Preparation of Large-Diameter "Molded" Porous Polymer Monoliths and the Control of Pore Structure Homogeneity

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The preparation of large cylindrical macroporous polymer monoliths with internal diameters of up to 50 mm has been studied for the first time for both styrenic and methacrylic monomer systems. The temperature profiles at different locations within the mold have been recorded during these polymerizations, and the occurrence of exotherms and temperature gradients was related to the creation of inhomogeneities in the pore structure. Several techniques, such as decreasing the rate of polymerization and a slow gradual addition of the polymerization mixture to the reaction vessel, were investigated in order to minimize the extent of the reaction exotherm. The latter approach proved especially powerful, as the absence of exotherm allowed the preparation of monoliths with homogeneous pore structures inaccessible by other methods for both monomer systems.

Introduction

Macroporous polymers possess fixed porous structures that persist even in the dry state. Discovered in the late 1950s, these materials are produced almost exclusively as spherical particles using a suspension polymerization process and have been commercially used in such applications as ion exchange, chromatographic separation, catalysis, adsorption, etc. The preparation of these spherical particles and the mechanism of pore formation have been extensively investigated.[1−3]

Recently, we have introduced a totally new class of macroporous polymeric materials that are prepared by polymerization within the confines of an unstirred mold.[4,5] The pore structure of the resulting polymer monolith, which is characterized by a bimodal pore-size distribution consisting of both large micrometer-sized and much smaller 10 nm range sized pores, is quite different from that produced when the identical reaction mixture is subjected to a suspension polymerization process.[6] High flow rates of a liquid through these monoliths can be obtained at moderate back pressures due to the network of large canallike pores which traverse the length of the monolith. The increased mass transfer that results from this ability to flow through the monoliths has been used to particular advantage in early test applications such as the chromatography of large molecules[5,7,8] and immobilized enzyme bioreactors.[9]

The flow-through properties of these monoliths can be tailored due to the control that can be exerted over the size of the large convective pores. Specifically, variables such as the polymerization temperature, composition of the porogenic mixture, and level of the divinyl cross-linker allow the tuning of the pore size over a broad range.[10] Temperature is an especially effective means of control, allowing the production of macroporous materials with a broad range of porosity profiles from a single polymerization mixture.[11] Careful control of the polymerization temperature has allowed the production of small size monoliths of different chemistries with pore diameters spanning over 2 orders of magnitude at the mode of the distribution curve.[11]

Although easy to effect on a small scale, the accurate control of the polymerization temperature for larger size monoliths would be expected to be far more problematic. The unstirred nature of the polymerization within the confines of a mold leads to a decreased capacity to effectively dissipate the heat of polymerization. In addition to an overall deviation from the desired polymerization temperature, the exotherm may also vary radially in magnitude across the contents of the mold. In light of the demonstrated effect of the polymerization temperature on the porosity of the resulting polymer,[10] any significant variation in temperature within the mold would be expected to lead to monoliths with heterogeneity in their pore structures. This is the most likely reason all the work reported to date has focused on the development of small size monoliths.

This report explores both the effects of temperature gradients within the polymerization mixture on the heterogeneity of the porous properties of the resulting monolith and methods useful for the control of the evolution of the heat of polymerization (reaction exotherms). It presents the first detailed study of the preparation of large-mold shape-conforming polymer monoliths with homogeneous porous structures from both styrenic and methacrylic monomers.

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Experimental Section

Preparation of Polymers. *Polymerization Mixtures.* Benzoyl peroxide (Aldrich, 1 wt % with respect to monomers) was dissolved in 4 parts of a mixture consisting of 60% glycidyl methacrylate (GMA) and 40% ethylene dimethacrylate (EDMA; both from Sartomer), or 50% styrene (Aldrich) and 50% divinylbenzene (DVB, 80% of divinyl monomer, Dow Chemicals). The porogenic solvents (6 parts total), cyclohexanol for the methacrylic system and a mixture of 75% 1-dodecanol and 25% toluene (all from Aldrich) for the styrenic system, were added slowly to the respective monomer mixtures.

Polymerization in Mold. All polymerizations were performed within the confines of a tubular glass mold 16, 26, or 50 mm in diameter and 200 mm long provided with a heating jacket. The bottom part of the tube was sealed, and the mold brought to the desired polymerization temperature using thermostated water circulated through the jacket. The polymerization mixtures were sparged with nitrogen for 15 min and poured into the thermostated mold. The top of the mold was sealed with a rubber stopper, and the polymerizations were allowed to proceed for 20 h. In some experiments, the polymerization mixture was added gradually to the heated column at a flow rate of 20 mL/h through a polyethylene tube using a syringe pump (Sage Instruments, Model 355).

Temperature Measurements. The temperature profiles were measured by placing K-type thermocouples (Omega) directly into the polymerizing mixtures. For the 26 mm mold, a thermocouple was placed at both the wall and center of the column ("outer" and "center" positions, respectively). A third thermocouple was added in the larger 50 mm mold halfway between the other two ("middle" position). All thermocouples were vertically positioned at approximately half the height of the column. In contrast, all three thermocouples were spaced equidistant from the center of the column at the "middle" position for the gradual addition polymerizations but were placed at heights of 2, 5, and 8 cm from the bottom of the 50 mm mold. Temperatures were recorded from each thermocouple once per minute and logged into a computer spreadsheet using a DAS08 circuit board, EXP16 thermocouple expansion board (both from Computer Boards, Inc., Mansfield, MA), and Labtech Notebook software (Laboratory Technology Corporation, Wilmington, MA).

Porous Properties in the Dry State. The monoliths were removed from the glass molds, and 1 cm portions from both ends were cut and discarded. The remaining length of monolith was cut into radial disks of equal thickness. These disks were further divided into inner and outer portions of approximately equal volume using punches of the appropriate diameter. The samples were cut into smaller pieces using a razor blade, extracted with methanol in a Soxhlet apparatus for 12 h, and vacuum-dried overnight at 40 °C. The porous properties of the samples were determined by mercury intrusion porosimetry using a custom-made combined BET sorptometer and mercury porosimeter (Porous Materials Inc., Ithaca, NY).

Results and Discussion

Standard "Bulk" Polymerization. The perceived difficulties in producing homogeneous materials were quickly confirmed during our initial attempt to prepare a monolith in the 26 mm mold using a typical polymerization mixture with azobisisobutyronitrile initiator (AIBN) at an initial temperature of 55 °C. A violent evolution of gas occurred during the polymerization, leading to a monolith with a badly scarred surface. The exotherm was sufficient to increase substantially the reaction temperature from its relatively low initial level, accelerate the polymerization dramatically, and cause a rapid decomposition of the initiator with a concomitant rapid release of nitrogen gas. The monolith thus prepared was of little use.
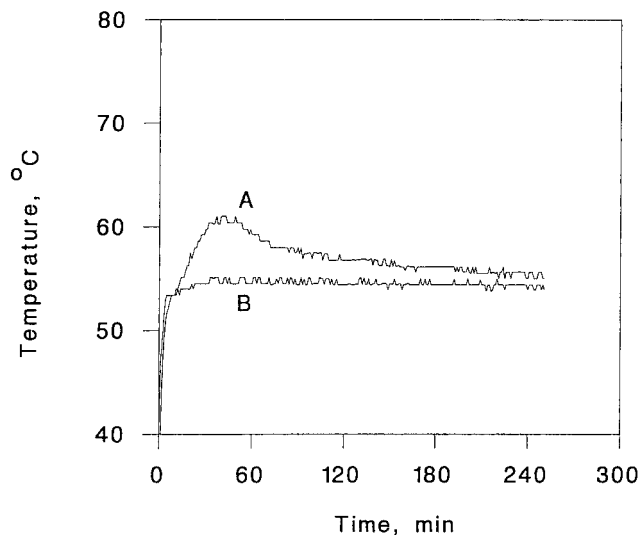
Figure 1. Temperature profile curves measured at the center (A) and outer (B) positions during the batch mode preparation of a poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monolith in the 26 mm mold at a nominal temperature of 55 °C. For conditions see Table 1.

Correlation of Polymerization Rate and Porosity Inhomogeneities. Due to the problem of the rapid autoaccelerated decomposition of the azo initiator, all further experiments were performed using benzoyl peroxide (BPO) as the initiator. BPO is advantageous as it decomposes at higher temperatures and with less gaseous side products than does AIBN. This switch to BPO allowed the close monitoring of exotherms in these larger scale polymerizations, and an evaluation of what effects, if any, they produce in the porosity profiles of the resulting monoliths.
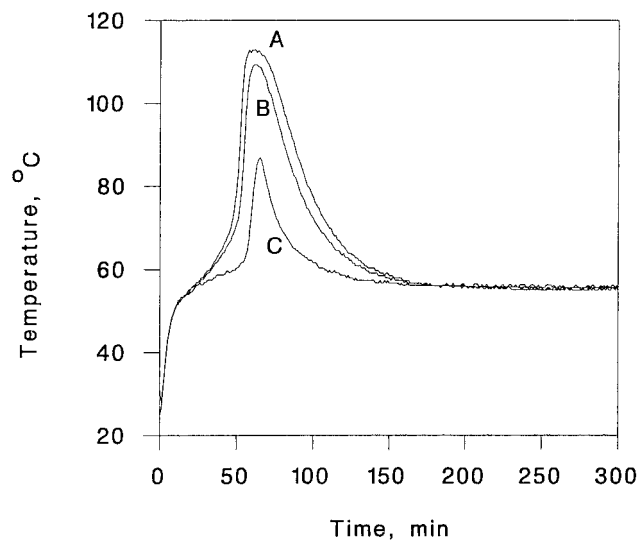
Figure 1 shows the temperature profile for a polymerization performed with BPO in the 26 mm diameter cylindrical mold at 55 °C using the methacrylic monomer system. The increase in temperature is minimal under these conditions, reaching a maximum of 61 °C at the center position and creating a temperature differential of only 7 °C across the radius of the column. As shown by the porosity profile of this material given in Table 1, the absence of a significant exotherm results in a monolith with a homogeneous pore structure both along its length and its width.

By contrast, Figure 2 shows the temperature profile for a polymerization performed under identical conditions in the 50 mm diameter cylindrical mold. Upon doubling the diameter of the mold and thus quadrupling its volume, the polymerization system is no longer able to effectively dissipate the heat of polymerization. As a result, the temperature rises to 113 °C at the center position, and a 25 °C temperature differential is recorded across the radius of the column. As shown in Table 1, these deviations from the desired polymerization temperature are clearly reflected in the radial differences in the porous properties of the resulting monolith. The inner core of the column has larger pores than the outer shell, as evidenced by both its larger mode pore size and the greater percentage of its total porosity originating from pores larger than 1 μm. This trend is different from that observed in the smaller scale columns.[11] However, these small-scale columns were all made in a temperature range lower than that for the observed exotherms. Additional experiments to

Table 1. Porous Properties of the Molded Poly(glycidyl methacrylate-*co*-Ethylene Dimethacrylate)[a] Prepared by Polymerization at 55 °C

sample		V_p,[b]	pore volume,[c] %				$D_{p, mode}$,[d]
position	portion	mL/g	<100	−500	−1000	>1000	μm
			26 mm Mold				
bottom	inner	1.55	13.72	8.52	13.71	64.04	1.50
	outer	1.61	14.02	8.23	12.16	65.63	1.54
middle	inner	1.52	14.39	8.33	12.52	64.75	1.56
	outer	1.63	12.91	8.31	12.54	66.24	1.55
top	inner	1.51	12.88	8.73	12.39	65.99	1.56
	outer	1.61	13.15	8.77	11.64	66.44	1.52
			50 mm Mold				
bottom	inner	1.64	18.98	11.64	9.24	60.14	2.02
	outer	1.45	17.25	14.09	15.56	53.11	1.57
middle	inner	1.60	18.79	12.86	10.40	57.95	1.96
	outer	1.46	19.48	19.71	19.36	41.45	1.42
top	inner	1.61	18.23	12.06	9.77	59.94	1.97
	outer	1.48	20.08	16.99	16.66	46.26	1.43

[a] Reaction conditions: polymerization mixture: glycidyl methacrylate 24%, ethylene dimethacrylate 16%, cyclohexanol 60%, benzoyl peroxide 1 wt % (with respect to monomers), 20 h, 55 °C. [b] Total pore volume. [c] Percentage of pore volume in the pores less than 100, 100−500, 500−1000, and over 1000 nm in size. [d] Pore diameter at the highest peak in the pore size distribution profile.
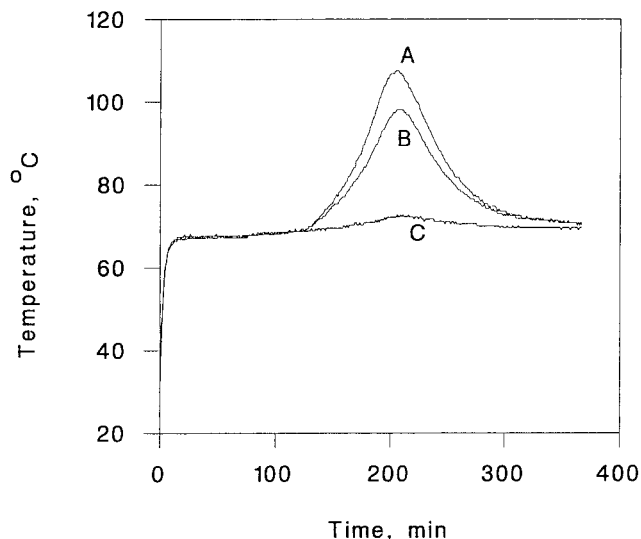

Figure 3. Temperature profile curves measured at the center (A), middle (B), and outer (C) positions during the batch mode preparation of a poly(styrene-*co*-divinylbenzene) monolith in the 50 mm mold at a nominal temperature of 70 °C. For conditions see Table 2.

Figure 2. Temperature profile curves measured at the center (A), middle (B), and outer (C) positions during the batch mode preparation of a poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monolith in the 50 mm mold at a nominal temperature of 55 °C. For conditions see Table 1.

Figure 4. Temperature profile curves measured at the center (A), middle (B), and outer (C) positions during the batch mode preparation of a poly(styrene-*co*-divinylbenzene) monolith in the 50 mm mold at a nominal temperature of 60 °C. For conditions see Table 2.
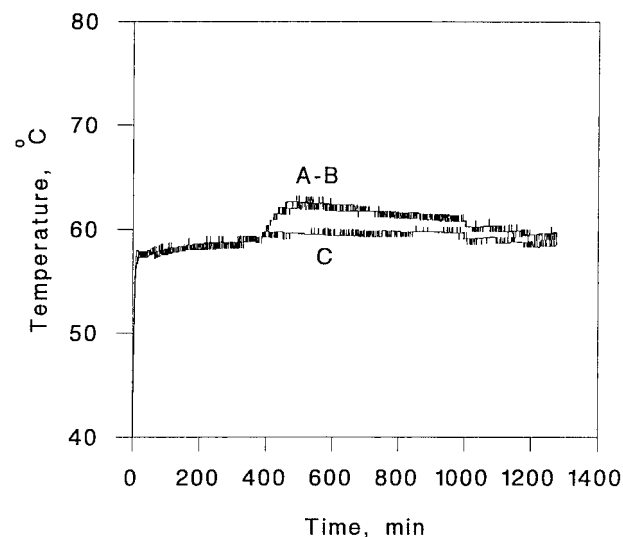
explain these unexpected porosimetry results are currently being performed.

The increase in temperature during such large-scale batch polymerizations can have consequences far more significant than a simple lack of homogeneity in the porous structure. Figure 3 shows the temperature profile for the polymerization of styrene and divinylbenzene performed in the 50 mm mold at 70 °C. A maximum exotherm temperature of 109 °C was recorded at the center position. In this case however, the resulting monolith exhibits numerous large cracks and other deformities along its length. The failure of this system to produce a regular macroporous monolith almost certainly arises from the fact that the temperature achieved during polymerization exceeds the boiling point of the co-porogen toluene.

Slow Polymerization. Clearly, the preparation of large-diameter monoliths that have homogeneous po-

rous structures requires the use of techniques that effectively decrease or even eliminate the occurrence of an exotherm. A simple solution to this problem is to run the polymerization at a rate slow enough to allow dissipation of the heat of polymerization. Figure 4 shows the temperature profile for the polymerization of styrene and divinylbenzene performed in the 50 mm mold at 60 °C. Unlike the polymerization at 70 °C, only a minimal increase in the temperature (3 °C) is observed. The absence of a significant exotherm again correlates with the formation of a completely homogeneous porous structure, as seen in Table 2. The homogeneity exhibited by this monolith is striking, considering the extremely large size of the pores produced (modal pore diameter of approximately 20 μm).

Although effective, this slow polymerization technique suffers from several disadvantages. Obviously, the polymerizations proceed slowly. After 20 h, the styrenic

Table 2. Porous Properties of the Molded 50 mm i.d. Poly(styrene-*co*-divinylbenzene)[a] Prepared by Batch Polymerization at 60 °C

sample position	portion	V_{p},[b] mL/g	pore volume,[c] % <0.1	−1	−10	>10	$D_{p, mode}$[d] μm
bottom	inner	2.28	14.36	1.93	32.76	50.95	20.08
bottom	outer	2.44	13.13	2.03	31.25	53.59	19.99
middle	inner	2.18	10.95	2.26	35.14	51.65	20.22
middle	outer	2.30	8.83	2.17	32.54	56.46	20.03
top	inner	2.32	13.98	2.31	29.27	54.44	20.88
top	outer	2.38	12.89	1.89	30.56	54.66	20.69

[a] Reaction conditions: polymerization mixture: styrene 20%, divinylbenzene 20%, 1-dodecanol 45%, toluene 15%, benzoyl peroxide 1 wt % (with respect to monomers), 20 h, 60 °C. [b] Total pore volume. [c] Percentage of pore volume in the pores less than 0.1, 0.1−1, 1−10, and over 10 μm in size. [d] Pore diameter at the highest peak in the pore size distribution profile.

system described reaches only a conversion of approximately 80%. In addition, numerous polymerizations defined and optimized previously on the small scale cannot be directly translated to the larger scale due to the occurrence of exotherms. In effect, certain combinations of chemistry and porosity profile are simply unattainable using this method. If the numerous potential applications of the polymer monoliths are ever to be effectively applied beyond the analytical scale, a different technique must be used.

Gradual Addition. Another approach to reducing the fast evolution of heat and the resulting uncontrolled increase in temperature during the preparation of large-diameter monoliths is to limit the amount of monomer that can react at any given time. This can be accomplished by slowly adding the polymerization mixture to the mold while the polymerization has started. For example, the glycidyl methacrylate/ethylene dimethacrylate system was fed at a rate of 20 mL/h for 12 h to the 50 mm diameter reaction vessel maintained at 55 °C. Using this technique, the polymer monolith grows slowly upward from the bottom of the reaction vessel. The monolith prepared in this manner is free of deformities, and its porosity profile, given in Table 3, shows a marked improvement in homogeneity compared to the monolith produced at the same temperature in the batch mode.

A temperature profile was recorded during this polymerization in order to confirm that this improvement in homogeneity indeed results from the minimization of the polymerization exotherm. However, instead of placing the thermocouples at different radial positions as for the batch mode profile, the thermocouples were positioned at the same radial ("middle") position but at different heights in the mold. The resulting temperature profile is shown in Figure 5. The maximum recorded temperature was 65 °C, only 10 °C more than the nominal polymerization temperature. This compares very favorably to the 110 °C observed in the batch polymerization and clearly documents that the use of the gradual addition technique nearly eliminates the problem of exotherm during the preparation of a large-diameter monolith within an unstirred mold.

The versatility of this technique is demonstrated by the preparation of a poly(styrene-*co*-divinylbenzene) monolith at a polymerization temperature of 70 °C in a 50 mm mold. When this reaction was attempted in the batch mode, the resulting monolith was cracked and unusable. The same polymerization performed in the

Table 3. Porous Properties of the Macroporous Polymer Monoliths Produced by the Gradual Addition Technique

sample position	portion	V_{p},[a] mL/g	pore volume,[b] % <100	−500	−1000	>1000	$D_{p, mode}$,[c] μm
Poly(glycidyl methacrylate-*co*-ethylene dimethacrylate)[d]							
bottom	inner	1.40	15.37	7.08	11.39	66.15	1.77
	outer	1.51	13.78	7.48	10.68	68.05	1.66
middle	inner	1.34	17.51	6.70	10.70	65.09	1.76
	outer	1.48	15.37	6.59	10.03	68.00	1.76
top	inner	1.43	18.94	6.41	8.63	66.02	2.04
	outer	1.53	17.42	7.12	8.59	66.87	1.92
Poly(styrene-*co*-divinylbenzene)[e]							
bottom	inner	2.27	10.16	7.60	14.80	67.44	1.42
	outer	2.40	8.81	8.01	15.51	67.68	1.41
middle	inner	2.52	9.35	4.40	6.40	79.84	2.34
	outer	2.49	9.43	4.34	5.63	80.59	2.32
top	inner	2.22	9.60	3.13	3.57	84.25	4.47
	outer	2.05	10.92	3.29	3.03	82.78	4.72

[a] Total pore volume. [b] Percentage of pore volume in the pores less than 100, 100−500, 500−1000, and over 1000 nm in size. [c] Pore diameter at the highest peak in the pore size distribution profile. [d] Reaction conditions: polymerization mixture: glycidyl methacrylate 24%, ethylene dimethacrylate 16%, cyclohexanol 60%, benzoyl peroxide 1 wt % (with respect to monomers), 12 h feed at 20 mL/h, 55 °C. [e] Reaction conditions: polymerization mixture: styrene 20%, divinylbenzene 20%, 1-dodecanol 45%, toluene 15%, benzoyl peroxide 1 wt % (with respect to monomers), 12 h feed at 20 mL/h, 70 °C.
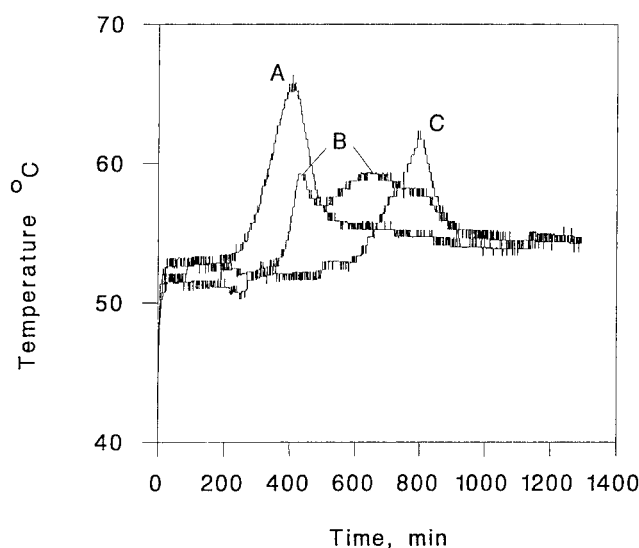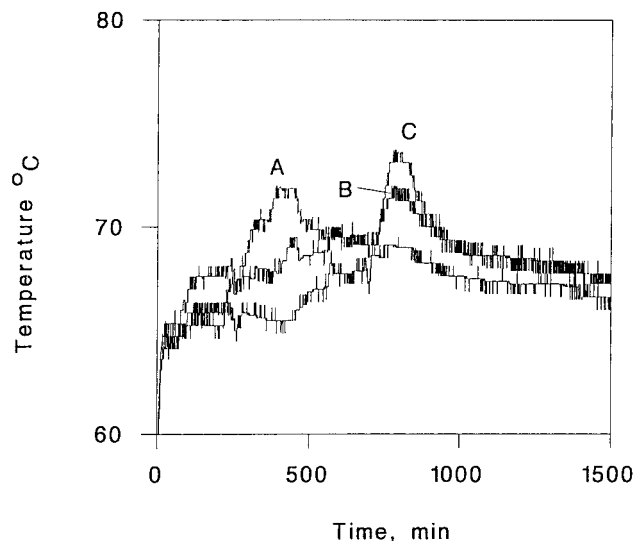

Figure 5. Temperature profile curves measured at heights of 2 (A), 5 (B), and 8 cm (C) from the bottom of the polymerization apparatus during the gradual addition mode preparation of a poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monolith in the 50 mm mold at a nominal temperature of 55 °C. For conditions see Table 3.

gradual addition mode produces a monolith that is completely free of deformities. The temperature profile for this reaction, shown in Figure 6, displays a maximum at 73 °C, compared to 100 °C for the batch polymerization. As seen in Table 3, this effective elimination of the polymerization exotherm again results in the production of a monolith with no radial inhomogeneities in its porous structure.

Conclusions

Our experimental results show that in contrast to materials prepared using a typical bulk polymerization process, large-diameter monoliths with completely homogeneous pore structures are produced when the heat of polymerization is effectively controlled. Of the dif-

Figure 6. Temperature profile curves measured at heights of 2 (A), 5 (B), and 8 cm (C) from the bottom of the polymerization apparatus during the gradual addition mode preparation of a poly(styrene-*co*-divinylbenzene) monolith in the 50 mm mold at a nominal temperature of 70 °C. For conditions see Table 3.

ferent methods shown to minimize the detrimental effects of polymerization exotherms, the gradual addition approach proved especially powerful, as it allows the preparation of monoliths of almost any size that cannot be otherwise obtained. This general technique, combined with the abilities to both mold and further functionalize the monolithic polymers, should allow the facile production of preparative-scale chromatographic columns, large-diameter plugs, thermally responsive devices,[12] etc. Additionally, the slow upward growth of the monolith that occurs as a result of the gradual addition provides a tool to produce more advanced mold shape conforming materials. Specifically, monoliths with a controlled *gradient of porosity* can be produced by simply changing the polymerization temperature during the course of the gradual addition, while monoliths with a *gradient of chemistry* can be obtained by changing the composition of the feed mixture over time.

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