Kinetic Control of Pore Formation in Macroporous Polymers. Formation of "Molded" Porous Materials with High Flow Characteristics for Separations or Catalysis

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The preparation of large macroporous polymer objects with controlled macroporous structures can be carried out in an unstirred mold through careful control of the polymerization kinetics. The polymerization is carried out in a mold using a mixture of monomers, porogenic solvent and free-radical initiator under conditions that afford macroporous objects with extremely large channels that provide for the high flow characteristics required for applications in separation or catalysis. In contrast, bead polymers prepared from identical polymerization mixtures but in a suspension polymerization process do not exhibit the same type of macroporous structure with large flow-through channels. The main differences between the two processes are the lack of interfacial tension between aqueous and organic phases and the absence of dynamic forces resulting from stirring in the case of the polymerization in an unstirred mold. Control of the kinetics of the overall process through changes in reaction time, temperature, and overall composition allows the fine tuning of the macroporous structure and provides an understanding of the mechanism of large pore formation within the unstirred mold. For example, a decrease in the reaction temperature that slows down the rate of polymerization and the use of shorter reaction times than required for complete monomer conversion lead to porous objects with larger flow through channels.

Introduction

Macroporous polymers are characterized by their rigid porous matrix that persists even in the dry state. These polymers are typically produced as spherical beads by a suspension polymerization process using a polymerization mixture that contains both a cross-linking monomer and an inert diluent, the porogen. Porogens can be solvating or nonsolvating solvents for the polymer that is formed, or soluble non-cross-linked polymers or mixtures of polymers and solvents. The mechanism of pore formation as well as the properties of macroporous polymers and their applications have been reviewed several times.[1−3]

The size distribution of pores within a porous polymer may cover a broad range from a few nanometers to several hundred nanometers. Pores with a diameter of less than 2 nm are classified as micropores, pores ranging from 2 to 50 nm are mesopores, while pores over 50 nm are macropores. The larger the pores, the smaller the surface area. Therefore, porous polymers with very large pores have relatively low specific surface areas, typically much less than 10 m^2/g.

The morphology of macroporous polymers is rather complex.[1,2,4−6] They consist of interconnected microspheres (globules) that are partly aggregated in larger clusters that form the body of the beads. The size of the spherical globules that form the bulk of the macroporous polymer ranges from 10 to 50 nm. The pores in the macroporous polymer actually consist of the irregular voids located between clusters of the globules (macropores), or between the globules of a given cluster (mesopores), or even within the globules themselves (micropores). The pore size distribution reflects the internal organization of both the globules and their clusters within the macroporous polymer and largely depends on the composition of the polymerization mixture and the reaction conditions. The most effective variables that control pore size distribution are the percentage of cross-linking monomer, the type and amount of porogen, the concentration of the free-radical initiator in the polymerization mixture, and the reaction temperature.[2]

In analogy to conventional sieving processes, the use of polymers with large pores is advantageous in promoting rapid mass transfer through a porous polymer. In chromatography this may be beneficial[7−11] for a variety of preparative as well as analytical applications. In catalysis, convection through a catalyst that has very large pores increases the catalyst effectiveness factor,[12] and large pore supports are therefore used in numerous

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(1) Seidl, J.; Malinsky, J.; Dusek, K.; Heitz, W. *Adv. Polym. Sci.* **1967**, *5*, 113.
(2) Guyot, A.; Bartholin, M. *Prog. Polym. Sci.* **1982**, *8*, 277.
(3) Hodge, P.; Sherrington, D. C., Eds. *Syntheses and Separations Using Functional Polymers*; Wiley: New York, 1989.
(4) Kun, K. A.; Kunin, R. *J. Polym. Sci., A1* **1968**, *6*, 2689.
(5) Pelzbauer, Z.; Lukas, J.; Svec, F.; Kalal, J. *J. Chromatogr.* **1979**, *171*, 101.
(7) Afeyan, N. B.; Gordon, N. F.; Maszaroff, I.; Varady, L.; Fulton, S. P.; Yang, Y. B.; Regnier, F. E. *J. Chromatogr.* **1990**, *519*, 1.
(8) Tennikova, T. B.; Bleha, M., Svec, F.; Almazova, T. V.; Belenkii, B. G. *J. Chromatogr.* **1991**, *555*, 97.
(9) Svec, F.; Fréchet, J. M. J. *Anal. Chem.* **1992**, *64*, 820.
(10) Wang, Q. C.; Svec, F.; Fréchet, J. M. J. *Anal. Chem.* **1993**, *65*, 2243.
(11) Fréchet, J. M. J. *Makromol. Chem., Makromol. Symp.* **70/71**,

catalytic processes.[13] Other areas of application of very large pore materials include supports for the growth of mammalian cell cultures[14] and the production of biomass.[15]

Two approaches are most frequently used for the preparation of porous polymers with very large pores: (i) Polymerization of a mixture containing a large volume fraction of a non-solvating diluent.[16] (ii) Polymerization in the presence of a linear polymer porogen.[4,17,18]

Most of the macroporous polymers prepared to date have been almost exclusively produced in a shape of spherical beads that are used as ion-exchange resins, chromatographic separation media, adsorbents, etc. Therefore, studies of the mechanism of formation of macroporous structures have focused exclusively on materials prepared by suspension polymerization.[1-3] For example, an extensive study[19] of the effects of different variables on the properties of macroporous poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) beads prepared by suspension polymerization has appeared. The average pore size of the copolymers prepared in this study that involved the use of cyclohexanol and dodecanol as porogens ranged from 20 to 150 nm.[19]

In our search for enhanced and simpler chromatographic separation media, we polymerized mixtures containing monomers and porogenic solvents directly within a chromatographic column used as a mold.[9-11] The macroporous material that is obtained contains two very different families of pores:[10] large channels and more conventional diffusive pores. Examination of the unusual pore size distribution curve of a typical poly(styrene-*co*-divinylbenzene) rod shows the existence of a sharp peak at about 1 000 nm and another small peak in a size range corresponding to small mesopores.[10] Rods prepared from poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) also contains similar bimodal pore size distribution including very large pores.[9]

Because the rod columns are essentially a single "molded" polymer monolith traversed by large channels and permeated by small pores, their hydrodynamic properties are excellent and even high flow rates can be used. They are unlike any of the existing porous materials that are typically used in packed beds because flow through the rod column does not involve *any* interstitial space but results entirely from the existence of the large flow-through channels that are built into the porous polymer monolith.

The continuous polymer rod media afford excellent resolution in the chromatographic separation of proteins, peptides, and small molecules.[7,8,20] Recently, our approach has been used for the preparation of continuous rods of molecularly imprinted polymers capable of molecular recognition of positional isomers and enantiomers.[21]

All of these rods were prepared from polymerization mixtures essentially identical to those that are used for the preparation of macroporous beads by suspension polymerization, yet beads prepared in parallel experiments by suspension polymerization do not contain any of the very large micrometer-size pores found in the molded continuous media.[19] This indicates that somewhat different mechanisms of pore formation must operate during the preparation of macroporous rods by our approach and of beads by the standard suspension polymerization technique.

This report explores the effects of polymerization conditions on the porous properties of rods prepared by polymerization of a mixture containing glycidyl methacrylate and ethylene dimethacrylate in a steel tube and provides an explanation for the formation of much larger pores during the polymerization in a tube as compared to the porous beads resulting from a suspension polymerization.

Experimental Section

Preparation of Polymers. Polymerization Mixture. Azobisisobutyronitrile (1% of the weight of monomers, Kodak) was dissolved in 4 vol parts of a mixture consisting of 60% glycidyl methacrylate (2-methyl-2-propenoic acid oxiranylmethyl ester, CAS reg. no. 106-91-2, Aldrich) and 40% ethylene dimethacrylate (2-methyl-2-propenoic acid 1,2-ethanediyl ester, CAS reg. no. 97-90-5, Sartomer). Cyclohexanol (Aldrich) was admixed slowly to the monomers followed by the addition of dodecanol (Aldrich); the total volume of the alcohols was 6 parts. The mixture was purged with nitrogen for 15 min. The stock polymerization mixture was stored in a closed flask in a refrigerator at a temperature of 5 °C and consumed within 7 days. Typically, polymerizations were repeated with two different fresh mixtures and with duplicate experiments done for each polymerization mixture.

Suspension Polymerization. The polymerization mixture (4 parts) was added to a 1% aqueous solution of poly(vinylpyrrolidone) (Aldrich) MW 360 000 (6 parts) and deaerated. The polymerization was carried out in a 250 mL glass reactor (Büchi BEP 280) equipped with an anchor stirrer and a heating jacket. The beads were washed with water, extracted in a Soxhlet apparatus with methanol for 24 h and dried at 60 °C.

Polymerization in Bulk Solution. A stainless steel tube (50-mm × 8-mm i.d., Labio) was charged with 2.5 mL of the polymerization mixture then sealed with rubber nut plugs. The polymerization was allowed to proceed in a water thermostat. The tubes either stood vertically in the bath or the contents were subjected to an end-over-end rotation while immersed. After the chosen polymerization time elapsed, the rubber plugs were replaced at one end by the column end fitting and the rod was forced out of the steel tube by applying a pressure of THF using a chromatographic pump. The length of the rod was measured using a ruler. The soluble compounds were removed from the rod by extraction in a Soxhlet apparatus with methanol for 24 h and the rod was dried at 60 °C. The conversion was calculated from the weight of the extracted dry rod.

In a modified procedure, the polymerization mixture was placed in a 5 mL polypropylene syringe barrel, the piston was left in the upper position, and the syringe was submerged in a water bath. Once the polymerization was completed, the end of the barrel was cut off and the rod was pushed out of the plastic tube using the syringe piston.

(13) Rodrigues, A. E.; Lopez, J. C.; Lu, Z. P.; Loureiro, J. M.; Dias, M. M. *J. Chromatogr.* **1992**, *590*, 93.
(14) Vournakis, J.; Ronstadler, P. *Bio/Technology* **1989**, *7*, 143.
(15) Brettenbucher, K.; Siegel, K.; Knupper, A.; Radke, M. *Water Sci. Technol.* **1987**, *5*, 835.
(16) Chung, D. Y.; Bartholin, M.; Guyot, A. *Angew. Makromol. Chem.* **1982**, *103*, 109.
(17) Hilgen, J.; deJong, G. J.; Sederel, W. L. *J. Appl. Polym. Sci.* **1975**, *19*, 2647.
(18) Guyot, A.; Revillon, A.; Yuan, Q. *Polym. Bull.* **1989**, *21*, 577.
(19) Horak, D.; Svec, F.; Ilavsky, M.; Bleha, M.; Baldrian, J.; Kalal, J. *Angew. Makromol. Chem.* **1981**, *95*, 117.

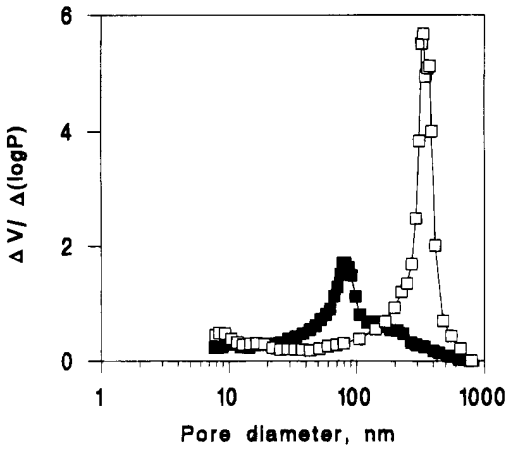

Figure 1. Differential pore size distribution curves of the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) beads (■) and rod (□) prepared at a temperature of 70 °C. For conditions see Table 1.

Porous Properties. Following washing or solvent extraction, the porous properties of the beads or rods 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 rods were cut to small pieces with a razor blade.

Gas Chromatography. Gas chromatographic determinations were carried out in a HP capillary column (crosslinked methylsilane gum, o.d. 0.32 mm, length 25 m, i.d. 0.17 mm, temperature gradient from 100 to 280 °C in 15 min) using a Hewlett-Packard 5890 chromatograph equipped with a HP-76739 automatic autosampler and TCD detector and helium as a carrier gas. The data were collected by a HP-3393 integrator.

Results and Discussion

Suspension polymerization is generally treated in the literature as a variant of bulk polymerization in which each droplet of the dispersed phase containing monomer is an individual bulk reactor.[22] Therefore, one might have anticipated that the properties of the products of both suspension and bulk polymerizations would be nearly identical. As indicated above, this is not the case, and properties such as pore size distribution are actually entirely different. Figure 1 shows the considerable discrepancy that exists between the pore size distributions of macroporous glycidyl methacrylate–ethylene dimethacrylate copolymers prepared by both suspension and the bulklike rod polymerization at 70 °C from an identical polymerization mixture containing 12% dodecanol, 48% cyclohexanol, 24% glycidyl methacrylate, and 16% ethylene dimethacrylate. The median pore size diameter for the beads is 85 nm while for the rod it is 315 nm. In contrast to the median pore diameter, the specific surface areas and the pore volumes do not exhibit such marked differences (Table 1). Since the reaction conditions in both polymerizations were comparable, this unprecedented difference in median pore size diameter has to result from the polymerization technique itself.

While suspension polymerization has already been analyzed in the literature several times,[1,2] little is known on how to control the properties of macroporous polymers obtained by a bulk polymerization within a mold. Therefore, we have studied this type of polymerization more thoroughly and investigated the effect of reaction variables such as composition of the porogenic solvent, reaction time, and reaction temperature on the porous properties of the molded rods. We did not take into consideration two other variables, the concentration of cross-linking agent and the monomers to porogenic solvent ratio.

Table 1. Polymerization Conditions and Properties of the Macroporous Poly(glycidyl methacrylate-*co*-ethylene dimethacrylate)[a]

expt	polymerization	dodecanol,[b] %	temp, °C	V_p,[c] mL/g	S_g,[d] m^2/g	$D_{p,max}$,[e] nm
1	suspension	0	70	1.23	96.0	53
2	suspension	6	70	1.29	173.6	63
3	PP tube	6	70	1.40	128.4	91
4	steel tube	6	70	1.33	137.2	93
5	PP tube	6	55	1.33	62.8	809
6	steel tube	6	55	1.10	65.6	935
7	steel tube	6	50–70[f]	1.33	103.1	214
8	suspension	12	70	1.39	102.8	85
9	PP tube	12	70	1.58	94.2	283
10	steel tube	12	70	1.46	102.7	315
11	PP tube	12	55	1.24	38.7	1530
12	steel tube	12	55	1.18	81.2	1527
13	steel tube	12	50–70[f]	1.50	172.3	1690

[a] Reaction conditions: polymerization mixture: glycidyl methacrylate 24%, ethylene dimethacrylate 16%, porogenic solvent (cyclohexanol + dodecanol) 60% [b] Percentage of dodecanol in the polymerization mixture. [c] Pore volume. [d] Specific surface area. [e] Median pore diameter. [f] Temperature was raised from 50 to 70 °C in steps by 5 °C lasting 1 h each and kept at 70 °C for another 4 h.

On the basis of our experience, we chose a standard composition of monomer mixture including 40% ethylene dimethacrylate and 60% glycidyl methacrylate for all experiments. This composition is deemed ideal because any lower concentration of the cross-linking agent could impair the mechanical properties of the final polymer rods, while a higher one would decrease the content of reactive epoxide groups that are needed for the subsequent functionalization of the rods. The 4:6 monomers/porogenic solvent ratio has already proven to be the most advantageous for the preparation of macroporous poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) materials.[23]

Effect of Polymerization Time. The influence of reaction time on conversion is well demonstrated for all reactions. Since the polymerization at 70 °C proceeds too fast to be monitored readily, we chose a temperature of 55 °C at which the rate of polymerization is low enough to be readily monitored (Figure 2). Although the conversion of monomers to polymer is close to quantitative after about 10 h, some additional structural changes still occur within the rod if the system is kept longer at the polymerization temperature. However, no significant changes are observed at reaction times exceeding 22 h.

The length of the completely polymerized rod prepared under the conditions specified in Table 2 in a tubular mold charged with 2 mL of the polymerization mixture is 35 mm. It would be expected that the length of the rod itself would not depend on the polymerization

Table 2. Porous Properties of Poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) Rods Prepared Using Different Polymerization Times[a]

	mercury porosimetry				BET			
t_{pol},[b] min	V_p,[c] mL/g	S_g,[d] m²/g	$D_{p,med}$,[e] nm	$D_{p,max}$,[f] nm	V_p,[c] mL/g	S_g,[d] m²/g	$D_{p,vol}$,[g] nm	$D_{p,surf}$,[h] nm
60	3.759	217.5	702	618	0.688	523.9	6.33	3.44
75	3.453	149.2	870	811	0.360	317.3	6.53	3.28
100	2.926	136.0	966	996	0.335	283.5	6.37	3.40
130	2.532	127.8	1124	1201	0.296	255.7	6.71	3.29
150	2.347	123.8	1090	1150	0.287	249.1	6.82	3.22
200	1.673	125.0	974	1099	0.239	239.8	6.32	3.28
300	1.312	73.0	966	1128	0.165	149.7	6.22	3.28
600	1.257	79.2	934	1125	0.153	138.0	6.18	3.33
1320	1.093	65.6	935	1154	0.139	120.1	6.78	3.33
1800	1.108	66.0	940	1148	0.140	119.8	6.49	3.29

[a] Reaction conditions: polymerization mixture: glycidyl methacrylate 24%, ethylene dimethacrylate 16%, cyclohexanol 54%, dodecanol 6%; polymerization temperature 55 °C. [b] Polymerization time. [c] Pore volume. [d] Specific surface area. [e] Median pore diameter. [f] Pore diameter at the maximum of the distribution curve. [g] Median pore diameter based on pore volume. [h] Median pore diameter based on surface area.

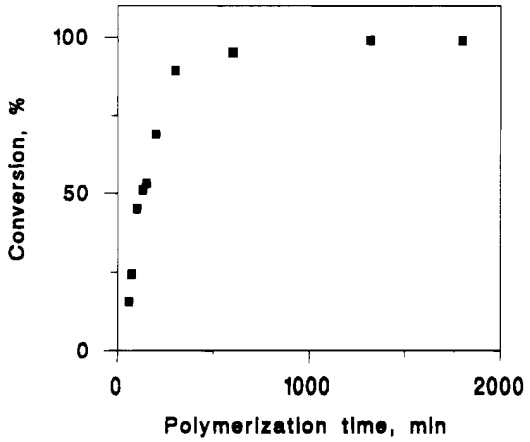

Figure 2. Kinetics of the polymerization of glycidyl methacrylate and ethylene dimethacrylate at a temperature of 55 °C. For conditions see Table 2.

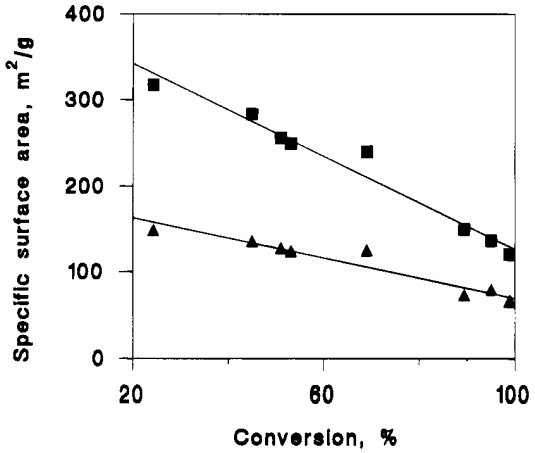

Figure 3. Effect of conversion on the specific surface area determined by BET method (■) and mercury intrusion porosimetry (▲) during the polymerization at a temperature of 55 °C. For conditions see Table 2.

time as the polymerization ought to take place throughout the entire volume of the mixture in the tube. However, this is not the case, and if tubular molds were held vertically during the polymerization reaction, the rods obtained after 60 and 75 min of polymerization were significantly shorter (21 and 25 mm, respectively) and occupied only the bottom part of the mold. The liquid remaining on the top of the rods under these conditions was removed with a syringe and analyzed by gas chromatography. Even after 150 min of polymerization a small amount of the liquid was still found, but this is most likely due to the oxygen inhibition of the polymerization at the surface of the rod because the tube was not completely filled with the polymerization mixture and the residual space can contain some air. The composition of all the liquids collected was generally close to that of the original polymerization mixture. The liquid did not contain any polymeric components as confirmed by the lack of precipitation during dilution of the samples with methanol for GC analysis.

Table 2 summarizes the porous properties of the rods. During the early stage of the polymerization, the pore volume is very high reaching almost 4 mL/g. This represents a porosity of about 82% at the low conversion of 15.7%. The pore volume decreases as the polymerization progresses, eventually reaching a value slightly above 1 mL/g that represents a porosity of about 60%. This porosity is directly related to the volume of the porogenic solvents used for the polymerization and

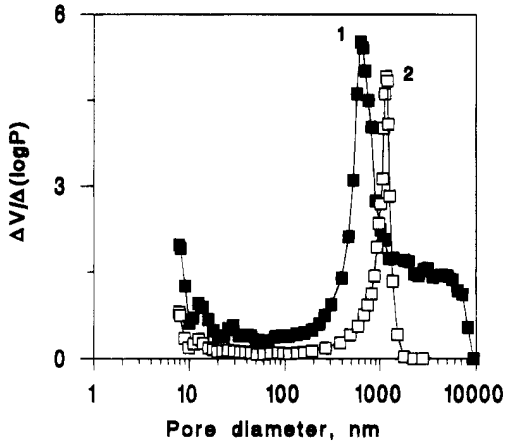

Figure 4. Differential pore size distribution curves of the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) rods after 1 h (■) and 14 h (□) of polymerization at a temperature of 55 °C. For conditions see Table 2.

The specific surface area, calculated from both mercury porosimetry and BET measurements, also decreases with the polymerization time. Figure 3 documents that the specific surface area decreases linearly within the range of conversions from 20 to 100%.

Figure 4 shows the pore size distribution curves for rods formed after 60 and 1320 min, respectively. Although the maximum of curve 1 (corresponding to the

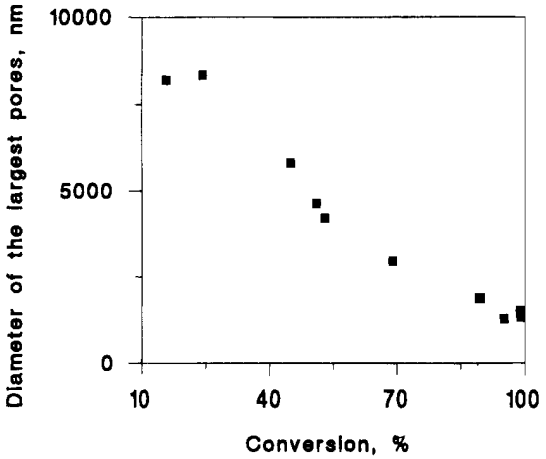

Figure 5. Diameter of the largest detectable pores in the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) rods prepared at a temperature of 55 °C as a function of conversion. For conditions see Table 2.

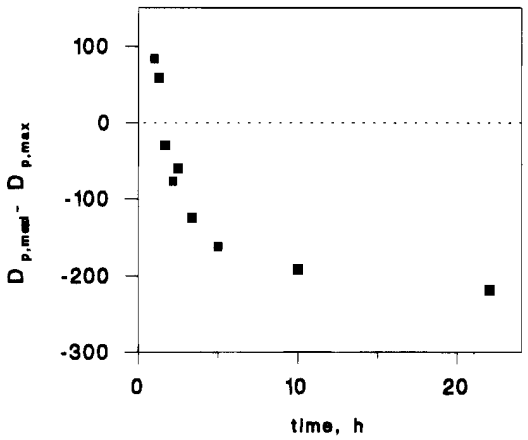

Figure 6. Difference between the calculated median pore diameter $D_{p,med}$ and the pore diameter corresponding to the maximum of the distribution curve $D_{p,max}$ for the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) rods prepared at a temperature of 55 °C as a function of polymerization time. For conditions see Table 2.

nm, the rod also contains a substantial amount of very large pores with diameters up to 10 mm. In contrast, the peak for curve 2 is located at 1154 nm, but it is narrower and without pores over 2 mm in diameter. The almost 4-fold difference in the pore volumes of the two molded rods obtained after 1 and 14 h, respectively, is also reflected in the much larger area beneath curve 1, particularly in the range of large pores. The pore size distribution narrows as the polymerization progresses because the largest pores disappear. Figure 5 shows the size of the largest pores detected by mercury porosimetry at different stages of the polymerization of the rod and documents that their size decrease is a function of the conversion.

Mercury porosimetry measurements provide two kinds of pore diameters: the calculated median pore diameter $D_{p,med}$ and the pore diameter that corresponds to the maximum read from the distribution curve $D_{p,max}$. Figure 6 shows that the difference $D_{p,med} - D_{p,max}$ decreases smoothly within the whole range of conversions. At low conversion, the median size exceeds the peak value. However, this already changes after about

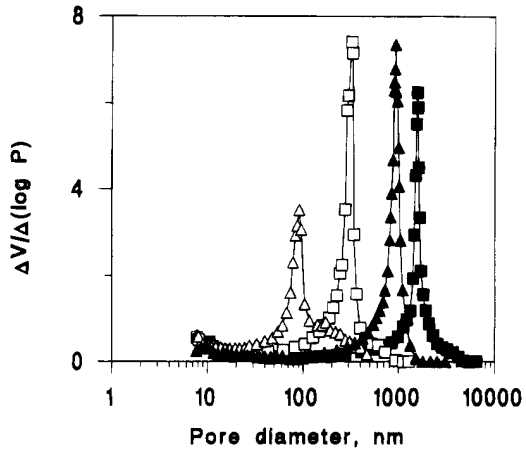

Figure 7. Differential pore size distribution curves of the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) rods prepared from mixtures containing 6% (▲, △) and 12% dodecanol (■, □) by a polymerization at a temperature of 55 °C (closed points) and 70 °C (open points). For general conditions see Experimental Section.

document that the very large pores that are characteristic of rods in the early stages of the polymerization and which contribute considerably to the median pore size, disappear as the polymerization progresses while the influence of the small pores on the average diameter becomes increasingly important. Table 2 shows that the size of the pore diameter $D_{p,max}$ reaches a plateau after about 2 h of polymerization. In contrast, the calculated median pore diameter $D_{p,med}$ initially increases, then reaches a maximum also after about 2 h, and then decreases again continuously.

It should be emphasized that any direct comparison of the BET and mercury porosimetry data would not be appropriate as each method covers a different range of pores. This can be confirmed by the comparison of the pore diameter data summarized in Table 2. While the mercury porosimetry monitors efficiently the significant changes affecting the pore diameters, the BET data do not show any change in the median pore diameters calculated from both pore volumes and surface areas during the polymerization. On the other hand, the surface areas measured by BET involve also the pores smaller than those detected by the mercury intrusion method. Therefore, the BET specific surface areas are about twice as large as those calculated from the mercury intrusion porosimetry. However, Figure 3 shows that the trends in changes of specific surface areas are similar for both the BET and the mercury porosimetry measurements.

Effect of the Porogenic Solvent. It was observed earlier that the addition of dodecanol to cyclohexanol used as the porogenic solvent results in the formation of larger pores in poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) beads.[19] This is also confirmed in this study. The median pore diameter for beads prepared at 70 °C in the presence of 0, 6, and 12% of dodecanol is 53, 63, and 85 nm, respectively (Table 1). Figure 7 shows the shift induced by dodecanol in the maxima of the pore size distribution curves for molded rods prepared at two different temperatures. For example, the median pore size of rods prepared with 6 and 12%

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