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# Novel Inorganic−Organic Hybrid Block Copolymers as Pore Generators for Nanoporous Ultralow-Dielectric-Constant Films

**Hyun Wook Ro,[†] Kook Ji Kim,[†] Patrick Theato,*[,‡] David W. Gidley,[§] and Do Y. Yoon*[,†]**

*School of Chemistry, Seoul National University, Seoul 151-747, Korea; Institut für Organische Chemie, University of Mainz, D-55099 Mainz; and Department of Physics, University of Michigan, Ann Arbor, Michigan 48109*

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Silsesquioxanes with the chemical formula $(RSiO_{1.5})_x$ have recently emerged as a new class of molecules for the preparation of nanostructured materials with novel properties. In this regard, polyhedral oligosilsesquioxanes (POSS) of octameric structure, $R_8Si_8O_{12}$ ($T_8$), have found much interest owing to their well-characterized cubic structure. For example, Laine et al. prepared novel inorganic−organic nanocomposite polymers by functionalization of POSS structures with appropriate organic moieties and subsequent polymerization, thereby opening new possibilities to improve material properties.[1] Another area of significant interest has been focused on polysilsesquioxanes (PSSQs) for low-dielectric-constant (low-*k*) thin films to reduce the interconnect delay times in next-generation microelectronic devices.[2−8] In particular, materials based on poly(methylsilsesquioxane) (PMSSQ) are the most promising spin-on candidates to replace the currently used chemical-vapor-deposited intermetal dielectrics such as $SiO_2$ ($k = 4.2$), fluorinated silicate glasses ($k = 3.6$), and carbon-doped oxides ($k = 2.9$). PMSSQ has a low dielectric constant of 2.7, but an ultralow dielectric constant smaller than 2.3 is needed for the next-generation logic devices with feature sizes smaller than 50 nm to be introduced around 2007−2010.[9]

To obtain such an ultralow dielectric constant ($k < 2.3$), air has to be incorporated into the material. Among the methods to generate discrete pores in PMSSQ thin films, a most promising approach involves the removal of a nanodispersed thermally labile pore generator (porogen) at high temperatures.[3] For this purpose, it is very critical to control the pore size, since the lateral dimension or the feature size of the intermetal dielectric films will soon be smaller than 50 nm. Therefore, the pore size should be smaller than ca. 4 nm, at least 1 order of magnitude smaller than the feature size. However, the maximum achievable nanoporosity, with pore sizes smaller than ca. 4 nm, from the conventional porogen approach is not very high owing to the nucleation-growth type phase separation of porogens in the PMSSQ matrix, which leads to the larger aggregates as the porogen content increases. Therefore, new approaches for introducing porosity with controlled pore sizes via templated porogen structures have been investigated, including the application of block copolymers,[4,8] ionic surfactants,[6] and unimolecular amphiphilic star polymers[7] as novel porogens. However, the pore sizes tend to be larger than 4 nm, or the templating requires complicated process conditions. In this regard, an ideal porogen molecule would be an inorganic−organic block copolymer, where the inorganic block is based on PMSSQ and undergoes secondary condensation during the curing process to be covalently linked to the matrix. The resultant grafted organic polymer segments will form phase-separated domains whose size does not vary substantially with the volume content of the thermally labile organic block. The final pore size will then be controlled primarily by the molecular weight of the organic block. In this way, one could obtain nanoporous ultralow-dielectric-constant films with the controlled pore sizes smaller than 4 nm.

Recently, atom transfer radical polymerization (ATRP) has gained a lot of attention as a versatile polymerization technique, where the fast exchange reaction between growing radicals and dormant species leads to a controlled radical polymerization.[10] One advantage of ATRP is that it is applicable to a broad range of monomers and allows a set of well-defined initiating species. Therefore, it is chemically possible to define the site of polymer chain growth, making it a perfect grafting-from technique.

In the current work, we concentrate on the functionalization of low-molecular-weight PMSSQ with PMMA blocks, the latter playing the role of phase-separated porogen upon mixing with a suitable PMSSQ-based matrix polymer. We first functionalize PMSSQ with a suitable ATRP initiator which will then result in the grafting-from polymerization of methyl methacrylate (MMA) to obtain hybrid block copolymer structures.

The synthesis of hybrid block copolymers starts with the synthesis of the inorganic PMSSQ block. Following a recently published procedure, it is possible to obtain highly branched PMSSQ structures with a high functionality of unreacted silanol groups.[11] Such highly branched PMSSQs, typically with 20−25 mol % free Si−OH groups, are required for further functionalization.

To graft an organic polymer from PMSSQ, we need to functionalize it with appropriate initiating sites. The synthesis of our initiator, described briefly elsewhere,[12] is shown in Scheme 1. Starting from 4-pentenol, the ester with 2-bromoisobutyroic acid is formed under general esterification. In the second step the dimethylchlorosilane group was introduced by hydrosilylation with an excess of chlorodimethylsilane. As a catalyst, platinum on carbon was used, which is reactive even in the presence of functional groups. The reaction was followed by NMR, and after complete reaction the pure product **1** was obtained.

The bifunctional initiator **1** was then allowed to react with PMSSQ containing 23.4 mol % silanol groups per Si atom, as shown in Scheme 1. The polymers were then purified by washing with water, and after drying in a vacuum PMSSQ prepolymers, which contained varying amounts of 2-bromoisobutyrate, were obtained as very viscous liquids. The resulting prepolymers generally retained considerable amounts of silanol groups, which are necessary for a later incorporation into the PMSSQ-based matrix, as listed in Table 1. The prepolymers were then used to initiate the polymerization of methyl

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[†] Seoul National University.
[‡] University of Mainz.
[§] University of Michigan.
* Corresponding authors: Tel +82-2-880-6814; Fax +82-2-877-6814; e-mail dyyoon@snu.ac.kr or theato@uni-mainz.de.

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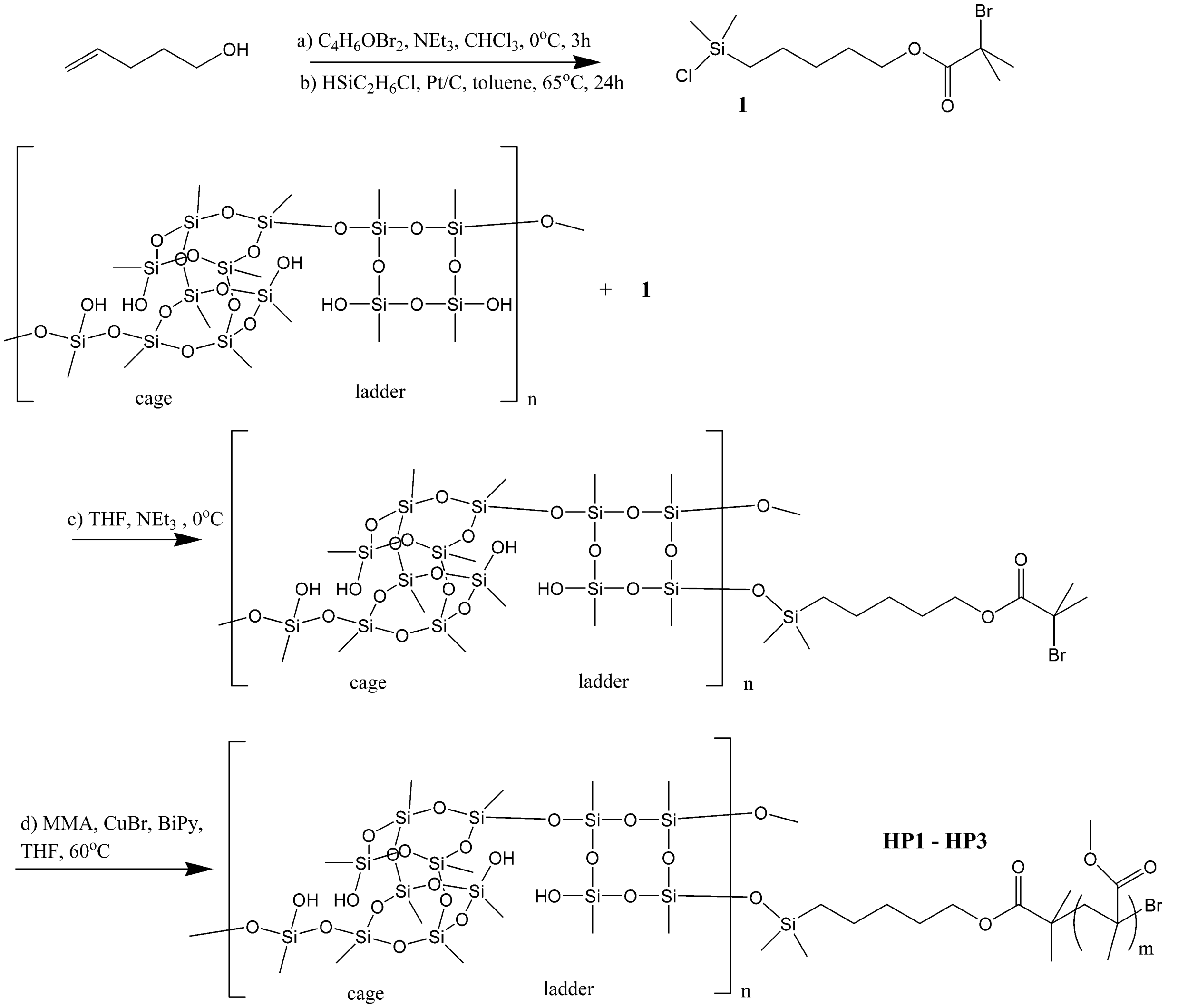
**Scheme 1. Outline of the Synthetic Scheme To Prepare Hybrid Block Copolymers Based on PMSSQ**[a]



[a] Note that the schematic drawing of PMSSQ represents a part of highly branched PMMSQ structure.

**Table 1. Compositions (mol %) and Molecular Weights of Hybrid Block Copolymers**

| | prepolymer | | | | |
|---|---|---|---|---|---|
| polymer | Si–OH [%][c] | initiator [%][c] | MSSQ [mol %][a] | $M_n$[b] | $M_w$[b] |
| **HP1** | 0 | 16 | 18 | 38 000 | 100 000 |
| **HP2** | 8.8 | 5.3 | 24 | 15 000 | 37 000 |
| **HP3** | 8.8 | 5.3 | 45 | 7 600 | 27 000 |
| **HP4** | 13.5 | 7.3 | 62 | 5 600 | 11 000 |
| **HP5** | 13.5 | 7.3 | 70 | 4 600 | 7 700 |

[a] The composition was determined by $^1$H NMR. [b] Average molecular weights were obtained from GPC with an RI detector, using polystyrene standards for calibration. [c] The composition refers to the mol % of OH and initiator groups, respectively, per Si atom.

methacrylate (MMA) to form hybrid polymers under general atom transfer radical polymerization (ATRP) conditions in THF solution, as shown in Scheme 1. After a defined polymerization time, usually 30 min, the copolymers were precipitated in hexane. Then, the copolymers were filtrated over basic $Al_2O_3$ and reprecipitated from THF solution into hexane to remove the residual copper used for the copolymer synthesis. This procedure yielded a white copolymer product, indicating that this method is quite effective in removing the residual copper as described in ref 13. The composition of copolymers were then characterized by $^1$H NMR. (A representative $^1$H NMR spectrum of the copolymer is shown in the Supporting Information, which also includes the details of the experimental procedures employed for this work.)

The PMSSQ had an initial number-average molecular weight ($M_n$) of 3700 according to the polystyrene standards prior to functionalization, while the hybrid **HP1** showed a higher molecular weight ($M_n$) of 38 000. The GPC trace of the block copolymer showed a monomodal distribution (see the Supporting Information), which indicated that initiation of MMA monomer started from the functionalized PMSSQ initiating sites, and hence the formation of PMMA homopolymer as a side reaction is negligible. The compositions of the hybrid block copolymers, together with those of the respective prepolymers, are listed in Table 1. Starting from a prepolymer with a low amount of functionalized initiating groups, the resulting hybrid polymers **HP4** and **HP5** contain a higher portion of PMSSQ than PMMA. This also results in lower molecular weight polymers with a molecular weight ($M_n$) of 4600 and 5500, respectively. In comparison, the hybrid polymers **HP2** and **HP3** exhibit increased molecular weights, caused by a higher MMA concentration during the polymerization reaction. In comparison, the hybrid polymer **HP1** contains only

**Table 2. Porosity (*P*), Positronium Lifetime (Ps), Estimated Pore Diameter (*D*), Modulus, and Hardness Determined for the Nanoporous Films**

| sample | loading [vol %] | expected *P* [%] | measured *P* [%] | Ps [ns] | *D* [nm] | modulus [GPa] | hardness [GPa] |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | | | 10.1 | 1.42 |
| 2 | 10 | 8.7 | 9.4 | 22.5 | 1.7 | 6.6 | 1.07 |
| 3 | 15 | 13.1 | 14.0 | 24.7 | 1.7 | 5.5 | 0.84 |
| 4 | 20 | 17.4 | 17.1 | 31.1 | 2.0 | 4.8 | 0.75 |
| 5 | 25 | 21.8 | 22.6 | 37.1[a] | 2.2[a] | 3.8 | 0.62 |
| 6 | 30 | 26.1 | 25.4 | 41.0[a] | 2.4[a] | 3.4 | 0.56 |

[a] The values were measured with films capped with thin $SiO_2$ layers to remove the signal from the positroniums escaping into the vacuum.[16]

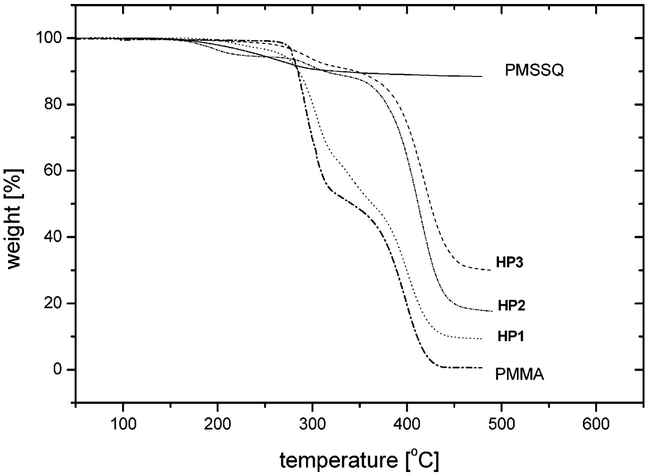


**Figure 1.** TGA results for PMMA, PMSSQ, and hybrid block copolymers **HP1**−**HP3** with varying compositions.

18 mol % PMSSQ monomers and a major fraction (82 mol %) of PMMA units, due to the higher amount of initiating groups in the prepolymer.

One of the most important features of the hybrid block copolymers as a successful pore generating material (porogen) is their thermal decomposition characteristics. In fact, it is an essential property for a porogen to show a well-defined decomposition behavior in an appropriate temperature range. Therefore, the thermogravimetric analysis (TGA) data for the hybrid block copolymers are plotted in Figure 1. The TGA curve of PMMA prepared under the same condition shows no weight loss up to 280 °C. Above that temperature, PMMA starts to decompose, and by 410 °C PMMA is quantitatively decomposed. Pure PMSSQ loses weight starting at around 150 °C, which is due to a secondary condensation process involving silanol and residual methoxy groups. At this stage the material mainly cross-links by the intermolecular condensation, whereby either water or methanol is eliminated. This secondary condensation process is complete before 300 °C. Afterward, no weight loss could be observed up to 500 °C.

The hybrid block copolymers, **HP1**−**HP3**, exhibit combined characteristics of PMMA and PMSSQ, as shown in Figure 1. Between around 175 and 275 °C a slight weight loss occurs, which is due to the intermolecular condensation of silanol and/or methoxy-silanol groups, as it is observed for pure PMSSQ. This is an important aspect because the free silanol or methoxy groups are needed in order to covalently bind the porogen to the PMSSQ-based matrix. The decomposition of the PMMA block starts at 280 °C and ends at 410 °C, as expected. The remaining weights are within the expected range of the weight of the PMSSQ fraction after secondary condensation.

As the TGA results suggest, the novel hybrid block copolymers exhibit all the characteristics needed to be used as successful porogens. They provide the functionalities to covalently bind into a PMSSQ-based matrix during the initial curing process, thereby fixing the PMMA block to the matrix, and the resultant grafted PMMA blocks would then form phase-separated domains, which lead to nanoporous films upon thermal decomposition of PMMA moieties. DSC measurements indeed showed the presence of a glass transition temperature around 110 °C for block copolymers, nearly the same as that for pure PMMA, indicative of pure PMMA domains dispersed in the PMSSQ matrix. (A representative DSC trace is shown in the Supporting Information.)

The hybrid copolymer **HP1** was therefore used as a porogen in a matrix of a PMSSQ terpolymer (MTMS:BTMSE:DMDMS = 7:2:1),[14] reported elsewhere.[15] The porous films prepared upon curing to 430 °C, with the final thicknesses in the range of 600 nm−1 $\mu$m, showed excellent film qualities with no cracks appearing when immersed in water. Their porosities, pore sizes, and mechanical properties were then investigated by ellipsometry, positronium annihilation lifetime spectroscopy (PALS),[16] and nanoindentation measurements, respectively. The results of six different samples with varying porogen loadings are summarized in Table 2. The porosities (*P*) were calculated on the basis of measured refractive indices of the thin films[15] and are found to match those expected. To convert the positronium lifetimes (Ps) into pore sizes (*D*), we used a cylindrical pore model for which the mean free path corresponds to the cross-sectional diameter. Sample 2 with a porosity of about 9% contains pores of 1.7 nm in diameter. With an increasing amount of hybrid polymer **HP1** blended into the matrix polymer, the resulting porosity increases up to 25.4%, but the pore sizes increase only slightly to 2.4 nm. The dielectric constant, estimated from the measured refractive index change for the same matrix polymer,[15] is ca. 2.2 for the nanoporous film with ca. 25% porosity. In other words, even with a porosity of 25%, the pore size remains nearly the same and smaller than 3 nm, fulfilling the pore size requirements as the ultralow-dielectric-constant films for the next-generation logic devices. Although the pore sizes are quite small, the mechanical modulus and hardness are still seen to decrease substantially as the porosity is introduced, as shown in Table 2. Therefore, it would be desirable to improve the mechanical properties of nanoporous films[5] in the future work, as well as to better define the pore size and the size distribution of nanopores by employing other experimental methods to complement the PALS method.[16]

In summary, we functionalized PMSSQ with 2-bromoisobutanoic acid 5-(chlorodimethylsilanyl)pentyl ester and obtained hybrid block copolymer under ATRP conditions in solution, using methyl methacrylate as the monomer. Upon the continuous heating of the hybrid copolymers, the secondary condensation of silanol groups and PMMA decomposition were observed to occur sequentially, thus making these polymers good candidates as pore generators to prepare nanoporous low-dielectric-constant materials. Using a PMSSQ-based matrix polymer, the hybrid copolymer porogens allowed a successful preparation of ultralow-dielectric-constant films with $k < 2.3$, for which the pore sizes were shown to be nearly independent of the porosity and to remain smaller than 3 nm. The incorporation of such porosity is accompanied by a substantial reduction in the mechanical modulus and hardness of the dielectric films.

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**Supporting Information Available:** Figures showing NMR spectrum of a hybrid block copolymer, GPC trace of the hybrid copolymer PMSSQ-*b*-PMMA compared to PMSSQ, and DSC heating curves of PMMA and PMSSQ-*b*-PMMA hybrid block copolymer; experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Costa, R. O. R.; Vasconcelos, W. L.; Tamaki, R.; Laine, R. M. *Macromolecules* **2001**, *34*, 5398.
(2) Miller, R. D. *Science* **1999**, *286*, 42. Peeray, P. S. *Nature (London)* **2000**, *406*, 1023. Havemann, R. H. *Proc. IEEE* **2001**, *89*, 586.
(3) Nguyen, C. V.; Carter, K. R.; Hawker, C. J.; Hedrick, J. L.; Jaffe, R. L.; Miller, R. D.; Remenar, J. F.; Rhee, H.-W.; Rice, P. M.; Toney, M. F.; Trollsas, M.; Yoon, D. Y. *Chem. Mater.* **1999**, *11*, 3080.
(4) Yang, S.; Mirau, P.; Pai, C. S.; Nalamasu, O.; Reichmanis, E.; Pai, J. C.; Obeng, S. Y.; Seputro, J.; Lin, E. K.; Lee, H. J.; Sun, J.; Gidley, D. W. *Chem. Mater.* **2002**, *14*, 369.
(5) Volksen, W.; Miller, R. D.; Hedrick, J. L.; Hawker, C. J.; Lee, V. Y.; Magbitang, T. P.; Toney, M. F.; Lynn, K. V.; Weber, M.; Petkov, M.; Ho, P.; Kiene, M.; Liu, J.; Rodbell, K. P.; Huang, E. In *Springer Series in Advanced Microelectronics;* Ho, P., Ed.; Springer-Verlag: Heidelberg, 2002; Vol. 9.
(6) Landskron, K.; Hatton, B. D.; Perovic, D. D.; Ozin, G. A. *Science* **2003**, *302*, 266.
(7) Conner, E. F.; Sundberg, L. K.; Kim, H.-C.; Cornelissen, J. J.; Magbitan, T.; Rice, P. M.; Lee, V. Y.; Hawker, C. J.; Volksen, W.; Hedrick, J. L.; Miller, R. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 3785.
(8) Pai, R. A.; Humayun, R.; Schulberg, M. T.; Sengupta, A.; Sun, J.-A.; Watkins, J. J. *Science* **2004**, *303*, 507.
(9) *The International Technology Roadmap for Semiconductors*, 2003.
(10) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337.
(11) Lee, J. K.; Char, K.; Rhee, H.-W.; Ro, H. W.; Yoo, D. Y.; Yoon, D. Y. *Polymer* **2001**, *42*, 9085.
(12) Theato, P.; Kim, K. J.; Yoon, D. Y. *Phys. Chem. Chem. Phys.* **2004**, *6,* 1458.
(13) Kickelbick, G.; Paik, H. J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2941. Honigfort, M. E.; Brittain, W. J.; Bosanac, T.; Wilcox, C. S. *Macromolecules* **2002**, *35*, 4849.
(14) MTMS = methyltrimethoxysilane; BTMSE = 1,2-bis(trimethoxysilyl)ethane; DMDMS = dimethoxydimethylsilane.
(15) Yoon, D. Y.; Ro, H. W.; Park, E. S.; Lee, J. K.; Kim, H. J.; Char, K.; Rhee, H.-W. Kwon, D.; Gidley, D. W. *Mater. Res. Soc. Symp. Proc.* **2003**, *766*, 241.
(16) Gidley, D. W.; Friez, W. E.; Dull, T. L.; Sun, J.; Yee, A. F.; Nguyen, C.; Yoon, D. Y. *Appl. Phys. Lett.* **2000**, *76*, 1282. Sun, J. N.; Hu, Y. F.; Frieze, W. E.; Gidley, D. W.; Yang, S. *Mater. Res. Soc. Symp. Proc.* **2002**, *726*, Q10.5. Sun, J. N.; Hu, Y. F.; Frieze, W. E.; Gidley, D. W. *Radiat. Phys. Chem.* **2003**, *68*, 345.

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