

# Effects of the Crosslinking Agent and Diluents on Bead Properties of Styrene–Divinylbenzene Copolymers

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**ABSTRACT:** Styrene–divinylbenzene copolymer beads were synthesized by radical suspension polymerization. Effects of the divinylbenzene concentration and composition of the toluene/heptane diluent were studied regarding the polymer bead formation, surface morphology, solvent swelling ratio, and glass transition temperature. The crosslinking density and diluent composition were responsible for solvent swelling. Interaction between the polymer and the diluents is attributed to phase separation, which controls the formation of a network-type or pore-type polymer, or a combination. For an optimum bead swelling in toluene, a combined morphology of more flexible polymer networks and a small amount of pores is essential for the desired absorption–desorption behavior. This article also combines several current findings with work presented elsewhere to explain the bead formation phenomenon. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 654–669, 2002

**Key words:** swelling; crosslinking; copolymerization; polystyrene

## INTRODUCTION

The development of crosslinked polymers of styrene and divinylbenzene with a well-defined porous structure and monodisperse size has received great interest. The versatile applications of this type of polymer beads include ion exchange resins, column-packing materials for gel permeation chromatography, polymer-supported catalysts, and standards for instrument calibration. The use of this type of polymer beads in environmental applications has

not yet received enough attention. Kiatkamjornwong et al.<sup>1–3</sup> have investigated the copolymerization technique of crosslinking polystyrene beads for improved performance in terms of solvent absorption and desorption properties for cleaning spilled solvent or oil drained (unfortunately) from production lines or accidentally leaked or discarded. The present work extends our previous work studying the relationship between the crosslinked molecular weight or crosslinking density and solvent swelling using the simplified equation of Flory and Rehner.<sup>4–7</sup> The solvent absorption and desorption properties of the imbibed beads are also investigated to obtain the diffusion coefficient, an indication of the swelling rate, which is network and porosity dependent.

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**Table I Basic Recipe and Reaction Conditions of Styrene-Divinylbenzene Copolymerization**

Ingredient	Crosslinking Agent, %						Heptane, %				
	D00	D03	D06	D09	D12	D15	H00	H20	H40	H60	H80
Sty, %	100	97	94	91	88	85	94	94	94	94	94
DVB, %	0	3	6	9	12	15	6	6	6	6	6
BPO, %	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tol, %	100	100	100	100	100	100	100	80	60	40	20
Hep, %	—	—	—	—	—	—	—	20	40	60	80

For all reactions, [PVA] = 0.1%; water-to-monomer ratio = 9 : 1; reaction temperature = 70°C; polymerization time = 10 h; and agitation rate = 270 rpm.

## EXPERIMENTAL

### Materials

Styrene, Sty (commercial grade, Shell Chemicals, Japan), or divinylbenzene, DVB (65% DVB isomers and 33% ethyl vinylbenzene measured by GC, technical grade, Merck, Darmstadt, Germany), was washed with 10% aqueous sodium hydroxide (BDH, Poole, Dorset, U.K.) solution and water, dried over anhydrous sodium sulfate (Carlo Erba, Milan, Italy), and passed through an activated  $\gamma$ -form aluminum oxide (100–125 mesh) column (Fluka, USA) to remove the residual inhibitors. These monomers were stored in a refrigerator prior to use. The diluents, toluene and heptane (analytical grade, J.T. Baker, USA), and other solvents were used as received.

### Polymerization

Sty-DVB copolymers were prepared by conventional suspension polymerization. Benzoyl peroxide initiator (BPO, 97% purity moistened with 25% of water, Merck, Darmstadt, Germany) of 0.5 wt % in relation to the monomers was dissolved in the selected monomer/diluent mixture. Poly(vinyl alcohol) (PVA, Fluka, having a MW average of  $10^5$ , a degree of polymerization of  $2 \times 10^3$ , and a degree of hydrolysis of 86–89%) of 0.1 wt % was used as a suspending agent. The monomer phase weight fraction for all reactions was 0.1.

The suspension copolymerization (shown in Table I) was carried out in a 1000-cm<sup>3</sup> reaction flask fitted with a variable mechanical stirrer, thermometer, N<sub>2</sub> inlet, and reflux condenser. The solution containing the monomers, the diluents (Tol and Hep), and the initiator was poured into the reactor, which contained the aqueous solution of the suspending agent in 270 cm<sup>3</sup> of distilled

water. The copolymerization was performed at 270 rpm and 70°C for 10 h in a thermostatically controlled oil bath. After the reaction period, the resulting copolymer beads were washed with hot water and extracted with acetone in a Soxhlet apparatus for 10 h to remove the diluents and residual monomers. Finally, the beads were dried under vacuum at 60°C for 24 h. Opaque spherical beads of 0.84–2.0 mm in diameter were obtained.

### Characterization

#### Particle Size and Distribution

The size and distribution of the beads were measured by sieve analysis as follows: wire gauze sieves of different mesh sizes were stacked over one another. The mesh size varied from 2 mm at the upper most stack to 0.84, 0.59, and 0.42 mm at the lower stacks, respectively. All the copolymer beads were first filled in at the top of the stack. The smaller beads were separated from the larger ones by passing through the upper gauze to the lower gauzes for further separation, whereas the larger ones had been retained on the upper wire gauze. Each percentage weight fraction of the sieved bead size was used to calculate the particle size distribution.<sup>3</sup>

#### Surface Morphology

The dried copolymer beads were coated with a thin layer of gold under a vacuum using a sputter coater, and photographed using a scanning electron microscope (Joel JSM-6400, Sweden) to characterize the surface morphology and average particle size of the copolymer beads.

#### Bead Density

The copolymer bead density was determined using a liquid displacement technique according to the ASTM D-792 test method.

### Swelling Ratio

Swelling measurements of the imbiber copolymer beads were carried out in toluene at room temperature for 24 h. The swelling ratio,  $S$ , was determined gravimetrically by immersing the dry copolymer beads in excess toluene in a test tube sealed with aluminum foil and closed with a cap. The excess solvent was filtered and the swollen beads were weighed. The swelling ratio of the beads was calculated by the following equation:

$$S = 1 + \left( \frac{W_s}{W_p} - 1 \right) \frac{\rho_p}{\rho_s}, \quad (1)$$

where  $W_p$  is the weight of the dry polymer before swelling,  $W_s$  is the weight of the fully swollen copolymer at equilibrium, and  $\rho_s$  and  $\rho_p$  are the densities of solvent and polymer, respectively.

### Crosslinking Density

The crosslinking densities of copolymer beads were determined using the Flory-Rehner theory.<sup>4-6</sup> To obtain this value, the volume fraction ( $\phi_p$ ) of the beads is first calculated by

$$\phi_p = \frac{V_p}{V_s + V_p}, \quad (2)$$

where  $V_s$  and  $V_p$  are the molar volumes of the solvent and polymer, respectively.

For a polystyrene system, the polymer-solvent interaction parameter ( $\chi_{12}$ ) was estimated using the following formula:<sup>7</sup>

$$\chi_{12} = 0.431 - 0.311\phi_p - 0.036\phi_p^2. \quad (3)$$

One of the most important structural parameters characterizing the crosslinking density is  $\bar{M}_c$ , the average molecular weight of the crosslinking network. According to the theory of Flory and Rehner,

$$\bar{M}_c = -V_s\rho_p \frac{(\phi_p^{1/3} - \phi_p/2)}{[\ln(1 - \phi) + \phi_p + \chi_{12}\phi_p^2]}. \quad (4)$$

Here the crosslinking density,  $q$ , is defined as the mole fraction of the crosslinking units:

$$q = \frac{M_o}{\bar{M}_c}, \quad (5)$$

where  $M_o$  is the molecular weight of the repeating units of the copolymer.

### Glass Transition Temperature

Differential scanning calorimetry (DSC) experiments were carried out using a Perkin-Elmer DSC-7 (USA) controlled by 7500 PC software. Copolymer beads in a pan were heated from 75 to 150°C at a heating rate of 20°C min<sup>-1</sup> under a nitrogen atmosphere, annealed for 5 min at 150°C and quenched to room temperature. Likewise, the second scan was recorded out at the same heating rate scanning up to 150°C. The glass transition temperature ( $T_g$ ) of the beads was determined as the midpoint of the endothermic displacement between linear baselines.

### Diffusion Coefficient

The diffusion coefficient ( $D$ ) of a liquid in the bead due to the porous microstructure was determined according to the method previously reported from the following equation:<sup>3</sup>

$$\tau = \frac{a^2}{D}, \quad (6)$$

where  $D$  is the diffusion coefficient of the the liquid in the bead,  $a$  is the final radius of the fully swollen gel, and  $\tau$  is the characteristic swelling time, providing a useful tool for measuring the absorption of imbiber beads.

### Pore Properties of Copolymer Beads

A mercury porosimeter (Micromeritic 9320, USA) was used to determine the pore volume, surface area, and average pore diameter of the copolymer beads.

### Surface Tension and Interfacial Tension of the Mixed Diluents

The surface tension and interfacial tension in water of the toluene/heptane diluent mixtures were measured by a Kruss Interfacial Tensiometer K8 (Germany) using the Wilhelming plate and DuNouy Ring techniques.

## RESULTS AND DISCUSSION

In the present work, an extremely low monomer phase weight fraction of 0.1 was used to obtain

**Table II** Effect of the Crosslinking Agent Concentration on Bead Properties<sup>a</sup>

Run	D03	D06	D09	D12	D15
DVB concentration, wt %	3.0	6.0	9.0	12.0	15.0
% Yield	39	51	58	66	70
Bead size distribution, wt %					
< 0.42 mm	—	0.99	2.82	6.23	4.37
0.42–0.59 mm	—	12.46	14.43	17.39	21.93
0.59–0.84 mm	—	15.71	21.55	21.71	27.23
0.84–2.0 mm	—	66.56	59.96	50.96	43.70
> 2.0 mm	—	4.28	1.53	3.71	2.67
Average bead size, mm	Fused	1.21	1.12	1.07	1.00
$\bar{M}_c$	53,400	12,300	7900	5800	3900
Crosslinking density	1.6	7.1	11.1	15.2	22.3
Swelling ratio	12.3	6.5	5.5	4.8	4.2
Diffusion coefficient, $\text{cm}^2 \text{s}^{-1} \times 10^5$	—	2.13	1.66	0.91	0.29
Bead density, $\text{kg m}^{-3}$	1050	1046	1046	1040	1036
Glass transition temperature, °C	99	107	112	123	129

<sup>a</sup> Toluene was used a diluent.  $M_0 = 8800$ .

pearl-like particles. Higher monomer phase weight fraction could not allow the copolymerization to form beads but gave aggregates or big lump of polymer mass. One may increase the amount of stabilizing agent such as PVA or droplet stabilization or increase the stirring rate to increase the monomer phase weight fraction as a normal commercial practice ( $\geq 0.5$ ). In this suspension copolymerization, low monomer phase weight fraction produces a relatively low conversion especially at low crosslinking agent concentration. To increase a higher monomer conversion, a larger amount of crosslinking agent should be used.

#### Effect of the Crosslinking Agent Concentration on Bead Formation

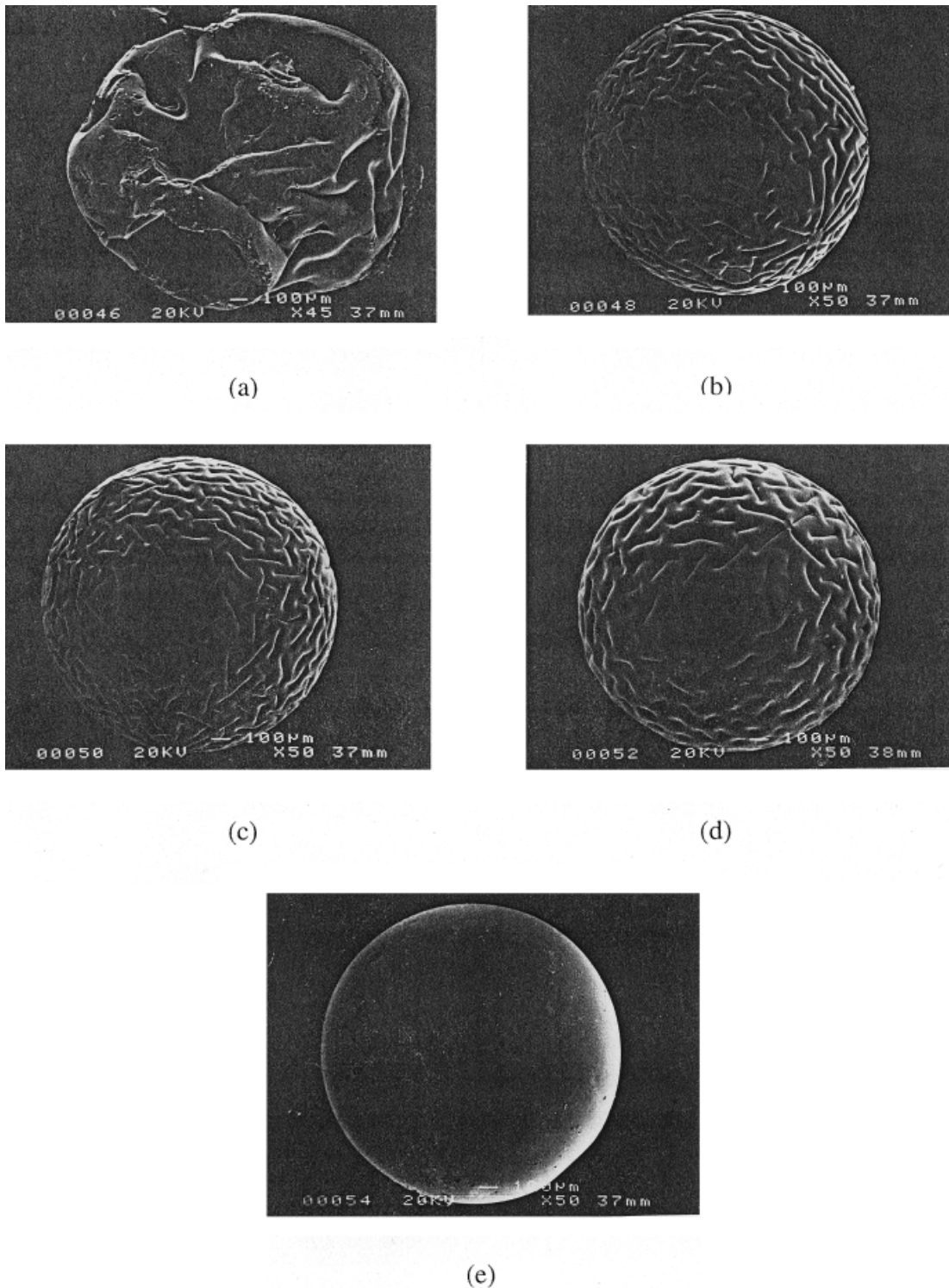
Table II shows the overall conversion, average particle size, and size distribution as a function of the concentration of the crosslinking agent, divinylbenzene (DVB). This shows that the overall conversion, expressed as the % yield, increased with increasing DVB content.

At a DVB percentage of 3.0 (Run D03), the polymeric beads formed were clustered and fused, and no bead formation could be observed, because the crosslinking agent concentration was too low to produce enough crosslinking sites to maintain the dimension of the beads. Thus, this amount of the crosslinking agent is not sufficient to help the bead formation. The corresponding consequence of low conversion or yield ( $< 50\%$ ) was observed at a low crosslinking agent concentration (D03). We

presumed that more soluble part of very lightly crosslinked poly(styrene-co-DVB) was the attribute to the low conversion.

When the DVB concentration was increased from 6 to 15% (D06 to D15), the average size decreased slightly and the particle shape was unchanged.

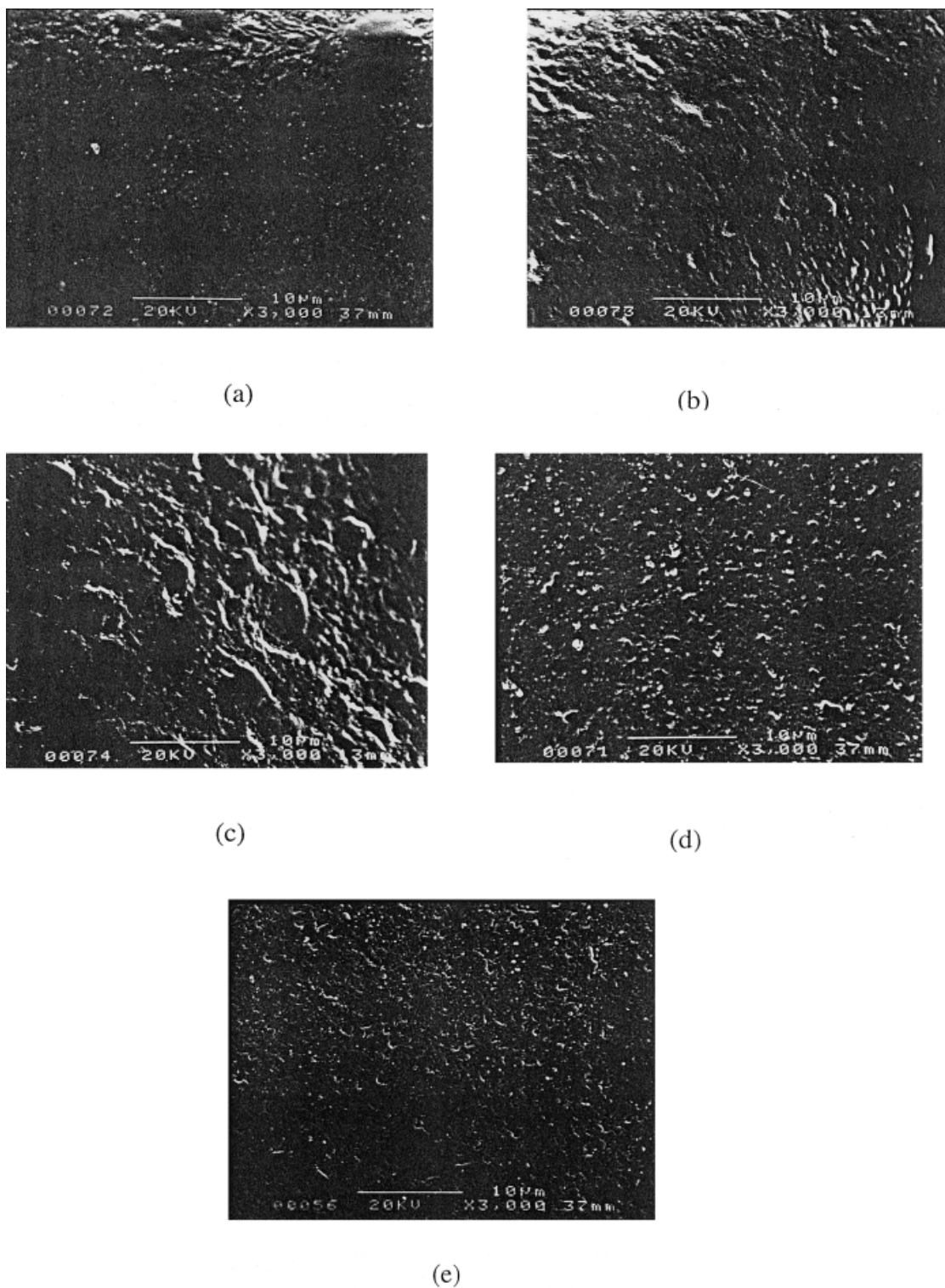
Figure 1 shows the surface morphology of Sty-DVB copolymer beads influenced by the crosslinking agent concentration at a magnification of 50. As mentioned above, the 3% DVB beads have a distorted dimension and deformed soft surface [Fig. 1(a)]. In general, an increase in the amount of DVB produces an increasing crosslinking density of the copolymer chains. The copolymer beads are thus harder and tougher leading to the decrease in shrinkage of the copolymer bead surface. Nonetheless, they appeared as small, uneven, and dented tracks on the bead surface. The bead surfaces become smoother when higher concentrations of the crosslinking agent were copolymerized [Fig. 1(b)–(e)]. The shrinkage of the copolymer bead surfaces in Figure 1(b)–(d) occurred because of the low crosslinking density resulting from a low DVB content. When the copolymers were being swollen by a good solvent during solvent extraction, an imbalance tension arose between the bead interior and the outer surface surrounded by the extracting solvent. The removal of the uncrosslinked copolymer beads caused the weak, expanded network of the bead outer surface to shrink and this shrinkage of some areas of the surface was enhanced as a



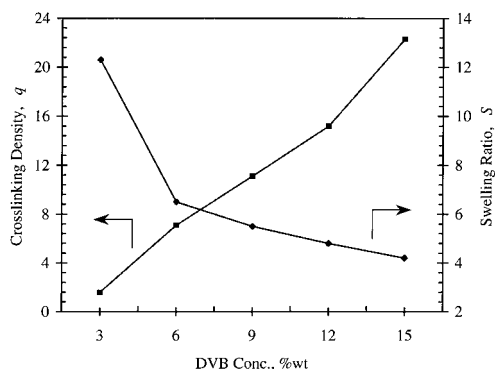
**Figure 1** SEM photographs of the copolymers prepared at different crosslinking agent concentrations: (a) D03, 3.0%; (b) D06, 6.0%; (c) D09, 9.0%; (d) D12, 12.0%; and (e) D15, 15.0% ( $\times 50$ ).

result of the cohesive forces when the solvated polymer chains approached each other due to loss of the solvent.

Figure 2 shows a higher magnification (3000 times) of the surface morphology of Sty-DVB copolymer beads to determine the effect of the



**Figure 2** SEM photographs of the copolymers prepared at different crosslinking agent concentrations: (a) D03, 3.0%; (b) D06, 6.0%, (c) D09, 9.0%; (d) D12, 12.0%, and (e) D15, 15.0% ( $\times 3000$ ).



**Figure 3** Effect of the crosslinking agent concentration on crosslinking density and swelling ratio.

crosslinking agent concentration. When styrene and divinylbenzene are copolymerized in the presence of a good diluent (toluene), two kinds of porous structure can be obtained: an expanded or macroporous gel. At a low DVB content, the final structure is an expanded gel [Fig. 2(a)–(c)], because the chains are fully solvated during the polymerization and they shrink less than those of the corresponding system do in the absence of a solvating diluent. However, the internuclear chains can collapse with the removal of the solvating diluent to make the approaching nuclei become a compact mass. A porous copolymer is obtained when the DVB content is relatively high

[Fig. 2(d) and (e)]. In this case, the collapse of the internuclear chains occurs before all the solvating diluents have been removed. The porosity is, of course, a result of a removal of the remaining diluent.<sup>8</sup> A bead with a relatively higher crosslinking density caused by the DVB content, as shown in Table II and Figure 3, results in a greater increase in the elastic-retractile force, which allows more formation of crosslinked microspheres with a porous structure.

Figure 3 shows the effect of a DVB concentration range of 3 to 15 wt % of the monomer content on the swelling ratio and crosslinking density of styrene–divinylbenzene beads. The swelling of the beads decreases with an increasing crosslinking density of the copolymer chains. The copolymer beads are therefore less flexible, leading to a decrease in the swelling ratio. These results also led to a decrease in the diffusion coefficient of the copolymer, as shown in Table II.

#### Effect of the Diluent Composition on Bead Formation

Table III shows the overall conversion, average particle size, and size distribution in relation to the diluent composition of toluene (Tol) and heptane (Hep) as a good solvent and bad solvent, respectively, for the newly synthesized copolymers in this work. It is shown that the overall

**Table III** Effect of the Toluene/*n*-Heptane Diluent Composition on Bead Properties<sup>a</sup>

Run	H00	H20	H40	H60	H80
Diluent composition (Tol/Hep), wt %	100/0	80/20	60/40	40/60	20/80
% Yield	51	48	49	50	48
Bead size distribution, wt %					
< 0.42 mm	0.99	1.79	3.33	6.66	8.86
0.42–0.59 mm	12.46	9.50	10.91	7.85	9.10
0.59–0.84 mm	15.71	12.32	11.87	13.39	12.16
0.84–2.0 mm	66.56	71.43	68.23	64.91	47.17
> 2.0 mm	4.28	4.96	5.66	7.19	22.71
Average bead size, mm	1.21	1.26	1.24	1.23	1.23
$\bar{M}_c$	12,300	12,900	17,400	11,800	7700
Crosslinking density	7.1	6.8	5.1	7.4	11.4
Swelling ratio	6.5	6.7	7.6	6.5	5.6
Diffusion coefficient, $\text{cm}^2 \text{s}^{-1} \times 10^5$	2.13	3.16	4.52	3.97	1.55
Bead density, $\text{kg m}^{-3}$	1,046	1,036	1,027	1,013	938
Glass transition temperature, °C	107	107	107	108	109
Average pore diameter, $\mu\text{m}$	0.0133	0.0137	0.0141	0.0167	0.0212
Surface area, $\text{m}^2 \text{g}^{-1}$	17.466	25.248	32.764	39.219	44.057
Pore volume, $\text{cm}^3 \text{g}^{-1}$	0.0581	0.0863	0.1158	0.1634	0.2337

<sup>a</sup> DVB concentration = 6 wt %.

conversion, expressed as %yield, does not depend on the diluent composition. Interestingly, changes in the diluent composition do not affect the average particle size of the copolymers. The function of a diluent mixture between a good and poor solvent is to develop the interior and surface morphology of the copolymers. The copolymer beads at low and high magnifications are shown by SEM photographs in Figures 4–5.

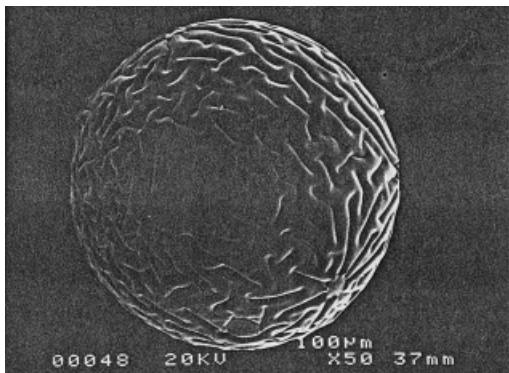
The most important factor controlling the heterogeneity of the porous network of polymers is the type and amount of diluent. Solvating diluents generally produce small pores while nonsolvating ones produce large pores.<sup>2</sup> Therefore, the polymer–solvent interaction ( $\chi$ ) is the main factor in determining the pore structure. The thermodynamic affinity of the diluent for the copolymer can be predicted using the concept of solubility parameter. Table IV describes the effect of the diluent ratio between a good solvent (toluene) and a poor solvent (heptane), with the presence of styrene and DVB monomers, on the surface appearance of Sty-DVB copolymer beads. Let  $\delta_1$  and  $\delta_2$  be solubility parameters of the diluent and polymer, respectively. When  $|\delta_1 - \delta_2| \approx 0$  or  $< 1.0$ , miscibility is favored, i.e., the diluent is a good solvent that produces expanded network gels. When  $|\delta_1 - \delta_2| > 3.0$  (MPa)<sup>1/2</sup>, miscibility does not occur spontaneously so that the diluent separates out; the polymer phase then produces rather large pores. In the presence of monomers, the diluent phase is more compatible with its polymerizing beads, because the  $|\delta_1 - \delta_2|$  is small (Table IV). In general, a diluent mixture composed of a balanced composition between a good and a poor solvent for a polymer produces intermediate pore structures.

Each monomer droplet contains a monomer (Sty), a crosslinking agent (DVB), a mixed solvent (HP/Tol) with the corresponding solubility parameter 19, 18, 15–18.2 (MPa)<sup>1/2</sup>, and an initiator (BPO). One can postulate that each droplet is composed of isolated cells in which active polymer radicals are dissolved in styrene-rich phase and surrounded by a relatively incompatible St/HP (continuous phase). Number of radicals in the droplet increases initially as the polymerization proceeds, HP-rich phase gradually separated, and finally forming macrodomains. The phase separation allows polystyrene chains to dissolve in a more favorable styrene phase, and the homogeneous bulk copolymerization takes place, and results in a gradual decrease in the average number of radicals in the droplets until the viscosity in-

crease to induce the formation of porous gel. When toluene is the sole solvent present in the droplet, the polymerization progresses in accordance with the solvent mechanism. Polystyrene can dissolve in the toluene/styrene monomer phase until a critical chain length is reached. When the styrene and DVB is copolymerized to transform to its crosslinked polystyrene, good solvency of the monomer (Sty) decreases and increases the immiscibility of the polymer in a poor solvent of heptane. Micro- or macrophase separation occurs in the droplet to produce porous gel. The conversion of mixed monomer causes the diluent phase composition to vary significantly during the course of polymerization. Because the styrene monomer and toluene are good solvent and heptane is a poor solvent, monomer conversion is a good indication of phase separation in a mixed solvent system. When more monomer concentration is used during the polymerization, such a copolymerization in the mixed solvent of low heptane content enhances the effect of toluene because the toluene content is high, and the resulting polymer can swell better in the good solvent portion. When the toluene is relatively low or the ratio of heptane is high, the polymer so formed is more porous. Comparing the two conditions, the swelling extent of the latter polymer of more porous nature is, of course, higher. On the other hand, if the rate of copolymerization of the monomer can be followed, the phase composition of the diluent in the polymerizing droplets could then be estimated or even quantified.

Figure 4 shows the scanning electron micrographs of the surface morphology of Sty-DVB copolymer beads from experiments H00 to H80 (in Table III) at the magnification of 50 times. To understand the effect of the diluent composition, a series of reactions was carried out with 6% DVB content in which the diluent ratio between toluene and heptane was 100/0, 80/20, 60/40, 40/60, or 20/80. All other reaction parameters including the temperature were held constant. The copolymer synthesized with Tol/Hep = 100/0 and 80/20 had deep channels regularly distributed on the bead surfaces [Fig. 4(a)–(c)]. The more the heptane in the polymerization recipe, the greater the distortion of the beads. Additionally, the beads obtained with larger contents of the poor solvent (heptane) had fewer and shallower channels irregularly distributed over a wide area [Fig. 4(d) and (e)]. All of these surface morphologies are basically caused by the different extent of phase separation due to

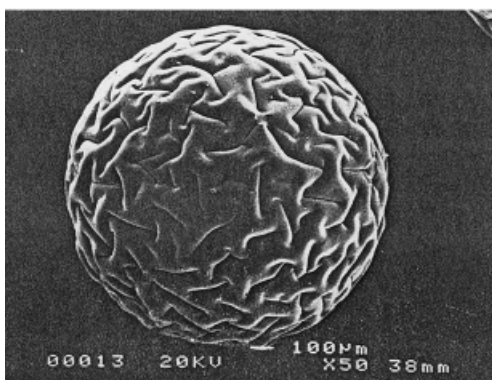




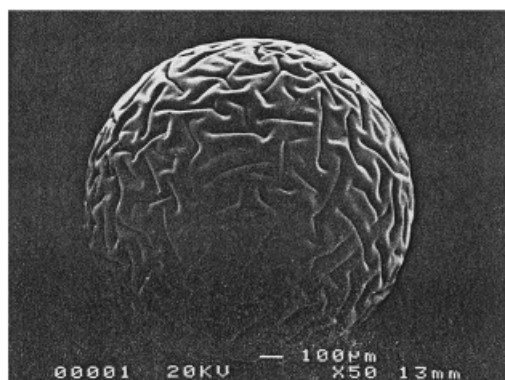
(a)



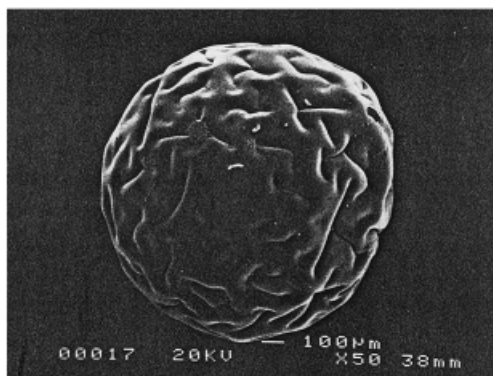
(b)



(c)

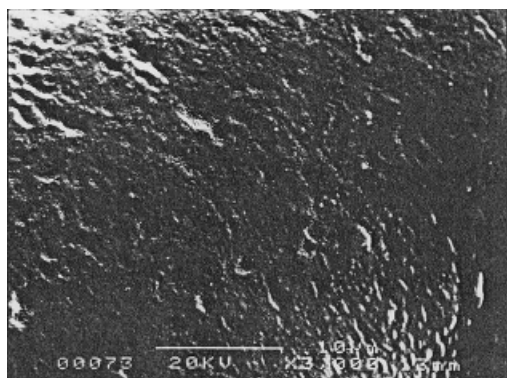


(d)

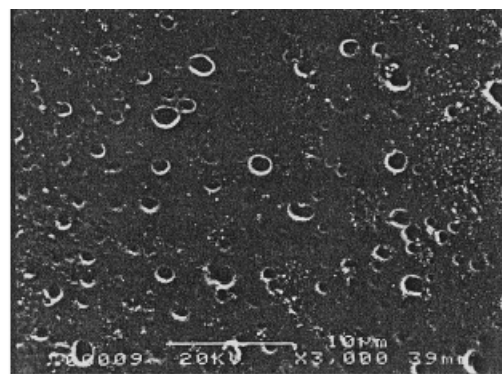


(e)

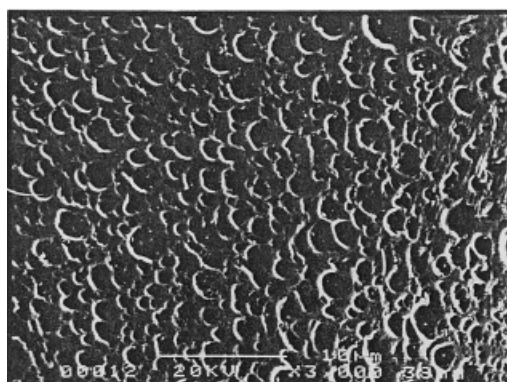
**Figure 4** SEM photographs of the copolymers prepared at different toluene/heptane ratios: (a) H00, 100/0; (b) H02, 80/20; (c) H04, 60/40; (d) H06, 40/60; and (e) H08, 20/80 ( $\times 50$ ).



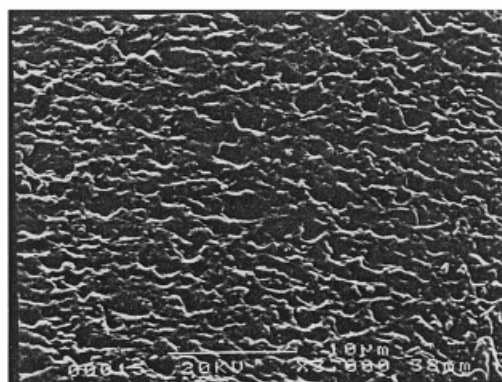
(a)



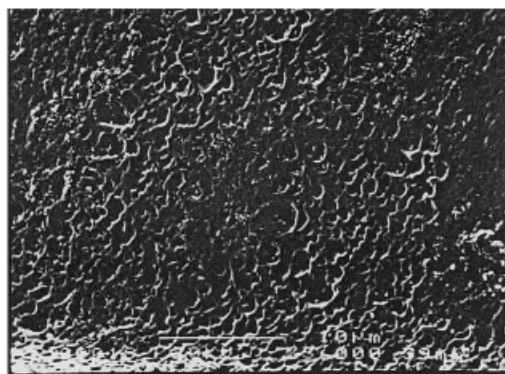
(b)



(c)



(d)



(e)

**Figure 5** SEM photographs of the copolymers prepared at different toluene/heptane ratios: (a) H00, 100/0; (b) H02, 80/20; (c) H04, 60/40; (d) H06, 40/60; and (e) H08, 20/80 ( $\times 3000$ ).

**Table IV Solubility Parameters of the Diluents Used with and without the Polymerizing Monomers**

Tol/Hep	Solubility Parameter, <sup>a</sup> (MPa) <sup>1/2</sup>	$ \delta_1 - \delta_2 $	Surface Appearance of the Copolymer Beads <sup>b</sup>
100/0	18.6 (18.2)	0.0 (0.4)	Gel
80/20	18.2 (17.5)	0.4 (1.1)	Heterogeneous
60/40	17.8 (16.8)	0.8 (1.8)	Heterogeneous
40/60	17.5 (16.2)	1.1 (2.4)	Heterogeneous
20/80	17.2 (15.6)	1.4 (3.0)	Porous

$\delta_{PS} = 22.5$  (MPa)<sup>1/2</sup>,<sup>9</sup>  $\delta_{DVB} = 18.0$  (MPa)<sup>1/2</sup>,<sup>10</sup> and  $\delta_{PS/DVB}$  or  $\delta_2 = 18.6$  (MPa)<sup>1/2</sup>,<sup>11</sup>  $\delta_{Sty} = 19.0$ , and  $\delta_{DVB} = 18.8$  (MPa)<sup>1/2</sup> are calculated from the group molar attraction constant.<sup>11</sup> The numbers in parentheses are the solubility values without considering the presence of the polymerizing monomers.

<sup>a</sup> Calculation from the equation

$$\delta_{\text{mix}} = \frac{\sum y_i v_i \delta_i}{\sum y_i v_i} = \sum \phi_i \delta_i,$$

where  $y_i$ ,  $v_i$  and  $\phi_i$  are the mol fraction, molar fraction, and volume fraction of component  $i$ .

<sup>b</sup> From SEM photographs.

good or poor solvency of the diluent and monomer of their corresponding copolymers.

Figure 5 shows electron micrographs of the surface morphology of Sty-DVB copolymer beads for diluent mixtures at a high magnification of 3000. The expanded network or gel-type structure is obtained when the good solvent (toluene) is used during the network formation. The solvent remained in the gel throughout the polymerization to cause the expanded networks to become a nonporous gel [Fig. 5(a)]. During removal or drying of the diluent, the expanded network reversibly collapses. It reexpands to its earlier state upon addition of a good solvent. Reducing the solvating power of the diluent mixture by adding heptane (toluene/heptane) could gradually produce copolymer beads with more porous structures due to the occurrence of greater microphase separation [Fig. 5(b)–(e)]. The diluent partially separates out of the network domain during the polymerization and disperses among the networks. Part of the diluent acts as a pore-forming agent, whereas the other part remains in the network structure.<sup>12</sup>

Thermodynamic affinity of the diluent for the Sty-DVB copolymer decisively determines the macroporous structure formation and the swelling properties. When styrene and divinylbenzene are copolymerized in the presence of a diluent and the monomer, they solvate the copolymers. As we already examined the solvation effect on the polymer bead appearance in the previous section, the expanded gel shown in Figure 5(a) at the low DVB

content was compared with the high content of DVB in toluene, the solvating diluent. A macroporous copolymer is only obtained when the DVB content is high, for example, 8 to 12%. In these cases, the collapse of the internuclear chains has occurred before all the solvating diluent is removed. The macroporosity of the copolymer beads is thus a result of the removal of the remaining diluent.<sup>13</sup>

On the other hand, when the diluent is a poor solvent for the polymer chains, a partial phase separation may eventually occur. As the polymerization progresses, the polymer chains are no longer extended, as in a good solvating system, and there is a tendency of the growing chains to become entangled inside the nuclei. Consequently, the nuclei of the final structure are large and connected by a relatively small number of coiled and crumpled internuclear chains. When the nonsolvating diluent is removed, the collapse of the system of interconnected nuclei can also occur.<sup>8</sup> When mixtures of solvating and nonsolvating diluents are used, the copolymers produce porous structures with intermediary characteristics [Fig. 5(b)–(e)] in relation to the copolymers prepared with the pure diluents [Figs. 2 and 5(a)]. The effects of synthetic conditions on the swelling properties are considerably more complex for copolymers obtained with diluent mixtures.<sup>8</sup>

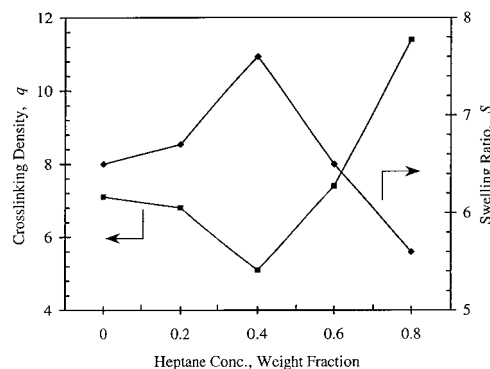
The mercury porosimetric technique was used to investigate the surface area, average pore diameter, and pore volume of the polymer porous beads. The copolymer beads that have diameters

in the range of 0.84–2.0 mm were studied by this technique. The average pore diameter, surface area, and pore volume of the polymer beads shown in Table III were about 0.0133–0.0212  $\mu\text{m}$ , 17.5–44.1  $\text{m}^2 \text{g}^{-1}$  and 0.0581–0.234  $\text{cm}^3 \text{g}^{-1}$ , respectively.

Table III shows the variation of pore properties, such as the average pore diameter, surface area, and pore volume, of the resulting copolymers when the diluent composition shifted from the good solvent (toluene) towards the poor solvent (heptane). We can see that increasing the fraction of heptane diluent increases the copolymer pore diameter and pore volume. When the solvating power changes, the formation of porous structure is determined by the critical concentrations of the polymer chains to precipitate and agglomerate in the microspheres, and the entanglement degree of nuclear and internuclear chains. In the presence of a solvating diluent (toluene), the nuclear chains become less entangled. The tendency of nuclei to agglomerate favors the formation of longer and less entangled internuclear chains. The microspheres are thus rather small, and the pores are consequently small (Run H00). On the other hand, when the diluent solvating power is reduced, the precipitated polymer chains tend to agglomerate rapidly to form large microspheres; consequently, the diluent molecules are distributed preferentially among the microsphere agglomerates to form big pores.<sup>8</sup>

The solvent uptake can appear in two ways: by filling the pores without affecting the gel regions (no volume change), and by chain displacement in the gel regions, causing bead expansion. The swelling of heterogeneous networks is governed by two separate processes.<sup>7</sup> First, the solvation of network chains is mainly driven by changes in the free energies of mixing and elastic deformation during the expansion of the network. The extent of network solvation is determined by the crosslinking density of the network and by the interactions between solvent molecules and network chains. Second, the filling of voids (pores) by the solvent is determined by the total volume of open pores, i.e., by the volume of diluent separated out of the network phase during the polymerization.

Figure 6 shows the effect of the diluent composition on the crosslinking density and swelling properties of Sty-DVB copolymer beads. When the copolymers were prepared in the presence of pure toluene (H00), an expanded gel could be obtained. The swelling of the copolymers takes place

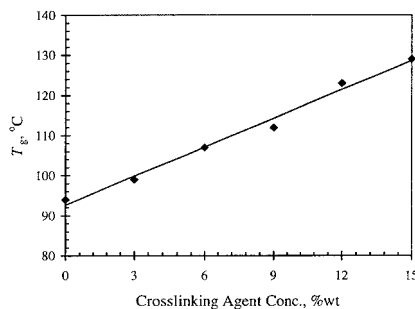


**Figure 6** Effect of the diluent composition on crosslinking density and swelling ratios.

through a partial solvent uptake by the gel portion of the networks due to the solvation of network chains only. When the copolymers were prepared with a lower heptane portion, copolymer structures were obtained with characteristic intermediate between an expanded gel and a heterogeneous porous network. The increased swelling of the copolymers takes place through the solvent partly taken by the whole network (gel + pores) due to both the solvation of network chains and the filling of voids by the solvent. When the heptane portion is increased, the copolymer structures with less of the gel portion and more of the heterogeneous network portion were obtained.<sup>12</sup> The swelling of the copolymers decreased because the polymeric chains of the copolymers prepared with a higher nonsolvent portion are more rigid and entangled than the gel-type chains.<sup>8</sup> Additionally, a greater phase separation could arise in a high concentration of heptane (0.8 wt %). A larger pore volume inside the beads might arise in order to decrease the spongy gel portion. We anticipate that this behavior is a major determinant of the swelling ratio.

### Glass Transition Temperatures of the Copolymers

The glass transition temperatures and incremental changes in heat capacity at  $T_g$  were measured calorimetrically. The  $T_g$  values of the synthetic copolymer beads for various contents of the DVB crosslinking agent (3–15 wt %) are shown in Table II. The  $T_g$  values were in the range of 99–129°C. It can be seen that the DVB content in the copolymer exerts a direct impact on the glass transition temperature of the resulting copolymers. The relation between  $T_g$  and the DVB content is presented in Figure 7. The higher the DVB



**Figure 7** Effect of the crosslinking agent concentration on glass transition temperature of the copolymer beads.

content, the higher the observed  $T_g$  value. Theoretically, the limited macromolecular relaxation by crosslinking site in the network reduces chain flexibility and elevates the  $T_g$  value of the beads<sup>14</sup> as well as decreasing the solvent swelling (Table II). Furthermore, the  $T_g$  values of the synthesized copolymer beads for various toluene/heptane ratios of 100/0, 80/20, 60/40, 40/60, and 20/80 as diluents for the monomers are shown in Table III. At a constant crosslinking agent concentration, the  $T_g$  range of these polymers is about 107–109°C, which indicates that the variation of the toluene/heptane ratio has an insignificant effect on the  $T_g$  values of the beads, because the composition of the monomer system is almost unchanged for crosslinking copolymerization.

#### Effect of the Crosslinking Agent and Diluent on Bead Properties

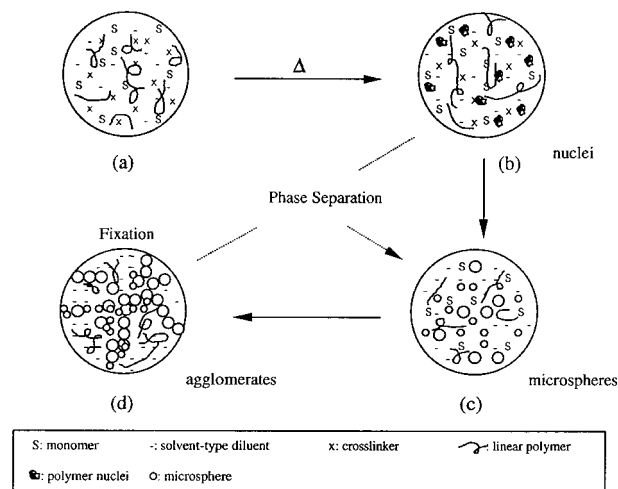
Tables II and III summarize the effects of the crosslinking agent concentration and diluent composition (Tol/Hep) on bead properties. Bead size distributions by weight caused by both effects have non-Gaussian distributions. High proportions (>50%) of the bead sizes are found, in all cases, in the range of 0.84–2.00 mm. The average bead size for all conditions is about 1.2 mm, leading to bead densities in the range of 940–1050 kg m<sup>-3</sup>. This range of bead densities allows all the beads to float on a water surface. The average molecular weight between the crosslinking points ( $\bar{M}_c$ ) depends greatly on the crosslinking density and diluent composition. The higher the crosslinking density, the lower the  $\bar{M}_c$  value. Higher crosslinking agent concentrations produce many active crosslinking sites, lowering the  $\bar{M}_c$  value. For very interesting values of the crosslinking density of around 11.2 (as shown in

Tables II–III) the crosslinking densities are 11.1 and 11.4, respectively, and  $\bar{M}_c$  values of about 7800 (actual values in Tables II–III are 7900 and 7700, respectively), the swelling ratio in toluene is the same at 5.5–5.6-fold. It may be possible to state that the combined effect of a medium crosslinking agent concentration in a good solvent is similar to that of a low crosslinking agent concentration in a poor solvent.

#### Mechanism of Porous Structure Formation

According to the observation of particle structure and solvent swelling, we could postulate a mechanism for pore formation during Sty-DVB copolymerization by suspension polymerization as a two-stage process based on the ideas of Cheng et al.<sup>13</sup>

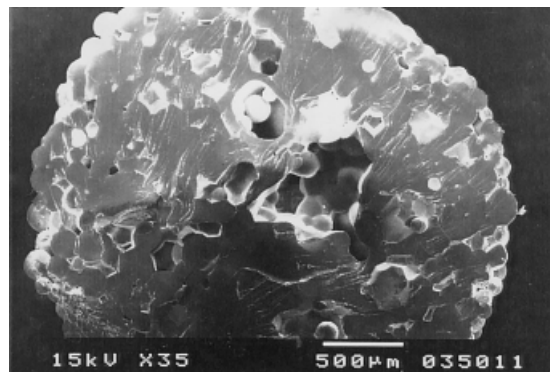
The first stage in the formation of a macroporous structure was described by Kun and Kunin<sup>15</sup> as a process consisting of three substages. In the first substage, each particle is composed of a solution of monomers, initiator, and diluents. It is suspended in an aqueous solution stabilized with surfactants. Because DVB has a high reactivity ratio ( $r = 1.18$ ), during the very early stages of the polymerization, DVB-rich copolymer molecules are formed, which are composed of straight chains with pendant vinyl groups.<sup>13</sup> During the early stages of the reaction, the so-called “primary” macromolecules resulted, as shown in Figure 8(a). When this bifunctional monomer molecule is consumed by a growing radical, one pendant double bond reacts. When such a pendant double bond reacts, a branch point is formed *in situ*. Further reaction leads to the increase of intermolecular linkages, with formation of small crosslinked polymer nuclei as shown in Figure 8(b).<sup>16</sup> Polymerization continues in the second substage to yield intermolecularly crosslinked microgels and linear molecular chains that are soluble in the monomers. The monomers are transformed into crosslinked copolymer as the reaction proceeds; a phase separation occurs between the copolymer, linear polystyrene, and diluent, which gives a copolymer-rich phase and a diluent-rich phase. The monomers are distributed between the two phases. So many linear polymers of low molecular weight are produced in the reaction that they could behave like a porogen in a swollen state, because the monomers themselves are good solvents for their polymers. Because the solvated and very lightly crosslinked copolymers can behave, in some respects, like a liquid, the interfacial tension at the polymer-rich phase is of low



**Figure 8** A schematic model for the process of pore formation in the copolymerization stage.

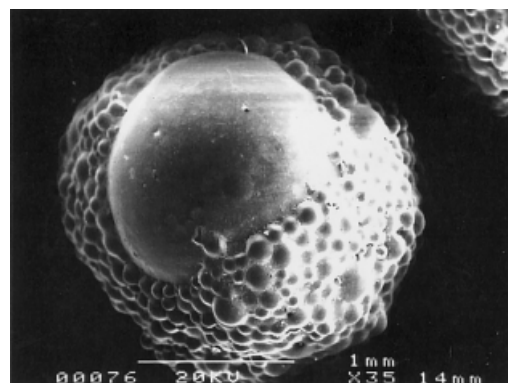
energy, and the spherical polymer is separated as a mass of microspheres [Fig. 8(c)].<sup>13</sup> In the third substage, the polymer macrogelation occurs and gives a gel type of particles composed of agglomerations of microspheres [Fig. 8(d)]. The porous structure of these copolymers consists of globules; the smallest, rather spherical particles of about 100–200 Å in diameter are the “nuclei,” and the aggregation of these nuclei results in the microspheres with diameters of 500–1000 Å; the microspheres are aggregated again into particles of about 2500–10,000 Å in diameter.<sup>17</sup>

The second stage in the pore-structure formation is the binding together and fixation of the microspheres and agglomerates, as shown in Figure 9. As the polymerization and formation of microspheres continue, the microspheres are bound together by the polymerization of the monomers, which have a higher percentage of monovinyl components in their composition, and act to solvate the microspherical polymers.<sup>13</sup> Primarily, internally compact crosslinked particles possessing a microgel character are formed, which are linked through their peripheral double bonds to yield a gel.<sup>18</sup> Some fraction of the high molecular weight linear polystyrene is trapped within the microspheres and agglomerates while they are binding together; the inclusion of linear low molecular weight polymer is dependent on the nature of the linear polymer and the extent of phase separation between the diluent phase and the copolymer phase. It is indeed during this stage that the macroporous structure is actually formed. Voids between microspheres and agglom-



**Figure 9** SEM photograph of the cross-sectioned copolymer of Sty/DVB ( $\times 35$ ) prepared by an Sty/DVB ratio of 84.5/15; BPO, 0.5%; PVA, 0.1%; SDS, 0.005%; HQ, 0.02%; heptane, 30% in a monomer weight fraction of 0.25, at the polymerization temperature of 70°C for 8 h with an agitation rate of 250 rpm.

erates are filled with diluent. The pore size and pore size distribution depend on the size, polydispersity, and arrangement or packing of agglomerated microspheres. In the diluent phase, entanglement of the linear polymer takes place, depending on the molecular weight of the polymer and interaction between the solvent and the linear polymer, thus explaining the sensitivity of the pore size distribution to the molecular weight of the linear polymer.<sup>13</sup> The pore formation inside the polymer bead could continue to the surface of the bead to provide open pores. After the removal of the diluents, polymer particles with macroporous structure are obtained. During the parti-



**Figure 10** SEM photograph of the copolymer of Sty/DVB ( $\times 35$ ) prepared by an Sty/DVB ratio of 84.5/15; BPO, 0.5%; PVA, 0.1%; SDS, 0.005%; HQ, 0.02%; heptane, 30% in a monomer weight fraction of 0.25, at the polymerization temperature of 70°C for 8 h with an agitation rate of 250 rpm.

cle formation, the secondary nucleation could occur in the later stage after a core macropolymer sphere had already been formed, as shown in Figure 10. The nucleation may proceed to form internal voids and pores at its new surface. Surface agglomeration of secondary particles is adsorbed on the seed polystyrene particle surface (Fig. 10). Because of a higher surface energy of PVA-absorbing polystyrene of  $40.7 \text{ mN m}^{-1}$ ,<sup>19</sup> the secondary particles, with the lower surface energy can adhere on its surface.

In a suspension polymerization system, the dispersed phase that contains mixed monomers and diluents mixture form monomer droplets in a continuous phase. These two phases tend to minimize the interfacial tension (or the excessive free energy at the interface) between the dispersed phase and the continuous phase. Thus, the concentration or orientation of the components in the dispersed phase at the interface will occur to minimize the interfacial tension. Table V shows the interfacial tensions of diluent mixture in an aqueous phase of each system. Interfacial tension between two liquids is smaller than the surface tension of the liquid having a higher surface tension, because the molecules of each liquid attract each other across the interface, thus diminishing the inward pull exerted by that liquid on its own molecules at the surface. The interfacial tension is determined by the internal forces in the liquid; thus, it will be related to the internal energy. The copolymer synthesized with toluene (with the highest surface tension) presented the lowest interfacial tension, although the copolymer prepared with heptane (with the lowest surface tension) presented the highest interfacial tension. The diluent mixtures between toluene/heptane presented the intermediate interfacial tension. These results indicate that the diluent composition and their interfacial tension affect the sizes

of monomer droplets and the copolymer microspheres. The higher the interfacial tension, the larger the copolymer microsphere size. The copolymer microspheres are therefore larger, leading to an increase in the size of voids between agglomerated microspheres.

## CONCLUSION

Crosslinking polymerization of styrene (Sty) and divinylbenzene (DVB) was performed by a suspension technique. A DVB concentration in the range of 3–15 wt % was used to produce spherical imbibed beads. A mixture of a good and a poor solvent of toluene and heptane was used to control the phase separation and pore formation in the beads. General polymerization properties in terms of the conversion (as yield), bead size distribution, average bead size, crosslinking density, and its corresponding average crosslinking molecular weight affecting the swelling ratio, diffusion coefficient, and bead density of the polymer were elucidated. A modification of the theory of Flory and Rehner was used for the investigation of  $\bar{M}_c$  and  $q$ ; the polymer–diluent interaction controlled the gel- or porous-type polymer beads through the phase separation or phase miscibility. The imbibed beads obtained from this research have a bead density in a range of 940 to 1050  $\text{kg m}^{-3}$  and a diffusion coefficient in the range of  $2.9 \times 10^{-6}$  to  $4.52 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , yielding bead-swelling ratios of 4 to 12.3. The surface tension of the diluent mixtures and their interfacial tension in the aqueous phase indicate the extent of pore formation. A simplified mechanism of bead formation was proposed based on previous work done by other leading research groups elsewhere and our results.

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**Table V** Surface and Interfacial Tensions of Diluent Mixtures vs. Water

Tol/Hep	Surface Tension, $\text{mN m}^{-1}$	Interfacial Tension, $\text{mN m}^{-1}$
100/0	27.6	33.1
80/20	26.4	35.0
60/40	25.1	37.8
40/60	23.8	40.0
20/80	22.6	42.4
0/100	21.4	45.4

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