Chem. Mater. **1996,** *8,* 744−750

Monolithic, “Molded”, Porous Materials with High Flow Characteristics for Separations, Catalysis, or Solid-Phase Chemistry: Control of Porous Properties during Polymerization

Camilla Viklund, Frantisek Svec, and Jean M. J. Fréchet*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Knut Irgum

Department of Analytical Chemistry, University of Umeå, S-901 87 Sweden

Received September 19, 1995. Revised Manuscript Received December 18, 1995⊗

The porosity and flow characteristics of macroporous polymer monoliths that may be used to prepare separation media, flow-through reactors, catalysts, or supports for solid-phase chemistry can be controlled easily during their preparation. Key variables such as temperature, composition of the pore-forming solvent mixture, and content of cross-linking divinyl monomer allow the tuning of average pore size within a broad range spanning 2 orders of magnitude. The polymerization temperature, through its effects on the kinetics of polymerization, is a particularly effective means of control, allowing the preparation of macroporous polymers with different pore size distributions from a single composition of the polymerization mixture. The choice of pore-forming solvent is also important, larger pores being obtained in a poor solvent due to an earlier onset of phase separation. Increasing the proportion of the cross-linking agent present in the monomer mixture not only affects the composition of the final monoliths but also decreases their average pore size as a result of early formation of highly cross-linked globules with a reduced tendency to coalesce. The synergy of different effects has also been observed under specific polymerization conditions using two monomer pairs, styrene−divinylbenzene and glycidyl methacrylate−ethylene dimethacrylate polymerized in close molds. Mercury intrusion porosimetry measurements, inverse size exclusion chromatography, and back pressure measured at different flow rates with the macroporous monoliths were used for the characterization of the porous properties. A good correlation between pore size and flow resistance that follows the Hagen−Poiseuille equation used previously to describe flow through a straight tube has been found.

Introduction

The preparation of macroporous polymer beads is generally achieved as a result of the phase separation which occurs during the polymerization of a monomer mixture containing appropriate amounts of both a cross-linking monomer and a porogenic solvent. This process, invented in the late 1950s, has been commercialized, and macroporous bead materials are widely used today for the preparation of ion-exchange resins, catalysts, adsorbents, chromatographic media, etc.[1] In contrast to common cross-linked polymers that must be swollen in a good solvent in order to acquire porous properties, these resin beads remain porous even in the dry state. The porous properties of such particulate resins can be controlled by many variables. The most important ones are generally thought to be the concentration of cross-linking monomer in the monomer mixture and the type and percentage of porogenic solvent present in the polymerizing system. Other variables such as content of initiator, reaction time, and polymerization temperature are considered to be of minor importance for the control of the porous properties of these materials.[1,2]

In 1992 we described a totally new type of macroporous material obtained by solution polymerization in an unstirred mold.[3] This macroporous material is obtained as a monolith with a shape that conforms to that of the mold and with a highly unusual pore structure allowing direct flow of a liquid through its large pores. Because direct flow through the monolithic molded medium, as opposed to flow around a classical bead, may offer new opportunities for applications as varied as chromatography or chemistry on solid support, it is important to control accurately the porous structure of the monoliths. We have recently shown that polymer beads prepared by classical suspension polymerization and polymer monoliths prepared by our process using the same monomer mixture, pore-forming solvent, initiator, and temperature have vastly different macroporous structures.[4,5] Only the molded monoliths contain the large channels that allow a liquid to flow through

---

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1996.

(1) Seidl, J.; Malinsky, J.; Dusek, K.; Heitz, W. *Adv. Polym. Sci.* **1967**, *5*, 11. Guyot, A.; Bartholin, M. *Prog. Polym. Sci.* **1982**, *8*, 277. Hodge, P., Sherrington, D. C., Eds. *Syntheses and Separations Using Functional Polymers*; Wiley: New York, 1989. Kun, K. A.; Kunin, R. *J. Polym. Sci., A1* **1968**, *6*, 2689. Sederel, W. L.; DeJong, G. J. *J. Appl. Polym. Sci.* **1973**, *17*, 2835.

(2) Horak, D; Svec, F.; Bleha, M.; Kalal, J. *Angew. Makromol. Chem.* **1981**, *95*, 109. Horak, D; Svec, F.; Ilavsky, M., Bleha, M.; Baldrian, J.; Kalal, J. *Angew. Makromol. Chem.* **1981**, *95*, 117.

(3) Svec, F.; Fréchet, J. M. J. *Anal. Chem.*, **1992**, *64*, 820. Svec, F.; Fréchet, J. M. J. US Patent No. 5,334,310, 1994.

(4) Svec, F.; Fréchet, J. M. J. *Chem. Mater.* **1995**, *7*, 707.

(5) Svec, F.; Fréchet, J. M. J. *Macromolecules* **1995**, *28*, 7580.

the medium at a low applied pressure. Typical macroporous beads obtained by suspension polymerization contain a more extensive network of smaller pores than the monolith but they allow mass transfer only through flow around the beads using the large interstitial spaces that unavoidably result from their spherical shape. Mass transfer is increased considerably in the perfusive beads that have been introduced recently for use in HPLC, diagnostics, and enzyme immobilization.[6] These beads have some pores that are large enough to allow up to about 5% of the mobile phase to flow through, and even this small convection has a positive effect on the chromatographic separations.[7]

The process used to prepare the monoliths and the beads differ only in the lack of interfacial tension between an aqueous and an organic phase, and the absence of dynamic forces resulting from stirring in the case of the polymerization in an unstirred mold. The kinetics of the overall process within the unstirred mold is also one of the most important variables that contributes to the formation of large pores and allows the control of the macroporous structure involving these flow-through channels.[5]

Once polymerized in a tubular or a flat mold, the porous material is an excellent support for the immobilization of biological catalysts or for use as a separation medium for high-performance liquid chromatography (HPLC) of a broad spectrum of molecules, large and small.[8] Our approach has also been used for the preparation of rods with molecularly imprinted templates that have been used in molecular recognition by HPLC and in separations by capillary electrophoresis.[9]

This study examines in detail the effects of the most important variables such as temperature, concentration of cross-linking monomer in the polymerization mixture, and composition of the porogenic solvent, on the porous structure obtained with the two chemically different systems of styrenic and methacrylate monomers.

Experimental Section

Preparation of Polymers. Polymerization Mixtures. Azobisisobutyronitrile (1 wt % with respect to monomers, Kodak) was dissolved in 4 vol parts of a mixture consisting of glycidyl methacrylate and ethylene dimethacrylate (both from Sartomer). In an alternative procedure, azobisisobutyronitrile (1 wt % with respect to monomers) was dissolved in 4 vol parts of a mixture consisting of styrene (Aldrich) and divinylbenzene (80% of divinyl monomer, Dow Chemicals). The porogenic solvents, mixtures of cyclohexanol with dodecanol or of dodecanol with toluene, respectively (all Aldrich), were admixed slowly to the monomers. The total volume of the porogenic mixture was 6 parts. The stock polymerization mixtures were stored in closed flasks in a freezer at a temperature of −18 °C and consumed within 2 days.

Polymerization in Solution. The polymerization mixtures were purged with nitrogen for 15 min in order to remove oxygen. The stainless steel tubular molds (100 mm × 8 mm i.d.) were sealed at one end with rubber septa fitted over a piece of polyethylene film, filled with the mixture, then sealed on the other end, and placed in a vertical position into a water bath. The polymerization was allowed to proceed for 24 h at 55−80 °C.[10] The seals were removed, the tube was provided with fittings, attached to the high-pressure pump, and 25 mL tetrahydrofuran was pumped through the column at a flow rate of 0.1−1 mL/min depending on the flow resistance of the rod to remove the porogenic solvents and any other soluble compounds that remained in the polymer rod after the polymerization was completed. After all of the in situ hydrodynamic and chromatographic measurements were completed, the polymer was forced out of the steel tube by applying a pressure of THF using the pump and dried prior to porosity studies.

Porous Properties in Dry State. The porous properties of the monoliths were determined by mercury intrusion porosimetry and the specific surface areas calculated from nitrogen adsorption/desorption isotherms using a custom-made combined BET sorptometer and mercury porosimeter (Porous Materials, Inc., Ithaca, NY). Prior to the measurements, the materials were cut into small pieces using a razor blade.

Chromatographic and Hydrodynamic Measurements. Inverse size-exclusion chromatography was carried out using a Nicolet IBM LC 9560 ternary gradient liquid chromatograph equipped with a Hewlett-Packard 1050 UV detector. The peaks of toluene, *o*-terphenyl, and polystyrene standards with molecular weights ranging from 1 250 to 2 950 000 were monitored in tetrahydrofuran as the mobile phase at 254 nm. Before and after these measurements, the outlet capillary was removed from the bottom fitting of the tube and the back pressure produced by a flow of tetrahydrofuran through the material was recorded.

Results and Discussion

The use of porous monolithic materials for applications such as dead-end filtration, membrane chromatography, and HPLC in which a liquid or gas have to flow through the medium requires that the flow be achieved at a reasonably low pressure. Because the pressure depends on the porous properties of the material, the pore size distribution of the monolith should be adjusted to match each of the applications. Typically, the material must contain a sufficient volume of large channels with a diameter of about 1 μm, and, for some of the applications, additional diffusive pores smaller than 100 nm. The key variables that allow the control of the pore size[5] are the polymerization temperature, the composition of porogenic solvent, and the percentage of cross-linking monomer.

Effect of Polymerization Temperature. Recently, we have formulated general guidelines for use of temperature in the control of pore sizes within macroporous polymers.[5] As a rule, the higher the polymerization temperature, the smaller the pores. We have now found this to be true for both the poly(styrene-*co*-divinylbenzene) and the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monoliths prepared in tubular molds. Indeed our findings summarized in Figure 1 confirm that adjustments in the polymerization temperature

---

(6) Afeyan, N. B.; Gordon, N. F.; Mazsaroff, I.; Varady, L.; Fulton, S. P.; Yang, Y. B.; Regnier, F. E. *J. Chromatogr.* **1990**, *519*, 1. Afeyan, N. B.; Fulton, S. P.; Regnier, F. E. *J. Chromatogr.* **1991**, *544*, 267. Fulton, S. P.; Afeyan, N. B.; Regnier, F. E. *J. Chromatogr.* **1991**, *547*, 452.

(7) Liapis, A. I. *Math. Modeling Sci. Comput.* **1993**, *1*, 397. Rodrigues, A. E.; Lu, Z. P.; Loureiro, J. M.; Carta, G. *J. Chromatogr.* **1993**, *653*, 93. Liapis, A. I.; McCoy, M. A. *J. Chromatogr.* **1994**, *660*, 85.

(8) Fréchet, J. M. J. *Makromol. Chem., Makromol. Symp.* **1993**, *70/71*, 289. Wang, Q. C.; Svec, F.; Fréchet, J. M. J. *J. Chromatogr.* **1994**, *669*, 230. Wang, Q. C.; Svec, F.; Fréchet, J. M. J. *Anal. Chem.* **1993**, *65*, 2243. Svec, F.; Fréchet, J. M. J. *J. Chromatogr. A* **1995**, *702*, 89. Tennikova, T. B.; Svec, F. *J. Chromatogr.* **1993**, *646*, 279.

(9) Matsui, J.; Kato, T.; Takeuchi; T., Suzuki, M.; Yokoyama, K.; Tamyia, E.; Karube, I. *Anal. Chem.* **1993**, *65*, 2223. Sellergren, B. *Anal. Chem.* **1994**, *66*, 1578. Sellergren, B. *J. Chromatogr. A* **1994**, *673*, 133. Nilsson, K.; Lindel, J.; Norrlow, O.; Sellergren, B. *J. Chromatogr. A* **1994**, *680*, 57.

(10) The time required for heating the polymerization mixture in the 8 mm tubular molds to the reaction temperature is assumed to be much shorter than the polymerization time[5] and is not considered to affect the properties of the final monolith.

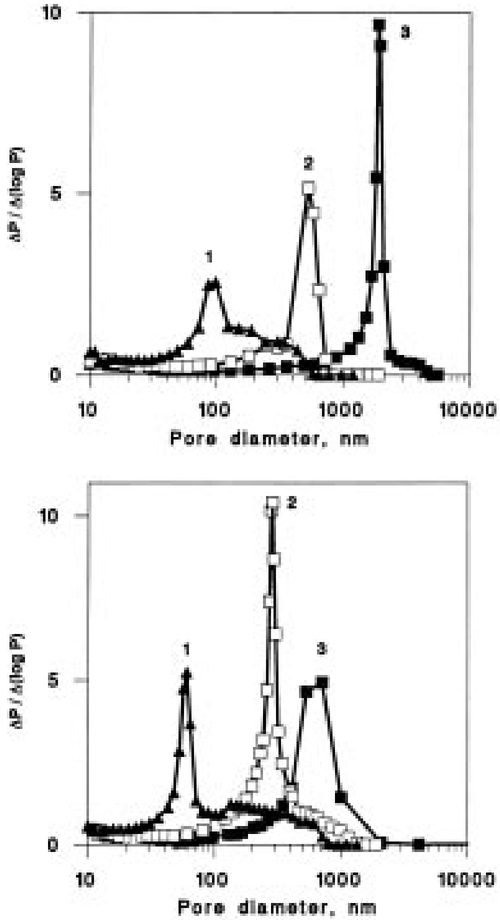

Figure 1. Differential pore size distribution curves of molded poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) and poly(styrene-*co*-divinylbenzene) monoliths polymerized at different temperatures. Conditions: Polymerization time 24 h. (a, top) Polymerization mixture glycidyl methacrylate 24%, ethylene dimethacrylate 16%, cyclohexanol 54%, dodecanol 6%, temperature 80 (1), 70 (2), and 55 °C (3). (b, bottom) Polymerization mixture styrene 20%, divinylbenzene 20%, dodecanol 40%, toluene 20%, temperature 80 (1), 70 (2), and 60 °C (3).

alone may be used to shift the maximum of the pore size distribution profile (modal pore diameter) within a range of 2 orders of magnitude. Tables 1 and 2 show that this shift is accompanied by changes in the volume fraction of the smaller pores, and, consequently, changes in specific surface areas. Obviously, a larger volume fraction of smaller pores translates into a higher overall surface area for the porous material.

The effect of temperature can be readily explained in terms of the nucleation rate. The free-radical initiator decomposes at a particular temperature and the resulting radicals initiate a polymerization in solution. However, the polymers that are formed soon become insoluble and precipitate in the reaction medium as a result of both their cross-linking and the choice of porogen, which is typically a poor solvent for the polymer. Precipitation leads to the formation of nuclei which grow to the size of globules as the polymerization proceeds further. The globules and their clusters constitute the elemental morphological units of the macroporous polymer. Because higher reaction temperatures lead to the formation of a larger number of free radicals by decomposition of the initiator, a larger number of growing nuclei and globules are formed. Since the volume of monomer used is the same for each polymerization, the formation of a larger number of globules is compensated by their smaller size. Because macroporous materials are composed of arrays of interconnected globules, smaller voids, or pores, are obtained if the globules are smaller and more numerous. Therefore, the shift in pore size distribution induced by changes in the polymerization temperature can be accounted for by the difference in the *number of nuclei* that result from such changes.

Temperature also affects the solvent quality, or solvency, that controls the phase separation of polymers from solution. With the exception of polymers with a lower critical solution temperature, the mixing of a polymer with a solvent is an endothermic process, and therefore an increase in temperature promotes dissolution of the polymer. Therefore, the phase separation required for the formation of a macroporous structure is likely to occur when the nuclei reach a higher molecular weight if the polymerization is run at a higher temperature. As a result, both the nuclei and the voids between them would be larger. Since this is actually not the case and indeed the opposite effect of temperature on pore size is observed, changes in the thermodynamic quality of the solvent resulting from temperature increases seem to be of no consequence to the pore formation process.

If a very poor solvent such as dodecanol is used for the polymerization of styrene and divinylbenzene, the temperature effect is suppressed by the even larger effect of porogen on the phase separation that occurs during polymerization (vide infra). As a result, for polymerizations in which dodecanol is the sole porogen, the size of large through pores increases as the temperature is raised in the range 60−80 °C. This finding does not apply to polymerizations done in mixtures of dodecanol and toluene (a very good solvent) for which the pore size is again controlled by the nucleation rate and decreases as the temperature increases (Table 2).

Effect of Composition of Porogenic Solvent. Phase separation of cross-linked nuclei is a prerequisite for the formation of the macroporous morphology. The polymer phase separates from the solution during polymerization because of its limited solubility in the polymerization mixture that results either, or both, from a molecular weight that exceeds the solubility limit of the polymer in the given solvent system or from insolubility derived from cross-linking.

The effect of the thermodynamic quality of the porogenic solvent system on the properties of the porous polymers can be documented for both monomer pairs studied.

Table 1 shows that porous polymers prepared from a cyclohexanol−dodecanol mixture with a higher content of dodecanol have larger pores. This results from phase separation (nucleation) occurring earlier in the system that contains more dodecanol because it is a more potent precipitant for poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) than cyclohexanol. Table 1 also shows that the effect of dodecanol is smaller for a polymerization done at 55 °C since the polymerization rate at this temperature is so slow that the pore size is always large. In contrast, the effect of dodecanol is clearly dominant at temperatures of 70−80 °C. For example, Figure 2a shows that the mode (pore diameter at the highest peak) of the pore size distribution curve for

Table 1. Porous Properties of the Molded Poly(glycidyl methacrylate-*co*-ethylene dimethacrylate)[a]

dodecanol,[b] vol %	EDMA,[b] vol %	temp, °C	pore vol,[c] %				V_p,[d] mL/g	$D_{p,mode}$,[e] nm	$D_{p,mean}$,[f] nm	S_g,[g] m^2/g
			<50	−500	−1000	>1000				
0	16	55	16.4	18.7	19.0	45.9	1.49	1250	1010	17.0
3	16	55	11.3	8.5	9.3	70.9	1.41	1930	1700	7.9
6	16	55	13.3	12.7	9.0	65.0	1.40	1900	1690	12.2
15	16	55	10.0	9.4	14.6	66.0	1.46	1840	1540	7.9
0	16	70	23.3	76.0	0	0.7	1.46	150	120	43.2
3	16	70	30.4	68.9	0	0.7	1.57	260	150	21.7
6	16	70	17.4	56.0	25.7	0.9	1.61	480	470	19.3
15	16	70	5.1	4.8	5.5	84.6	1.39	2570	2490	6.0
0	16	80	35.6	60.0	3.8	0.6	1.29	80	90	68.1
3	16	80	40.3	59.1	0	0.7	1.55	60	70	58.1
6	16	80	27.0	71.7	0.4	0.9	1.59	100	100	54.2
15	16	80	12.1	7.7	7.3	72.9	1.89	1330	1440	23.6
6	16	55	13.3	12.7	9.0	65.1	1.40	1900	1690	12.2
6	24	55	27.5	23.0	48.6	0.9	1.85	860	540	24.0

[a] Reaction conditions: polymerization mixture: monomers (glycidyl methacrylate + ethylene dimethacrylate) 40%, porogenic solvent (cyclohexanol + dodecanol) 60%. [b] Percentage of dodecanol and ethylene dimethacrylate in the polymerization mixture, respectively. [c] Percentage of pore volume in the range less than 50, 50−500, 500−1000, and over 1000 nm. [d] Total pore volume. [e] Pore diameter at the highest peak in the pore size distribution profile. [f] Mean pore diameter. [g] Specific surface area.

Table 2. Porous Properties of the Molded Macroporous Poly(styrene-*co*-divinylbenzene)[a]

toluene,[b] vol %	DVB,[b] vol %	temp, °C	pore vol,[c] %				V_p,[d] mL/g	$D_{p,mode}$,[e] nm	$D_{p,mean}$,[f] nm	S_g,[g] m^2/g
			<50	−500	−1000	>1000				
0	20	60	14.2	4.0	2.4	79.4	2.34	5660	4830	8.6
10	20	60	8.7	1.9	3.7	85.7	1.81	4370	6790	8.4
15	20	60	12.1	11.1	14.7	62.1	1.86	1750	1540	14.4
20	20	60	9.9	27.4	60.0	2.7	2.23	680	600	48.4
0	20	70	10.1	2.9	2.1	84.9	1.79	7090	5660	12.0
10	20	70	11.7	2.2	1.0	85.1	1.83	7355	7365	8.4
15	20	70	9.7	8.4	21.7	60.2	2.12	1250	1160	14.5
20	20	70	12.7	76.6	9.9	0.8	2.18	290	270	54.7
0	20	80	9.4	2.6	0	88.0	2.11	9590	8030	9.1
10	20	80	20.6	17.2	17.8	44.4	2.22	1070	950	19.1
15	20	80	12.0	78.2	8.3	1.5	2.21	180	180	82.0
20	20	80	28.3	67.1	4.2	0.5	2.01	60	70	160.5
15	20	70	9.7	8.4	21.7	60.2	2.12	1250	1160	14.5
15	28	70	4.6	42.4	52.7	0.3	2.02	540	550	30.4

[a] Reaction conditions: polymerization mixture: monomers (styrene + divinylbenzene) 40%, porogenic solvent (dodecanol + toluene) 60%. [b] Percentage of toluene and divinylbenzene in the polymerization mixture, respectively. [c] Percentage of pore volume in the range less than 50, 50−500, 500−1000, and over 1000 nm. [d] Total pore volume. [e] Pore diameter at the highest peak in the pore size distribution profile. [f] Mean pore diameter. [g] Specific surface area.

monoliths polymerized at a temperature of 70 °C decreases from 2570 nm to 480, 260, and 150 nm for mixtures that contains 15, 10, 5, and 0 vol % dodecanol, respectively.

Dodecanol is also a poor solvent for poly(styrene-*co*-divinylbenzene) while toluene is an excellent solvent. Table 2 shows that the addition of even a relatively small percentage of toluene to the polymerization mixture results in a dramatic decrease in pore sizes. Figure 2b shows an example of actual pore size distribution profiles.

The effect of adding a better solvent to shift the distribution toward smaller pore sizes can be readily explained by considering that phase separation occurs in the later stages of polymerization where cross-linking dominates the phase-separation process. The addition of a poorer solvent to the polymerizing system results in an earlier phase separation of the polymer. The new phase swells with the monomers because these are thermodynamically much better solvents for the polymer than the porogenic solvent. As a result of this preferential swelling, the local concentration of monomers in the swollen gel nuclei is higher than that in the surrounding solution and the polymerization reaction proceeds mainly in these swollen nuclei rather than in the solution. Those newly formed nuclei obtained in the solution are likely to be adsorbed by the large preglobules formed earlier by coalescence of many nuclei and further increase their size. Overall, the globules that are formed in such a system are larger and, consequently, the voids between them (pores) are larger as well. As the solvent quality improves, the good solvent competes with monomers in the solvation of nuclei, the local monomer concentration is lower and the globules are smaller. As a result, porous polymers formed in more solvating solvents have smaller pores.[1,5] Obviously, the porogenic solvent controls the porous properties of the monolith through the *solvation of the polymer chains in the reaction medium* during the early stages of the polymerization.

Effect of Cross-Linking Monomer. In contrast to the effects of temperature and porogenic solvent that affect the porous properties of the resulting material but not its composition, variations in the monovinyl/divinyl monomer ratio not only induce the formation of different porous structures but also lead to materials with different compositions. A higher content of divinyl monomer directly translates into the formation of more highly cross-linked polymers in the early stages of the polymerization process and therefore lead to earlier phase separation. Although this is similar to the effect of poor solvent, the nuclei are more cross-linked and because

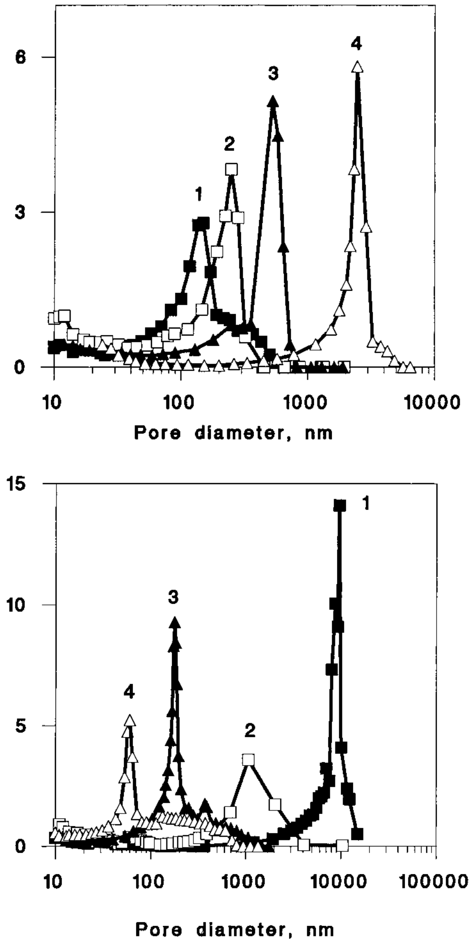

Figure 2. Effect of dodecanol (a, top) and toluene (b, bottom) in the porogenic solvent on differential pore size distribution curves of molded poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) and poly(styrene-*co*-divinylbenzene) monoliths. Conditions: polymerization time 24 h; (a) polymerization mixture: temperature 70 °C, glycidyl methacrylate 24%, ethylene dimethacrylate 16%, cyclohexanol and dodecanol contents in mixtures 60 + 0 (1), 57 + 3 (2), 54 + 6 (3), and 45 + 15% (4). (b) Polymerization mixture: temperature 80 °C, styrene 20%, divinylbenzene 20%, dodecanol and toluene contents in mixtures 60 + 0 (1), 50 + 10 (2), 45 + 15 (3), and 40 + 20% (4).

this affects their swelling with the monomers, they remain relatively small in size. The preglobules can still capture the nuclei generated during the later stages of polymerization, but true coalescence does not occur. Since the final macroporous structure that results consists of smaller globules, it also has smaller voids. Experiments with monomer mixtures containing 40% and 60% ethylene dimethacrylate and 50% and 70% divinylbenzene shown in Tables 1 and 2 clearly document the shift in the pore size distributions toward smaller pore sizes as the percentage of cross-linker is increased. The experimental results imply that, in this case, the pore size distribution is controlled by the *swelling of cross-linked nuclei*.

Because this approach to the control of the porous structure is accompanied by changes in polymer composition, it may not be suitable for some applications in which the highest possible content of a functionalized monovinyl monomer and a large surface area are desirable.

Characterization of Smaller Pores. Many applications of porous materials such as catalysis, adsorption, ion exchange, chromatography, solid-phase synthesis, etc., require contact with a surface that supports the active sites. To obtain a large surface area, a large number of smaller pores should be incorporated into the polymer. The most substantial contributions to the overall surface area comes from the micropores with diameters smaller than 2 nm followed by the mesopores ranging from 2 to 50 nm. Large macropores with diameters over 50 nm make only an insignificant contribution to surface area. However, in order to achieve interaction with as many active sites as possible, the pores must also have a size that allows their penetration by a variety of compounds. While small molecules might penetrate even some of the larger micropores, linear macromolecules with a molecular weight exceeding 10^4 are totally excluded and can reach only mesopores and macropores. Because the surface area of the macropores is insignificant, the mesopores constitute the most important part of the entire porous structure for applications involving large molecules.

The porosity data presented in Tables 1 and 2 and the pore size distribution profiles shown in Figures 1 and 2 were obtained by means of mercury intrusion porosimetry. This technique is well suited for the determination of large pores, but its accuracy for the measurement of small pores is limited due to the compressibility of the polymeric matrix itself. Therefore, inverse size exclusion chromatography (ISEC)[11] is often used for the determination of pores smaller than about 50 nm. The concept of ISEC is based on the measurement of pore volumes that are accessible to polymer standards of well-defined molecular sizes. For example, narrow polystyrene standards with molecular weights of 9 000 and 2 950 000 in tetrahydrofuran solution have hydrodynamic diameters of 1.3 and 40.7 nm, respectively. Such polymers can penetrate only into pores that are larger than their hydrodynamic volume. Because ISEC measurements are carried out with porous polymers immersed in a liquid, this measurement is particularly well-suited to predict the accessibility of sites to external reagents in solution. Figure 3 shows the calibration curves obtained by ISEC for different molded monoliths. As expected, polymers with very large pores do not exhibit any difference in retention of the polystyrene standards within a broad range of molecular weights. In other words, all of the standards can gain access the same volume of pores without any noticeable separation thus indicating the absence of mesopores. This is in good agreement with the mercury porosimetry data. In contrast, the monoliths for which mercury porosimetry shows a pore-size distribution profile including a larger proportion of smaller pores exhibit differences in the retentions of the various polymer standards.

Flow Resistance. Application of the porous monoliths in chromatography, solid-phase chemistry, or catalysis requires that a liquid be able to flow through the pores. As a result, resistance to flow is an important issue and the pressure needed to drive the liquid through the molded monolith should be as low as

---

(11) In contrast to standard size-exclusion chromatography (SEC) which is typically used for the determination of the molecular weight distribution of an unknown polymer, inverse SEC (ISEC) uses well-defined narrow polymer standards for the characterization of the pore-size distribution of porous polymer materials (Knox, J. H.; Scott, H. P. *J. Chromatogr.* **1984**, *316*, 311. Freeman, D. H.; Poinescu, I. C. *Anal. Chem.* **1977**, *49*, 1183).

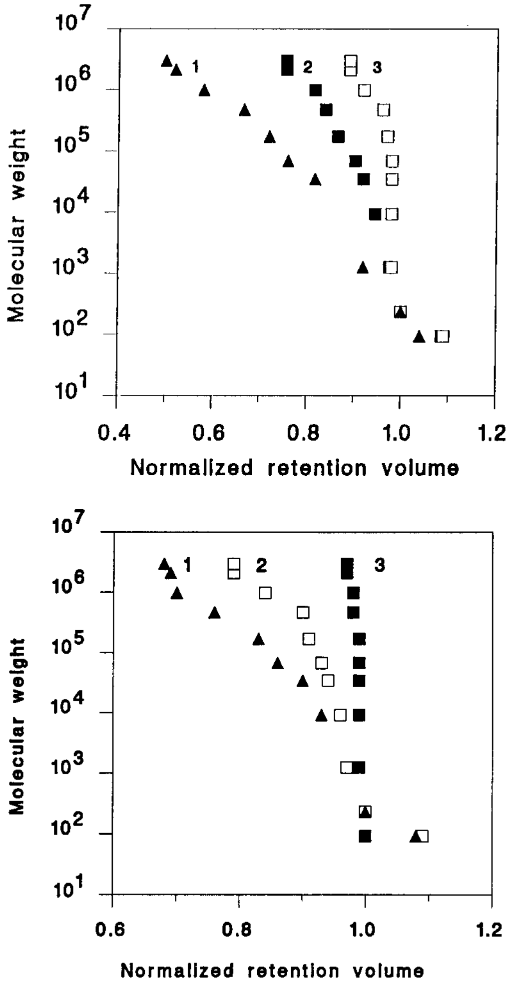

Figure 3. Inverse size exclusion chromatography calibration curve of the molded poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) and poly(styrene-*co*-divinylbenzene) 100 mm x 8 mm monoliths. Conditions: flow rate 0.5 mL/min; mobile phase tetrahydrofuran; UV detection at 254 nm. (a, top) Polymerization mixture glycidyl methacrylate 24%, ethylene dimethacrylate 16%, cyclohexanol and dodecanol contents in mixtures 57 + 3%, respectively (1), 54 + 6 (2), and 45 + 15% (3), temperature 70 °C. (b, bottom) Polymerization mixture styrene 20%, divinylbenzene 20%, dodecanol 45%, toluene 15%, temperature 80 (1), 70 (2), and 60 °C (3).

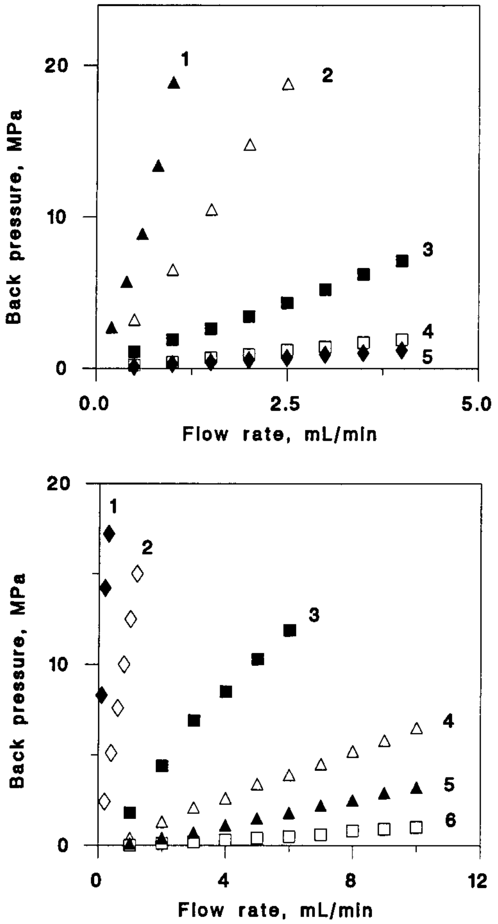

Figure 4. Effect of flow velocity on back pressure in the molded poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) and poly(styrene-*co*-divinylbenzene) 100 mm × 8 mm monoliths. Conditions: mobile-phase tetrahydrofuran. (a, top) Polymerization mixture: glycidyl methacrylate 24%, ethylene dimethacrylate 16%, cyclohexanol and dodecanol contents in mixtures 54 + 6%, respectively; temperature 80 °C (1), 54 + 6, 70 °C (2), 54 + 6, 55 °C (3), 57 + 3, 55 °C, and 45 + 15% 70 °C (5). (b, bottom) Polymerization mixture: styrene 20%, divinylbenzene 20%, dodecanol and toluene contents in mixtures 40 + 20%, respectively, temperature 80 °C (1), 40 + 20, 70 °C (2), 45 + 15, 80 °C (3), 45 + 15, 60 °C (4), 50 + 10, 70 °C (2), and 60 + 0%, 70 °C.

possible. Obviously, this can be achieved with materials that have a high content of large pores. However, as discussed earlier, the same applications may also require a large surface area and therefore a compromise has to be found for the seemingly contradictory requirements of low flow resistance and high surface area.

Figure 4 shows the effect of flow rate through cylindrical rods of the molded porous polymers prepared under different conditions. Typically, the pressure needed to sustain even a very modest flow rate is quite high for materials that have mean pore diameter of less than about 500 nm, while high flow rates can be achieved at low pressures with materials that have pores larger than 1000 nm.

According to the Hagen–Poiseuille law, the average laminar flow velocity, v, through a tube of radius r and length L is[12]

$$v = \Delta P r^2 / 8\eta L \tag{1}$$

where ΔP is the pressure drop along the liquid path and η is the viscosity of the liquid. After rearranging this equation to:

$$\Delta P / v = 8\eta L / r^2 \tag{2}$$

which shows that the pressure drop per unit of flow rate increases exponentially with decreasing tube diameter. This function is linear in its logarithmic form:

$$\log(\Delta P / v) = C - 2 \log r \tag{3}$$

where $C = \log(8\eta L)$. Figure 5 shows the back pressure per unit of flow rate (the slope of the back pressure vs flow rate) as a function of pore diameter at the highest peak of the pore size distribution profile (mode). The graph is a straight line as predicted by eq 3. A single curve can fit the experimental points obtained for both types of materials studied, because the mold geometry is identical for all of the materials tested and, as expected, the flow does not depend on the chemistry of the material itself. The dotted line, also shown in

---

(12) Bird, R. B.; Steward, W. E.; Lightfoot, E. N. *Transport Phenomena*; J. Wiley: New York, 1960.

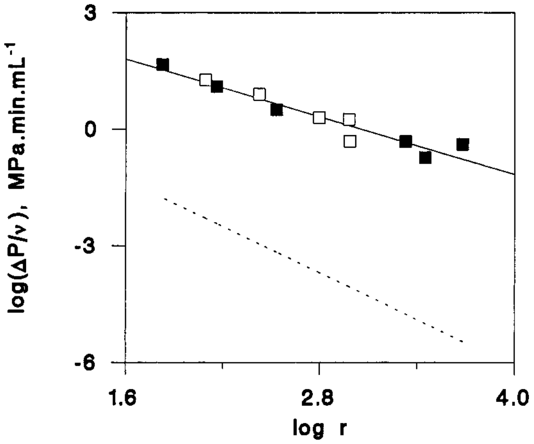

Figure 5. Flow resistance (back pressure per unit of flow rate) of the molded poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) (open points) and poly(styrene-*co*-divinylbenzene) (closed points) 100 mm × 8 mm monoliths as a function of pore diameter at the mode of pore size distribution curve (full line) and flow resistance calculated from Hagen−Poiseuille equation (dotted line).

Figure 5, was calculated from experimental pore radii using the eq 2. Both the experimental and the calculated lines have similar slopes of 2.00 and 1.24, respectively. This suggests that the linear function essentially also holds true for the flow through the molded monoliths. The shift toward higher back pressure for the molded materials reflects the substantial difference between the shape of the pores within the monoliths and the shape of a tube.

Conclusion

Our experimental data obtained for polymerizations of the monomer pairs styrene−divinylbenzene and glycidyl methacrylate−ethylene dimethacrylate show that it is possible to control accurately the porous properties of molded macroporous materials within a very broad range. This is achieved by changing the reaction temperature, the composition of pore-forming solvent, or the content of divinyl monomer in the polymerization mixture. The polymerization temperature is the most convenient variable to adjust the pore-size distribution because it does not require any change in the composition of the reaction mixture. A higher content of a poor solvent such as dodecanol used as porogen leads to monolithic materials that have larger pores while an increase in the content of cross-linking monomer results in a decrease in pore size. All of these variables represent very important tools for the engineering of molded macroporous materials that contain large pores and are therefore easily permeable. Under extreme conditions, such as very low polymerization temperature or very poor porogenic solvent, a synergistic combination of different effects can lead to products with properties different from those that would be expected from a simple extrapolation of the effect of a single variable.

Inverse size-exclusion chromatography data correlates well with results obtained from mercury intrusion porosimetry. Materials that do not contain small pores cannot separate polystyrene standards and are therefore characterized by very steep SEC calibration curves. These macroporous polymers are well suited for flow-through systems since they are permeable to liquids even at high flow rates. In contrast, monoliths that separate the polymer standards and provide a calibration curve typical of SEC stationary phases do not contain sufficiently large pores to allow flow through at very low back pressures. A correlation between pore size and flow resistance can be made using the Hagen−Poiseuille law originally derived for flow through a tube.

Acknowledgment. Support of this research by a grant of the National Institute of Health (GM 48364-03) is gratefully acknowledged. This work also made use of MRL Central Facilities supported by the National Science Foundation under Award No. DMR-9121654. Thanks are also due to University of Umeå, Sweden for partial support of C.V. during her stay at Cornell University and Dow Chemical for a gift of high-grade divinylbenzene.

CM950437J