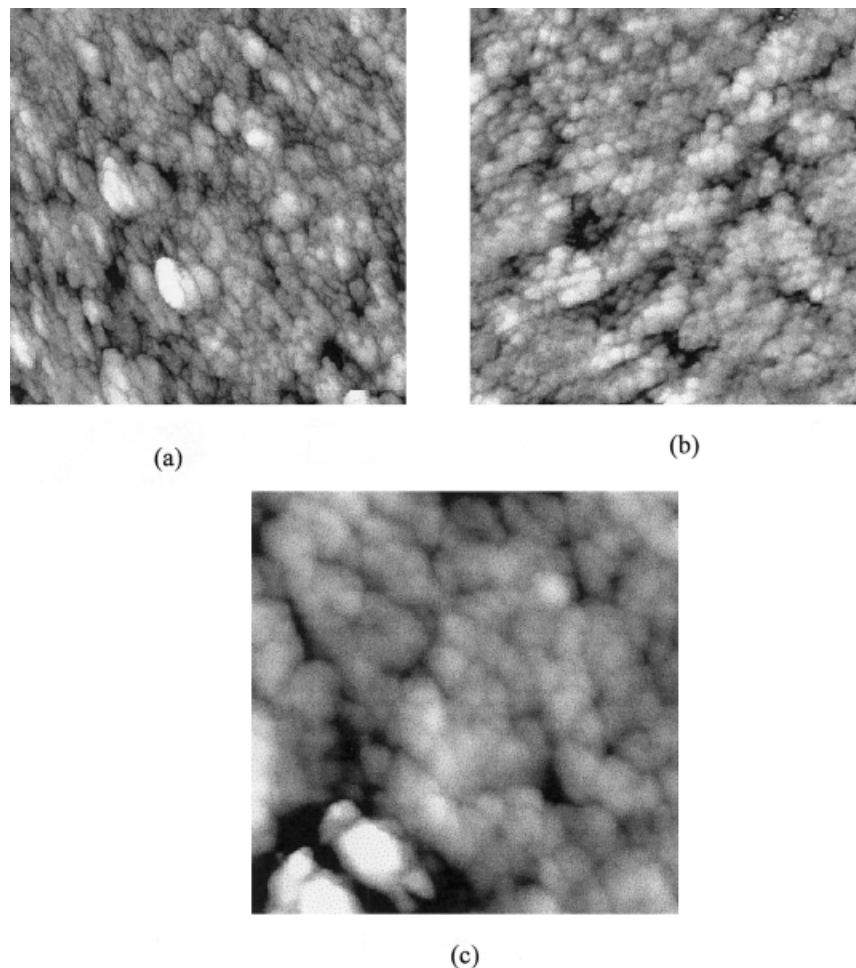


Figure 7 Atomic force image of poly(divinylbenzene) beads prepared at different dilution degrees: (a) 100%, (b) 150%, and (c) 200% (lateral dimensions $1.4 \mu\text{m}$).

mean value of the peak spacing was also quantified.

RESULTS AND DISCUSSION

The synthesis conditions to produce beads of poly(styrene-*co*-divinylbenzene) and poly(divinylbenzene) and their physical characteristics that are the subject of analysis in this work are summarized in Tables I and II. The morphology of the copolymer beads was examined by using one of the most recent techniques in the study of polymer morphology, the AFM, and compared with the traditional technique was used to determine the porosity of macroporous copolymers in the dry state, the nitrogen adsorption, that is employed to measure mesopores (20–500 Å). In this work, all the AFM analyses were carried

out by using AC-Mode of operation. We have found in our studies that the use of noncontact mode allowed more reliable and reproducible images of the copolymer bead surface than the contact mode.

The AFM image presented in Figure 2 shows the bead surface of poly(styrene-*co*-divinylbenzene). Three beads of about $10 \mu\text{m}$ in diameter are clearly shown in that image. Because of the low magnification, microspheres and pores cannot be visualized. Thus, to examine the microspheres and the pores of the beads, higher magnifications were used.

Beads of Poly(styrene-*co*-divinylbenzene)

The first study of this work is the morphology evaluation of poly(styrene-*co*-divinylbenzene) synthesized by using the conditions presented in

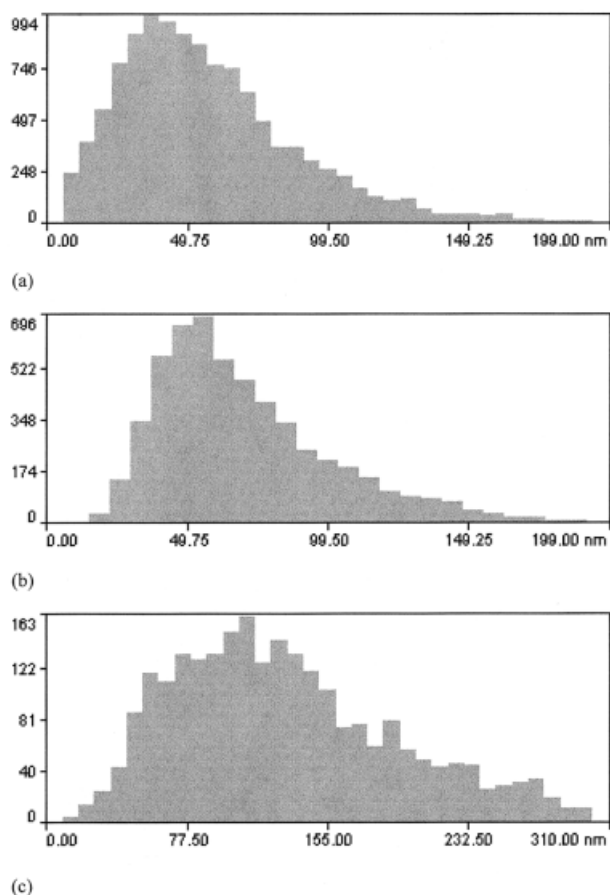


Figure 8 Peak spacing distribution of microspheres of poly(styrene-*co*-divinylbenzene) beads prepared at different dilution degrees: (a) 100%, (b) 150%, and (c) 200%.

Table I [i.e., 60% of DVB, expressed as molar percentage in relation to styrene, dilution degree of 100% (volume percentage of the total volume of the monomers), and varied tol/hep ratios]. The surface area and fixed pore volume of the beads of poly(styrene-*co*-divinylbenzene) synthesized by using as diluent tol/hep = 100/0 and 70/30 were nonmeasurable by nitrogen adsorption. These results indicate that the beads did not present mesopores in the dry state. However, the atomic force images, Figure 3(a,b), show the surface of these beads of poly(styrene-*co*-divinylbenzene) where it is possible, in both cases, to see that these materials are formed by microspheres and channels between microsphere aggregates that are the pores of the beads. The AFM image of beads of poly(styrene-*co*-divinylbenzene) synthesized by using as diluent tol/hep = 100/0 [Fig. 3(a)] shows microspheres of nonuniform sizes.

These beads of poly(styrene-*co*-divinylbenzene) are formed by large microspheres and small ones with small channels between them. These channels are probably the pores that are nonmeasurable by nitrogen adsorption method. The bead synthesis in the presence of solvating diluent provokes the later occurrence of phase separation in the polymerization process; thus, the size of microspheres increases and their size distribution broadens. Figure 4(a) presents the size distribution curve of the microspheres showing that these microspheres present a bimodal size distribution, the average size being 135 nm. As expected,¹¹ the addition of the nonsolvating diluent [i.e., addition of heptane to the diluent (tol/hep = 70/30)] provoked the earlier occurrence of phase separation. As a consequence, the size of the microspheres decreased [Fig. 3(b)]. However, further increases of heptane proportional in the diluent mixture (50/50, 30/70, and 0/100) [Fig. 3(c–e)] made the size of the microspheres increase. The microspheres size distribution curves of those beads are presented in Figure 4(b–e). Those figures show that a displacement of the distribution curves to high values occurs as the proportion of heptane increases. The average diameters of microspheres (D_m) are presented in Table I. The increase of the microsphere size and microsphere size distribution may be attributed to the occurrence of phase separation when the microspheres still were in the sticky stage. Thus, probably some small microspheres agglomerated forming larger ones. In Table I, the beads of poly(styrene-*co*-divinylbenzene), synthesized by using as diluent tol/hep = 70/30, also did not present measurable fixed pore volume and surface area by nitrogen adsorption method, but by AFM images, it is possible to visualize channels between the microspheres that may be the pores of the beads. The nitrogen adsorption method requires the removal of adsorbed molecules from the external and internal (pores) surfaces. Thus, an exhaustive sample pretreatment is necessary before carrying out the analysis (heating at 140°C and 10 μ m Hg vacuum).¹⁵ As the beads of poly(styrene-*co*-divinylbenzene) have the capacity of shrinking and swelling,⁹ the heating and high-vacuum application during the pretreatment may provoke a decrease in the pores size, giving rise to differences in the values obtained by nitrogen adsorption and AFM techniques. The beads of poly(styrene-*co*-divinylbenzene) synthesized by using tol/hep in ratios of 50/50, 30/70, and 0/100 presented pores in the range of mesopores, measured by nitrogen de-

sorption, as may be seen in Figure 5. The pores size distribution was displaced to higher values as the heptane proportion in the diluent mixture was increased. That behavior is confirmed by AFM [Fig. 3(c–e)]. At a fixed dilution degree, an increase in the heptane proportion in the diluent mixture provoked an increase in the size of microspheres. Thus, we may expect that the channels between the microspheres increased and consequently the pores size also increased. Observing the 3D images of the surface of the beads of poly(styrene-*co*-divinylbenzene) [Fig. 6(a,b)], it is easier to visualize the difference between them. The copolymer synthesized by using tol/hep = 70/30 as diluent presented small channels regularly distributed while the beads of poly(styrene-*co*-divinylbenzene) prepared by using tol/hep = 30/70 presented larger channels, more irregularly distributed. Thus, the increase of heptane proportion in the diluent mixture contributed to an increase in the size of microspheres and the size of pores. Those materials presented surface area around 100 m²/g and the pore volume increased as the proportion of heptane in the porogen agent increased (Table I).

Beads of Poly(divinylbenzene)

The effect of the dilution degree on the morphology of the beads surface of the copolymers pro-

duced by using the conditions presented in Table II was analyzed by AFM and nitrogen adsorption method. Thus, the second part of this work is the evaluation of the highly crosslinked poly(divinylbenzene) beads synthesized in the presence of the diluent mixture, tol/hep = 30/70, at varied dilution degrees, by using as monomer commercial divinylbenzene containing approximately 55 wt % *m*- and *p*-divinylbenzene, ≈ 38 wt % *m*- and *p*-ethyl styrene, and other nonpolymerizable compounds. In Figure 7(a–c), it is possible to see that the microspheres obtained when 100 and 150% of dilution degree was used are more uniform than the microspheres produced when 200% of dilution degree was used. The size distributions of the microspheres are presented in Figure 8(a–c). The microsphere size distribution curves were displaced to higher values as the dilution degree was increased. At 200% of dilution [Fig. 8(c)], the curve of the microspheres size distribution is wider than those at 100 and 150% of dilution degree [Fig. 8(a,b)]. That behavior should be expected, because by increasing the proportion of the crosslinking monomer (DVB) in the presence of a diluent mixture with a high proportion of nonsolvating compound, highly entangled crosslinked structures are formed. As the microspheres become more crosslinked, the phase separation occurs earlier. However, at high-dilution

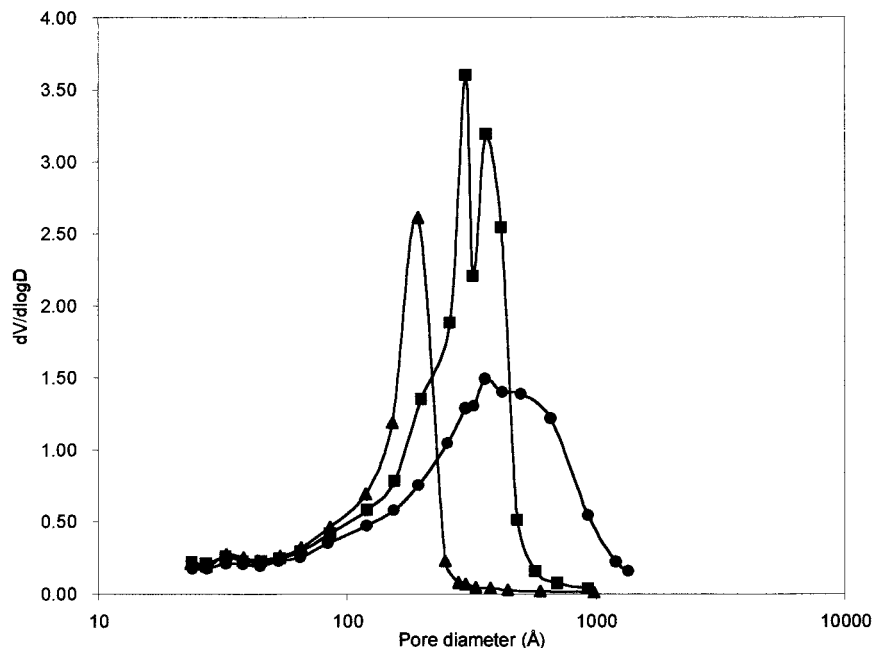


Figure 9 Differential pore size distribution curves of poly(divinylbenzene) beads measured by nitrogen desorption at different dilution degrees: (▲) 100%, (■) 150%, and (●) 200%

degree, in a diluent rich in bad solvent (heptane), the phase separation occurs when microspheres still were in the stick stage, provoking the microspheres agglomeration and consequently the sizes and size distribution increase. Another aspect that should be observed in Figure 7(a–c) is the channels between the microspheres that increased with the dilution degree. It is evident by nitrogen adsorption measurements that the beads of poly(divinylbenzene) synthesized at 150 and 200% of dilution degree present larger pores than those synthesized at 100% (Fig. 9). All distribution curves, in Figure 9, start at the same size of pores, because the high concentration of divinylbenzene that was fixed for all reactions generated small pores, but with the increase of dilution degree, the size of pores was displaced to higher values. Observing the pore size distribution curves of the beads of poly(divinylbenzene), it is possible to see that the pores size is directly related to the dilution degree. As the dilution degree increases, more diluent is present among the microspheres, increasing the size and the number of channels among the microspheres. When 200% of dilution degree was employed, the size distributions of microspheres and pores became wider than those produced at 100 or 150% of dilution degree. As expected, the surface area and pore volume of these materials are higher than those of the beads of poly(styrene-*co*-divinylbenzene). The small pores formed in the beads of poly(divinylbenzene) contributed accentuatedly to the high values of surface area shown in Table II. The fixed pore volumes of poly(divinylbenzenes) (Table II) were higher than those of poly(styrene-*co*-divinylbenzene) (Table I). This behavior is a consequence of the earlier occurrence of phase separation during the polymerization because of the higher proportion of crosslinking agent (DVB) employed in poly(divinylbenzene) synthesis.

CONCLUSION

AFM technique is a good tool to study the mechanism of pore formation of beads of poly(styrene-*co*-divinylbenzene) with sizes around 10 μm . By

AFM, it was possible to see that each bead of the copolymer consists of microspheres with channels between them, identified as the bead pores. It was possible to confirm by AFM the results obtained by nitrogen adsorption. The size of the microspheres and the porosity of the beads of the poly(styrene-*co*-divinylbenzene) are dependent on the synthesis conditions (i.e., the diluent composition, the dilution degree, and divinylbenzene content).

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