Macromolecules **2009**, *42*, 455−458 **455**

Synthesis of Photocleavable Poly(styrene-*block*-ethylene oxide) and Its Self-Assembly into Nanoporous Thin Films

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Received October 31, 2008
Revised Manuscript Received November 14, 2008

Introduction

Self-assembled nanostructures of block copolymers have been used to fabricate nanoporous thin films by selective removal of one of the two block domains. These materials are promising in a wide range of applications such as templates for nanostructure fabrication,[1] separation membranes,[2] and sensors.[3] So far, diverse examples of nanoporous materials obtained from block copolymer by selective removal of one block domain were reported such as chemical etching,[4] ozonolysis,[5] and UV degradation.[6] However, most of these protocols usually demand harsh conditions, are limited to the polymers bearing specific functional groups (i.e., alkenes), or both. Among the many extensively studied block copolymers that aim for these applications, poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO) has drawn much attention because it forms well-ordered cylindrical nanostructures normal to the surface with long-range order without the use of a neutralizing layer by the simple solvent annealing process, which is tremendously beneficial as a template from a practical point of view.[7] However, selective removal of the PEO domain from a well-ordered PS-*b*-PEO film has been a challenging problem. Hillmyer and coworkers reported a method using a strong nucleophilic acid, HI, to remove PEO domains selectively.[8] Hawker and coworkers prepared highly ordered films using a PS-*b*-PMMA-*b*-PEO triblock copolymer and used the short mid-PMMA block as a sacrificial domain, which was degraded by UV irradiation.[9] Recently, Venkataraman and coworkers reported the synthesis of PS-*b*-PEO block copolymer having an acid-sensitive trityl ether linkage and demonstrated that PEO domains could be selectively removed from the nanostructured film by acid treatment.[10] Although these strategies provide the successful removal of PEO domains, they still have drawbacks in the sense that they require the use of harsh chemicals and the preparation of synthetically more elaborate triblock copolymers.

In this Note, we describe the synthesis of an easily cleavable PS-*b*-PEO by UV irradiation in which a photochemically sensitive *ortho*-nitrobenzyl (ONB) group is installed as a linker. We also demonstrate its utility in the fabrication of nanoporous thin films. We take advantage of the ONB group that has been used in organic synthesis as a light-sensitive protecting group, a masking group for biological molecules, and a readily cleavable linker for solid-phase synthesis.[11] We have prepared the desired ONB-linked PS-*b*-PEO block copolymer, ONB-(PS-*b*-PEO), by atom transfer radical polymerization (ATRP)[12] using a ONB-functional PEO macroinitiator.

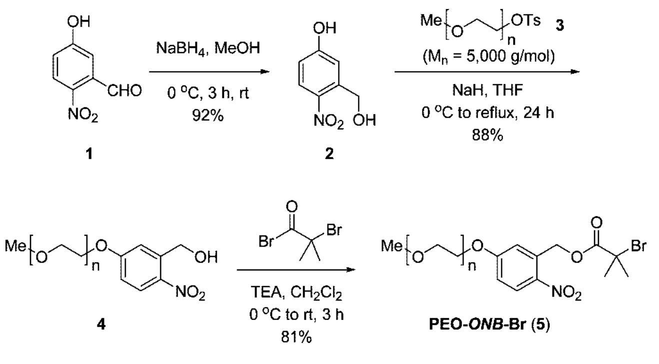
Experimental Section

Materials and Characterization. All commercially obtained solvents and reagents were used without further purification except as noted below. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Dry methylene chloride was obtained by distilling from calcium hydride. Monomethoxy PEO (5000 g/mol) was purchased from Aldrich. We prepared 5-hydroxy-2-nitrobenzaldehyde (**1**) in three steps starting from 3-hydroxybenzaldehyde by following the literature procedure[13] in 43% overall yield, or it can be obtained from a commercial source. We prepared α-methoxy-*ω*-toluenesulfonyl-PEO (**3**) starting from monomethoxy PEO by following the literature procedure.[14] ^{1}H and ^{13}C NMR spectra were obtained using a Varian Gemini-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometer. Elemental analyses were performed by the Organic Chemistry Research Center at Sogang University using a Carlo Erba EA 1180 elemental analyzer. Polymer molecular weights were estimated using a Sykam GmbH GPC system equipped with a Sykam S1122 HPLC pump, an S5200 autosampler, an S3580 differential RI and an S3210 UV/vis detector, and three Jordi Gel DVB GPC columns (500, 1000, and 10 000 Å; 300 × 7.8 mm^2) using $CHCl_3$ as an eluent at a flow rate of 1 mL/min. Photolysis of thin films was carried out using a UV light system (model LZC-ORG, Luzchem Research) equipped with eight Hitachi FL8BL-B (350 nm, 8 W) lamps. Atomic force microscopy (AFM) measurements were carried out using a Digital Instrument nanoscope IV-A in a tapping mode. Field emission transmission electron microscopy (TEM) imaging was performed on a JEOL JEM-2100F electron microscope operated at 200 kV. Film thicknesses were measured by a Stokes ellipsometer LSE (Gaertner Scientific).

3-Hydroxymethyl-4-nitrophenol (2). Sodium borohydride (635 mg, 16.8 mmol) was slowly added to a solution of 5-hydroxy-2-nitrobenzaldehyde (**1**) (1.4 g, 8.4 mmol) in MeOH (50 mL) at 0 °C and the resulting solution was stirred for 3 h at the same temperature. The reaction was cautiously quenched by the addition of a 10% HCl solution, and it was extracted with EtOAc (50 mL × 3). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated in vacuo. The yellow solid residue was purified by flash column chromatography with hexanes/EtOAc (1:1) to give 3-hydroxymethyl-4-nitrophenol as a yellow solid (1.3 g, 92% yield). $R_f = 0.4$ (Hex/EtOAc 1:1). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 10.89 (s, 1H), 8.07 (d, $J = 9.0$ Hz, 1H), 7.29 (s, 1H), 6.81 (d, $J = 9.0$ Hz, 1H), 5.52 (s, 1H), 4.85 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): 163.12, 142.98, 137.98, 127.84, 113.89, 113.86, 60.41. Anal. Calcd for $C_7H_7NO_4$: C, 49.71; H, 4.17; N, 8.28. Found: C, 50.02; H, 4.169; N, 7.884.

PEO-ONB-OH (4). Sodium hydride (77 mg, 3.2 mmol) was suspended in dry THF (5 mL). To the resulting suspension was slowly added 5-hydroxy-2-nitrobenzyl alcohol (**2**) (541 mg, 3.2 mmol) in THF (5 mL) at 0 °C. After stirring for 30 min at 0 °C, a solution of α-methoxy-*ω*-toluenesulfonyl-PEO **3** (4 g, 0.8 mmol, $M_n = 5000$ g/mol) in THF (10 mL) was added at 0 °C. The solution was allowed to warm to 70 °C and was stirred overnight. The reaction was quenched by the addition of distilled water (1 mL), then the mixture was filtered through a short pad of basic alumina. The filtrate was dripped in diethyl ether to precipitate the desired

Scheme 1. Synthesis of the ATRP Macroinitiator PEO-ONB-Br 5



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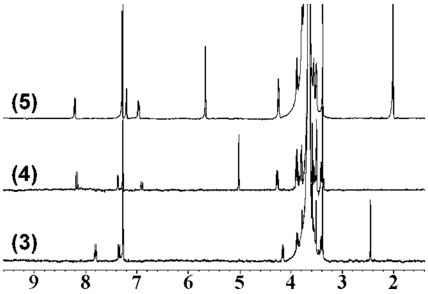


Figure 1. ^{1}H NMR spectra of functionalized PEO **3**, **4**, and **5** (300 MHz, $CDCl_3$).

polymer. The resulting white powder was collected by filtration and dried under vacuum for 1 day to give polymer **4** in 88% yield (3.5 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.16 (d, J = 9.0 Hz, 1H), 7.38 (s, 1H), 6.91 (d, J = 9.0 Hz, 1H), 5.01 (s, 2H), 4.27 (t, J = 4.5 Hz, 2H), 3.40−3.80 (br, $-CH_2CH_2-$), 3.38 (s, 3H).

PEO-ONB-Br (5). A 250 mL round-bottomed flask was equipped with a stir bar, PEO-ONB-OH (**4**) (800 mg, 0.16 mmol), and 4-dimethylaminopyridine (DMAP, catalytic amount, ∼10 mg). After the flask was capped with a rubber septum, the flask was filled with dry nitrogen by three vacuum−nitrogen cycles. Dry methylene chloride (10 mL) was added to the flask via a syringe to dissolve the mixture. Then, triethylamine (TEA, 0.4 mL) and 2-bromo-2-methylpropanoyl bromide (80 μL, 0.64 mmol) were sequentially added. The resulting solution was stirred for 20 h at room temperature. After 20 h, the reaction was quenched by the addition of methanol (1 mL) and was diluted with THF. HBr·TEA salt was removed by filtration through a short pad of basic alumina. The filtrate was dripped in diethyl ether to precipitate the polymer. The precipitates were collected by filtration and dried under vacuum overnight to provide the PEO-ONB-Br **5** as a white solid (650 mg, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.20 (d, J = 9.0 Hz, 1H), 7.21 (s, 1H), 6.96 (dd, J = 9.3 and 2.4 Hz, 1H), 5.66 (s, 2H), 4.24 (t, J = 4.5 Hz, 2H), 3.40−3.80 (br, $-CH_2CH_2-$), 3.38 (s, 3H), 2.01 (s, 6H).

Synthesis of ONB-(PS-*b*-PEO). PEO-ONB-Br **5** (300 mg, 0.06 mmol) and CuBr (9 mg, 0.06 mmol) were placed in a Schlenk flask. After the flask was filled with dry nitrogen by three vacuum−nitrogen cycles, styrene (3 mL, 29 mmol) was added. Then, three freeze−pump−thaw cycles were repeated, and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 12 μL, 0.06 mmol) was added. The mixture was heated to 90 °C for 8 h. After 8 h, the mixture was filtered through a short pad of basic alumina. The filtrate was precipitated by dripping in *n*-hexanes. After filtration and vacuum drying, ONB-(PS-*b*-PEO) was obtained as white powder (1.2 g, 36% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.4−7.3 (br, aromatic H), 3.4−3.8 (m, $-CH_2CH_2-$), 1.3−2.3 (br, $-CH_2CH-$).

Preparation of Nanoporous Thin Films. ONB-(PS-*b*-PEO) diblock copolymer was doped with KI (ratio of [O]/[K] = 64) in benzene,[15] and the solution (0.5 wt %) was spin-cast onto a silicon wafer (1.5 × 1.5 cm^2). After spin coating (3000 rpm, 50 s), the thin film substrates (thickness = 43 nm) were annealed for 2 h via a solvent annealing procedure (benzene/water at humidity of ∼85%).[16] Then, the thin films were exposed to UV light (350 nm) for 2 h in a UV reactor (LZC-ORG, Luzchem Research) equipped with eight Hitachi FL8BL-B (350 nm, 8 W) lamps (5.3 mW/cm^2). After the UV exposure, the films were rinsed with MeOH/H_2O (8:1) to remove PEO domains.

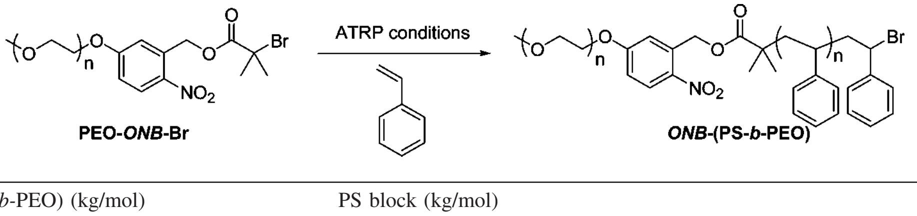
Results and Discussion

Ortho-nitrobenzyl (ONB) end-functionalized ATRP macroinitiator **5** was prepared in three steps starting from 5-hydroxy-2-nitrobenzaldehyde (**1**), as shown in Scheme 1. 5-Hydroxy-2-nitrobenzaldehyde (**1**) was reduced with sodium borohydride ($NaBH_4$) to give 5-hydroxy-2-nitrobenzyl alcohol **2** in 92% yield.

To introduce an ONB group at the chain end of poly(ethylene oxide), etherification of **2** with α-methyl-ω-*p*-toluenesulfonyl poly(ethylene oxide) (MeO-PEO-OTs, **3**)[14] was achieved in THF at 70 °C, providing polymer **4** in 88% yield. Finally, PEO-ONB-Br **5** was prepared in 81% yield by treatment of ONB-functionalized poly(ethylene oxide) **4** with 2-bromo-2-methylpropanoyl bromide in the presence of TEA and DMAP. The chain end functionality of each poly(ethylene oxide) was determined to be >95% by the ^{1}H NMR spectroscopic analyses of the polymers by comparing the resonance integrals of $-\mathbf{CH_2}OAr$ against that of $-OC\mathbf{H_3}$ (δ 3.37 (s)) (Figure 1). The resonances from the aromatic protons (δ 7.80 (d) and 7.35 (d)) and the methyl group (δ 2.45 (s)) from the *p*-toluenesulfonyl (OTs) group at the chain end are clearly seen in the NMR spectrum of MeO-PEO-OTs **3**. The appearance of the triplet at δ 4.15 ($C\mathbf{H_2}OAr$) indicates that the chain end is actually functionalized with a *p*-toluenesulfonyl group. After substitution of the OTs group with an ONB group, the peaks of the OTs group disappeared, and new peaks at δ 8.16 (d, $Ar-H_5$), 7.38 (s, $Ar-H_2$), 6.91 (d, $Ar-H_6$), and 5.01 (s, Ar-CH_2) appeared. The triplet at δ 4.15 in **3** has been shifted to δ 4.27 while maintaining its relative intensity to the end-OMe group, which indicates almost quantitative functional group transformation (spectrum 4 in Figure 1). ^{1}H NMR of PEO-ONB-Br **5** (spectrum 5 in Figure 1) also indicates complete functional group transformation, which is inferred from the chemical shift change in the CH_2OAr resonances from δ 5.01 to 5.66 and the appearance of a new resonance at δ 2.01 for the gem-dimethyl group.

Having synthesized PEO-ONB-Br **5**, we investigated the polymerization of styrene by ATRP using **5** as the macroinitiator. We prepared several ONB-(PS-*b*-PEO) block copolymers by using the typical ATRP conditions (CuBr, PMDETA, or dNbpy) with a good control of molecular weight and narrow polydispersity, as verified by GPC analysis and ^{1}H NMR

Table 1. Molecular Weight and Polydispersity Data of ONB-(PS-*b*-PEO)



	ONB-(PS-*b*-PEO) (kg/mol)			PS block (kg/mol)						
entry	M_n[d]	M_w[d]	PDI[d]	$M_{n,theor}$	$M_{n,calcd}$[d]	M_n[a]	M_w	PDI[d]	conversion (%)[a][yield (%)][e]	time [temp] h [°C]
1[b]	48.6	55.7	1.15	28.7	22.3	27.8	23.2	1.04	69 [36]	10 [110]
2[b]	41.6	45.5	1.09	22.5	24.6	23.7	25.5	1.04	45 [36]	8 [90]
3[c]	25.1	26.9	1.07	10.0	10.1	11.3	10.4	1.03	30 [39]	17 [110]

[a] Calculated by ^{1}H NMR integration compared with the intensity of PEO backbone resonances. [b] PMDETA was used. [c] dNbpy was used. [d] Determined by GPC using polystyrene standards. [e] Isolated yields of the polymers obtained by precipitation into *n*-hexanes.

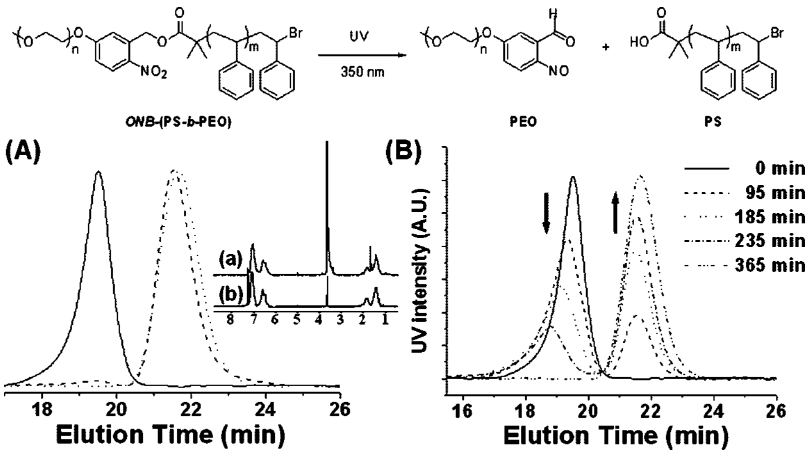


Figure 2. (A) GPC traces (UV detector) of ONB-(PS-*b*-PEO) (23.7-*b*-5.0 K, entry 2 in Table 1) before (—) and after (•••, solution; ---, film) UV light exposure (350 nm, 5.3 mW/cm^2) for 6 h. Inset shows ^{1}H NMR spectra: (a) ^{1}H NMR of the ONB-(PS-*b*-PEO) block copolymer in $CDCl_3$ showing the characteristic signals of PS and PEO regions and (b) ^{1}H NMR of the precipitates formed in MeOH after UV irradiation. (B) Monitoring of the photocleavage reaction of ONB-(PS-*b*-PEO) (23.7-*b*-5.0 K, entry 2 in Table 1) in THF by GPC.

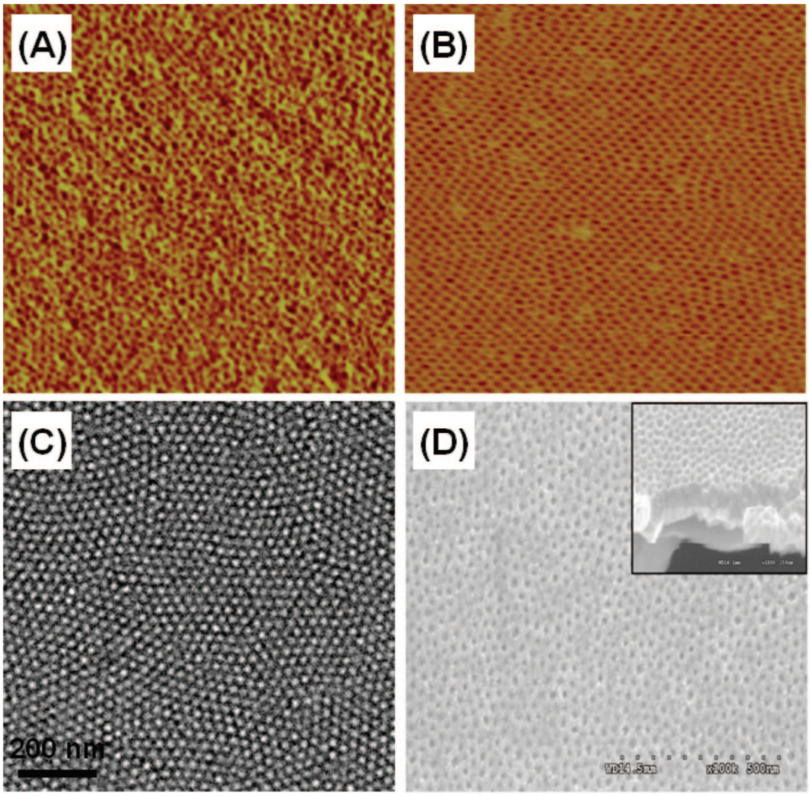


Figure 3. AFM images (1 × 1 μm^2) of ONB-(PS-*b*-PEO) (23.7-*b*-5.0 K) films (thickness = 43 nm) (A) as cast on a silicon wafer and (B) after solvent annealing for 2 h (benzene/water). (C) TEM image of the nanoporous PS thin film fabricated by UV irradiation followed by selective solvent rinse (MeOH/H_2O (8:1)) of the ONB-(PS-*b*-PEO) film. This image was obtained without metal staining. (D) SEM image of the same nanoporous PS thin film. A side view (45°) is shown in the inset image.

spectroscopy (Table 1). To determine the molecular weight of the resulting PS block more accurately, each block copolymer was cleaved by UV irradiation (350 nm, THF, 6 h), and the resulting polystyrene blocks were analyzed by GPC after purification by precipitating in MeOH. The use of PMDETA as the ligand (entry 1 and 2 in Table 1) resulted in faster polymerization of the polystyrene block than did the use of dNbpy (entry 3 in Table 3).

The ONB-(PS-*b*-PEO) block copolymer (23.7-*b*-5.0 K, entry 2 in Table 1, 20 mg) was then dissolved in THF (2 mL), and the solution was exposed to UV light at 350 nm (5.3 mW/cm^2) for 6 h. After 6 h, the cleaved polystyrene block was obtained by trituration into MeOH and collection of the precipitate. ^{1}H NMR analysis of the precipitates indicated that most of the PEO was removed, as shown in Figure 2 (inset b). GPC analysis of the precipitate also showed that the block copolymer was completely cleaved under these conditions (dotted line in Figure 2A). Furthermore, the cleavage could be efficiently achieved in not only solution but also solid phase under similar conditions. An ONB-(PS-*b*-PEO) polymer film on a glass slide was prepared by drop casting of the polymer solution (2 wt % in THF) and was exposed to UV light (350 nm) for 2 h. The film was then dissolved in $CHCl_3$ and checked by GPC. As shown in Figure 2A, the GPC trace (dashed line) is similar to that obtained in the solution phase (dotted line), which indicates that the photocleavage of the polymer in the solid state was complete in 2 h. It is noteworthy that no detectable high-molecular-weight polystyrene peak was observed under these long-wavelength UV irradiation conditions. The time dependence of the photocleavage of ONB-(PS-*b*-PEO) in solution (1 wt % in THF) was monitored by GPC (Figure 2B). The GPC traces were recorded after the designated time periods of irradiation with 350 nm UV light. The ONB-(PS-*b*-PEO) peak gradually disappeared, and the cleaved PS homopolymer peak appeared accordingly. The reaction was determined to be complete in 6 h under these conditions (total dose of ~114 J/cm^2).

Once the photolytic cleavage behavior of ONB-(PS-*b*-PEO) was successfully characterized, we attempted the selective removal of the PEO domains from a solvent annealed ONB-(PS-*b*-PEO) film by photolysis. To promote the vertically aligned cylinders of PEO domains, ONB-(PS-*b*-PEO) (23.7-*b*-5.0 K) was doped with KI (ratio of $[O]/[K] = 64$) in benzene,[15] and the resulting solution (0.5 wt %) was spin-cast on a silicon wafer. The as-cast ONB-(PS-*b*-PEO) film showed vertically aligned cylindrical morphology without long-range ordering (Figure 3A). After solvent annealing of this film with benzene/water for 2 h, significantly improved long-range ordering was observed, as shown in Figure 3B, where PEO domains are mostly seen as a cylinder form in a PS matrix. The resulting film was exposed to UV light (350 nm) for 2 h and washed with MeOH/H_2O (8:1). The TEM image (Figure 3C) of the resulting film shows the nanoporous structure. The bright circles correspond to the nanopores where the cylindrical PEO domains were removed after UV light irradiation and selective solvent rinse. The SEM image of the film (Figure 3D) also supports the fact that the PEO domains were successfully removed.

Conclusions

We have successfully synthesized a selectively photocleavable PS-*b*-PEO block copolymer (ONB-(PS-*b*-PEO)) by ATRP with a good control of molecular weight and polydispersity. The key in the design of this unique block copolymer was to incorporate a photocleavable linking unit, ONB, in the middle of the block copolymer. The facile photocleavage of ONB-(PS-*b*-PEO) was carried out by simple irradiation with long-wavelength UV light (350 nm) for several hours with low-power UV lamps (8 × 8 W, 5.3 mW/cm^2) in both solution and thin films. Fabrication of nanoporous PS films was easily achieved using this block copolymer. We are aiming to exploit the utility of this polymer by taking advantage of the functionality inside the nanopores because COOH groups should be generated by ONB group cleavage.

Acknowledgment. This work was supported by the Center for Bioactive Molecular Hybrid (CBMH) of KOSEF. B.M. acknowledges the Sogang University grant (200811016), and M.K. gratefully acknowledges a fellowship of the BK21 program from the Ministry of Education and Human Resources Development.

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MA802434G