

Correlations for Prediction of Specific Surface Area and Bulk and Apparent Densities of Porous Styrene-Divinylbenzene Copolymers

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ABSTRACT: Macroporous styrene-divinylbenzene copolymers with different degree of crosslinking were prepared by suspension polymerization in presence of different binary mixtures of toluene and heptane, as diluent. Specific surface area, bulk and apparent densities, and pore volume of the resulting beads were determined experimentally. Applying the least square method to the experimental data, correlations for prediction of these properties were obtained. Effects of divinylbenzene concentration, dil-

uent to comonomer volume ratio, and composition of the diluent mixture were considered in developing the aforementioned correlations. The influence of the reaction recipe on porous structure of the samples was also studied using scanning electron microscope (SEM). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1942–1949, 2011

Key words: macroporous polymers; styrene-divinylbenzene; specific surface area; density; pore volume

INTRODUCTION

Preparation of the macroporous styrene-divinylbenzene (S-DVB) copolymer beads, which are widely used as starting materials in synthesis of ion exchange resins, solid acid catalysts, and specific sorbents, has been the subject of many research and review articles.^{1,2} The copolymer beads are generally produced via suspension polymerization of styrene and divinylbenzene (DVB), in the presence of a diluent as porogen. Removal of the diluent after polymerization leaves porous crosslinked beads. The most important characteristics of the macroporous S-DVB beads are pore volume, pore size distribution, and specific surface area which can be controlled by type and amount of diluent, and also by the amount of crosslinking divinyl monomer used in the reaction recipe.³

The use of several porogens including pure solvating or nonsolvating diluents^{4–7} or mixtures thereof^{8–15} has been reported in the synthesis of macroporous S-DVB copolymer beads. In the binary diluent systems, a mixture of good and bad solvents is used. The good solvent can dissolve linear polymer in addition to the monomer and also is capable of swelling the network to generate more specific

surface area, whereas the bad solvent can only dissolve the monomer, and is responsible for higher porosity and consequently lower specific surface area. Therefore, desired porosity and specific surface area could be properly controlled by selecting a mixture of diluents.

Although a few experimental works have been performed to investigate the effect of the diluent system and crosslinking on the porous structure of the copolymers, less attention has been paid to the prediction of the structure as a function of the reaction conditions. Okay^{16,17} developed a theoretical model based on thermodynamic and kinetic aspects of free-radical crosslinking copolymerization for prediction of the porosity of S-DVB copolymers depending on reaction conditions. Malik et al. proposed correlations for prediction of the pore volume¹⁸ and specific surface area¹⁹ of the S-DVB copolymers based on bulk density of the dry copolymer beads. Similar methods were also used for prediction of the pore volume and specific surface area in methylmethacrylate-ethyleneglycol dimethacrylate,²⁰ methylmethacrylate-DVB,²¹ and 4-vinylpyridine-DVB²² copolymers. Because the bulk density in these correlations is itself a polymer property, which is a function of reaction conditions, an additional correlation is required for its prediction. In another work, Malik et al.²³ used the solubility parameters and corresponding weight fractions of the monomers and diluents present in the polymerization reaction mixture, to predict the pore volume of the resulting

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copolymers through a correlation. The correlation is based on a constant solubility parameter of the mixture, which is calculated using the initial composition of the reaction mixture by ignoring the changes in the solubility parameter during the polymerization reaction. The proposed correlation has a good accuracy but has a very limited application because the effect of DVB concentration on the porous structure is not included.

In this work, macroporous S-DVB copolymers with different degree of crosslinking are prepared by suspension polymerization in presence of different toluene/heptane binary mixtures as diluent at two diluent to comonomer volume ratio. Based on experimental data, bulk and apparent (particle) densities, as well as specific surface area of the resulting beads are correlated to DVB concentration and composition of the diluent in the reaction mixture at two dilution levels.

EXPERIMENTAL

Materials

Commercial grade styrene was distilled under reduced pressure and stored in a refrigerator before use. DVB (Fluka), comprising of 80% DVB isomers and the rest being mostly ethylvinylbenzenes, was freed from the inhibitor by successively washing with a 5% aqueous NaOH solution and water. Benzoyl peroxide, toluene, *n*-heptane, and acetone were supplied from Merck. Polyvinylpyrrolidone (Fluka) was used as suspending agent.

Preparation of macroporous S-DVB copolymers

Conventional suspension polymerization technique was used for synthesis of the S-DVB copolymer beads. Polymerization was conducted in a 2 L jacketed glass reactor equipped with a reflux condenser, nitrogen inlet, a variable speed mechanical stirrer, and a temperature indicator. The solution containing monomers, initiator (1% by weight) and diluents mixture with appropriate composition and volume ratio (with respect to comonomer), was poured into the reactor, containing 0.1% aqueous solution of the suspending agent. Samples with three different amounts of DVB were synthesized at two diluent/comonomer volume ratio of 1.2 and 2.0, and in the presence of five different ratios of toluene/heptane. The organic/aqueous phase ratio was set to 1 : 9 for all reactions. The reaction was carried out at 75°C for the first 4 h and then temperature was raised to 90°C for the next 3 h. At the end of the reaction, the resulting copolymer beads were washed with water and acetone, respectively. After the solvent treatment, copolymer beads were dried in a vacuum oven at 50°C for 24 h.

Characterization

Bulk density of dry copolymer beads was determined using a 10 mL measuring cylinder, by dividing the weight of the packed beads by the occupied volume. For determination of the apparent density of the particles which well describes the porous structure of the samples, a known volume of water was added to the predetermined weight of the sample in a 10 mL measuring cylinder. After removing of the air bubbles and exclusion of the volume of water in the bed, the volume of the beads were measured. Apparent density was calculated by dividing the weight, by the volume of the beads. In this method, it was assumed that water molecules could not diffuse into the particles through the pores because of hydrophobicity of the particles. In practice, diffusion of water molecules into the pores is performed by a solvent replacement method, using methanol impregnated beads.²⁴

By having the apparent density of the particles, the pore volume is easily calculated using the true density of the homogeneous S-DVB copolymer as follows:

$$V_p = \frac{1}{d_a} - \frac{1}{d_t} \quad (1)$$

where V_p is the pore volume, and d_a and d_t are apparent and true densities, respectively.

The surface area of the copolymer beads were determined by the nitrogen desorption, BET method using a CHEMBET 3000 (Quantachrom, USA) instrument. The morphology of the particles was studied using scanning electron microscopy (TESCAN, VEGAII, XMU, Czech Republic).

Curve fitting

Correlations for bulk and apparent densities and specific surface area of the samples were obtained using least square method through a two-stage curve fitting procedure. First, for each set of DVB concentration, experimental data for densities and surface area were plotted as a function of the composition of the toluene in the diluents mixture and different equations were fitted. The coefficients of the resulting equations were then similarly correlated to DVB concentration, using second degree polynomials.

RESULTS AND DISCUSSIONS

Table I shows experimental data for bulk and apparent densities, specific surface area, and pore volume of the copolymer samples containing 16, 28, and 40 wt % of DVB.

TABLE I
Specific Surface Area, Bulk and Apparent Densities and Pore Volume of the Samples

Experiment	Dilution ratio	DVB%	Tol/Hep	S_A (m ² /g)	d_b (g/cm ³)	d_a (g/cm ³)	V_p (cm ³ /g)
1	1.2	16	0/100	67.866	0.320	0.512	0.993
2			15/85	63.336	0.405	0.683	0.502
3			50/50	0.243	0.539	0.943	0.099
4			85/15	0.161	0.641	0.959	0.040
5			100/0	0.195	0.662	0.999	0.039
6		28	0/100	100.715	0.286	0.469	1.170
7			15/85	131.109	0.330	0.521	0.957
8			50/50	65.915	0.511	0.870	0.236
9			85/15	0.111	0.603	0.991	0.048
10			100/0	0.191	0.643	0.992	0.047
11	2.0	40	0/100	177.781	0.262	0.421	1.412
12			15/85	251.190	0.279	0.440	1.313
13			50/50	320.888	0.399	0.662	0.549
14			85/15	103.240	0.540	0.855	0.208
15			100/0	2.123	0.562	0.877	0.179
16		16	0/100	0.431	0.177	0.277	2.649
17			15/85	62.610	0.263	0.440	1.313
18			50/50	0.203	0.617	0.963	0.077
19			85/15	0.206	0.620	0.987	0.052
20			100/0	0.107	0.632	1.010	0.029
21	28	0/100	7.440	0.162	0.252	3.011	
22		15/85	101.647	0.211	0.331	2.060	
23		50/50	0.138	0.602	0.959	0.081	
24		85/15	0.157	0.610	0.980	0.059	
25		100/0	0.181	0.620	0.999	0.040	
26	40	0/100	21.520	0.163	0.265	2.811	
27		15/85	196.420	0.187	0.290	2.487	
28		50/50	351.110	0.287	0.455	1.235	
29		85/15	11.164	0.518	0.790	0.304	
30		100/0	0.995	0.522	0.799	0.290	

Figures 1–6 reveal experimental data and corresponding fitted curves for bulk and apparent densities and specific surface area, versus volume fraction of toluene in the reaction mixture at different

dilution ratios and DVB concentrations, respectively. In order to correlate the experimental data, several equations were examined, however, only exponential functions could well describe the behavior of the

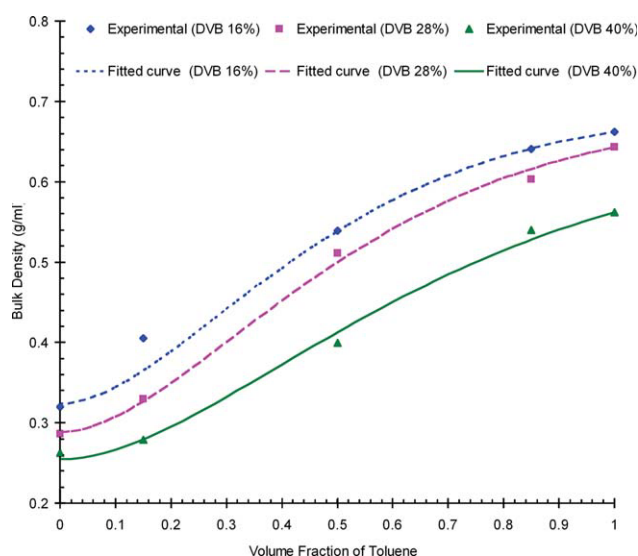


Figure 1 Experimental data and fitted curves for bulk density (dilution ratio = 1.2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

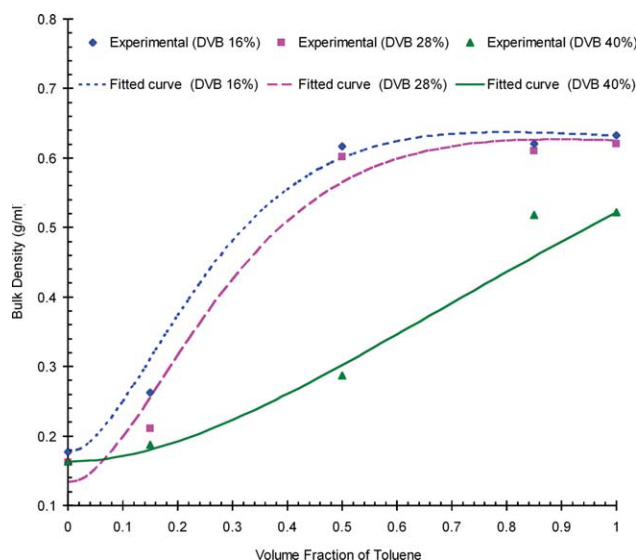


Figure 2 Experimental data and fitted curves for bulk density (dilution ratio = 2.0). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

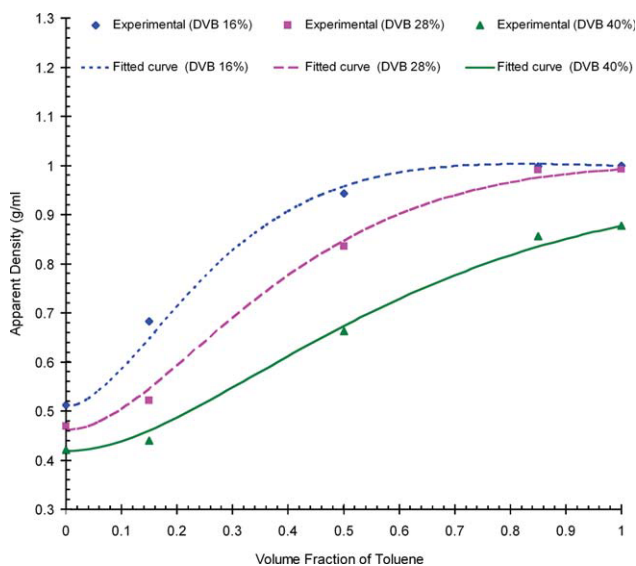


Figure 3 Experimental data and fitted curves for apparent density (dilution ratio = 1.2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

system, particularly for the surface area of the samples obtained at the higher volume ratio of the diluents. Thus, at each degree of dilution, three general correlations for prediction of bulk and apparent densities and specific surface area as a function of the diluent composition and DVB mass fraction in the copolymer were obtained. The calculated coefficients for each equation are shown in Table II. Applying the numerical values of apparent density calculated based on the proposed correlations, in eq. (1), gives the predicted pore volume profiles. The ex-

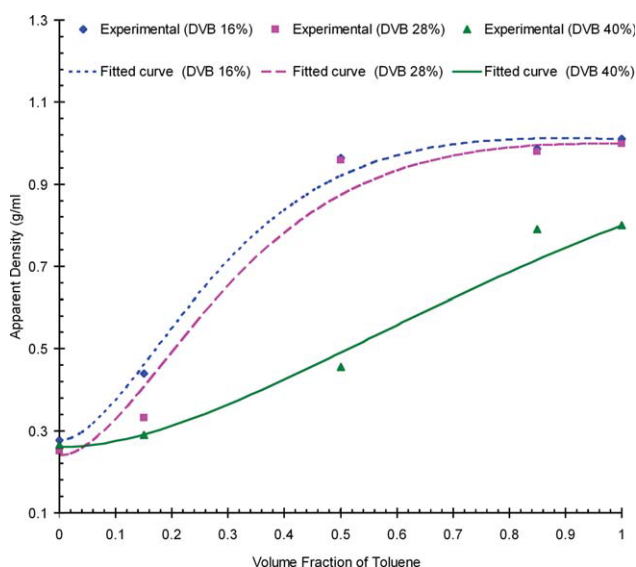


Figure 4 Experimental data and fitted curves for apparent density (dilution ratio = 2.0). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

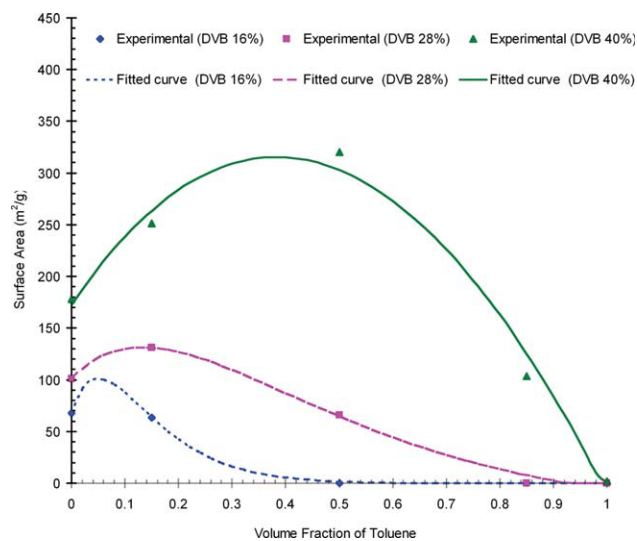


Figure 5 Experimental data and fitted curves for surface area (dilution ratio = 1.2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

perimental data and predicted pore volumes are shown in Figures 8 and 9 for two dilution ratios. Because of differences in the polymerization conditions and reaction recipes for preparation of the macroporous S-DVB copolymers, the experimental data reported in this work cannot be compared with those reported in the literature. However, the trends observed in this work are in accordance with data reported in Refs. 10 and 13 in which reaction conditions are relatively similar to those used in this work.

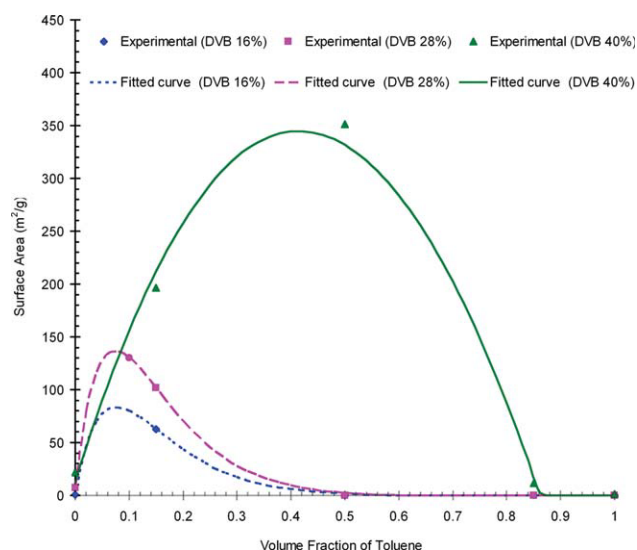


Figure 6 Experimental data and fitted curves for surface area (dilution ratio = 2.0). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Correlation Parameters for Prediction of Bulk and Apparent Densities, and Specific Surface Area

Dilution ratio	Correlation	$Y = A \exp(-ax) + Bx \exp(-ax) + C$ $S_A = \max(0, Y)$		
	Parameter	Bulk density	Apparent density	Surface area
1.2	a	$-9.2431z^2 + 2.0069z + 2.6466$	$15.115z^2 - 19.435z + 7.5887$	$189.8958z^2 - 159.6742z + 33.6864$
	A	$-1.2326z^2 + 0.7765z + 0.2454$	$-1.7951z^2 + 1.134z + 0.3319$	$1596506.95z^2 - 701937.61z + 71507.78$
	B	–	–	$362418.31z^2 - 171821.19z + 20746.53$
	C	$0.0278z^2 - 0.3047z + 0.372$	$0.2049z^2 - 0.4968z + 0.5841$	$-1595160.55z^2 + 701619.45z - 71423.47$
2.0	a	$-97.981z^2 + 38.663z + 1.3363$	$-81.469z^2 + 32.772z + 1.3274$	$-444.4395z^2 + 195.5534z - 6.911$
	A	$6.853z^2 - 2.7556z + 0.7021$	$3.059z^2 - 1.1618z + 0.8043$	$3152150.48z^2 - 1386884.23z + 141207.47$
	B	–	–	$460380.83z^2 - 187582.49z + 21180.19$
	C	$2.5377z^2 - 1.4778z + 0.3482$	$1.9514z^2 - 1.1628z + 0.4131$	$-3152211.64z^2 + 1386969.57z - 141219.12$

z and x are the mass fraction of DVB in the sample and volume fraction of toluene in the diluent mixture, respectively.

The trends for variation of bulk and apparent densities of samples as a function of the diluent composition and DVB content which are shown in Figures 1–4, clearly show that by increasing the proportion of the good solvent in the diluent mixture, bulk and apparent densities tend to increase due to decrease in the pore volumes illustrated in Figures 7 and 8. The increase in DVB content for the samples compared at the same diluent compositions, results in particles with higher porosity and lower density.

In the case of specific surface area, the situation is more complicated. As shown in Figure 5, the samples prepared in the presence of pure toluene and at the dilution ratio of 1.2 show gel-type structures with no internal surface area, whereas the samples prepared in presence of pure *n*-heptane show macro-

porous structures with relatively high-surface area as expected. Such results are generally related to the high and low affinity of toluene and *n*-heptane as good and bad solvents for the copolymer, respectively. Similarly, as shown in Figure 6, for the samples prepared in the presence of pure toluene and at the dilution ratio of 2.0, gel-type structures with no internal surface area are established; however, the samples prepared in the presence of pure *n*-heptane show macroporous structures with lower surface area with respect to those shown in Figure 5. As increasing the degree of dilution using a bad solvent in the reaction recipe promotes the early phase separation, therefore, as can be seen in Figure 8 (in comparison with Fig. 7), higher pore volumes are obtained at the expense of lower specific surface area.

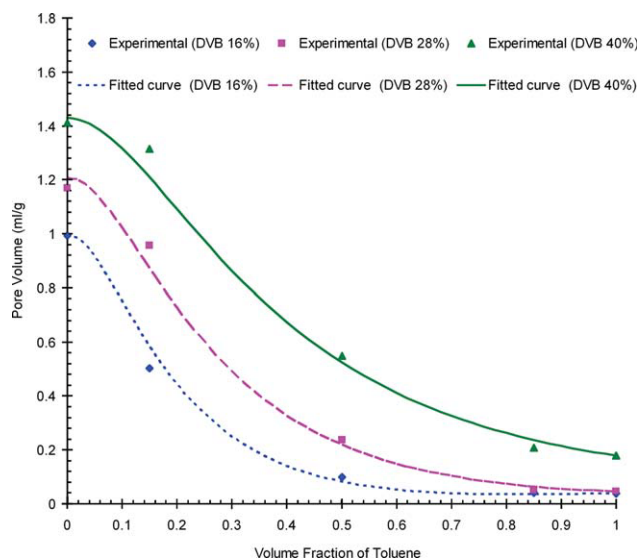


Figure 7 Experimental data and predicted curves for pore volume (dilution ratio = 1.2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

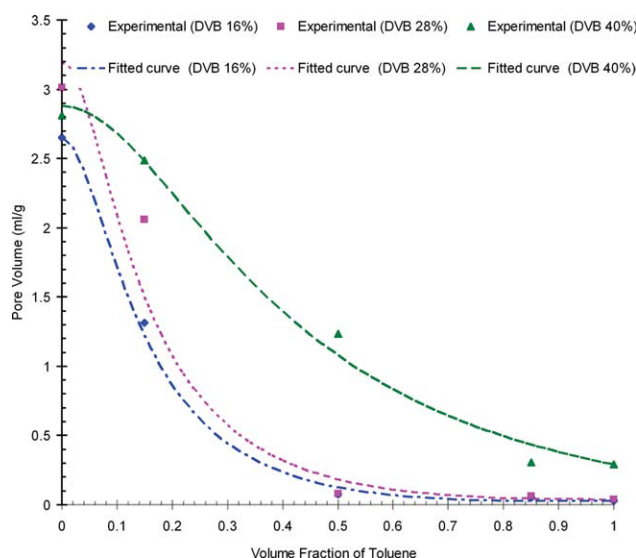


Figure 8 Experimental data and predicted curves for pore volume (dilution ratio = 2.0). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

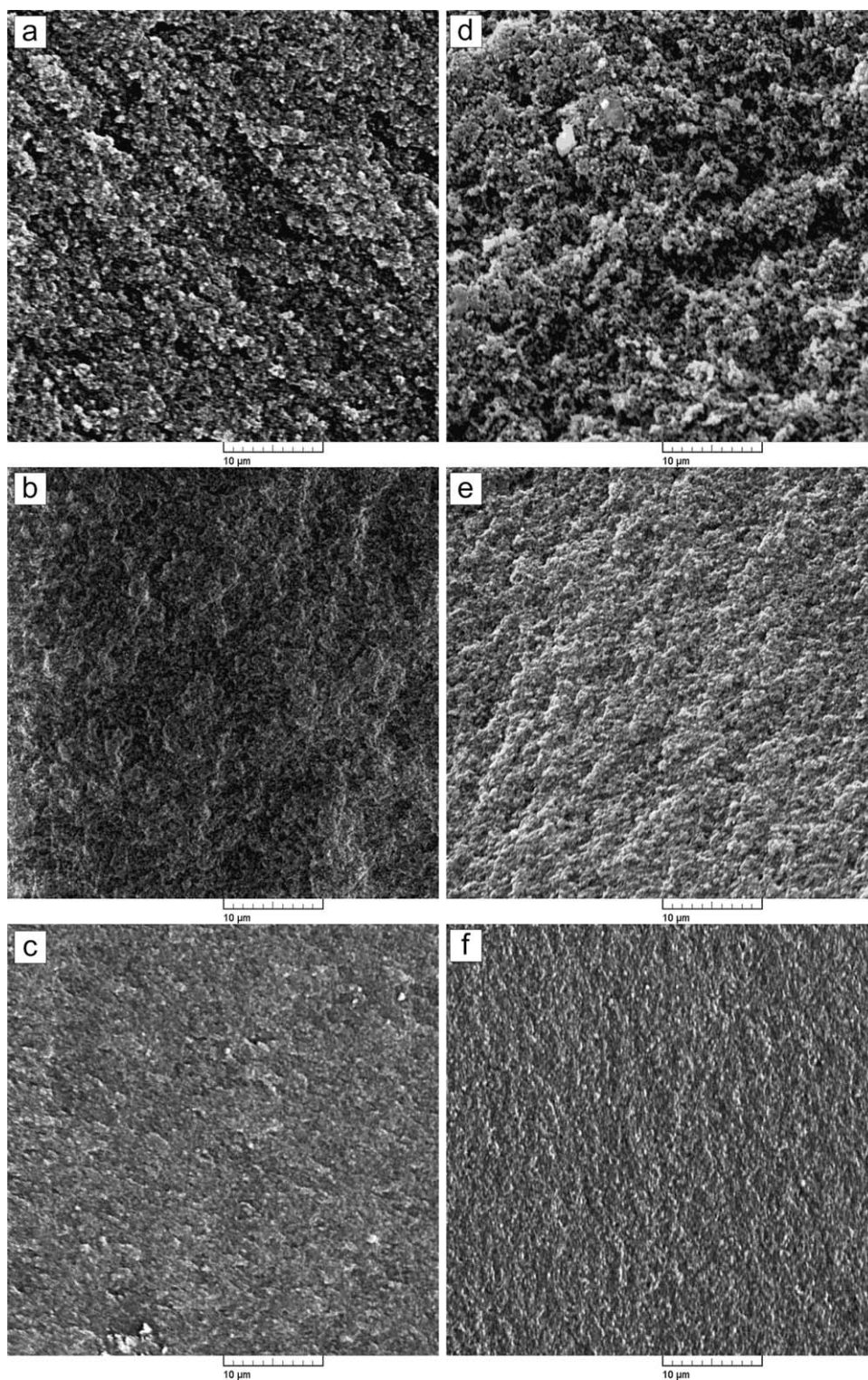


Figure 9 SEM micrographs for macroporous samples obtained in (a) Run 2, (b) Run 12, (c) Run 14, (d) Run 27, (e) Run 28, and (f) Run 29 (see Table I for details). Magnification: $\times 5000$.

In addition, as depicted in Figures 5 and 6, for the samples with high DVB contents, the use of binary diluent mixtures having intermediate compositions gives even more surface area in comparison with the same samples prepared in presence of

pure *n*-heptane. These observations are well described by considering the pore formation mechanisms represented by Dusek.²⁵ At a constant DVB content, when a good solvent, e.g., pure toluene is used, an expanded network is obtained. Removal

of the diluent at the end of the polymerization reaction leaves a collapsed nonporous structure without any internal surface area. As shown in Figure 6, this effect is more pronounced in the case of higher diluent/comonomer ratio. On the other hand, by using a small amount of a bad solvent, e.g., *n*-heptane in the monomer mixture, due to some decrease in the solvating power of the diluent, phase separation occurs and consequently porous structures with small pore diameters start to form. By increasing the proportion of the bad solvent in the diluent mixture up to a critical point, a gradual increase in both internal surface area (see Figs. 5 and 6) and pore volume (see Figs. 7 and 8) is observed. As shown, this critical point which appears as a maximum in the surface area curve is a function of the crosslink density of the sample. It can be seen that by increasing DVB content, this maximum point is shifted toward higher toluene fractions. It means that if DVB content is increased, due to formation of a dense crosslinked network, more good solvent is needed to produce smaller pores with maximum surface area. Increasing the bad solvent content in the diluent mixture to higher amounts passing through this critical point, leads to the very large pores with smaller internal surface area. As shown in Figure 6, increasing dilution ratio at higher heptane compositions, results in even larger pores with a very small surface area, due to the bad solvency power of the diluent mixture including porogens and unreacted comonomer.

Effect of DVB contents on the specific surface area of the samples can also be seen in Figures 5 and 6. As shown in Figure 5, for diluent/comonomer volume ratio of 1.2, for a constant diluent composition in the whole range, increasing in DVB content increases the resulting surface area. This effect is more pronounced for the samples prepared in the presence of diluents having intermediate compositions. Because at the first stages of free radical crosslinking polymerization of S-DVB copolymers, microgels which are responsible for developing of the macroporosity are formed, therefore by increasing the DVB content, the higher number of microgels and consequently higher number of pores with relatively high-surface area are obtained.

Figure 9 shows SEM micrographs of the samples with different morphologies obtained in runs 2, 12, 14, 27, 28, and 29. As depicted in Figure 9(a,b), at dilution ratio of 1.2 and Tol/Hep ratio of 15/85, by increasing DVB content from 16% to 40% (run 2 → run 12) a tortuous structure having more surface area and pore volume is observed. The change in Tol/Hep ratio of 15/85 to 85/15 at constant DVB content of 40% and at the same dilution ratio (run 12 → run 14), results in a more uniform structure

with lower pore volume and internal surface area [Fig. 9(c)]. Effects of the increasing in dilution ratio and changes in diluent composition on morphology of the samples at a constant DVB content of 40% are shown in Figure 9(d–f). As illustrated in Figure 9(b,d), increasing in dilution ratio at constant DVB content of 40% and Tol/Hep ratio of 15/85 (run 12 → run 27) results in larger pore diameters which are responsible for higher pore volume and smaller internal surface area. The increase in Tol/Hep ratio of 15/85 to 50/50 (run 27 → run 28) at the same dilution ratio of 2.0 and DVB content of 40% generates smaller pore diameters with lower pore volume but increased internal surface area as shown in Figure 9(d,e). As can be seen in Figure 9(f), increasing the Tol/Hep ratio to higher extents (run 28 → run 29) under the same condition eliminates the porosity and as a result leaves a nearly uniform nonporous structure with a very low-pore volume and internal surface area.

CONCLUSIONS

Using experimental data, correlations for prediction of the bulk and apparent densities and specific surface area of the macroporous S-DVB copolymer beads were proposed. The proposed correlations can be used to predict the above polymer properties as a function of the composition of toluene in the diluent mixture and DVB content in the copolymers at two dilution ratios. The pore volume of the samples is also predicted using true and correlated apparent densities. The predictions obtained from proposed correlations are in a good agreement with experimental data.

References

1. Okay, O. *Prog Polym Sci* 2000, 25, 711.
2. Liu, Q.; Wang, L.; Xiao, A. *Des Monomers Polym* 2007, 10, 405.
3. Kun, K. A.; Kunin, R. *J Polym Sci Part A-1: Polym Chem* 1968, 6, 2689.
4. Jacobelli, H.; Bartholin, M.; Guyot, A. *Angew Makromol Chem* 1979, 80, 31.
5. Poinescu, I. C.; Beldie, C.; Vlad, C. *J Appl Polym Sci* 1984, 29, 23.
6. Rabelo, D.; Coutinho, F. M. B. *Polym Bull* 1994, 33, 479.
7. Tank, R.; Beldar, A.; Saxena, A.; Gupta, D. C. *J Appl Polym Sci* 2008, 108, 1531.
8. Coutinho, F. M. B.; Cid, R. C. A. *Eur Polym J* 1990, 26, 1185.
9. Coutinho, F. M. B.; Rabelo, D. *Eur Polym J* 1992, 28, 1553.
10. Rabelo, D.; Coutinho, F. M. B. *Eur Polym J* 1992, 30, 675.
11. Rabelo, D.; Coutinho, F. M. B. *Polym Bull* 1994, 33, 487.
12. Rabelo, D.; Coutinho, F. M. B. *Polym Bull* 1994, 33, 493.
13. Coutinho, F. M. B.; Neves, M. A. F. S.; Dias, M. L. *J Appl Polym Sci* 1997, 65, 1257.
14. Coutinho, F. M. B.; Torre, M. L. A.; Rabelo, D. *Eur Polym J* 1998, 34, 805.
15. Erbay, E.; Okay, O. *J Appl Polym Sci* 1999, 71, 1055.

16. Okay, O. *Polymer* 1999, 40, 4117.
17. Okay, O. *J Appl Polym Sci* 1999, 74, 2181.
18. Malik, M. A.; Rehman, E.; Naheed, R.; Alam, N. M. *React Funct Polym* 2002, 50, 125.
19. Malik, M. A.; Ali, S. W.; Waseem, S. *J Appl Polym Sci* 2006, 99, 3565.
20. Malik, M. A. *e-Polymers* 2006, no. 040.
21. Ali, S. W.; Waseem, S.; Malik, M. A. *Polym Test* 2007, 26, 505.
22. Malik, M. A.; Ali, S. W. *J Appl Polym Sci* 2008, 109, 3817.
23. Malik, M. A.; Ahmed, M.; Ikram, M. *Polym Test* 2004, 23, 835.
24. Yan, J.; Wang, X.; Yang, Y. *React Funct Polym* 2000, 43, 227.
25. Dusek, K. In *Polymer Networks-Structure and Mechanical Properties*; Chomppff, A. J., Newman, S., Eds.; Plenum Press: New York, 1971.