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Control of Porous Properties and Surface Chemistry in "Molded" Porous Polymer Monoliths Prepared by Polymerization in the Presence of TEMPO

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Introduction. "Living" radical polymerizations have received a great deal of recent attention due to their potential for combining the chemical robustness of free radical polymerizations with the high level of control over polymer composition and architecture characteristic of traditional living polymerization methods.[1] Although the overwhelming majority of reports have focused on the polymerization of monovinylic monomers in bulk or solution, both emulsion[2] and dispersion[3] polymerizations utilizing 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO)-based initiating systems have also been described.

We have recently introduced a new class of macroporous polymers in the form of monoliths prepared by polymerization within the confines of an unstirred closed mold.[4] Although these materials have found use in a variety of applications,[5] the range of porosity profiles that can be produced is limited by the kinetics of standard free radical polymerization. Here we report the first use of a "living" radical polymerization for the preparation of macroporous polymers by the direct copolymerization of monovinyl and divinyl monomers in the presence of a porogenic solvent. The combination of slower kinetics and elevated reaction temperatures characteristic of the TEMPO-mediated polymerization employed enables the preparation of materials with completely different porosity profiles. In addition, the resulting monolithic structure contains TEMPO-capped latent radicals that can later be used to grow polymer chains from its internal pore surface and thus potentially impart additional unique properties to these monolithic flow-through supports.[6]

Results and Discussion. **1. Porous Properties.** It has been well documented that changes in the temperature of polymerization of the macroporous monoliths cause shifts in their pore size distribution profiles.[7] These changes result from differences in the number of polymer nuclei formed at different temperatures at constant initiator concentration as well as the rate of their formation. However, all of our earlier studies were performed within the range of temperatures typically employed in conventional free radical polymerization initiated with AIBN or BPO (55−80 °C). In this study, we carried out several experiments at the much higher temperature of 130 °C in both the presence and absence of TEMPO. These experiments have led to macroporous monoliths with entirely different porous structures. Table 1 details the porous properties of these monoliths. It should be noted that almost identical porosity data were obtained for monolithic materials produced with and without TEMPO at elevated temperatures. This indicates that the unique porous structure results not from the controlled free radical nature of the polymerization but rather from the effect of the elevated reaction temperature on the solvency of the specific porogen employed (dodecanol). In addition, the pore volumes determined by mercury intrusion porosimetry are distributed over a very broad range of pore sizes (10−1000 nm). In contrast, monoliths prepared at lower temperature typically exhibit a relatively narrow distribution of pore sizes.[7] For example, the "conventional" monolith listed in Table 1 derives the majority of its pore volume from pores with diameters of 500−1000 nm.[9] The significant increase in volume arising from pores smaller than 50 nm in the polymers prepared at 130 °C is reflected in their specific surface areas that exceed 300 m^2/g and are much higher than those for monoliths prepared at lower temperature.[7b]

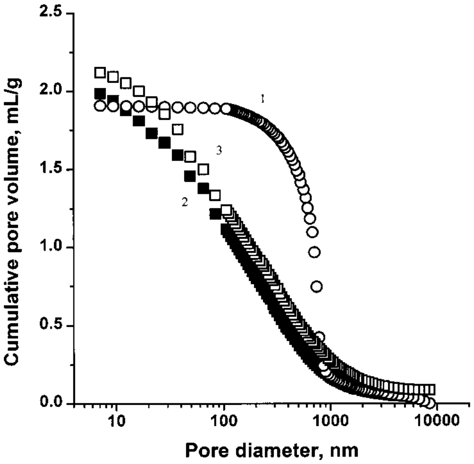

Figure 1. Integral pore size distribution profiles of porous polymer monoliths prepared by a typical polymerization at 70 °C (1)[8b] and in the presence (2) and the absence (3) of TEMPO at 130 °C. For reaction conditions see Table 1 and ref 11.

The substantial differences in porous structures can be easily seen in Figure 1 which shows the cumulative pore volume distribution curves determined in the dry state for the monoliths listed in Table 1.[9] These differences also persist in the solvent "swollen" state as shown by inverse size-exclusion chromatography (ISEC), which measures the pore volumes that are accessible to polymer standards of well-defined molecular sizes.[10] While traditional monoliths exhibit no real SEC separation ability,[7b] Figure 2 shows that the ISEC curve of a monolith prepared at 130 °C is almost linear for an extremely broad range of polystyrene molecular weight standards.[11]

2. Polymerization Kinetics. Although not responsible for the formation of this unique final pore structure, the TEMPO-mediated polymerization of monoliths provides other potential advantages. Figure 3 shows the kinetics of monomer incorporation under a variety of reaction conditions. As reported elsewhere,[1c,d] the TEMPO-mediated polymerization (curve 1) is much slower than the reaction performed in the absence of TEMPO (curve 3), reaching a final conversion level of only 85% after 48 h. Several groups have reported an acceleration of the rate of polymerization upon the

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Table 1. Polymerization Conditions and Properties of Monoliths Prepared at High Temperature

polymerization conditions[a]						percentage of pore volume in pores			
t,[b] h	TEMPO	*T*,[c] °C	conv,%	S_g,[d] m^2/g	V_p,[e] mL/g	<50 nm	50−500	500−1000	>1000
46	yes	130	83	342	2.46	19.4	51.2	15.0	14.3
8	no	130	94	312	2.12	25.5	52.8	11.9	9.8
24[f]	no	70	98	18.4	1.85	9.9	27.4	60.0	2.7

[a] General reaction conditions: polymerization mixture—styrene, 20 wt %; divinylbenzene, 20 wt %; 1-dodecanol, 60 wt %; BPO, 0.5 wt % (with respect to monomers); TEMPO, 1.2 molar excess (with respect to BPO). [b] Reaction time. [c] Temperature. [d] Specific surface area. [e] Pore volume. [f] Polymerization mixture consisted of 40% monomers, 40% dodecanol, and 20% toluene [ref 7b] to obtain pores in range similar to the other two monoliths.

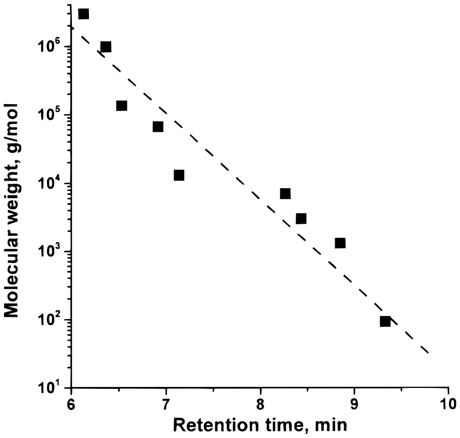

Figure 2. Inverse size-exclusion chromatography calibration curve of a poly(styrene-*co*-divinylbenzene) monolithic column prepared by TEMPO-mediated polymerization.[11]

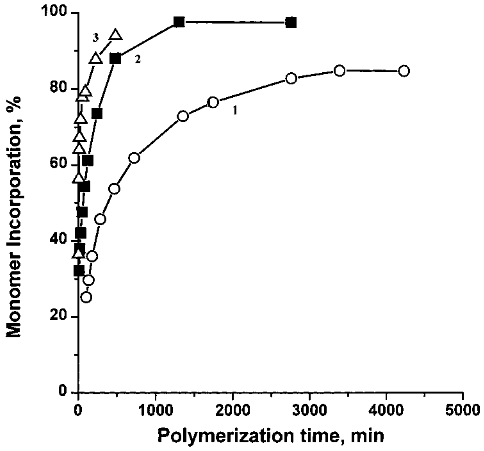

Figure 3. Reaction kinetics of the polymerization of styrene and divinylbenzene in the presence of TEMPO alone (curve 1) and TEMPO and 2 mol % acetic anhydride (with respect to monomers) (curve 2) and without TEMPO (3).[8]

addition of camphorsulfonic acid[12a] or various acylating agents.[12b] A similar rate acceleration was also observed in our system upon the addition of acetic anhydride,[12b] resulting in nearly quantitative monomer incorporation within 20 h (curve 2).

The reduced rate of polymerization in these systems resulting from the greatly reduced concentration of free radicals present at any given time has proven advantageous for the preparation of larger diameter monoliths. Such materials with homogeneous pore structures are difficult to prepare due to the inefficient dissipation of the heat of polymerization from the center of the unstirred mold.[13] Georges' group has earlier reported the absence of the Trommsdorff effect in TEMPO-mediated polymerizations.[14] This is reflected in the batch preparation of a 5 cm diameter poly(styrene-*co*-divinylbenzene) monolith in the presence of TEMPO, as an exotherm of only 6 °C was recorded at the center of the mold, and the resulting monolith did not exhibit any radial or axial heterogeneity.[15]

3. Grafting Studies. Yet another advantage of the TEMPO-mediated preparation of monoliths at 130 °C is the fact that chain ends remain capped with TEMPO, and these may act as latent initiators for the subsequent grafting of additional monomers to the internal pore surface of the monolith. To demonstrate this concept, sections of a monolith prepared in the presence of TEMPO were submerged separately in solutions of either 2-hydroxyethyl methacrylate (HEMA) or vinylbenzyl chloride (VBC). The mixtures were then heated in unstirred vials at 130 °C in the absence of other initiators or additional TEMPO.[16] After thorough extraction of the samples, their FT-IR spectra clearly exhibit new peaks at 1725 or 1265 cm^{-1} characteristic of the ester and benzyl chloride moieties of the respective grafted monomers. Significantly, the FT-IR spectra from control experiments run identically, but containing sections of monoliths prepared using only BPO as the initiator do not exhibit these bands, discounting the possibility that the previously observed peaks arose from thermally initiated polymerizations and subsequent grafting or physical absorption.

Although much remains to be done, these monolithic materials possessing completely redesigned pore size distribution profiles will undoubtedly further extend the range of applications of the macroporous polymer monoliths. For example, this new approach can afford materials in both column and capillary formats with specifically tailored porous structures and vastly enhanced resolution and efficiency for the separations of macromolecules in size-exclusion mode and for the rapid isocratic reversed-phase chromatography of small molecules. The use of TEMPO derivatives operating at lower temperature may also be suitable for the control of properties of macroporous beads prepared by conventional polymerization in aqueous suspension. Finally, the latent grafting potential of the TEMPO-capped chain ends should enable the preparation of a variety of macroporous composite materials with different chemistries and enhanced capacities.

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(8) Benzoyl peroxide (BPO; 0.5 wt % with respect to the monomers) and TEMPO when specified (1.2 molar excess with respect to BPO) were dissolved in a mixture of 20 wt % divinylbenzene (80% grade), 20 wt % styrene, and 60 wt % 1-dodecanol. Equal portions of this mixture (5 g) were weighed into glass ampules and deaerated using three freeze−pump−thaw cycles. The ampules were then sealed under vacuum and submerged in a 130 °C oil bath. The monoliths obtained after different polymerization times were extracted with methanol for 12 h, dried at 60 °C, and weighed to determine the percentage of monomer incorporation.

(9) The pore size distribution and specific surface area were determined in the dry state by mercury intrusion porosimetry and nitrogen adsorption/desorption (BET), respectively, using Autopore III and ASAP 2010 instruments (Micromeritics, Norcross, GA).

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(11) The monolithic column for ISEC was prepared by polymerization of a TEMPO-containing mixture at 130 °C for 20 h in a 50 × 8 mm i.d. stainless steel tube fitted with a 10 mm long Teflon tubular extension to eliminate the formation of void volume at the top of the column. After attachment to a Waters HPLC system and washing for 3 h with THF at a flow rate of 0.2 mL/min, solutions of toluene and polystyrene standards in THF were injected at a flow rate of 0.2 mL/min to obtain the calibration curve.

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(15) The large diameter column experiments were performed as described in ref 13.

(16) Grafting was carried out in a glass vial at 130 °C for 20 h with a mixture of 0.4 g of crushed monolith prepared in the presence of TEMPO and 4 mL of a 25 vol % solution of the appropriate monomer in cyclohexanol. The product was extracted with methanol for 48 h, dried, and analyzed by FT-IR spectroscopy and elemental analysis.

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