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Notes

Porogen and Cross-Linking Effects on the Surface Area, Pore Volume Distribution, and Morphology of Macroporous Polymers Obtained by Bulk Polymerization[§]

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Introduction

Macroporous polymers, polymers containing a permanent pore structure, have been used extensively as ion-exchange resins and as acid catalysts in industrial applications.[2] These resins are generally formed under free radical suspension polymerization conditions with high cross-linking agent levels and in the presence of a porogen, generally an inert solvent. Many studies have investigated the complex physicochemical process for forming macroporous polymers in suspension polymerization.[3] As might be expected, several factors influence the polymer properties and morphology, including the type and amount of porogen used, the degree of cross-linking, and the temperature and time of polymerization.

More recently, macroporous polymers have been used as supports for transition metal catalysts.[4] In this application, a high surface area material that provides good access to internal catalytic sites is desirable. An important characteristic of macroporous supports is that all solvents can access the permanent pore structure of the polymer; i.e., swelling is not critical to accessibility. For example, even water can penetrate a macroporous divinylbenzene/styrene matrix.[5] This property is advantageous as it allows solvent/reaction matching with minimal considerations for polymer swelling. In contrast, lightly cross-linked supports necessitate a swelling solvent; for example, MeOH collapses a Merrifield resin.

In the context of developing catalysts that are immobilized into highly cross-linked macroporous polymer supports,[4c−e] we found that many metallomonomers were only soluble in certain porogen/comonomer combinations and that their air and water sensitivity precluded suspension polymerization techniques. Moreover, Frechét and co-workers have described significant differences[6] between macroporous polymer morphologies obtained by suspension and "bulk" polymerization techniques.[7] Because of this recently recognized difference, and our desire to use common organic solvents as porogens, we initiated a study examining the effect of porogen and cross-link density on surface area/pore size distribution in "bulk" polymerizations.[8] Although many surface area measurements have been reported in the molecular imprinting literature,[9] these data come from different laboratories, and so a quantitative evaluation of various synthesis variables is difficult. A common data set obtained under carefully controlled conditions should be beneficial.

Table 1. BET Surface Area[a] and BJH Cumulative Pore Volume for DVB/STY Polymers

porogen	100% DVB (80% tech) BET[b] (BJH[c])	4:1 DVB:STY BET[b] (BJH[c])	1:1 DVB:STY BET[b] (BJH[c])
THF	820 (0.75)	625 (0.55)	0 (0)
acetonitrile	375 (0.80)	250 (0.70)	115 (0.70)
toluene	810 (0.90)	680 (0.80)	310 (0.30)
chlorobenzene	850 (0.90)	700 (0.70)	0 (0)
hexane	515 (1.00)	420 (0.90)	220 (0.70)
methanol	1 (0.01)	1 (0.01)	1 (0.01)
DMF	755 (1.10)	630 (1.00)	410 (0.90)
methyl *tert*-butyl ether	700 (1.00)	615 (1.00)	360 (0.90)

[a] Surface area for repeat polymer batches were reproducible within ±5%. [b] BET surface area (m^2/g polymer). [c] BJH cumulative pore volume for pores between 1.7 and 300 nm in diameter (mL/g polymer).

In the present study, two classes of resins were investigated: divinylbenzene/styrene (DVB/STY) and ethylene dimethacrylate/methyl methacrylate (EDMA/MMA). Three cross-link feed ratios were investigated for each system: 100, 80, and 50% cross-linking by weight.[10] Porogens with boiling points >55 °C were chosen: THF, CH_3CN, toluene, chlorobenzene, *n*-hexane, methanol, DMF, and methyl *tert*-butyl ether were utilized at a 1:1 vol:vol ratio to the monomers. The effect of these variables on the accessible surface area (BET) and the pore size distributions (BJH) of the resulting materials is reported herein.

Results and Discussion

DVB/STY. The BET surface areas and the BJH cumulative pore volumes of a family of DVB/STY polymers generated by varying the porogen and the DVB/STY ratio are listed in Table 1. Most of the DVB polymers have high surface areas, with the polymers using THF, toluene, and chlorobenzene as porogens exceeding 800 m^2/g polymer (Figure 1). Methanol was the exception as it led to surface areas of <1 m^2/g. For comparison, a common silica gel used for chromatography has a surface area of 518 m^2/g (EM Science silica gel 60, 230−400 mesh), and a lightly cross-linked Merrifield resin has a surface area <1 m^2/g.

The BET surface area values were observed to decrease with decreasing cross-linking ratio for all poro-

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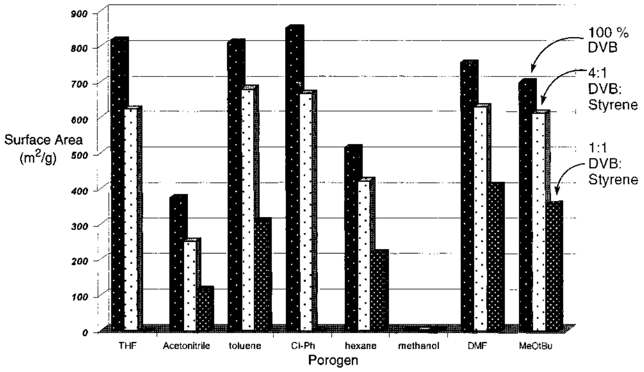


Figure 1. BET surface areas of the DVB/styrene polymers.

Table 2. BET Surface Area[a] and BJH Cumulative Pore Volume for EDMA/MMA Polymers

porogen	100% EDMA BET[b] (BJH[c])	4:1 EDMA: MMA BET[b] (BJH[c])	1:1 EDMA:MMA BET[b] (BJH[c])
THF	580 (0.60)	310 (0.50)	60 (0.25)
acetonitrile	390 (0.80)	225 (0.60)	105 (0.50)
toluene	470 (0.90)	255 (0.70)	90 (0.50)
chlorobenzene	460 (0.80)	285 (0.65)	10 (0.05)
hexane	5 (0.01)	1 (0.01)	1 (0.01)
methanol	335 (0.40)	210 (0.35)	50 (0.25)
DMF	510 (0.70)	270 (0.50)	10 (0.05)
methyl *tert*-butyl ether	405 (0.65)	290 (0.55)	15 (0.05)

[a] Surface area for repeat polymer batches were reproducible within ±5%. [b] BET surface area (m^2/g polymer). [c] BJH cumulative pore volume for pores between 1.7 and 300 nm in diameter (mL/g polymer).

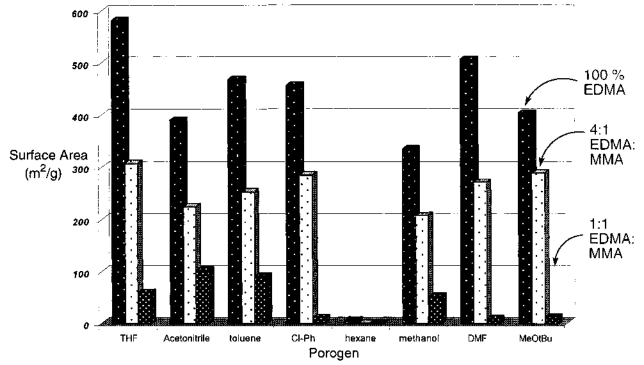


Figure 2. BET surface areas of the EDMA/MMA polymers.

gens (Figure 1).[11] The decrease was especially dramatic for THF and chlorobenzene, where the 1:1 DVB:STY polymers had reproducibly low surface areas (<1 m^2/g).[12] It should also be noted that *n*-hexane is a moderately good porogen for the DVB/STY system, giving surface areas of 515, 422, and 218 m^2/g.

EDMA/MMA. The BET surface areas and the BJH cumulative pore volumes for the EDMA/MMA polymers are listed in Table 2. The surface areas of the 100% EDMA polymers are also high, with THF and DMF polymers exceeding 500 m^2/g (Figure 2). The EDMA/MMA polymers generally had lower surface areas than the DVB/STY polymers. Once again, surface areas decrease with decreasing cross-link ratio for each of the porogens.[10] Several of the polymers also showed a drastic dropoff in surface area at a 1:1 ratio of cross-linker and monomer; notably the materials made with chlorobenzene, DMF, and methyl *tert*-butyl ether as porogens (surface areas = 11, 9, and 13 m^2/g, respectively).[11]

Especially dramatic differences are observed in the accessible surface areas of DVB/STY and EDMA/MMA using *n*-hexane and MeOH as porogens (Figures 1 and 2). In the nonpolar DVB/STY system (Figure 1), the nonpolar porogen *n*-hexane effectively generates high surface areas (515, 422, and 218 m^2/g), while the polar porogen MeOH gives low surface areas (<1 m^2/g). In the more polar EDMA/MMA system (Figure 2), the solvent roles are reversed, and *n*-hexane gives low surface area materials (<10 m^2/g),[13] while the polar porogen MeOH leads to high surface area materials (335, 298, and 52 m^2/g). In both polymer systems the use of MeOH as a porogen is unique to bulk polymerization as it is, of course, soluble with water and precludes its usage in suspension polymerization.

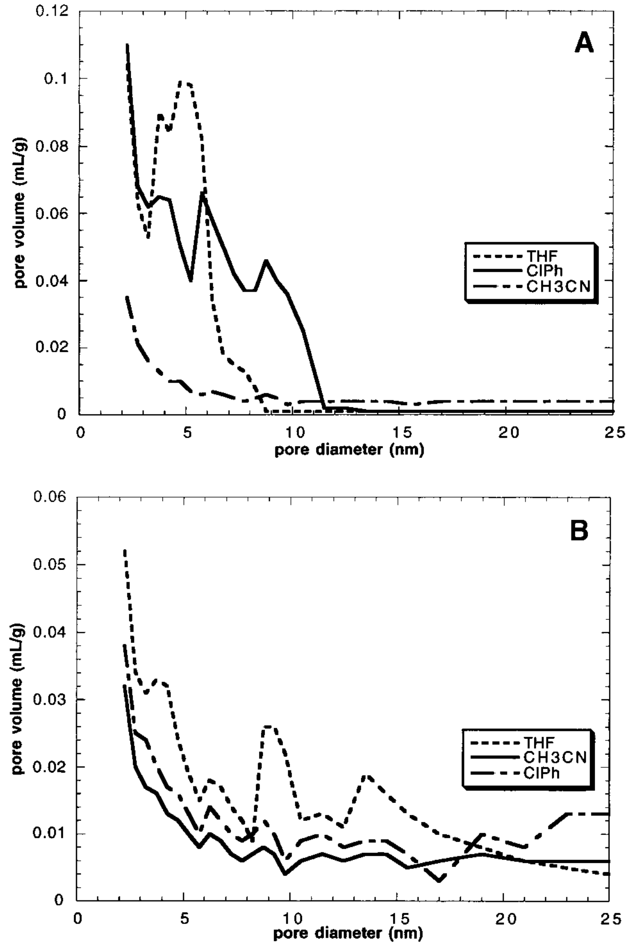
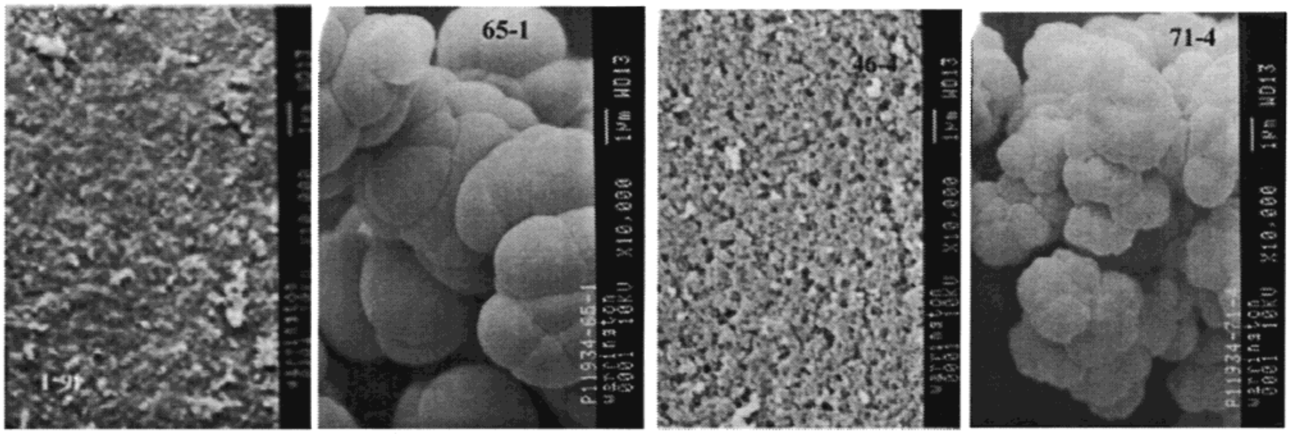


Figure 3. (A) Pore volume distributions for the 100% DVB polymers (2–25 nm). (B) Pore volume distributions for the 100% EDMA polymers (2–25 nm).

The physical properties of the polymers were also qualitatively different for the high and low surface area materials. For all the high surface area samples the polymer fractures into large sections upon extended physical abuse. The low surface area samples, however, could only be removed from the reaction vessel by scraping, yielding a white powder.

Since solvation/desolvation protocols often fracture larger polymer chunks (0.2–0.5 cm^3) into small pieces, we investigated the effect of a solvation/desolvation (in vacuo) cycle on the pore structure and surface area. These experiments were chosen to simulate the effect of repeated usage of the polymer in a catalytic application. Three toluene/DVB:STY (4:1) polymers were synthesized under the standard conditions. After porogen removal, each polymer was immersed in toluene, THF, or CH_2Cl_2 and stirred for 6 h, and the solvent was then



toluene/100% DVB ($810\ m^2/g$)   MeOH/100% DVB ($1\ m^2/g$)   toluene/100% EDMA ($470\ m^2/g$)   hexane/100% EDMA ($5\ m^2/g$)

Figure 4. SEM images of polymers at 10 000× (1 μm bar in the upper right corner).

removed from each polymer sample in vacuo. The surface areas of the dried polymers were 640, 660, and 686 m^2/g, respectively, values similar to the untreated polymer (Table 1, 681 m^2/g). Thus, a single solvation/desolvation cycle does not appreciably alter the accessible surface area and by inference the micro- and mesopore structure.

The BET surface area data indicate that a wide range of solvents can be used as porogens under bulk polymerization conditions to yield high surface area macroporous polymers. Choosing solvents that both dissolve metallomonomers and give high surface areas should maximize the chances for accessible and thereby reactive supported catalysts.

BJH Pore Volume Distribution. Pore volume distributions were measured by the BJH method from the dinitrogen desorption isotherms.[14] Not surprisingly, the polymers having high surface areas had pore size distributions in the micropore (<2 nm diameter) and mesopore regime (2−50 nm diameter). A representative plot of pore volume distributions for the 100% DVB system is shown in Figure 3A. This plot compares two high surface area systems (THF (820 m^2/g) and chlorobenzene (850 m^2/g)) with a relatively low surface area material (CH_3CN as porogen (390 m^2/g)).[15] The polymers show tangential behavior near the micropore boundary (<5 nm), with the higher surface area materials having steeper slopes in this region. In the high surface area materials, the pore volumes drop to near zero past about 15 nm pore diameters. In the 100% EDMA system (Figure 3B) the pore volume distribution trends were similar for THF, ClPh, and CH_3CN (580, 457, and 391 m^2/g, respectively). In both systems, the appearance of fine structures suggests that some pore sizes are preferred over others.

Polymer Morphology. Scanning electron micrographs were obtained for several of the macroporous polymers (Figure 4). Comparison of the polymers at 10 000× reveal differences in the high and low surface area samples in both the DVB and EDMA systems. The toluene/DVB and toluene/EDMA systems, both high surface area materials with small pores, have a grainy appearance at 10 000×. The low surface area materials such as MeOH/DVB and *n*-hexane/EDMA look like large bubbles at this magnification.[16] From these and other images (see Supporting Information), we find that SEM images can be used to qualitatively rank the relative surface area of these materials.

Conclusion

Bulk polymerization techniques and high degrees of cross-linking make several common organic solvents good porogens for synthesizing macroporous DVB/STY and EDMA/MMA polymers with high surface areas and permanent pores in the micro- and mesopore regime. Surface areas are found to decrease with decreasing cross-link ratio, sometimes falling to <1 m^2/g in some systems. Low surface area materials are obtained with MeOH as a porogen for the DVB/STY system and *n*-hexane as a porogen for the EDMA/MMA system. Large differences are observed in the SEM images between the high and low surface area polymers, which can be correlated to measured surface areas. We hope that the data contained herein will serve as a helpful guide to optimizing the solubility of functionalized monomers and the accessible surface area of the resulting macroporous polymers.

Experimental Section

General. All reagents were purchased from Aldrich. 80% tech grade divinylbenzene, styrene, ethylene glycol dimethacrylate, and methyl methacrylate were passed through a plug of activated alumina and freeze−pump−thaw degassed prior to use. All solvents were used as received. AIBN was recrystallized from MeOH and dried under vacuum.

Typical Polymerization Conditions. In a dinitrogen-filled glovebox, AIBN (1.5 wt % of monomers), monomers (ratio of monomers by weight), and porogen (monomer:porogen, 1:1 v:v) were added to a 20 mL vial fitted with a Teflon-coated screwcap. The vial was capped, removed from the glovebox, and placed in a temperature-controlled oil bath (toluene, chlorobenzene, DMF, CH_3CN = 80 °C; MeOH, *n*-hexane, MeO*t*Bu, THF = 65 °C).[17] The bulk solution was heated for 24 h[18] to give white insoluble polymers. The solvent was removed in vacuo.

Surface Area/Pore Volume Distribution. Dinitrogen adsorption/desorption measurements were performed at 77.3 K on Micrometrics ASAP model 2400/2405 porosimeters. Samples were degassed at 150 °C under vacuum for 16 h prior to data collection. Surface area measurements utilized a five-point adsorption isotherm collected over 0.05 to 0.20 p/p_0 and analyzed via the BET method.[19] Pore volume distributions utilized a 27-point desorption isotherm and were analyzed via the BJH method.[20]

SEM. All samples were mounted on aluminum stubs with double-sided tape, sputtered with Au/Pd convective, and imaged on a JEOL 840A SEM using secondary electron imaging at 10 kV.

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Supporting Information Available: Pore volume distribution plots for all 48 polymers listed in Tables 1 and 2 and SEM images for the following polymers: 100% DVB/THF, 100% DVB/*n*-hexane, 100% EDMA/THF, and 100% EDMA/MeOH. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) This work was carried out by BPS while an industrial intern at DuPont.

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(6) As pointed out by a referee, some of the reasons for this might include the fact that monomer droplets in suspension polymerization are water-saturated and are highly agitated. The latter might act to reduce the number of entanglement cross-links and affect the onset of phase separation.

(7) Svec, F.; Fréchet, J. M. J. *Chem. Mater.* **1995**, *7*, 707−715. (b) Viklund, C.; Svec, F.; Fréchet, J. M. J.; Irgum, K. *Chem. Mater.* **1996**, *8*, 744−750.

(8) For a series of polymer morphology studies of macroporous trimethylolpropane trimethacrylate (TRIM) resins made under bulk polymerizations conditions, see: (a) Rosenberg, J. E.; Flodin, P. *Macromolecules* **1986**, *19*, 1543−1546. (b) Rosenberg, J. E.; Flodin, P. *Macromolecules* **1987**, *20*, 1518−1522. (c) Rosenberg, J. E.; Flodin, P. *Macromolecules* **1987**, *20*, 1522−1526.

(9) See for example: (a) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812−1813. (b) Sellergen, B.; Shea, K. J. *J. Chromatogr.* **1993**, *635*, 31−49. (c) Wulff, G. *ACS Symp. Ser.* **1986**, *308*, 186−230. (d) Wulff, G.; Schauhoff, S. *J. Org. Chem.* **1991**, *56*, 395−400.

(10) The true cross-link density is generally substantially lower than the feed ratio. See: Law, R. V.; Sherrington, D. C.; Snape, C. E.; Ando, I.; Kuroso, H. *Macromolecules* **1996**, *29*, 6284−6293.

(11) For similar results in porous polymer monoliths, see: Xie, S.; Svec, F.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 4072−4078, and references therein.

(12) For lucid descriptions of these phenomena in suspension and bulk polymerizations, see: footnote 3 and Viklund, C.; Svec, F.; Fréchet, J. M. J.; Irgum, K. *Chem. Mater.* **1996**, *8*, 744−750.

(13) Heptane (and benzyl alcohol) similarly lead to low surface areas (<1 m^2/g) in TRIM resins.[7b]

(14) For nitrogen adsorption measurements, pore size ranges become uncertain at the upper limit of the mesopore region: Cheng, C. E.; Micale, F. J.; Vanderhoff, J. W.; El-Aasser, M. S. *J. Colloid Interface Sci.* **1992**, *150*, 549−558.

(15) See the Supporting Information for a complete set of pore volume distribution plots.

(16) For similar SEM images, see: (a) Footnote 8a. (b) Viklund, C.; Pontén, E.; Glad, B.; Irgum, K.; Hörstedt, P.; Svec, F. *Chem. Mater.* **1997**, *9*, 463−471.

(17) Control experiments indicate that under these conditions the polymerization temperature did not have a large effect on the surface area of the resulting polymers.

(18) For a DVB polymer morphology study addressing the length of polymerization, see: Nyhus, A. K.; Hagen, S.; Berge, A. *J. Polym. Sci., Part A* **1999**, *37*, 3973−3990.

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