Synthesis and Simple Method of Estimating Macroporosity of Methyl Methacrylate–Divinylbenzene Copolymer Beads

Muhammad Arif Malik, Syed Wasim Ali

Applied Chemistry Laboratories, Nilore, Islamabad 44000, Pakistan

Received 17 January 2008; accepted 18 March 2008
DOI 10.1002/app.28556

ABSTRACT: Macroporous methyl methacrylate–divinylbenzene copolymer beads having diameter ∼ 300 μm were synthesized by free radical suspension copolymerization. The macroporosity was generated by diluting the monomers with inert organic liquid diluents. The macroporosity was varied in the range of ∼ 0.1 to ∼ 1.0 mL/g by varying a number of porosity controlling factors, such as the diluents, solvent to nonsolvent mixing ratios when employing a mixture of the two diluents, degree of dilution, and crosslinkage. Increase in pore volume from 0.1 to 0.45 mL/g resulted in a sharp increase in mesopores having diameters in the range of 3–20 nm whereas the macropores remained negligible when compared with mesopores. Increase in pore volume from 0.45 to 1 mL/g resulted in a sharp increase in macropores, whereas mesopores having diameters in the range of 3–20 nm remained almost constant. The mesopores having diameters in the range of 20–50 nm showed an increase with the increase in pore volume throughout the whole range of pore volume studied. Macroporosity characteristics, i.e., pore volume (V_m), surface area (SA), and pore size distributions were evaluated by mercury penetration method. Statistical analysis of the data obtained in the present study shows that the macroporosity characteristics can be estimated with a reasonable accuracy from the pore volumes, which in turn are determined from the densities of the copolymers. These results are explained on the basis of pore formation mechanism. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3817–3824, 2008

Key words: methyl methacrylate–divinylbenzene; macroporosity; suspension polymerization; adsorbent; macroporous copolymer

INTRODUCTION

The porous polymeric adsorbents[1] in beaded form are synthesized by free radical suspension copolymerization.[2–4] The monomers are diluted with some inert organic liquid, which is removed at the end of polymerization, leaving behind a porous copolymer matrix.[2] Macroporosity, i.e., the pores of permanent nature that do not disappear upon drying, provides fast access to the reagents into the inner portions of the copolymer beads.[5] The macroporosity is controlled by the amount and nature of the diluent and by the degree of crosslinkage.[2,6,7] This subject has been extensively investigated for styrene-divinylbenzene and other related copolymers as it is clear from review[8] and recent research[9] on the subject. However, the literature on the synthesis of macroporous methyl methacrylate–divinylbenzene copolymers is rare.[8,10] Here, we report the results of a comprehensive study on the synthesis and control of macroporosity of methyl methacrylate–divinylbenzene. The amount and nature of the diluent/s and the degree of crosslinkage were varied in a practically useful range.

The methyl methacrylate–divinylbenzene copolymers were chosen for the present study because they can have a broad range of polar and hydrophilic characters when compared with the conventional porous polymeric adsorbents which are either nonpolar and hydrophobic, e.g., styrene-divinylbenzene,[1,11] or polar and hydrophilic, e.g., methyl methacrylate–ethylene glycol dimethacrylate.[1] Further, the ester group of the methyl methacrylate has been chemically transformed into other functional groups, e.g., hydrolyzed to weak acid cation-exchanger,[12] sulfonated to cation-exchanger,[13] converted to other functional groups that can be used for immobilization of biological molecules,[14] etc. In such chemical transformations, the crosslinkage with divinylbenzene is chemically stable when compared with the ethylene glycol dimethacrylate.

The macroporosity characteristics, i.e., pore volume, surface area, and the pore size distribution, are usually evaluated by mercury penetration method,[2] which requires expensive instruments, relatively longer analysis time and handling with toxic mercury. Therefore, we have developed a relatively simple,

---

Correspondence to: M. A. Malik (marifmalik@gmail.com).

Journal of Applied Polymer Science, Vol. 109, 3817–3824 (2008)

cheaper yet accurate method of estimating pore volume,[15] surface area, and pore size distribution from the density of the copolymer beads and applied it successfully in the case of styrene-divinylbenzene,[16] 4-vinylpyridine-divinylbenzene[17] and methyl methacrylate-ethyleneglycol dimethacrylate.[18] In this study, the simple method of estimating the macroporosity characteristics from the densities of the copolymers is applied for methyl methacrylate–divinylbenzene copolymers for the first time. The empirical relationships derived from the experimental data will be helpful to the professionals for synthesizing and characterizing macroporous methyl methacrylate–divinylbenzene copolymer beads of desired macroporosity.

EXPERIMENTAL

Methyl methacrylate (98% from Fluka) and divinylbenzene (60%, containing ~ 40% ethylvinyl benzene, from Panreac) were washed with dilute sodium hydroxide followed by three washings with water. Diluents and other chemicals were of analytical grade and were used as such. The polymerizing mixture (also called organic phase in this manuscript) was prepared by mixing monomers and diluents followed by addition of benzoylperoxide (1% by weight to the organic phase). The aqueous phase was prepared by dissolving 1.5 g gum Arabic, and 1.5 g gelatin per 100 mL of water. One part of the organic phase was suspended in five parts of the aqueous phase (volume-to-volume ratios), under mechanical stirring. The suspension was left under stirring for half an hour at room temperature. The temperature was then raised to 80°C in ~ 20 min and maintained at 80°C for 20 h, while the mechanical stirring was continued. Then, the copolymer beads were filtered out in a Buckner funnel and washed with hot water. The diluents and unreacted monomers or homopolymers were extracted with acetone.

The beads were left to swell in acetone 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 dried beads were packed in a measuring cylinder with tapping and their volume (V_d) was measured. Density (d) of the dried beads was calculated from the weight and volume of the dried beads. The swellability coefficient in acetone (SC_a) was calculated by using the following formula: $\mathrm{SC}_a = (V_s - V_d)100/V_d$. The recovered yield of the copolymers was more than 80% in all experiments. Volume of divinylbenzene (V_{DVB}), and volume of methyl methacrylate (V_{MMA}) employed were used to calculate the crosslinkage in the copolymers by using the following formula: Crosslinkage (%) = $60V_{\mathrm{DVB}}/(V_{\mathrm{DVB}} + V_{\mathrm{MMA}})$. Volume of diluents ($V_{\mathrm{diluents}}$) and volume of monomers (V_{monomers}) employed were used to calculate the dilution by using the following formula: Dilution (%) = $100V_{\mathrm{diluents}}/(V_{\mathrm{monomers}})$. Pore volumes, surface areas, and pore size distributions of the dried beads were determined by a mercury porosimeter, Autopore II 29220 from Micromeritics. The pore size distributions are 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 volumes and surface areas, between pore volumes and swelling coefficients in acetone, and between densities and pore volumes were obtained by the best fit regression equations using Microsoft Excel. R^2 was calculated by the software. The pore volumes were measured by mercury penetration and they represent macroporosity. The mercury porosimeter could not analyze the pore having diameter < 3 nm. Nitrogen adsorption–desorption (BET) equipment, which is considered suitable for analysis of pores having diameter < 3 nm, was not available to us. So, analysis of the pores having diameter < 3 nm was not done in this study. The compositions of the polymerization mixtures and the characteristics of the resulting methyl methacrylate–divinylbenzene copolymers are listed in Table I.

The copolymer of Exp no. 14 was converted to cation-exchanger by the following procedure: 5 g oven dried copolymer was mixed with 40 mL of 98% sulfuric acid at 100°C for 2 h. Then the slurry from the reaction vessel was poured into 1 L of cold demineralized water and the ion-exchanger beads were filtered out and washed with demineralized water. One step dilution of the slurry with cold water, instead of stepwise dilution, may damage the resin due to osmotic the thermal shock. However, we observed no cracks or damage to the resin beads in our experiments showing that the resin beads had good enough mechanical strength to withstand the shocks.

The capacity of the cation-exchanger was determined by the following procedure: the cation-exchanger was packed in a column and washed with 100 mL of 2*M* HCl followed by 100 mL of demineralized water. Then 100 mL of 2*M* NaCl solution was passed on it followed by 100 mL of demineralized water and the 200 mL effluent was titrated to determine the milliequivalent (meq) of HCl produced. The weak acid capacity was then calculated as meq/mL of the cation-exchanger, which is equal to the millimoles of $—\mathrm{COO^-H^+}$ groups per mL of the cation-exchanger. Then 200 mL of 0.36*M* NaOH was passed through the same cation-exchanger followed by 50 mL of demineralized water and the 250

TABLE I
Composition of Polymerization Mixtures and Macroporosity Characteristics of Methyl Methacrylate–Divinylbenzene Copolymers Synthesized in This Study

Exp No.	Diluent/s	Dilution (%)	Crosslinkage (%)	Density (g/mL)	Pore volume (ml/g)	Surface area (m^2/g)
1	Diethylphthalate	100	15	0.48	0.3883	159
2	Dibutylphthalate	100	15	0.47	0.3888	156
3	Bis-2-ethylhexylphthalate	100	15	0.37	0.8000	194
4	*n*-Heptane+Toluene 0 : 100	100	15	0.66	0.0670	34
5	*n*-Heptane+Toluene 20 : 80	100	15	0.65	0.1446	88
6	*n*-Heptane+Toluene 30 : 70	100	15	0.52	0.4326	155
7	*n*-Heptane+Toluene 50 : 50	100	15	0.41	0.6999	175
8	Cyclohexanone	100	20	0.68	0.0900	49
9	Dimethylphthalate	100	20	0.49	0.3900	151
10	Methyl-isobutyl ketone	100	20	0.47	0.4543	151
11	Cyclohexanol	100	20	0.61	0.2633	117
12	*n*-Heptane+Toluene 0 : 100	100	20	0.62	0.1961	93
13	*n*-Heptane+Toluene 10 : 90	100	20	0.55	0.2596	123
14[a]	*n*-Heptane+Toluene 20 : 80	100	20	0.52	0.4433	164
		100	20	0.52	0.4550	144
15	*n*-Heptane+Toluene 40 : 60	100	20	0.40	0.6821	181
16	*n*-Heptane+Toluene 50 : 50	100	20	0.36	0.8747	197
17	Dimethylphthalate	100	30	0.35	0.7480	189
18	Diethylphthalate	100	30	0.33	0.8916	206
19	Dibutylphthalate	100	30	0.32	1.0447	228
20	Bis-2-ethylhexylphthalate	100	30	0.30	1.0505	209
21[b]	Toluene	100	30	0.51	0.2682	120
				–	0.2788	130
22	*n*-Heptane+Toluene 1 : 1	43	20	0.53	0.2897	123
23	*n*-Heptane+Toluene 1 : 1	67	20	0.48	0.4453	147
24	*n*-Heptane+Toluene 1 : 1	100	20	0.36	0.8747	197
25	*n*-Heptane+Toluene 1 : 1	150	20	0.28	1.1931	200
26	Toluene	100	15	0.66	0.0670	34
27	Toluene	100	20	0.62	0.1961	93
28	Toluene	100	30	0.51	0.2682	120
29	Toluene	100	40	0.49	0.3558	125
30	*n*-Heptane+Toluene 20 : 80	100	15	0.65	0.1446	88
31	*n*-Heptane+Toluene 20 : 80	100	20	0.52	0.4433	164
32	*n*-Heptane+Toluene 20 : 80	100	30	0.44	0.5410	158

[a] Synthesis and porosity analysis was repeated.
[b] Porosity analysis was repeated.

mL of effluent was titrated to analyze the NaOH concentration. The strong acid capacity was calculated from the meq of NaOH consumed per mL of the cation-exchanger, which is equal to the millimoles of —$SO_3^-H^+$ groups per mL of the cation-exchanger.

RESULTS AND DISCUSSIONS

Effect of different diluents on macroporosity

Different diluents created different pore volumes in methyl methacrylate–divinylbenzene copolymers as shown in the case of Exp nos. 1–21 in Table I. This different pore volumes can be related with the difference in the solubility parameters of the diluents and the copolymers, i.e., the larger the difference the more porous the copolymer.[19,20] For the case of good solvents, the difference in the solubility parameters of the solvent (the diluents) and the copolymers is small. Therefore, the literature on the related porous copolymers concludes that the diluents that are good solvents for the copolymer create less pore volume and the diluents that are nonsolvent for the copolymer create more pore volume under the same experimental conditions.[2,6,7,8,19]

In Exp nos. 4–7 *n*-heptane, a nonsolvent, was mixed with toluene, a good solvent. With the increase in *n*-heptane content in the diluent from 0 to 50%, the pore volume increased from ~ 0.1 to ~ 0.7 mL/g and the surface area increased from 34 to 175 m^2/g. In Exp nos. 12–16, where the crosslinkage was 20% (instead of 15% in previous set of experiment), the increase in *n*-heptane content in the diluent from 0 to 50% resulted in an increase in the pore volume from ~ 0.2 mL/g to ~ 0.9 mL/g and increase in surface area from 93 to 197 m^2/g. When *n*-heptane was more than 50% in the diluent, the

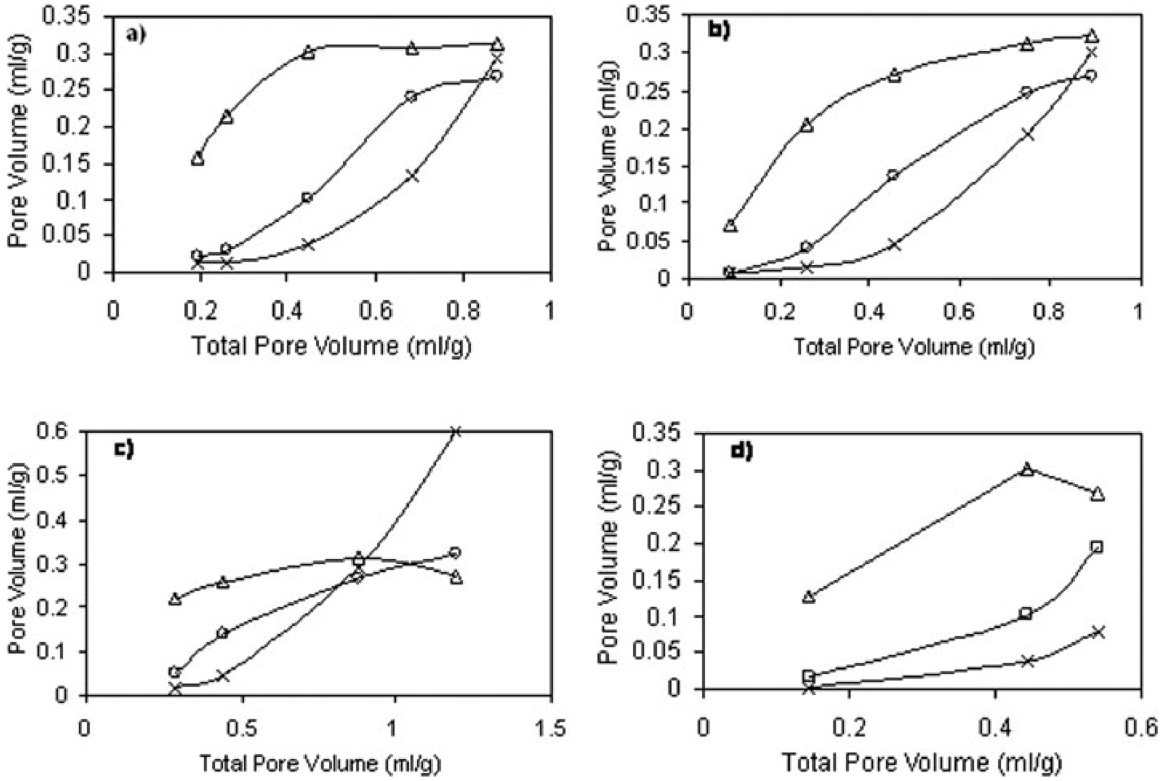

Figure 1 Variation of masopore and macropore contents with changes in the total pore volume of the copolymers: x, macropores having diameters > 50 nm; o, mesopores having diameters in the range of 20–50 nm; Δ, mesopores having diameter in the range of 3–20 nm. The pore volume was varied by: (a) varying *n*-heptane contents in the *n*-heptane+toluene mixture dilute, i.e., Exp nos. 12–15 in Table I; (b) by employing different diluents under different experimental conditions, i.e., Exp no. 8, Exp no. 11, Exp no. 10, Exp no. 17, and Exp no. 18; (c) by varying dilution, i.e., Exp nos. 22–25; (d) by varying the crosslinkage, i.e., Exp nos. 30–32.

copolymer beads were very fragile and broke during post reaction processing. It was observed that whenever the pore volume of the methyl methacrylate–divinylbenzene copolymers was more than 1 mL/g the copolymer bead were very fragile and practically not useable. Therefore, all the statistical analyses in this study were preformed on the results of the copolymers having pore volume less than 1 mL/g.

The pore volumes and surface areas discussed above belong to macroreticular porosity, i.e., pores of permanent nature which do not disappear upon drying. The macroreticular pores are subdivided into three classes namely macropores having diameters > 50 nm, mesopores having diameters in the range of 50–2 nm, and micropores having diameters < 2 nm.[21] Mercury penetration method analyzes macroreticular pores having diameter greater than 3 nm, i.e., macropores and mesopores. Figure 1(a,b) illustrate the changes in the pore volumes of mesopores having diameters less than 20 nm, mesopores having diameters more than 20 nm and macropores with respect to increase in overall pore volume from ~ 0.1 to ~ 1.0 mL/g. Both mesopores and macropores increase as the overall pore volume increases. It shows that new pores are added in the copolymer matrix with the increase in pore volume, which explains the increase in surface area as observed in this study. The mesopores having diameter less than 20 nm show a significant increase when the total pore volume is increased from ~ 0.1 to ~ 0.45 mL/g and appear to remain almost constant in the range of total pore volume from ~ 0.45 to ~ 1.0 mL/g. The mesopores having diameter greater than 20 nm increase with increase in total pore volume in the whole range of total pore volume studied. The macropores show a significant increase when the pore volume increases in the range ~ 0.45 to ~ 1.0 mL/g.

Effect of amount of diluents on macroporosity

In Exp nos. 22–25 of Table I, the dilution was gradually increased from 43 to 150%, keeping all other experimental parameters constant. The increase in dilution resulted in increase in pore volume from ~ 0.3 to 1.0 mL/g and increase in surface area from 123 to 200 m^2/g. These results are in accordance with the literature for styrene-divinylbenzene and other related copolymers, which concludes that the pore volume increases with increase in amount of diluent.[2,8] The effect of increase in pore volume with dilution on the mesopore and macropore contents is illustrated in Figure 1(c), which was similar to that of the effect of different dilutes ,i.e., the pores shift toward larger diameter with increase in overall pore volume. The surface area is increased because of the introduction of new pores with increase in the pore volume under our experimental conditions, as discussed in the previous section.

Effect of crosslinkage on macroporosity

In Exp nos. 26–29 of Table I the crosslinkage was gradually increased from 15 to 40% keeping all other experimental parameters constant. It resulted in increase in pore volume from ~ 0.1 to ~ 0.4 mL/g and increase in surface area from 34 to 125 m^2/g. In Exp nos. 30–32 of Table I the crosslinkage was gradually increased from 15 to 30% under a new set of experimental conditions. Again it resulted in an increase in pore volume from ~ 0.1 to ~ 0.5 mL/g and increase in surface area from 88 to 158 m^2/g. These results are in accordance with the literature for styrene-divinylbenzene and other related copolymers, which concludes that the pore volume, in general, increases with increase in crosslinkage.[7,8] The effect of crosslinkage on mesopore and macropore contents is illustrated in Figure 1(d), which was almost the same as the effect of different diluents, i.e., new pores are introduced and the pores distribution shift toward larger diameter with increase in the overall pore volume.

It can be observed from Figure 1 that increase in the total pore volume results in the introduction of new pores in the whole range of pore sizes and shift of average pore diameters toward larger pores, irrespective of how the pore volume was increased. These results can be explained on the basis of pore formation mechanism discussed in the next section.

Pore formation mechanism

The pore formation mechanism that was initially proposed for styrene-divinylbenzene copolymers[2] and later found applicable for other related copolymers[8] is the following. As the polymerization starts in the suspended droplet, the initially formed copolymer chains are swollen in the surrounding mixture of monomers and diluent. When more polymer chains accumulate the phase separation takes place between copolymer phase and the monomers+diluent mixture. The copolymer chains acquire spherical shapes called mirogel nuclei within the polymerizing droplet. The microgel nuclei grow into microspheres. The microspheres agglomerate with each other forming a primary porous network, which upon further polymerization and crosslinkage becomes porous copolymer bead. The macroporosity is the void spaces between the microspheres. Dilution of the monomers with nonsolvent or increasing the dilution or increasing the crosslinkage results in early phase separation and consequently, more porous copolymer network having higher pore volume and higher surface area as observed in this study.

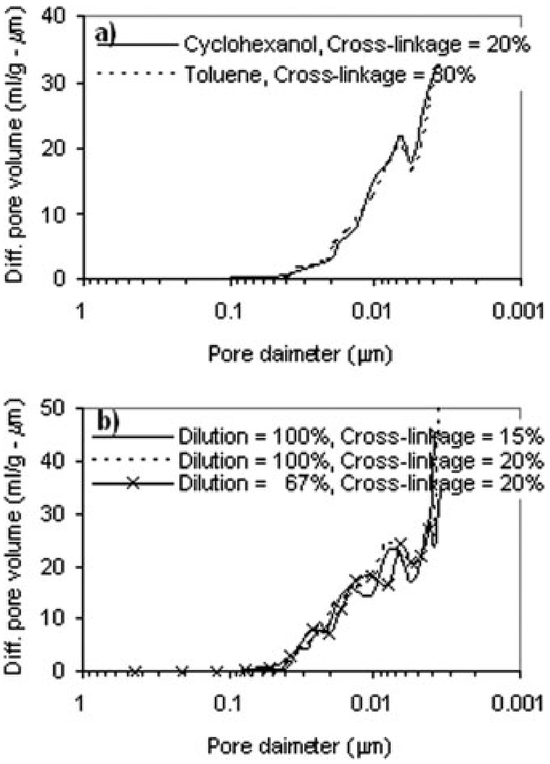

Figure 2 Similar pore size distributions for the copolymers synthesized under different experimental conditions but having nearly the same pore volumes: (a) the copolymers from Exp no. 11 and Exp no. 21, both having pore volume ~ 0.26 mL/g and (b) the copolymers from Exp no. 6, Exp no. 14, and Exp no. 23, all having pore volume ~ 0.45 mL/g.

Estimation of pore size distributions

It can be deduced from the pore formation mechanism and from the discussion in the previous sections that any change in the nature of diluent, amount of diluent, or crosslinkage changes the pore volume and pore size distribution, simultaneously. This deduction leads to the conclusion that each value of pore volume should be associated with a specific pore size distribution under our experimental conditions. This deduction is supported by the practical results illustrated in Figure 2 showing almost the same pore size distributions for the copolymers having nearly the same pore volume, irrespective of the diluent or crosslinkage employed in their synthesis. The deduction is also supported by several practical examples reported earlier for styrene-divinylbenzene,[16] 4-vinylpyridine-divinyl-

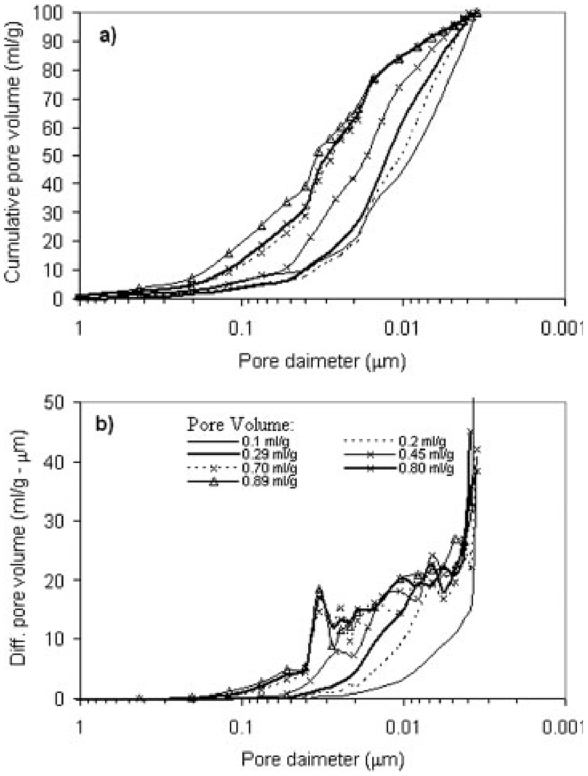

Figure 3 Representative pore size distribution curves for methyl methacrylate–divinylbenzene copolymers having pore volumes in the range of 0.1 to 0.9 mL/g: (a) cumulative pore size distributions, and (b) pore volume density distributions.

benzene,[17] and methyl methacrylate-ethyleneglycol dimethacrylate[18] copolymers. Therefore, the pore size distributions of several methyl methacrylate–divinylbenzene copolymers having pore volumes gradually varying from ~ 0.1 to ~ 1.0 mL/g are illustrated in Figure 3. If the pore volume of methyl methacrylate–divinylbenzene copolymer is known, one can predict its pore size distribution from the reference pore size distribution curves shown in Figure 3.

Estimation of surface area

Assuming pores to be cylindrical, the surface area ''SA'' is related to the pore volume ''V_m'' and average pore diameter ''D'' by the following relation: SA $= 4V_m/D$. The average pore diameter is dependent on the pore size distribution. The fact that each value of pore volume is associated with a specific pore size distribution leads to the deduction that each value of pore volume should be associated with a specific value of surface area. This deduction is supported by our results illustrated in Figure 4, where the surface areas are plotted against the pore volumes. The best fit equation to the data is the following logarithmic equation:

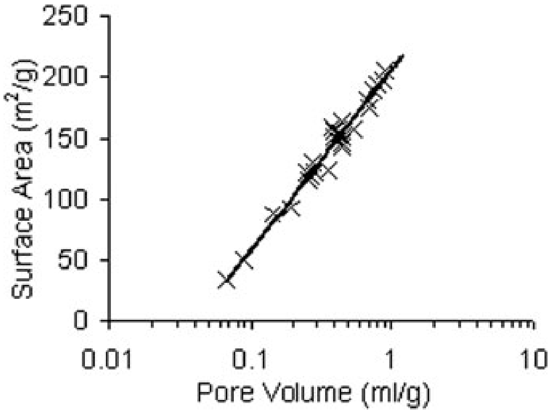

Figure 4 Plot of surface areas versus pore volumes: Crosses are experimental values and thick line is the best-fit equation eq. (1).

$$\mathrm{SA} = 64.192\mathrm{Ln}\,(V_m) + 205.95 \qquad (1)$$

Square of the Pearson product-moment correlation coefficient (R^2) between the estimated surface area and the surface area experimentally measured by mercury penetration method is 0.97. A visual observation from Figure 4 and the R^2 value close to one proves that the surface area can be estimated if the pore volume of the copolymer is known.

Estimation of swelling coefficient in acetone

The copolymers swell to a different extent depending on their pore volumes as shown in Figure 5. The best fit equation for the swelling coefficient in acetone (SC_a) as a function of the pore volume (V_m) was found as given below.

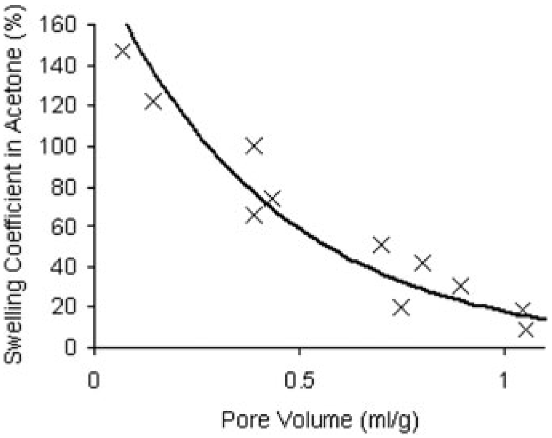

Figure 5 Swelling coefficients in acetone versus pore volumes of some copolymers synthesized in this study with crosslinkage in the range of 15–30% and dilution in the range of 67–100%: Crosses are the experimental values and the line is the best fit equation eq (2).

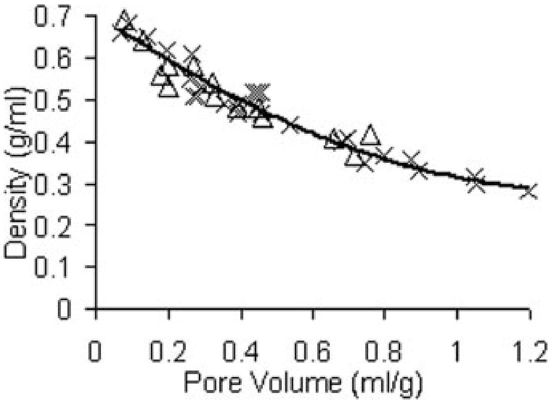

Figure 6 Plot of densities versus pore volumes: Crosses are the experimental values from this study, thick line is the best-fit equation eq. (7) based on the crosses and triangles are the experimental values obtained from Ref. 22.

$$SC_a = 192.75e^{-2.3649V_m} \quad (2)$$

The $R^2 \sim 0.9$ and visual observation from Figure 5 show that the swelling coefficient in acetone can be estimated with a good accuracy by using eq. (2). The range of experimental parameters of the data points used to obtain the Eq. (2) were crosslinkage 15–30% and dilution 67–100%. So, the eq. (2) should be used within the stated ranges, which, according to our experience, cover the most often used ranges of the parameters.

Estimation of pore volume

In the case of ideally packed spherical beads, the interparticle void occupies a constant fraction of the total volume of the packed beads. Therefore, any difference in the density ''d'' of the packed spherical beads of porous methyl methacrylate–divinylbenzene should be related to pore volume ''V_m'' of the beads. This deduction is supported by the plot of the densities verses pore volumes from this study and from literature[22] as illustrated in Figure 6. The best fit equation to the data is the following second degree polynomial:

$$V_e = 5.1014d^2 - 7.5077d + 2.862 \quad (3)$$

where ''V_e'' is the estimated pore volume. The R^2 through data points between the estimated pore volumes (V_e) and the pore volumes experimentally measured by mercury penetration method (V_m) was 0.96, i.e., close to one, proving that the pore volume of methyl methacrylate–divinylbenzene copolymer can be estimated with a good accuracy if its density is known. These results are in agreement with our earlier studies on styrene-divinylbenzene, 4-vinylpyridine-divinylbenzene and other related copolymers.[15]

Preestimation of pore volume

Figure 7 shows the plot of weight average solubility parameter of the polymerizing mixture verses the pore volume of the copolymers synthesized for nonpolar diluents, by the procedure explained earlier.[19] The following second degree polynomial was found the best fit for our data with R^2 more than 0.9:

$$V_{pe} = 10.224\left(\sum \delta_i f_i\right)^2 - 179.64\left(\sum \delta_i f_i\right) + 789.24 \quad (4)$$

where ''V_{pe}'' is the preestimated pore volume by the eq. (4), and $\sum \delta_i f_i$ is the weight average solubility parameter of the polymerizing mixture, i.e., δ_i is the solubility parameter of methyl methacrylate, divinylbenzene, and diluent/s and f_i is their respective weight fraction in the polymerizing mixture. However, such a correlation was not found for moderately polar or strongly polar and H-bonding diluents. These results are almost in agreement with our earlier results for styrene-divinylbenzene copolymers where preestimation of the pore volume was proven to be possible for nonpolar and moderately polar diluents.[19]

Conversion of the copolymers to cation-exchanger

The methyl methacrylate based porous copolymers have been converted to cation-exchanger by treatment with HSO_3Cl.[13] The sulfonation reaction can also be performed by H_2SO_4.[23,24] In this study methyl methacrylate–divinylbenzene copolymer from Exp no. 14 was treated with H_2SO_4 and the resultant

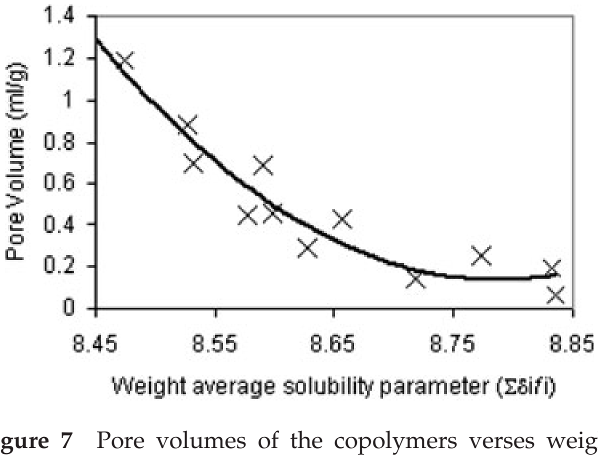

Figure 7 Pore volumes of the copolymers verses weight average solubility parameters of the polymerizing mixture ($\sum \delta_i f_i$) for the case of nonpolar diluents: Crosses are the calculated values of ($\sum \delta_i f_i$) and the thick line is the best-fit equation eq. (4).

cation-exchanger was found to have ~ 3 meq/g weak acid capacity due to —COO$^-$H$^+$ groups and ~ 2 mq/g strong acid capacity due to —SO$_3$$^-H^+$ groups on the cation-exchanger. The total capacity was ~ 5 meq/g (~2 meq/mL), which is noticeably higher as compared to ~ 4 meq/g (~1.5 meq/mL) capacity of the macroporous styrene-divinylbenzene copolymers of comparable porosity and sulfonation under the same conditions.[24] This difference can be explained on the basis of the fact that —C$_6$H$_4$SO$_3$$^-H^+$ group on the cation-exchanger derived from styrene-divinylbenzene is bulky and, consequently, occupies more space as compared to —COO$^-$H$^+$ group on the cation-exchanger derived from methyl methacrylate–divinylbenzene.

CONCLUSIONS AND GENERAL COMMENTS ON ESTIMATING MACROPOROSITY CHARACTERISTICS

It is concluded that the pore volumes of the copolymers can be estimated from the densities of the copolymers by using eq. (3) with reasonable accuracy. The surface area, swelling coefficient in acetone, and pore size distribution of mesopores and macropores, can be estimated by using eqs. (1)–(3), respectively, with a reasonable accuracy. All that is required is a measuring cylinder and a balance. For nonpolar diluents the pore volume can be preestimated from the solubility parameters and weight fractions of the polymerizing mixture by using equation eq. (4). The R^2 values between the estimated values and experimentally determined values are ≥0.9, indicating the estimations are reasonably close to the actual values.

The proposed method of estimation is simple, inexpensive but yet accurate. The proposed method will not be applicable if this copolymer is synthesized by some other procedure, e.g., if the porosity is generated by using some template, or when some polymer is employed as diluent,[6] or when some sublimable solid is employed as diluent.[25] Furthermore, a fraction of the porosity of the copolymer may be temporarily lost during some post processing conditions.[26,27] Therefore, the proposed method should be applied under the very experimental conditions given in this study, which off course are the most often used experimental conditions in practice. It should be mentioned that the proposed method can not fully replace the mercury porosimetry. Observations from Figure 6 show that absolute error in estimated pore volume could be as high as 0.15 mL/g. Based on the facts presented above, it can be said that the proposed method is best suited for applications in quality assurance where the copolymer is produced repeatedly. However, this method can be employed in those research laboratories also where the copolymers are produced for applications as adsorbents, chromatographic media, etc, and where the mercury porosimetry facility is not available. In such situations, the proposed method of estimating the macroporosity characteristics can prove to be the best alternate.

The authors thank Mr. Hafiz Altaf Hussain (SA-I) of ACL for performing mercury porosimetry.

References

1. Kunin, R. In Dorfner, K., Ed.; Ion Exchangers: Polymeric Adsorbents; Walter de Gruyter: Berlin, 1991; p 659.
2. Kun, K. A.; Kunin, R. J Polym Sci Part A-1: Polym Chem 1968, 6, 2689.
3. Arshady, R. J Chromatogr 1991, 586, 181.
4. Arshady, R. J Chromatogr 1991, 586, 199.
5. Patell, S.; Turner, J. C. R. J Sep Proc Technol 1980, 1, 31.
6. Sederel, W. L.; De Jong, G. J. J Appl Polym Sci 1973, 17, 2835.
7. Jacobelli, H.; Bartholin, M.; Guyota, A. J Appl Polym Sci 1979, 23, 927.
8. Okay, O. Prog Polym Sci 2000, 25, 711.
9. Sherrington, D. C.; Lanver, A.; Schmalz, H. G.; Wilson, B.; Ni, X. W.; Yuan, S. Angew Chem Int Ed 2002, 41, 3656.
10. Anand, P. S.; Pall, G.; Reddy, K. A.; Dasare, B. D. J Polym Mater 1985, 2, 227.
11. Liu, Q.; Want, L.; Xiao, A. Des Monomers Polym 2007, 10, 405.
12. Thanoo, B. C.; Jayakrishnan, A. J Appl Polym Sci 1990, 39, 1153.
13. Beldie, C.; Poinescu, C. L.; Cotan, V. J Appl Polym Sci 2003, 29, 13.
14. Ding, L.; Yao, Z.; Li, T.; Qiu, M.; Yue, Q.; Chai, J. Iranian Polym J 2003, 12, 491.
15. Malik, M. A.; Rehman, E.; Naheed, R.; Alam, N. M. React Funct Polym 2002, 50, 125.
16. Malik, M. A.; Ali, S. W.; Waseem, S. J Appl Polym Sci 2006, 99, 3565.
17. Malik, M. A. e-Polymers 2006, no. 040.
18. Ali, S. W.; Waseem, S.; Malik, M. A. Polym Test 2007, 26, 505.
19. Malik, M. A.; Ahmed, M.; Ikram, M. Polym Test 2004, 23, 835.
20. Scheler, S. J Appl Polym Sci 2007, 105, 3121.
21. Hearn, J.; Smelt, P. L.; Wilkinson, M. C. J Colloid Interface Sci 1989, 133, 284.
22. Cardoso, A. M.; Lucas, E. F.; Barbosa, C. C. R. Polímeros 2004, 14, 201.
23. Pepper, K. W. J Appl Chem 1951, 1, 124.
24. Ahmed, M.; Malik, M. A.; Pervez, S.; Raffiq, M. Eur Polym J 2004, 40, 1609.
25. Malik, M. A.; Naheed, R. e-Polymers 2007, no. 135.
26. Hilgen, H.; De Jong, G. J.; Sederel, W. L. J Appl Polym Sci 1975, 19, 2647.
27. Erbay, E.; Okay, O. J Appl Polym Sci 1999, 71, 1055.