

A Simple Method for Estimating Parameters Representing Macroporosity of Porous Styrene–Divinylbenzene Copolymers

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ABSTRACT: A quick, easy, and novel method to estimate pore volume (PV), pore size distribution, surface area (SA), and swelling coefficient in acetone (SC_a) of porous styrene–divinylbenzene copolymer beads on the basis of their density (d) in dry state is developed. The density is determined by measuring cylinder method. The equation to calculate the parameters are $11.993 d^2 - 14.04 d + 4.2$ for PV, $68.449 \ln(PV) + 208.08$ for SA, and $136.47 e^{-1.8323(PV)}$ for SC_a . Regression analysis shows a close match between the estimated values and the corresponding values measured by

mercury porosimetry, with square of the Pearson product moment correlation coefficient through data points in known y 's and known x 's (R^2) values in the range of 0.93–0.99. The pore size distribution can be estimated from the given curves for the corresponding pore volume value. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3565–3570, 2006

Key words: styrene–divinylbenzene copolymers; macroporous resins; suspension polymerization; porosity formation; swelling

INTRODUCTION

Macroporous styrene–divinylbenzene copolymers are produced as spherical beads by suspension polymerization^{1–4} in the presence of inert organic liquid (diluent or porogen), which is miscible in monomers and immiscible in water.^{5,6} The copolymers have two types of pores; macroreticular pores where the interconnected pores in the matrix persist in dry state, and microreticular pores where the shrinkable pores are the spaces between polymer chains and crosslinks in the polymer phase. The porosity of the copolymers is controlled by the nature and amount of diluent, and the amount of the crosslinker in the polymerization mixture.^{5–7} A number of reviews have been published on this subject.^{8–13}

Pore volume, pore size distribution, and surface area are important parameters describing the porous structure of copolymers. These parameters are analyzed by nitrogen desorption (BET method)¹⁴ or mercury penetration method.^{5,15–17} The mercury porosimeter analyzes macroporosity in dry state for pores of diameter $>0.003 \mu\text{m}$. Mercury porosimetry and the BET method require expensive equipments and relatively lengthy analytical procedures. Therefore, some inexpensive and simple methods are reported in literature, e.g., pore volume determination by water up-

take.^{18,19} We have proposed a simple, inexpensive, yet reasonably accurate method of pore volume estimation, based on the density of the dried copolymer beads.²⁰ In this study, the simple and inexpensive method of pore volume estimation was extended to the estimation of pore size distribution, surface area, and swelling coefficient in acetone of macroporous styrene–divinylbenzene copolymers. This was achieved by establishing empirical relationships between pore volume and surface area, and the swelling coefficient in acetone.

EXPERIMENTAL

The styrene–divinylbenzene copolymers were synthesized using the suspension polymerization method reported earlier.²¹ Styrene (St; 99%), divinylbenzenes (comprises 60% divinylbenzene isomers (DVB), and 40% ethylvinylbenzene isomers (EVB)), and diluents were mixed. Benzoylperoxide (1% by weight) was dissolved in the mixture to initiate polymerization. The mixture was suspended in water at a 1 : 5 volume-to-volume ratio, under mechanical stirring at room temperature. Gum Arabic, gelatin, and NaCl, 1.5, 1.5, and 1% of water by weight, respectively, were predissolved in the water. After stirring for half an hour at room temperature, the temperature was raised to 80°C and maintained at 80°C for 20 h. Then, the copolymer beads were filtered out in a Buchner funnel and washed with hot water. The diluent and any unreacted monomers or homopolymers were extracted with acetone in a Soxhlet apparatus. The washed

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TABLE I
Composition of the Polymerization Mixture and Characteristics of the Styrene–Divinylbenzene Copolymers Synthesized in This Study

Exp No.	Diluent	FS	%X (%)	d g/ml	PV_m mL/g	SA m^2/g	SC_a (%)
Styrene–Divinylbenzene—Effect of diluent amount							
1	<i>n</i> -Heptane	0.30	30	0.67	0.1655	82	62
2	<i>n</i> -Heptane	0.40	30	0.49	0.3093	127	34
3	<i>n</i> -Heptane	0.45	30	0.36	0.6257	170	39
4	<i>n</i> -Heptane	0.50	30	0.32	0.8666	194	29
Styrene–Divinylbenzene—Effect of crosslinker							
5	<i>n</i> -Heptane	0.50	15	0.37	0.7673, 0.7579	168, 171	45
4	<i>n</i> -Heptane	0.50	30	0.32	0.8666	194	29
6	<i>n</i> -Heptane	0.50	60	0.31	1.1673	250	16
Styrene–Divinylbenzene—Effect of good-solvent nonsolvent mixture of diluent							
7	<i>n</i> -Heptane:Toluene, 60:40	0.50	15	0.65	0.0931	54	122
8	<i>n</i> -Heptane:Toluene, 80:20	0.50	15	0.65	0.1407	78	88
9	<i>n</i> -Heptane:Toluene, 90:10	0.50	15	0.65	0.2137	100	106
10	<i>n</i> -Heptane:Toluene, 95:5	0.50	15	0.45	0.4772	149	54
5	<i>n</i> -Heptane:Toluene, 100:0	0.50	15	0.37	0.7673	168	45
Styrene–Divinylbenzene—Effect of nature of diluent							
11	Toluene	0.50	30	0.56	0.0951	52	122
12	Diethylptthalate	0.50	30	0.50	0.1635	83	93
13	Methyl-iso-butylketone	0.50	30	0.56	0.2140	103	73
14	Dibutylptthalate	0.50	30	0.47	0.3582	143	85
15	Dimethylphthalate	0.50	30	0.37	0.6397, 0.7501	174, 186	53
16	bis-2-Ethyl-hexylphthalate	0.50	30	0.37	0.6608	171	57
4	<i>n</i> -Heptane	0.50	30	0.32	0.8666	194	29

beads were left in acetone at room temperature for ~16 h. Excess acetone was removed by centrifugation and the volume of the acetone-swollen beads (V_s) was recorded. The beads were dried at 110°C until constant dry weight (W_d). The volume of the dried beads (V_d) was measured by measuring cylinder method.²⁰ Density (d) of the dried beads was calculated by using the following formula:

$$d = W_d / V_d \quad (1)$$

The swellability coefficient in acetone (SC_a) was calculated by using the following formula:

$$SC_a = (V_s - V_d)100 / V_d \quad (2)$$

The yield of the product (Y) was calculated from volume (V_{St}) and density (d_{St}) of styrene, volume (V_{DVB}) and density (d_{DVB}) of divinylbenzene, and dry weight (W_d) of the copolymer, by the following formula:

$$Y = W_d / 100(V_{St}d_{St} + V_{DVB}d_{DVB}) \quad (3)$$

Yield was more than 80% in all cases. Fraction of diluent (FS) was calculated by the following formula:

$$FS = V_d d_d / (V_{St}d_{St} + V_{DVB}d_{DVB} + V_d d_d) \quad (4)$$

where V_d and d_d are the volume and density of diluent. Degree of crosslinkage (%X) of the polymer was calculated by the following formula:

$$\%X = (V_{DVB}d_{DVB})60 / (V_{St}d_{St} + V_{DVB}d_{DVB}) \quad (5)$$

where 60 appears in the numerator because divinylbenzene is 60% pure. Pore volume (PV_m), surface area (SA), and pore size distribution of the dried beads were determined by mercury porosimeter, Autopore II 29,220 from Micromeritics. Manufacturer of the instrument quotes ± 1 accuracy of results. The pore size distribution is presented as cumulative pore size distribution. The pore volume density distribution is defined as the linear derivative of the cumulative pore volume curve with respect to the pore diameter. The empirical relationships between pore volume and surface area, and between pore volume and swelling coefficient in acetone were obtained by the best fit regression equations, using Microsoft Excel. Square of the Pearson product moment correlation coefficient through data points in known y 's and known x 's (R^2) was calculated by the software. The R^2 value close to one proves to be a close match between y 's and x 's.

RESULTS AND DISCUSSION

The composition of the polymerization mixture and characteristics of the copolymers are listed in Table I. The pore volume and surface area values were in-

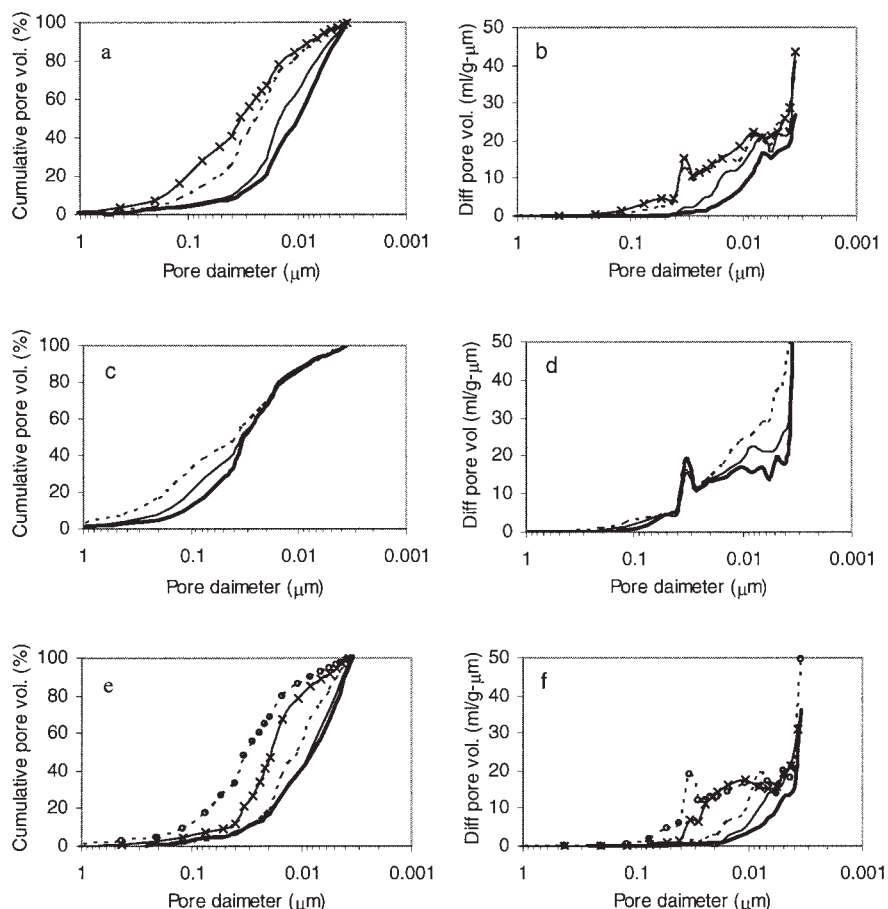


Figure 1 Pore size distributions, cumulative pore size distribution [(a), (c), and (e)], and pore volume density distribution [(b), (d), and (f)]. (a) and (b): Effect of amount of diluent. Thick line, thin line, dotted line, and crossed line are for FS value of 0.3, 0.4, 0.45, and 0.5, respectively for Exp 1–5. (c) and (d): Effect of degree of crosslinkage. Thick line, thin line, and dotted line are for %X value of 15, 30, and 60, respectively, for Exp 5, 4, and 6. (e) and (f): Effect of good-solvent non-solvent component in diluents. Thick line, thin line, dotted line, thin line with cross symbols, dotted line with circle symbols are for *n*-heptane:toluene ratio of 60 : 40, 80 : 20, 90 : 10, 95 : 5, and 100 : 0, respectively, for Exp 7–10, and 5.

creased, and the pore size distribution shifted towards larger pores by increasing: (a) amount of diluent, (b) amount of crosslinking monomer, or (c) the ratio of nonsolvent component in the diluents, as shown in Table I and Figure 1. The nonsolvent component was *n*-heptane, and good-solvent component was toluene in the mixture of diluents. These results are in agreement with published literature.^{5–13,22,23}

The effect of diluent and crosslinking monomer on the porosity can be explained by the pore formation mechanism.^{5–7,24} The polymerization reaction takes place in a suspended droplet during the suspension polymerization. As the reaction progresses, the copolymer precipitates within the droplet, i.e., phase separation takes place between polymer phase and the surrounding diluent + monomers phase. The precipitated polymer forms spherical shapes, called nuclei, within the droplet. The nuclei grow into microspheres (also called microgel) and the microspheres agglomerate with each other resulting in the primary net-

work. Upon further polymerization and crosslinkage, the primary network becomes the crosslinked porous network, as illustrated in Figure 2. The void space between microsphere-agglomerates is called macropo-

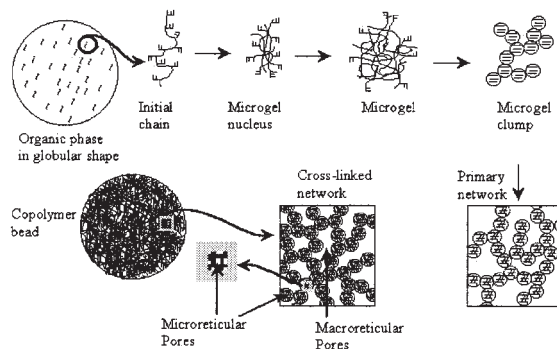


Figure 2 Mechanism of porous structure formation during suspension copolymerization of styrene-divinylbenzene.

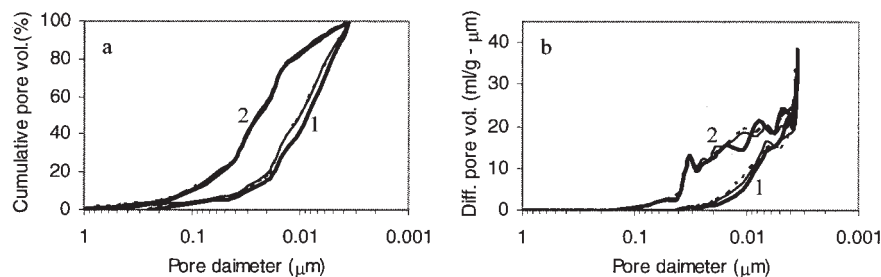


Figure 3 Examples showing same pore size distribution for a nearly same pore volume values. Set 1: Thick line, thin line, and dotted line are for Exp 8, 1, and 12, respectively having pore volume of ~ 0.15 mL/g. Set 2: Thick line, thin line, and dotted line are for Exp 3, 16, and 15, respectively, have pore volume of ~ 0.65 mL/g. In (a) the thin line and dotted lines in the set 1 and all three lines in the set 2 are completely overlapped.

rosity or macroreticular porosity, which persist upon drying the polymer. The shrinkable pores, that are spaces between chains and crosslinks in the polymer phase, define the microreticular porosity. Increasing the amount of diluent, increasing the amount of crosslinking monomer, or replacing good-solvent with a nonsolvent diluent results in more porous matrix because of early phase separation and highly entangled and compact copolymer phase in the microspheres. This explains the observed trend of pore volume, surface area, and the pore size distribution.

It can be deduced from the pore formation mechanism that both the pore volume and the pore size distribution are changed simultaneously by any change in the diluent or crosslinking monomer. This deduction leads to the hypothesis that each value of pore volume should be associated with a specific pore size distribution. This hypothesis has been verified by the experimental results of this study, as shown in Figure 3. It can be observed from Figure 3 that same pore volume can be obtained with different compositions of the polymerization mixture, but this pore volume is associated with a specific pore size distribution. Although some exceptions to this general rule were noticed in this study, the exceptional differences were small and within the error range usually associated with the mercury porosimetry technique. Therefore, it can be said that if the value of pore volume is known, the pore size distribution can be predicted from some reference pore size distribution spectrum. For this purpose, the pore size distribution curves of styrene–divinylbenzene copolymers with pore volume values ranging from 0.1 to 1.2 mL/g are illustrated in Figure 4. We have selected 0.1 to 1.2 mL/g range, as, according to our experience, represents the useful range of porosity. It can be concluded from the above discussion that if pore volume value is known, the pore size distribution can be predicted.

The surface area (SA) is related with pore volume (PV_m) and average pore diameter (assuming cylindrical pores) by the following formula:

$$SA = 4PV_m / \text{average pore diameter} \quad (6)$$

The average pore diameter is dependent on the pore size distribution. Therefore, the hypothesis that each value of pore volume is associated with a specific pore size distribution leads to the conclusion that each value of pore volume should be associated with a specific value of surface area. This conclusion has been verified by the results of this study as well as by the results of our earlier study,²⁵ as shown in Figure 5. The best fit equation between pore volume (PV_m in mL/g) and surface area (SA in m^2/g), with R^2 value of 0.97, is:

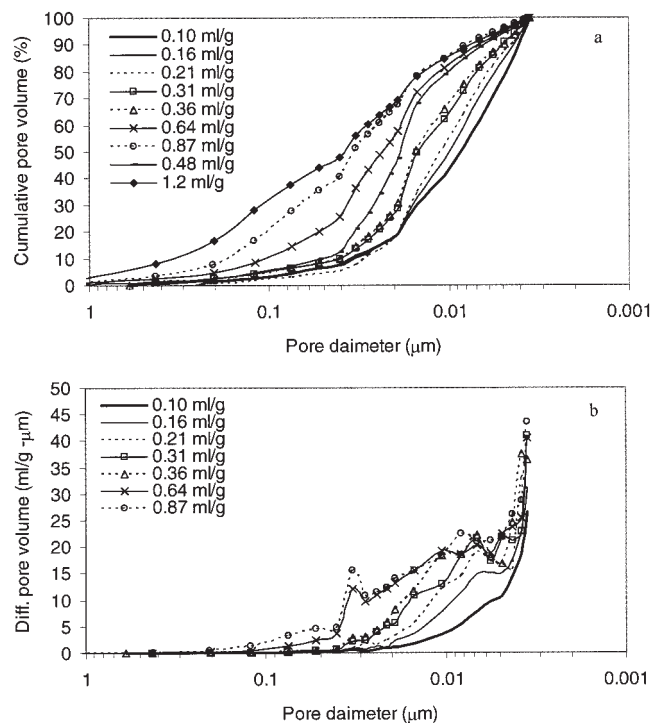


Figure 4 (a) Pore size distributions, cumulative pore size distribution, and (b) pore volume density distribution for styrene–divinylbenzene copolymers from Exp 11, 12, 13, 2, 14, 15, 4, 10, and 6 having pore volume 0.1, 0.16, 0.21, 0.31, 0.36, 0.64, 0.87, 0.48, and 1.2 mL/g, respectively. The curves of Exp 10 and 6 have been omitted from pore volume density distribution curves in order to improve clarity of the figure.

$$SA = 68.449 \ln(PV_m) + 208.08 \quad (7)$$

The polymers swelled in acetone to a different extent depend on their pore volume, as shown in Figure 6. The best fit equation between the swelling coefficient in acetone (SC_a) and pore volume (PV_m), with R^2 value of 0.95, is:

$$SC_a = 136.47 e^{-1.8323(PV_m)} \quad (8)$$

Equation (8) was found to be valid for the data from this study, as well as for the data from earlier literature.^{21,26} This trend of swelling in acetone can be explained by the fact that the higher pore volume values are achieved by employing higher amount of crosslinking monomer, higher amount of diluent, or nonsolvating diluent. These three factors lead to early phase separation between copolymer phase and surrounding liquid phase during the polymerization, and make the copolymer chains more compact and entangled with each other in the polymer phase. Consequently, the polymer becomes less swellable. Further, a fraction of the polymer swelling may have resulted by a decrease in macroporosity in the wet state.

The pore volume (PV_c) values can be calculated from the density (d) of the copolymers in dry state using the following equation:²⁰

$$PV_c = 11.993d^2 - 14.04d + 4.2 \quad (9)$$

The density (d), in turn, can be measured by measuring cylinder method described earlier.²⁰ The R^2 value between PV_c and PV_m was 0.99 in our earlier study,²⁰ and was found to be 0.93 when the data of this study was analyzed.

The R^2 values of ≥ 0.95 between the calculated data and experimentally measured data shows that eq. (7) and eq. (8) can be used to estimate surface area and swelling coefficient in acetone, respectively, from the pore volume values with reasonable accuracy. Similarly, The R^2 value of 0.93–0.99 shows that PV_c values

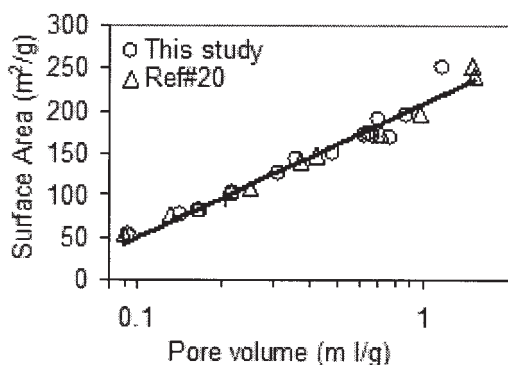


Figure 5 Pore volume vs. surface area. The line in figure represents the best fit logarithmic eq. (7).

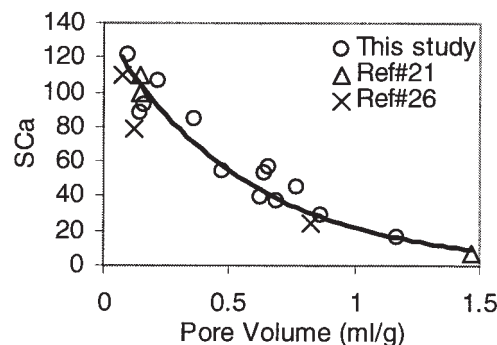


Figure 6 Pore volume vs. swelling coefficient in acetone (SC_a). The line in figure represents the best fit exponential eq. (8).

calculated from eq. (9) are fairly close to PV_m values measured experimentally. In other words, the PV_c values can be used in the place of PV_m for estimation of pore size distribution, surface area, and swelling coefficient in acetone.

In conclusion, the results of this study show that one can measure density of the porous styrene-divinylbenzene copolymers by a measuring cylinder and a balance, and can estimate their pore volume, pore size distribution, surface area, and swelling coefficient in acetone from the density values with reasonable accuracy. The method can potentially be extended for other related porous copolymers, such as macroporous 4-vinylpyridine-divinylbenzene, glycidylmethacrylate-divinylbenzene, etc., provided, enough data from porosimetry and density measurements become available for the statistical analysis. It should be mentioned, that pore volume, pore size distribution, and surface area values estimated by the method proposed in this article belong to macroreticular porosity, and should be used only in the place of the corresponding values that can be obtained by mercury porosimetry. Further, the assumptions and hypothesis discussed in this article are valid for the case of organic liquid diluents, and they are not valid when porosity is generated by some other means, e.g., by using some template or by using polymeric diluents. It should be kept in mind that the polymeric diluents can generate pores of relatively large diameter with relatively small pore volume values, as compared with the case of organic liquid diluents.^{6,27}

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