Use of Stable Free Radicals for the Sequential Preparation and Surface Grafting of Functionalized Macroporous Monoliths

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Received May 9, 2000

ABSTRACT: Porous polymer monoliths have been prepared by polymerization of styrene and divinylbenzene in the presence of porogenic solvents initiated by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane. Although the polymerization reaction initiated by this alkoxyamine initiator is slower than that initiated by typical free-radical initiators, almost complete conversions were obtained at temperatures of 95 and 110 °C. The porous properties of the monolithic materials were easily controlled in a broad range by adjusting the composition of the porogenic solvents in the polymerization mixture. The capped radicals located at the surface of the pores of the monolith were used for subsequent grafting of functionalized linear chains from monomers such as *tert*-butyl methacrylate, chloromethylstyrene, or vinylpyridine at 110 °C. The extent of grafting within the pores could be controlled by adjusting the reaction time or diluting the monomer with an inert solvent.

Introduction

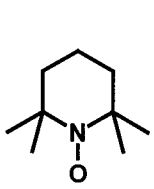
The need for porous materials in which slow diffusion within pores filled with a stagnant pool of liquid is minimized has led to the development of porous structures with entirely new shapes in which mass transfer is considerably enhanced by convective flow through the pores.[1] Macroporous disks, rolled woven matrices, and compressed polyacrylamide gels placed in a cartridge or column are representative examples of this new class of materials. These approaches were recently detailed in a series of excellent review articles.[2]

In the early 1990s, we developed novel rigid macroporous monoliths formed by a very simple "molding" process in which a mixture of monomers and porogenic solvents is polymerized within a closed tube or other container under carefully controlled conditions.[3] Polymerization occurs with the formation of co-continuous phases, one of which, the solvent, is removed to leave behind a porous network capable of sustaining flow. The monoliths have shown excellent performance in a number of applications including HPLC of biopolymers, synthetic oligomers and polymers, capillary electrochromatography, solid-phase extraction, enzyme immobilization, and supports for solid-phase reactions.[4] The unique feature of these materials is the high permeability of their pores, a radical departure from the beads used in today's technologies for which flow occurs mainly through the interstitial voids between particles. Monoliths intended for rapid separation processes must have sufficiently large pores to enable high flow-through velocities. The larger the pores, the smaller the flow resistance. Unfortunately, large-pore materials only possess very modest specific surface areas, usually less than 10−20 m^2/g.[5] Macroporous polymer beads with large internal surface area are useful in applications based on adsorption/desorption processes such as chromatography and catalysis and in systems such as ion-exchange and polymer-supported reactions for which a high degree of surface functionalization is required. However, the large surface area of beads typically results from the presence of a great number of small pores. Therefore, such materials are not well suited for applications in the flow-through mode since their flow resistance is excessively high. Obviously, a combination of these positive features, low resistance to flow, large surface area, and high concentration of functional groups, in a single monolith would be highly desirable for numerous applications. Hence, we are seeking alternative preparation methods to control the porous structure and the surface chemistry of monolithic macroporous polymers.

Living free-radical polymerization has attracted considerable attention since it enables the preparation of polymers with well-controlled composition and molecular architecture previously the exclusive domain of ionic polymerizations, using very robust conditions akin to those of a simple radical polymerization.[6] While the vast majority of these polymerizations are carried out in bulk or solution, emulsion,[7] dispersion,[8] and suspension processes[9] have also been reported for free radical polymerizations mediated by 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO, **1**). The living radical process not only is suited for the synthesis of narrow molecular weight distribution homopolymers but also allows the preparation of well-defined block and graft copolymers.[10] We have already demonstrated the use of TEMPO-mediated cross-linking polymerization for the preparation of macroporous polymers.[11] We also found that the latent TEMPO capped free radicals had a great potential for the preparation of a variety of macroporous materials with different chemistries and enhanced capacities using grafting provided the polymerization

10.1021/ma000797e CCC: $19.00
Published on Web 09/28/2000

conditions can be modified to obtain monoliths with suitable porous properties.[11]



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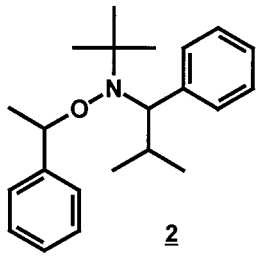

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Typically, stable free-radical polymerizations require high temperatures to proceed. Our earlier study had shown that temperature had a remarkable effect on the process of pore formation during the preparation of monoliths as an increase in temperature led to a rapid decrease in the size of the pores that are formed.[12] This initial study only covered a narrow temperature range from 55 to 90 °C. This was later extended to 130 °C, leading to dramatic changes of the monoliths prepared using benzoyl peroxide (BPO) as the initiator. This high-temperature monolithic material had very large specific surface areas of several hundred m^2/g but only very small pores not well suited to sustain flow.[11] When TEMPO was used in conjunction with BPO at 130 °C, the rate of polymerization decreased considerably, but the porous structure of the resulting monolith did not change, thus indicating that the stable free radical has little, if any, effect on porosity. However, the polymerization afforded monoliths with reactive TEMPO moieties still attached to the numerous chain ends of the monolith providing ready access to subsequent grafting.[11]

The preparation of monoliths by copolymerization of functional monovinyl and divinyl monomers requires optimization of the polymerization conditions for each new set of functional monomers and cross-linkers in order to obtain monoliths with the desired properties.[3] Since the functional monomer constitutes both the bulk and the active surface of the monolith, a substantial percentage of the functional units remains buried within the highly cross-linked polymer matrix and is inaccessible for the desired interactions. A better utilization of a rare functional monomer might involve its graft polymerization within large pores of a "generic" monolith using the terminal nitroxide moieties of a monolith prepared in the presence of a stable free radical. In this way, the monolith is prepared first, and its dormant free-radical ends can be used in a subsequent step involving growth of the functional polymer within the pores of the previously formed monolith. This makes the stable free-radical-assisted two-step polymerization process a versatile tool, since it allows the preparation of functionalized porous materials with a large variety of surface chemistries that originate from only a single type of parent monolith.

Our previous communication clearly demonstrated that the preparation of monoliths in the presence of TEMPO and their grafting is feasible.[11] However, this polymerization led to products with a less permeable porous structure as a result of the rather high reaction temperature of 130 °C required to obtain high conversions in the preparation of the original monolith using TEMPO as a stable free radical. A "library" of nitroxides and nitroxide-based alkoxyamines containing compounds suitable for the living free-radical polymerization of a broad range of monomers at temperatures as low as 85 °C has recently been described.[13] Since the use of these "low"-temperature mediators in the preparation of porous monoliths may substantially simplify the control of porous properties, the first objective of this study was to explore the bulklike polymerization of styrene and divinylbenzene in the presence of one of these alkoxyamine initiators, 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TPPA, **2**). Finally, pore surface grafting of these monoliths with different functional monomers was examined.

Experimental Section

Materials. Styrene, divinylbenzene (80% grade), *tert*-butyl methacrylate, and chloromethylstyrene (mixture of isomers) were purchased from Aldrich and distilled in a vacuum prior to use. 2-Acrylamido-2-methyl-1-propanesulfonic acid (99%) and benzoyl peroxide (97%), both from Aldrich, were used as obtained. TPPA was prepared using a procedure described elsewhere.[13] All alcohols and solvents were purchased from Aldrich in the best available quality and used without further purification. Commercial polystyrene with a weight-average molecular weight of 2.8×10^5 was purchased from Aldrich.

Preparation of Monoliths. Benzoyl peroxide or TPPA (0.4 mol % with respect to monomers) was dissolved in a mixture consisting of 2 parts of divinylbenzene and 2 parts of styrene. Acetic anhydride (2 equiv with respect to TPPA) was added to the mixtures containing TPPA. Porogenic solvent, a higher aliphatic alcohol and toluene (6 parts), was admixed to the monomers. Equal portions of this mixture (typically 0.9 g) were placed in glass ampules that were attached to a vacuum line. The contents of ampules were deaerated using three freeze−pump−thaw cycles. The ampules were sealed under vacuum and submerged in an oil bath heated to the desired temperature to effect the polymerization. After the polymerization time elapsed, the ampules were removed from the bath and immediately cooled on ice. Then they were carefully opened, and the monolith formed by the bulk polymerization was sliced into smaller pieces using a razor blade. The slices of cut monolith were extracted in THF for 24 h in a Soxhlet apparatus to remove any soluble components and subsequently vacuum-dried at 60 °C overnight. These slices of polymer were used in the grafting studies and porosimetric measurements.

Grafting. The grafting was performed with pure *tert*-butyl methacrylate or its solutions in 1,4-dioxane, pure chloromethylstyrene, 4-vinylpyridine in toluene solution, and 2-acrylamido-2-methyl-1-propanesulfonic acid dissolved in a 25/75 water/methanol mixture. The small pieces of porous polymer were placed in glass ampules, pretreated with three cycles of vacuum pumping and filling with nitrogen at 60 °C. After the addition of 10-fold weight excess of monomer the mixture was deaerated by three repeated cycles of freeze−pump−thaw, and the ampules were sealed under vacuum. The grafting polymerization was then allowed to proceed in an oil bath thermostated at 110 °C. The resulting product was extracted with THF for 24 h in a Soxhlet, dried under vacuum at 60 °C overnight, ground using a pestle, extracted with THF again for an additional 48 h, and dried in a vacuum. The extent of grafting was initially estimated from the difference in weight of the sample before and after grafting.

Specific Example. To a solution of 0.0421 g of TPPA in 1.8649 g of styrene was added 1.8354 g of divinylbenzene, 4.1778 g of dodecanol, 0.8682 g of toluene, and 0.0282 g of acetic anhydride. A 5 mL glass ampule was charged with 0.9 g of this polymerization mixture, sealed after three freeze−pump−thaw cycles, and polymerized at 110 °C for 168 h. This procedure yields 0.3558 g of porous polymer (97.8% conversion in respect to added monomers) that has a pore volume of 1.56 mL/g, a modal pore size of 53 nm, and a specific surface area of 305 m^2/g. To 0.0415 g of this polymer in an ampule was added 0.4318 g of *tert*-butyl methacrylate; the contents were deaerated and sealed. The grafting reaction was allowed to

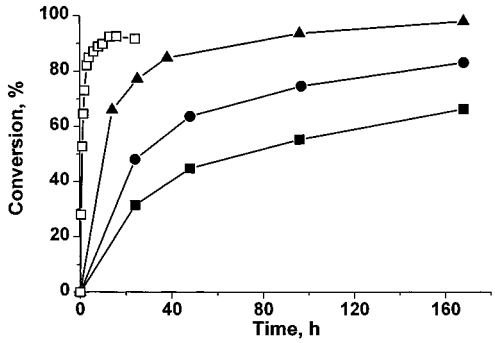

Figure 1. Reaction kinetics of polymerization of a mixture consisting of 20% styrene, 20% divinylbenzene, 50% dodecanol, and 10% toluene initiated by benzoyl peroxide at 85 °C (□) and 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane with acetic anhydride at 85 (■), 95 (●), and 110 °C (▲).

proceed at 110 °C for 1 h, affording 0.0847 g (104% weight increase) of grafted monolith.

Analytical Procedures. The pore size distribution and specific surface area of the monolithic materials in the dry state were determined by mercury intrusion porosimetry and nitrogen adsorption/desorption, respectively, using Autopore III and ASAP 2010 instruments (both Micromeritics, Norcross, GA). Thermogravimetric measurements (Seiko Instruments Inc., TGA/DTA 220) were performed in a nitrogen atmosphere at a heating rate of 10 °C/min. Calibration of this method for the determination of grafting was performed with poly(*tert*-butyl acrylate) homopolymer. A weight decrease of 45.7 wt % has been measured for the homopolymer corresponding to the liberation of isobutylene and water as well as anhydride formation. The surface grafting was also confirmed by FTIR and quantified by nitrogen and chlorine elemental analyses.

Results and Discussion

Kinetics of Polymerization. A number of previous reports[6,11,13] demonstrated that stable free-radical-mediated polymerizations are much slower than those performed using typical free-radical initiators in the absence of these stable free radicals. Although the rate of polymerization in the presence of TEMPO can be accelerated by the addition of acylating agents[15] or acids,[16] a relatively high temperature of about 130 °C is still required to obtain high conversions. In contrast, 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and acetic anhydride initiated polymerization of styrene at 85 °C, affording a conversion of 90% after 90 h.[13] Therefore, we utilized this novel initiating system for the preparation of porous monoliths using mixtures of styrene and divinylbenzene. However, Figure 1 documents that the alkoxyamine-initiated polymerizations of monoliths are still very slow. For example, a conversion of only 66.3% is achieved after 168 h (7 days) at 85 °C while a comparable polymerization initiated by benzoyl peroxide affords a conversion of 90% in less than 10 h at the same temperature. As expected, increasing the temperature to 95 and 110 °C increases the polymerization rate which conversions reach 83.0 and 97.8% after 168 h, respectively. The much lower rate of polymerization for the monolith when compared to the bulk polymerization of pure styrene[13] likely results from the dilution of the polymerization system that contains 40 vol % of monomers diluted with 60 vol % of porogenic solvents. Since the initial reaction rate is considerably higher at the highest reaction temperature, a conversion of 90% is achieved already after 80 h at 110 °C.

The plots of $\ln([M_0]/[M_t])$ vs time are linear and indicate that the first-order kinetics typical of polymerizations mediated by stable free radicals also apply to this system. The observed rate constants are 1.0×10^{-6}, 1.7×10^{-6}, and 4.3×10^{-6} s^{-1} for the temperatures of 85, 95, and 110 °C, respectively. These values are about 1 order of magnitude lower than those found for the bulk polymerization of styrene in the presence of TEMPO at 135 °C.[17]

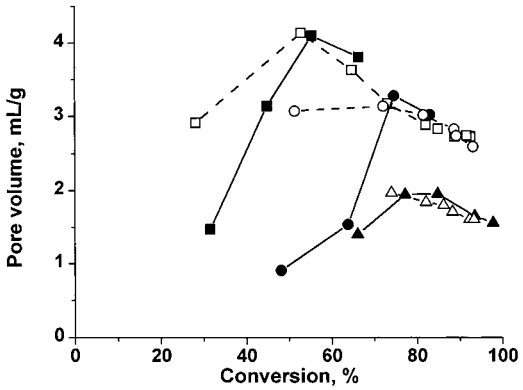

Figure 2. Effect of conversion of polymerization of a mixture consisting of 20% styrene, 20% divinylbenzene, 50% dodecanol, and 10% toluene initiated by benzoyl peroxide (open points) and 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane with acetic anhydride (close points) at 85 (■, □), 95 (●, ○), and 110 °C (▲, △) on pore volume determined in the dry state by mercury intrusion porosimetry.

Porous Properties. The pore volume and pore size distribution of porous monoliths prepared using standard initiators and lower temperature depend on the conversion.[18] The same effect is also observed for polymerizations at higher temperatures. Figure 2 compares pore volumes of materials prepared at 85 °C. In the BPO-initiated system, the pore volume increases from 2.91 mL/g at 28% conversion (reaction time 30 min) to reach a maximum of 4.14 mL/g at 53% and then decreases to 2.72 mL/g at a conversion of 90%. The general pattern of the porosity development for polymers prepared using TPPA-initiated polymerization is similar. However, the overall range of pore volumes is broader than that for BPO starting at 1.47 at a conversion of 31% (reaction time 24 h) and reaching 4.10 mL/g at 55% conversion. The pore volume also varies with the volume of porogen added to the polymerization mixture. For example, an increase from 50 to 55% and to 60% dodecanol in the polymerization mixture increases the pore volume from 1.56 mL/g to 1.72 and 1.99 mL/g, respectively, at comparable conversions (Table 1). A similar effect is also observed for hexadecanol as a porogenic solvent.

Obviously, the pore volume of the porous polymer formed at any time of the polymerization process should be close to the sum of the volumes of the porogenic solvent and the unreacted monomers. However, the less cross-linked porous structure formed at the early stages of polymerization lacks rigidity and collapses on drying. Therefore, the apparent values of pore volume measured in the dry state using mercury intrusion porosimetry are initially lower than predicted. Once a strong, noncollapsing superstructure is formed, the porous polymer has the largest pore volume. The lower the conversion at which this point is achieved, the larger the pore volume. The cross-linked polymer that is formed during subsequent polymerization beyond this point fills the pores and decreases their overall volume.

The results presented in Figure 2 show that this

Table 1. Effect of Aliphatic Alcohols and Their Percentage in the Polymerization Mixture on Porous Properties of Polymer Monoliths Prepared by TPPA and Acetic Anhydride Initiated Polymerization at 110 °C[a]

porogen	porogen (vol %)	conv (%)	$D_{p,mode}$ [b] (nm)	V_p [c] (mL/g)	surf. area (m^2/g)
butanol	60	97.53	53.8	1.57	266.0
hexanol	60	96.13	136.5	1.72	300.8
octanol	60	95.38	119.9	1.77	258.4
decanol	60	96.69	54.7	1.77	258.2
dodecanol	60	93.91	23.5	1.99	155.8
dodecanol	55	96.31	53.1	1.72	239.6
dodecanol	50	97.77	53.8	1.56	305.4
tetradecanol	60	93.54	54.9	2.06	122.0
hexadecanol	60	88.75	152.7	2.17	54.3
hexadecanol	50	97.63	37.1	1.63	274.0
octadecanol	60	87.46	1024.1	2.13	17.4
polystyrene[d]	60		1124.7	0.82	178.4

[a] For polymerization conditions see Experimental Section. [b] Pore diameter at the maximum of the pore size distribution curve. [c] Pore volume. [d] 5 wt % solution of polystyrene (M_w 2.8 × 10^5) in toluene used as a porogen.

mechanism also holds for polymerizations carried out at high temperatures. However, less rigid superstructures are initially formed in the process of TPPA-initiated polymerizations compared to the equivalent BPO-initiated process. Analogous patterns were observed earlier for the TEMPO-mediated polymerization of similar monomer mixtures at 130 °C.[19] Obviously, the mechanism of "living" polymerization is somewhat different from that of the "classical" free-radical process. While growing polymer chains continue to propagate for a long period of time during the "living" polymerization process, termination reactions limit the lifetime of each propagating radical to only a few seconds in the best case when classical initiators are used. This affects the phase separation and formation of interconnected microglobules that are the primary building blocks of all macroporous polymers. The process of termination by combination of radicals propagating from two neighboring nuclei serves to quickly reinforce the superstructure. This "strengthening" process is missing in the "living" system. Once the self-supporting superstructure is created, the pore volumes are identical for both types of polymerizations. The larger decrease in the pore volume observed for products of polymerizations at 110 °C likely reflects the increasing volume of pores smaller than 6 nm, a value that represents the detection limit of our current mercury porosimetry equipment.

Control of Pore Size. Although the above results demonstrate the feasibility of the preparation of porous monoliths with controlled properties using the alkoxyamine initiator, the pores of the resulting materials are too small to make the monolith easily permeable. Figure 3 shows a typical pore size distribution profile of a monolith prepared at 110 °C. The modal pore diameter is only about 40 nm with almost no pores larger than 100 nm. Since pores with a diameter in the range of a few hundred nanometers are required to obtain highly permeable monoliths,[5] additional experiments targeting an increase in the pore size had to be carried out.

The well-established tools that enable the control of porous properties of macroporous beads and monoliths prepared using standard radical polymerization such as the type and percentage of porogenic solvent[3,5,20] were also useful for the preparation of monoliths at high temperature. Table 1 summarizes results of TPPA initiated polymerizations using different aliphatic alcohols and a solution of polystyrene as porogens. Dodecanol, which is the porogenic solvent of choice for the preparation of monoliths at the lower temperatures, affords monolith with a mode pore diameter of only 23.5 nm, actually the lowest value observed in the set of alcohols used (Figure 4). The apparent trend of increasing pore size as the length of the alcohol decreases was initially promising but did not yield the extrapolated large value for butanol. Figure 5 demonstrates the effect of various alcohols on the pore size distribution profiles. Of all porogenic alcohols used in this study, only the monolith prepared in the presence of octadecanol features pores in the desired 1 μm size range.

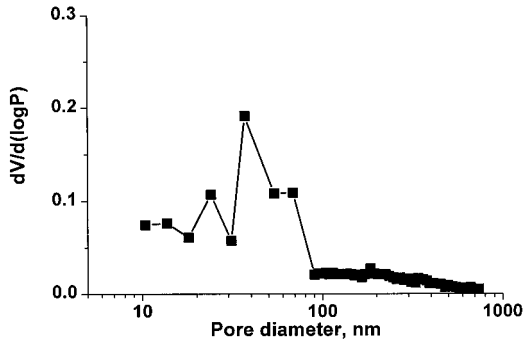

Figure 3. Differential pore size distribution profile determined by mercury intrusion porosimetry for a monolith prepared by polymerization of a mixture consisting of 20% styrene, 20% divinylbenzene, 50% dodecanol, and 10% toluene initiated by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and acetic anhydride at a temperature of 110 °C.

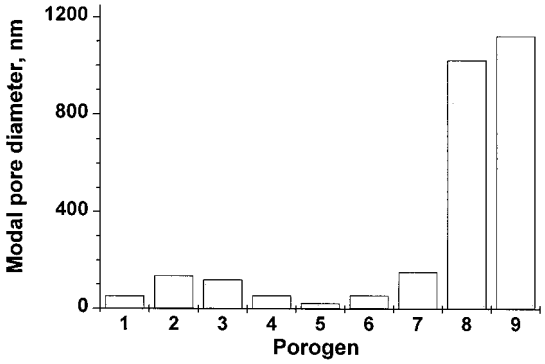

Figure 4. Effect of various porogens on modal pore size determined by mercury intrusion porosimetry for monoliths prepared by polymerization of a mixture consisting of 20% styrene, 20% divinylbenzene, and 60% porogenic solvent initiated by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and acetic anhydride at a temperature of 110 °C. Porogens: butanol (1), hexanol (2), octanol (3), decanol (4), dodecanol (5), tetradecanol (6), hexadecanol (7), octadecanol (8), and 5% polystyrene (M_w 280 000) solution in toluene (9).

We assume that the effect of the increasing alcohol alkyl chain length on porous properties might be related to the simultaneous decrease in solubility of both the monomers and the polymer in the system that contains higher alcohols. This decrease in solubility of the polymer formed in a system that contains higher alcohols leads to a phase separation (nucleation) at an earlier stage of the polymerization process. The separated nuclei preferentially "extract" the monomers from the surrounding liquid polymerization mixture containing the alcohol because the monomers favor the chemically similar environment of the nuclei. The enlarged nuclei can also attract and coalesce with the newly precipitated chains and further increase their sizes. As

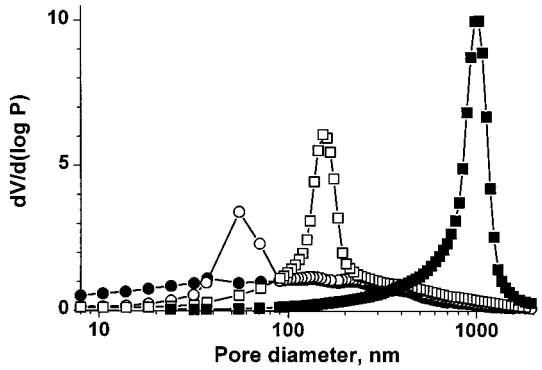

Figure 5. Differential pore size distribution profile determined by mercury intrusion porosimetry for monoliths prepared by polymerization of a mixture consisting of 20% styrene, 20% divinylbenzene, and 60% porogenic solvent initiated by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and acetic anhydride at a temperature of 110 °C. Porogens: tetradecanol (○), hexadecanol (□), octadecanol (■).

a result, both larger microglobules and larger pores are formed. In addition, the increase in viscosity resulting from the use of higher alcohols may also prevent the growing nuclei from assembling to better-organized arrays, thus leaving larger voids within the final structure.

Although octadecanol has the ability to promote formation of monoliths with large and well-defined pores, it has a melting point of 61 °C, a value that complicates the thawing of the polymerization mixture for the freeze−pump−thaw cycles, required for the removal of oxygen. Therefore, we also tested soluble polymers that are very powerful porogens.[21] For example, a 5% polystyrene solution in toluene was used as a porogen. The modal pore size of the monolith obtained with this polystyrene porogen was 1125 nm, well within the targeted range. However, the pore volume was only about 0.82 mL/g, less than half that obtained with alcohols. Despite its early promise, the use of porogenic systems involving polymer solutions obviously requires further development.

Grafting of Pore Surface. *tert*-Butyl Methacrylate. The chain ends capped with the alkoxyamine initiating groups at the pore surface within the monolith were used as latent free-radical initiator species for grafting of a variety of functional monomers. We chose *tert*-butyl methacrylate (*t*-BMA) since methacrylate homo- and copolymerizations have successfully been initiated by nitroxide-terminated polystyrene.[22] Because this monomer has a structure that is very different from that of the parent monolith, the grafting can easily be followed by FTIR. Figure 6 compares the FTIR spectrum of the grafted monolith with that of the original porous polymer. Strong new carbonyl bands appear at 1724 cm^{-1}, while the *tert*-butyl and C−O stretch at 1249 and 1140 cm^{-1}, respectively, clearly document the presence of poly(*tert*-butyl methacrylate) grafted to surface of the monolith. Thermal treatment of the grafted material using TGA equipment at a temperature near 240 °C leads to the simultaneous loss of isobutylene and water resulting from decomposition of the ester and the formation of anhydride groups, respectively.[23] The TGA trace also enables an estimation of the percentage of grafting. For example, a monolith was grafted with a 20% *t*-BMA solution in dioxane at 110 °C for 24 h. The content of *t*-BMA in this monolith calculated from TGA data was 7.4% or 0.51 mmol/g. This value is a good

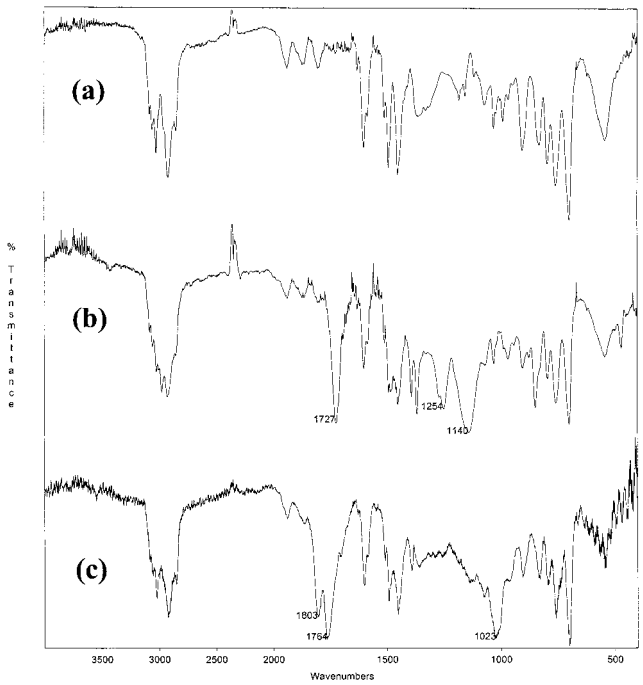

Figure 6. FTIR spectra of original poly(styrene-*co*-divinylbenzene) monolith prepared by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and acetic anhydride initiated polymerization at a temperature of 110 °C (a), monolith grafted with poly(*tert*-butyl methacrylate) (b), and grafted monolith heated to a temperature of 250 °C for 10 min (c).

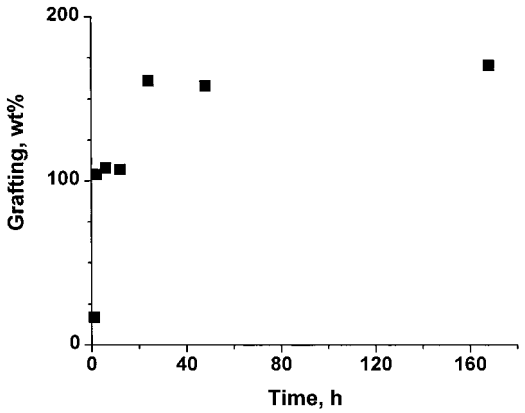

Figure 7. Kinetics of grafting of poly(styrene-*co*-divinylbenzene) monolith prepared by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and acetic anhydride initiated polymerization with *tert*-butyl methacrylate at a temperature of 110 °C.

match for the weight increase of 7.9% determined gravimetrically immediately after the grafting and work-up.

Figure 7 shows the kinetics of the grafting reaction using pure *t*-BMA. The content of grafted polymer increases rapidly, demonstrating high reactivity of the alkoxyamine initiating groups at 110 °C. The rate of grafting slows and finally almost levels off once the newly formed polymer fills the pores. At this point the weight of the materials almost triples, and the loading of the poly(*tert*-butyl methacrylate) is 4.33 mmol/g. This result corresponds well with a capacity of 4.23 mmol/g calculated for a monolith with 60% porosity (volume percentage of pores within the material) for which all of the pores have been completely filled with poly(*tert*-butyl methacrylate). Although the "living" polymerization can continue at the actual surface of the irregular

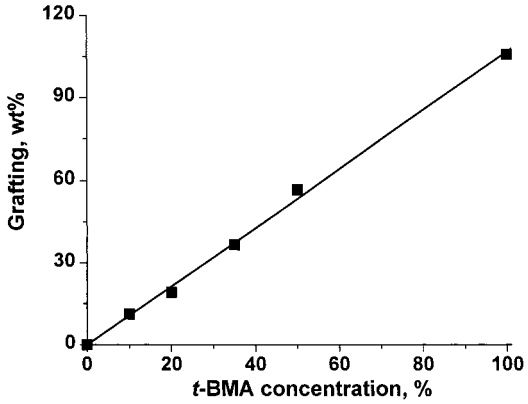

Figure 8. Effect of monomer concentration in 1,4-dioxane on extent of grafting of poly(styrene-*co*-divinylbenzene) monolith prepared by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and acetic anhydride initiated polymerization with *tert*-butyl methacrylate at a temperature of 110 °C.

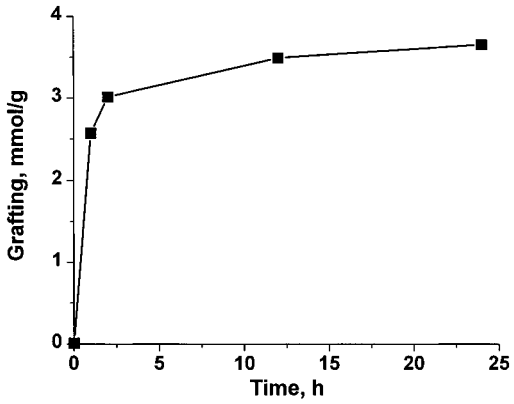

Figure 9. Kinetics of grafting of poly(styrene-*co*-divinylbenzene) monolith prepared by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and acetic anhydride initiated polymerization with chloromethylstyrene at a temperature of 110 °C.

particles, the weight increases only slowly since this surface is small. It is worth noting that the spontaneous polymerization of pure *t*-BMA in the absence of the porous polymer under analogous conditions only affords a conversion of 5.7% after 24 h of heating to a temperature of 110 °C.

Obviously, the length of the grafts and thus the overall extent of grafting can be controlled by the reaction time (Figure 7). Since the grafting is very rapid in the early stages of the polymerization within the pores, its fine control may be difficult. However, the polymerization rate generally depends on the concentration of monomer in the system. Therefore, diluting the monomer with an inert solvent was expected to decrease the reaction rate. Indeed, Figure 8 shows that in 1,4-dioxane the percentage of grafting is a linear function of *t*-BMA concentration. The linearity of this function in the range of 0−100% allows an easy control of the grafting reaction. A blank experiment did not reveal any spontaneous polymerization for a 50% *t*-BMA solution after 24 h at 110 °C.

Grafting of Other Monomers. Since one of our targets is the preparation of a variety of functionalized monoliths, we also studied the grafting of other functional monomers. Commercially available chloromethylstyrene contains a reactive benzylic halide functionality that is often used for the preparation of functional polymers.[24] Figure 9 shows kinetics of the graft polymerization with neat chloromethylstyrene. The functionalization reaches a value of 3.65 mmol/g after 24 h at 110 °C as determined by elemental analysis of chlorine. The weight of the original porous polymer almost doubles at this point. Under similar reaction conditions (110 °C, 24 h) 4-vinylpyridine can also be grafted from its 20% solution in toluene. The weight increase found after the reaction is 61.7 wt %, which corresponds well with the amount of nitrogen determined by elemental analysis (3.6 mmol/g).

Conclusion

This study demonstrates that the preparation of monolithic macroporous materials using stable free radicals is a viable alternative to the typical polymerization process initiated by "conventional" initiators. In contrast to TEMPO-mediated polymerizations that require temperatures in excess of 130 °C, the new generation of alkoxyamine initiators enables polymerizations to be run at lower temperatures. This, in turn, facilitates the control of porous properties using techniques such as variations in the composition of the porogenic solvents. The latent free radicals that remain in the polymer after preparation of the porous monolith can be used to graft a variety of monomers and form composite materials with different chemistries and well-controlled functional capacities. This approach has the potential to vastly simplify the preparation of monoliths with various chemistries since it separates the steps of preparation of the porous polymer framework from the modification of the surface chemistry within the pores. Thus, the polymerization conditions have to be optimized only once to obtain the parent material with the required porous properties, and a variety of surface functionalities can then be obtained through an independent grafting step. Although much remains to be done, this promising approach to porous monoliths with redesigned properties may lead to materials useful in applications such as catalysis, chromatography, adsorption, and solid-phase chemistry.

Acknowledgment. Support of this research by grant of the National Institute of General Medical Sciences, National Institutes of Health (GM-48364), is gratefully acknowledged.

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MA000797E