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Thermally Induced Mesophase Development in Ethanesilica Films *via* Macromolecular Templating Approach

Whirang Cho and Kookheon Char*

School of Chemical and Biological Engineering, Center for Functional Polymer Thin Films, Seoul National University, Seoul 151-744, Korea

Suyong Kwon

Division of Physical Metrology, Korea Research Institute of Standards and Science, Daejeon 305-340, Korea

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Abstract: Mesoporous ethanesilica thin film was prepared using PEO-PLGA-PEO triblock copolymers as structure-directing agents and (1,2-bis(triethoxysilyl) ethane BTESE; bridged organosilicates) as inorganic precursors via one-step sol-gel condensation of ethanesilica precursors. The mesostructure of ethanesilica films is critically dependent on the processing experimental parameters after the hydrolyzed silica sol mixture was spin-cast. This study examined the effects of the block copolymer template/organosilica precursor ratio in the casting solution and aging period before calcination of the mesostructure. It was further demonstrated that mesoscopic ordering of organosilicate thin films is induced by the rearrangement of block copolymer template/organosilica hybrid during thermal decomposition of the PEO-PLGA-PEO triblock copolymer. The mesoporous structure and morphology were characterized by SAXS, TEM and solid-state NMR measurement.

Keywords: mesoporous thin film(s), block copolymer template(s), organosilicate(s), structural rearrangement.

Introduction

Preparation of mesoporous materials in thin film form has attracted considerable attention due to their possible applications in the separations, chemical sensors, optical devices, and electronic devices such as low-k dielectrics.[1-11] In particular, organic modification of the mesoporous silica framework is regarded as an important technique because it changes the physical and chemical properties of porous materials needed for various applications. A new class of mesoporous materials has been reported such as periodic mesoporous organosilicas (PMOs) through the sol-gel condensation of organo-bridged silsesquioxanes.[12-19] Until recently, there have been a few reports on surfactant-templated PMO films with bridge-bonded organic groups in the presence of low molecular-weight surfactants.[16,18-20] A simple way to synthesize mesoporous silica films on the substrate has been developed by dip-coating[21-23] or spin-coating[24,25] utilizing evaporation induced self-assembly (EISA) route.[26,27] From a practical standpoint, spin coating would be an efficient process method for the rapid preparation of mesostructured films on a substrate.[28-30]

In the present study, we describe an approach for the synthesizing ordered mesoporous organosilicate films by spin coating method employing 1,2-bis(triethoxysilyl)ethane (BTESE) as an inorganic precursor and poly(ethylene oxide)-poly (DL-lactic acid-*co*-glycolic acid)-poly(ethylene oxide) (PEO-PLGA-PEO: LGE49) as a structure-directing agent. Previously, more hydrophobic PLGA block than the PPO block in typical PEO-PPO-PEO block copolymers is proven to provide more efficient contrast between hydrophilicity and hydrophobicity such that the organosilicate is effectively confined in the PEO matrix phase.[31] A key idea for realizing ordered mesophases in ethanesilica films involves restructuring silica/block copolymer hybrid *via* preferential decomposition of block copolymer template during calcination process. It is further demonstrated that the ordering of mesoporous organosilicate thin film can be tuned by block copolymer/organosilica precursor ratio in the casting solutions and drying period before calcinations process.

*Corresponding Author. E-mail: khchar@plaza.snu.ac.kr

Experimental

Synthesis of Block Copolymer Templates. We have synthesized a PEO-PLGA-PEO ($EO_{16}(L_{28}G_3)EO_{16}$) triblock copolymer (denoted as LGE49) through the ring-opening polymerization from mixtures of distilled 3,6-dimethyl-1,4-dioxane-2,5-dione (DL-lactide) (Aldrich) and glycolide (Polyscience)

with mono-methoxypoly(ethylene oxide) (Aldrich) and hexamethylene diisocyanate (Sigma) as a coupling agent. The molecular weight (4,900) and polydispersity index (1.23) were determined by GPC and their functional compositions were quantified with ^{1}H NMR analysis. The weight fraction of PEO blocks (f_{PEO}) for the triblock copolymer prepared in the present study was found to be 0.38.[31-35]

Preparation of Mesoporous Organosilica as Thin Film Form. Mesoporous organosilicate thin films were prepared using a silica sol solution containing PEO-PLGA-PEO ($EO_{16}(L_{28}G_3)EO_{16}$) copolymer as a structure-directing agent. The required amount of LGE 49 template was mixed with EtOH, H_2O, HCl, and BTESE then stirred for 1 h at 40 °C. One of the typical molar compositions of the final mixture was BTESE:LGE49:H_2O:EtOH:HCl=1:0.02:13:26:0.02. The homogeneous sol mixture then spin cast on Si wafer followed by evaporating the residual solvent under oven at 35 °C. The substrate used for SAXS measurement was polished thin glass (cover slide, MARIENFELD) since the glass is transparent to X-ray. Samples were cured at 450 °C for 1 h after pre-annealing at 200 °C for 30 min with a homemade furnace under N_2 purge.

Thin Film Characterization. Small angle X-ray scattering measurements were conducted at the 3C2 beamline in Pohang Light Source (PLS).[36] Samples deposited on the glass substrate were put vertically toward to the incident X-ray beam. The wavelength (λ) of the synchrotron beam was 1.54 Å and the energy resolution ($\Delta\lambda/\lambda$) was 5×10^{-4}. The range of moving angle of goniometer was varied between 0.2° and 4.2°. A JEM-2000EXII electron microscope operating at 200 KV was used for the TEM investigation. Film specimen was made as follows: First epoxy resin was put on the spin-cast film and then it was aged at 60 °C in oven. Si-wafer was removed by quenching in liquid nitrogen. The film was then coated with 20 nm gold layer as a marker to aid identification, next embedded in an epoxy resin mold. Cross sectional slices were obtained by cutting with a diamond knife using a microtome.

Results and Discussion

In order to favor fast hydrolysis and slow condensation of silica, pH condition is controlled to be close to the isoelectric point of silica (pH~2).[37] In addition, an important experimental parameter that should be controlled in the synthesis of ordered mesoporous organosilicates is the miscibility between the organosilica precursor and the hydrophilic PEO block. In a previous study, it was demonstrated that increased miscibility at higher temperature is due to increase in the relative hydrophobicity of the PEO block with the increase in temperature. It is thus matched with the relative hydrophobicity of the BTESE precursor in the range of 40-50 °C for forming ordered mesophases.[31]

The mesophases of the films were investigated by SAXS measurement with changing thermal treatment temperature. Figure 1 shows the primary scattering (100) peak starts to appear at 200 °C and gradually increases its intensity with a concomitant increase of calcination temperature in the range of 250 to 400 °C. It suggests that the assembly of silica/block copolymer hybrids into periodic mesostructure is strongly correlated with the template degradation and progressive silica condensation during calcination step. The d (100) spacing of ordered domains decreased from 12.3 to 10.6 nm with increasing calcination temperature due to structural shrinkage normal to the substrate. It has already been reported that the degree of silica condensation and the change in the interface of the silica/organic structure-directing agents critically impacts on the reconstruction of mesophases by the release of trapped water or organic groups.[37-42] It is thus expected that a low degree of silica polymerization and consequent appropriate silica network flexibility allows the rearrangement of block copolymer template/silica hybrid moieties during the decomposition of LGE49 triblock copolymer templates.

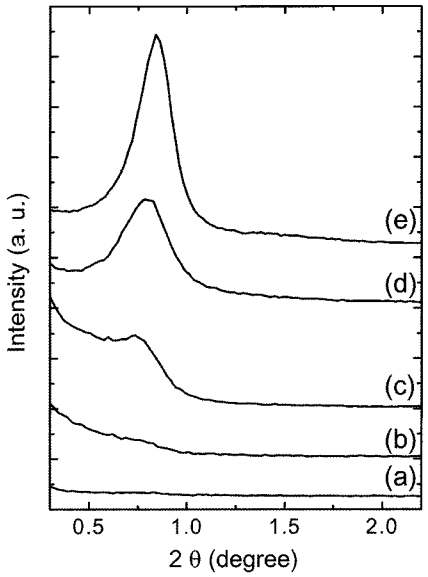

Figure 1. SAXS patterns of organosilicate films prepared with increasing calcination temperature: (a) 100 °C; (b) 200 °C; (c) 250 °C; (d) 300 °C; (e) 400 °C. As-synthesized films were spin-coated from block copolymer/silica sol mixture (ϕ_{bcp}=0.3) and dried at 35 °C for 72 h before calcination.

Mesosporous organosilica films were obtained upon drying of silica/block copolymer composite films at 35 °C and following calcination step for the removal of block copolymer templates. Figure 2(a) shows the 24 h drying-treated sample has no scattering peaks, implying disordered mesophases. However, ordered pore arrangement is appeared as a consequence of over 36 h drying treatment and the thermal calcination step confirmed by pronounced (100) scattering peak. Drying treatment could lead to a decrease in the number of dangling silanol groups and consequent decrease

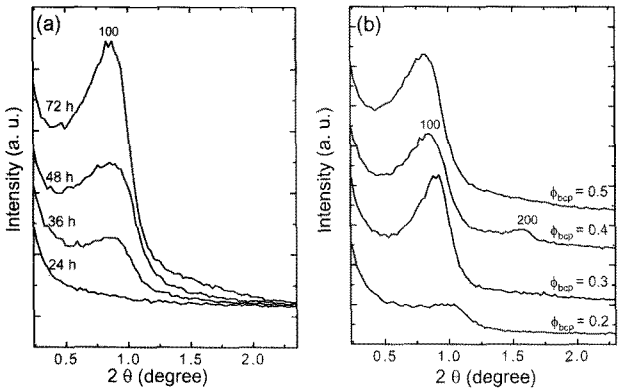

Figure 2. SAXS patterns of calcined mesoporous organosilicate films prepared by varying (a) drying treatment time before calcination (when ϕ_{bcp}=0.3); (b) volume ratio of block copolymer template to organosilicates.

in the mechanical strain during calcination.[43] Therefore, prolonging the aging treatment period for silica/block copolymer composite films leads to structural integrity for enduring high temperature during calcination process. To study the effect of block copolymer contents on the mesophases, samples were prepared by varying the amount of PEO-PLGA-PEO templates in the starting silica sol mixture. Then, as-synthesized films were dried at 35 °C for 72 h in the same way. Figure 2(b) shows SAXS patterns of mesoporous organosilicate films with varying the volume ratio, ϕ_{bcp} ([block copolymer]/([block copolymer]+[organosilica precursor])) ranged from 0.2 to 0.5. When the volume ratio, ϕ_{bcp} was 0.4, two well-resolved peaks indexed as (100) and (200) appears as represented in SAXS patterns. The presence of scattering peaks at these spacings indicates a 2D hexagonal mesophase. The intense (100) peak shows the lattice spacing of d=10.5 nm corresponding to the 2D-hexagonal unit cell parameter a =12.1 nm. The absence of (110) peak in 2D-hexagonal mesostructure of powdered samples indicates that planes of the hexagonal unit cell is oriented parallel to the substrate.[44] It is noted that the ordered mesoporous films can be obtained in a wide range of block copolymer compositions ($0.2<\phi_{bcp}<0.5$) with initial increase of d-spacing (ϕ_{bcp}=0.2; 8.9 nm) followed by almost same d-spacing of 10.5 nm for ϕ_{bcp}=0.4 and ϕ_{bcp}=0.5 as well. Taking into account that well-defined 2D-hexagonal mesophase is pronounced in the range of $0.4<\phi_{bcp}<0.5$, it leads us to conclude that cooperative self-assembly of silica/block copolymer composite is highly dependent on the balanced hydrogen and electrostatic interaction between them at the preceding range.

Figure 3 shows the thermal decomposition of block copolymer template and silica/block copolymer composite films containing structure-directing agents with thermal gravimetric analysis (TGA). A significant weight loss in the TGA scans of typical P123 block copolymer is observed in the temperature range from 300 to 400 °C (Figure 3(a)(A)). In contrast, a stepwise decomposition of LGE49 block copolymer template is observed as depicted in Figure 3(a)(B). Based on the molar ratio of each block, the weight loss up to 300 °C is mainly associated with the removal of PLGA block and the following decomposition of PEO block is completed at 300 to 400 °C, showing the weight loss of 60% and 40%, respectively. It is important to note that the decomposition temperature of the LGE49 block copolymer is lower than that of the P123 block copolymer. For SBA-15 mesostructured silica film synthesized with P123 block copolymer template exhibits a single oxidation step in the temperature range from 350 to 400 °C well correlated with that of P123 block copolymer templates as shown in Figure 3(b)(A). In contrast, mesostructured organosilica film containing LGE49 block copolymer shows a stepwise degradation in the range from 200 to 260 °C and 260 to 400 °C, respectively. The

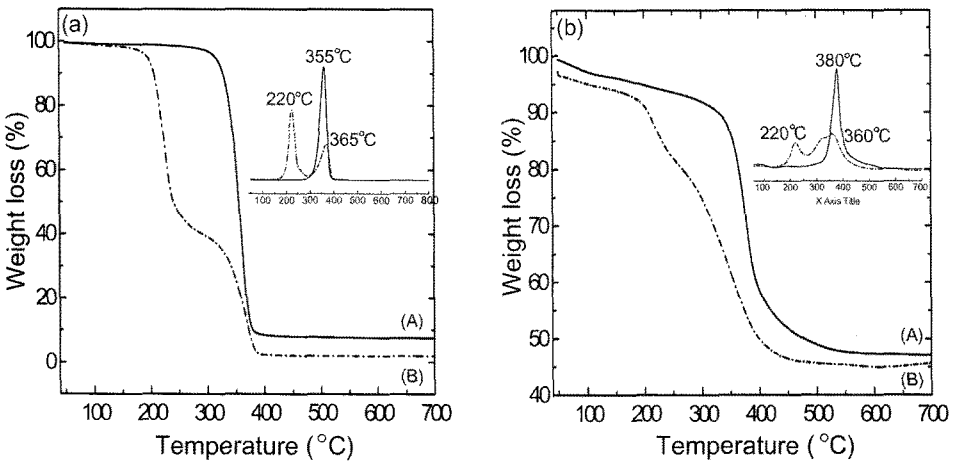

Figure 3. TGA and DTG (inset) spectra of (a) block copolymer template and (b) mesostructured silica films prepared with: (A) Pluronic P123 ($EO_{20}PO_{70}EO_{20}$: Mw=5,800) triblock copolymer template; (B) LGE 49 ($EO_{16}(L_{28}G_3)EO_{16}$) triblock copolymer template. The thermal analysis was performed in N_2 flow with heating rate of 5 °C/min.

former weight loss can be associated with the water originating from the polycondensation reaction as well as the partial decomposition of LGE49 block copolymer template, which is well in accordance with that of pure LGE49 block copolymer templates. Taking into account the previous SAXS results, this suggests that the preferential degradation of LGE49 template plays a crucial role in proceeding to the ordered mesophases in the temperature range between 200 and 250 °C.

Further evidence on the different mode of template degradation and information on the degree of silica condensation can be found from the analysis of FTIR measurements with continuous increase of calcination temperature as shown in Figure 4. All infrared spectra of mesoporous organosilica films were normalized using peak area corresponding to Si-CH_3 around 1270 cm^{-1}, due to its thermal stability up to 420 °C. We observed that the peak intensity at 1760 cm^{-1} assigned to carbonyl groups in the PLGA blocks of LGE49 templates notably decreases above 200 °C and completely disappears at 350 °C while a small amount of residual methylene (-CH_2-) group is left even after curing at 450 °C. Under acidic conditions, silica moieties co-assemble with the EO block through (S^0H^+)(X^-T^+) pathway, therefore it is believed that the EO block is stabilized by the condensed silica and degraded at a higher temperature compared with pure block copolymer.[37] As increasing temperature, the intensity of the vibrational band assigned to Si-O stretching at around 1040 cm^{-1} increases while the intensity of the band assigned to the cage-like Si-O stretching at 1130 cm^{-1} decreases, implying the increased dense matrix structure above 300 °C. This spectroscopic result suggests that structural rearrangement of silica/block copolymer hybrid is facilitated by the flexible inorganic framework and loss or partial block copolymer template at the early stage of silica condensation below 300 °C.

Representative film was prepared using 45 vol% LGE49 block copolymer template and characterized by transmission electron spectroscopy (TEM). Figure 5(a), (b) display images of a film deposited from reference silica/bcp sol while Figure 5(c) corresponds to a film produced from diluted sol mixture in order to decrease its thickness (diluted to 1:3 with EtOH). A randomly oriented mesophase can be seen before calcination (Figure 5(a)) while well-defined hexagonal mesostructure is located near the air/film interface after

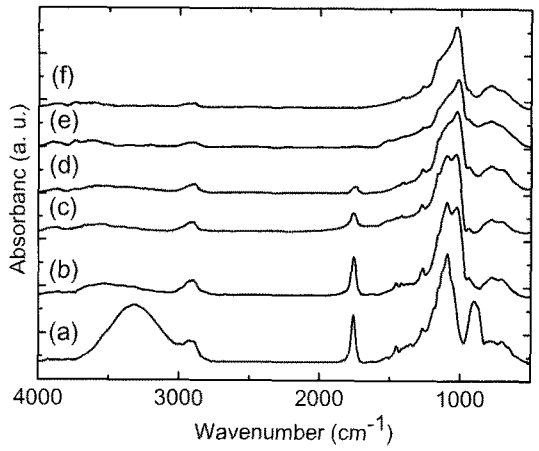

Figure 4. FTIR spectra of mesoporous organosilicate films with increasing calcination temperature: (a) as-synthesized; (b) 200 °C; (c) 250 °C; (d) 300 °C; (e) 400 °C; (f) 450 °C.

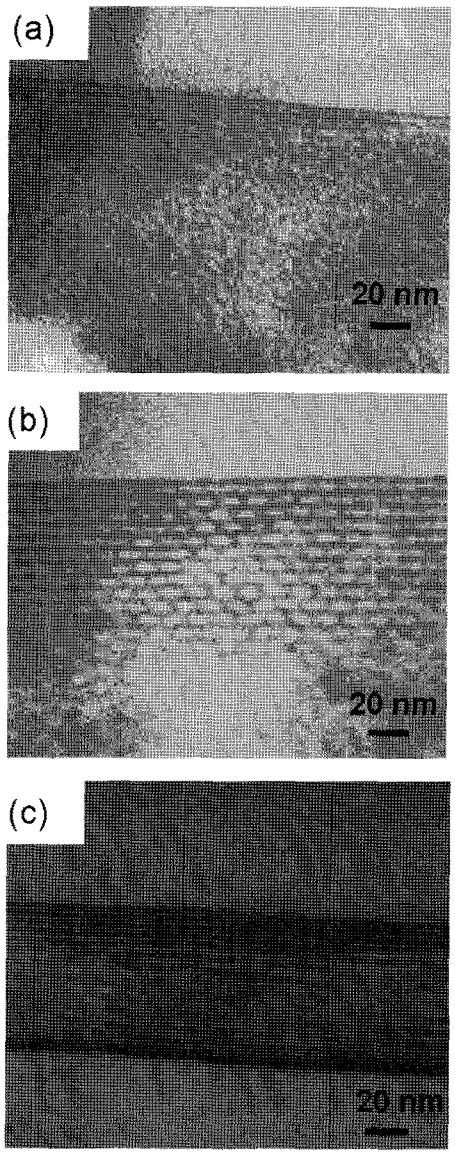

Figure 5. TEM image of (a) mesostructured organocilia before calcination and (b) mesoporous organosilica after calcination prepared with LGE 49 ($EO_{16}(L_{28}G_3)EO_{16}$) triblock copolymer template. (c) Thinner mesoporous organosilica film by dilution with EtOH. As-synthesized films were spin-coated from block copolymer/silica sol mixture (ϕ_{bcp}=0.45) and dried at 35 °C for 72 h before calcination. Then, composite silica/block copolymer films were cured at 450 °C for 1 h after pre-annealing at 200 °C for 30 min under N_2 purge.

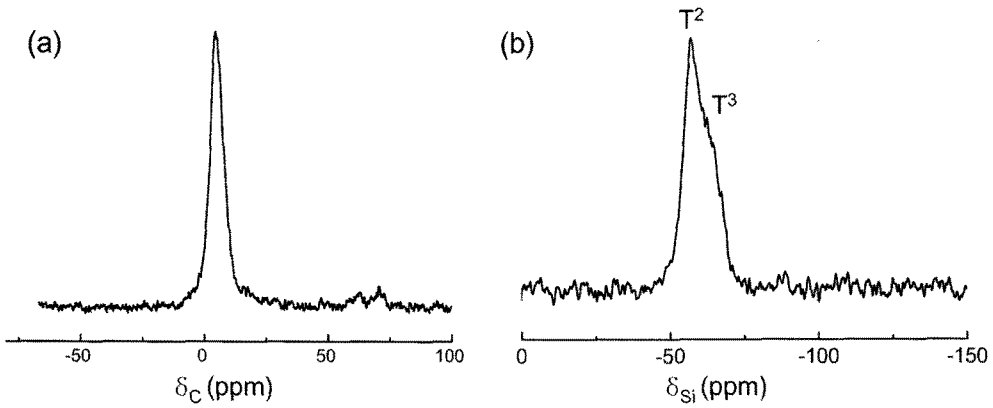

Figure 6. Solid-state (a) ^{13}C CP-MAS NMR and (b) ^{29}Si CP-MAS NMR spectra of mesoporous organosilicate films prepared with LGE 49 ($EO_{16}(L_{28}G_3)EO_{16}$) triblock copolymer template after calcination.

template removal as shown in Figure 5(b). The inter-pore spacing of hexagonal unit cell is about 10 nm in good agreement with the SAXS results. These images confirm the hypothesis of development of mesostructure during calcination suggested by combined preceding SAXS patterns (Figure 1) and TGA profiles (Figure 3). It is plausible that the propagation of cooperative self-assembly of silica/bcp hybrid was triggered by interfacial alignment from the interface to the center of the film. At a certain time, the mesostructure of the film kinetically freezes out as the silica network is too rigid to undergo further reorganization.[45] As film thickness is decreased, most of the domains had time to realign with the interfaces before rigidification of the silica networks. This suggests that the dilution and consequent decrease in film thickness leads to an extended proportion of well-textured mesophases ranging over almost entire film (~70 nm) as shown in Figure 5(c).[46]

In order to verify that the BTESE is incorporated into the oragnosilica matrix framework, solid state ^{13}C and ^{29}Si CP-MAS NMR experiments on the calcined samples were performed. The ^{13}C CP-MAS NMR spectrum of Figure 6(a) shows single resonance peak assigned to the ethane carbon δ -4 indicating complete removal of the LGE templates by calcination and retaining bridged ethane groups. The ^{29}Si CP-MAS NMR spectrum of Figure 6(b) shows the characteristic signals assigned to $CSi(OSi)_3$ (T^3, δ-65) and $CSi(OSi)_2(OH)$ (T^2, δ-57), respectively, confirming the presence of ethane moieties inside the organosilica framework. The absence of Q^n sites in the ^{29}Si CP-MAS NMR spectra indicates that the cleavage of Si-C bonds during polymerization of organosilicate is negligible.

Conclusions

In summary, we have successfully obtained ordered 2D hexagonal (*p6mm*) mesoporous ethanesilicate films by employing PEO-PLGA-PEO triblock copolymers containing more hydrophobic poly(DL-lactic acid-*co*-glycolic acid) block, as compared with typical PPO block, and BTESE as silica precursors. To prepare such an ordered mesophase, we controlled the drying time of the as-synthesized films before calcination and volume ratio of [block copolymer template]/[organosilica precursor] in casting solution for enhancing the cooperative organization between block copolymer micelles and silica precursor. Thermally benign poly(DL-lactic acid-*co*-glycolic acid) blocks played a key role in allowing the rearrangement of block copolymer template/organosilicate hybrid during its preferential decomposition. It is demonstrated that there is an optimum window to achieve highly ordered mesophases in organosilica thin films during thermal treatment when silicate network is still flexible.

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References

(1) M. Ogawa, *J. Am. Chem. Soc.*, **116**, 7941 (1994).
(2) I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger, and S. M. Gruner, *Science*, **273**, 892 (1995).
(3) H. Yang, A. Kuperman, N. Coombs, S. Mamich-Afara, and G. A. Ozin, *Nature*, **379**, 703 (1996).
(4) N. Nishiyama, A. Koide, Y. Egashira, and K. Ueyama, *Chem. Commun.*, 2147 (1998).
(5) J. Y. Ying, C. P. Mehnert, and M. S. Wong, *Angew. Chem. Int. Ed.*, **38**, 56 (1999).

(6) S. Y. Kwon, J. C. Kim, and B. I. Choi, *Thin Solid Films*, **516**, 2843 (2008).
(7) S. Walheim, E. Schaffer, J. Mlynek, and U. Steiner, *Science*, **283**, 520 (1999).
(8) E. Huang, M. F. Toney, W. Volksen, D. Mecerreyes, P. Brock, H. C. Kim, C. J. Hawker, J. L. Hedrick, V. Y. Lee, T. Magbitang, R. D. Miller, and L. B. Lurio, *Appl. Phys. Lett.*, **81**, 2232 (2002).
(9) J. L. Hedrick, R. D. Miller, C. J. Hawker, K. R. Carter, W. Volksen, D. Yoon, and M. Trollsas, *Adv. Mater.*, **10**, 1049 (1998).
(10) A. Stein, B. J. Melde, and R. C. Schroden, *Adv. Mater.*, **12**, 1403 (2000).
(11) (a) B. J. Cha, S. Kim, and K. Char, *Macromol. Res.*, **13**, 176 (2005). (b) S. Kim, K. Char, J. Hahn, J. K. Lee, D. Y. Yoon, H. W. Rhee, and M. Y. Jin, *Macromol. Res.*, **15**, 1 (2007).
(12) S.-S. Kim, T. R. Pauly, and T. J. Pinnavaia, *Chem. Commun.*, 1661 (2000).
(13) T. Asefa, M. J. MacLachlan, N. Coombs, and G. A. Ozin, *Nature*, **402**, 867 (1999).
(14) G. J. Kim, H. S. Kim, Y. S. Ko, and Y. K. Kwon, *Macromol. Res.*, **13**, 499 (2005).
(15) B. J. Melde, B. T. Holland, C. F. Blanford, and A. Stein, *Chem. Mater.*, **11**, 3302 (1999).
(16) Y. Lu, H. Fan, N. Doke, D. A. Loy, R. A. Assink, D. A. Lavan, and C. J. Brinker, *J. Am. Chem. Soc.*, **122**, 5258 (2000).
(17) J. Joo, T. Hyeon, and J. Hyeon-Lee, *Chem. Commun.*, 1487 (2000).
(18) O. Dag, C. Yoshina-Ishii, T. Asefa, M. J. MacLachlan, H. Grondey, N. Coombs, and G. A. Ozin, *Adv. Funct. Mater.*, **11**, 213 (2001).
(19) B. D. Hatton, K. Landskron, W. Whitnall, D. D. Perovic, and G. A. Ozin, *Adv. Funct. Mater.*, **15**, 823 (2005).
(20) (a) S. S. Park and C. S. Ha, *Chem. Commun.*, 1986 (2004). (b) S. S. Park and C. S. Ha, *Chem. Mater.*, **17**, 3519 (2005).
(21) Y. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. Gong, and J. I. Zink, *Nature*, **389**, 364 (1997).
(22) A. Selinger, P. R. Weiss, A. Nguyen, Y. Lu, R. A. Assink, W. Gong, and C. J. Brinker, *Nature*, **394**, 256 (1998).
(23) D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Bradley, F. Chmelka, and G. D. Stucky, *Adv. Mater.*, **10**, 1380 (1998).
(24) M. Ogawa, *Chem. Commun.*, 1149 (1996).
(25) M. Ogawa and N. Masukawa, *Micropor. Mesopor. Mater.*, **38**, 35 (2000).
(26) M. Ogawa, *J. Am. Chem. Soc.*, **116**, 7941 (1994).
(27) C. J. Brinker, Y. Lu, A. Sellinger, and H. Fan, *Adv. Mater.*, **11**, 579 (1999).
(28) N. Nishiyama, S. Tanaka, Y. Egashira, Y. Oku, and K. Ueyama, *Chem. Mater.*, **14**, 4229 (2002).
(29) S. Tanaka, N. Nishiyama, Y. Oku, Y. Egashira, and K. Ueyama, *J. Am. Chem. Soc.*, **126**, 4854 (2004).
(30) J.-I. Jung, J. Y. Bae, and B.-S. Bae, *J. Mater. Chem.*, **14**, 1988 (2004).
(31) (a) E.-B. Cho, K.-W. Kwon, and K. Char, *Chem. Mater.*, **13**, 3837 (2001). (b) E.-B. Cho and K. Char, *Chem. Mater.*, **16**, 270 (2004).
(32) Y. I. Jeong, D. G. Kim, and M. K. Jang, *Macromol. Res.*, **16**, 717 (2008).
(33) J. H. Do, J. H. An, and Y. S. Joun, *Macromol. Res.*, **16**, 695 (2008).
(34) M. J. Kim, J. H. Kim, and G. Yi, *Macromol. Res.*, **16**, 345 (2008).
(35) H. Park, K. Y. Lee, and S. J. Lee, *Macromol. Res.*, **15**, 238 (2007).
(36) M. Ree and I. S. Ko, *Phys. High Tech.*, **14**, 2 (2005).
(37) (a) D. Grosso, F. Cagnol, G. J. de A. A. Soler-Illia, E. L. Crepaldi, H. Amenitsch, A. B.-Bruneau, A. Bourgeois, and C. Sanchez, *Adv. Funct. Mater.*, **14**, 30 (2004). (b) M. Choi, B. Lim, and J. Jang, *Macromol. Res.*, **16**, 200 (2008).
(38) S. Besson, T. Gacoin, C. Jacquiod, C. Ricolleau, D. Babonneau, and J.-P. Boilot, *J. Mater. Chem.*, **10**, 1331 (2000).
(39) S. P. Naik, S. Yamakita, M. Ogura, and T. Okubo, *Micropor. Mesopor. Mater.*, **75**, 51 (2004).
(40) S. P. Naik, M. Ogura, H. Sasakura, Y. Yamaguchi, Y. Sasaki, and T. Okubo, *Thin Solid Films*, **495**, 11 (2006).
(41) M. Ogura, H. Miyoshi, S. P. Naik, and T. Okubo, *J. Am. Chem. Soc.*, **126**, 10937 (2004).
(42) D. Grosso, F. Babonneau, G. Soler-Illia, P. A. Albouy, and H. Amenitsch, *Chem. Commun.*, 748 (2002).
(43) X. Li, S. Barua, K. Rege, and B. Vogt, *Langmuir*, **24**, 11935 (2008).
(44) M. Ogawa, *J. Chem. Soc., Chem. Commun.*, 1149 (1996).
(45) D. Grosso, A. R. Balkenende, P. A. Albouy, A. Ayral, H. Amenitsch, and F. Babonneau, *Chem. Mater.*, **13**, 1848 (2001).
(46) S. Besson, T. Gacoin, C. Jacquiod, C. Ricolleau, D. Babonneaud, and J.-P. Boilot, *J. Mater. Chem.*, **10**, 1331 (2000).