

Low-Dielectric, Nanoporous Organosilicate Films Prepared via Inorganic/Organic Polymer Hybrid Templates

Cattien V. Nguyen,[‡] Kenneth R. Carter,[†] Craig J. Hawker,[†] James L. Hedrick,[†] Richard L. Jaffe,[§] Robert D. Miller,[†] Julius F. Remenar,[†] Hee-Woo Rhee,^{||} Philip M. Rice,[†] Michael F. Toney,[†] Mikael Trollsås,[†] and Do Y. Yoon^{* ,[⊥]}

IBM Research Division, Almaden Research Center, 650 Harry Road,
San Jose, California 95120; ELORET Inc., 690 W. Fremont, Sunnyvale, California 94087;
NASA-Ames Research Center, Moffett Field, California 94035;
Department of Chemical Engineering, Sogang University, Seoul, Korea;
and Department of Chemistry, Seoul National University, Seoul 151-742, Korea

Received February 24, 1999. Revised Manuscript Received August 3, 1999

Dielectric insulator materials containing nanometer-scale closed-cell pores with low dielectric constants ($k < 2.2$), good mechanical properties, and high dielectric breakdown strengths are required for future semiconductor devices. In this paper we present a novel method for preparing nanoporous polyorganosilicate films, which promise to satisfy the key requirements, via inorganic/organic polymer hybrid templating. The nanometer-scale inorganic/organic polymer hybrids are generated in situ upon heating mixtures of methylsilsesquioxane (MSSQ) prepolymer with star-shaped hydroxy-terminated poly(ϵ -caprolactone) (PCL) to ~ 250 °C, causing chain extension and cross-linking of MSSQ. Subsequent heating to 430 °C results in the thermal decomposition and volatilization of PCL components from the vitrified poly(methylsilsesquioxane) (PMSSQ) matrix, leaving behind porous PMSSQ films with pores with the size and shape of the original hybrid morphology. A dielectric constant as low as 2.1 has been achieved for closed-cell nanoporous PMSSQ films with hydrophobic surfaces and excellent breakdown strengths close to that of SiO₂. Moreover, conductance measurements on inorganic/organic polymer hybrids offer insight into the development of interconnected PCL domains as the PCL content is increased above $\sim 25\%$.

Introduction

According to the *National Technology Roadmap for Semiconductors*,¹ the feature dimension in integrated circuits will shrink to 0.15 micrometer around year 2001. At this dimension and below, the resistance \times capacitance (RC) delay and the crosstalk between metal interconnects would overwhelm the traditional gain in performance derived from the decreasing feature sizes in semiconductor devices. In addition to switching from Al metal to lower resistive Cu, replacing the currently used insulator, SiO₂, for which the dielectric constant (k) is 4.0–4.2, with a significantly lower k material will also be needed to reduce the RC delay. For example, the *National Technology Roadmap* indicates a need for materials with dielectric constants of 2.0–2.5 in year 2001 and materials with $k = 1.5$ –2.0 for dimensions below 0.13 micrometer by year 2003. Moreover, current chip manufacturing processes require the insulating materials to be thermally stable to at least 400 °C (including a high glass transition temperature, T_g), to

have low moisture absorption, to have good adhesion to metals and passivation coatings (oxides and nitrides), to have mechanical toughness to prevent crack propagation, and to exhibit coating hardness to withstand the rigors of chemical mechanical planarization (CMP), to name just a few of the requirements.

Decreasing the dielectric constants well below 2.2 is possible only with the incorporation of air voids ($k = 1$) in a suitable insulator. Therefore, the development of new porous insulator films has been very actively pursued. For example, porous aerogel and xerogel silica,^{2,3} and mesoporous silica obtained by silica-surfactant self-assembly processes^{4,5} have been shown to exhibit low dielectric values in the range of 1.3–2.5. Film fabrication processes to obtain small pore sizes (< 10 nm) have also been reported for the porous silica films, but the pores are normally interconnected, making them questionable for electroplated metal deposi-

* To whom correspondence should be addressed.

[†] IBM Research Division.

[‡] ELORET Inc.

[§] NASA-Ames Research Center.

^{||} Sogang University.

[⊥] Seoul National University.

(1) *The National Technology Roadmap for Semiconductors*; Semiconductor Industry Association: San Jose, CA, 1997.

(2) Prakash, S. S.; Brinker, C. J.; Hurd, A. J., *J. Non-Cryst. Solids* **1995**, *190*, 264.

(3) Jin, C. M.; Luttmar, J. D.; Smith, D. M.; Ramos, T. A. *Mater. Res. Soc. Bull.* **1997**, *30*, 39.

(4) Lu, Y.; Ganguli, R.; Drewien, C. A.; Anderson, M. T.; Brinker, C. J.; Gong, W.; Guo, Y.; Soye, H.; Dunn, B.; Huang, M. H.; Zink, J. I. *Nature* **1997**, *389*, 364.

(5) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548. Zhao, D.; Yang, P.; Melosh, N.; Feng, B. F.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1998**, *10* (16), 1380.

tion. Very recently, closed-cell porous silica films have been prepared by self-assembly of silica templated with block copolymer surfactants.⁵ However, the self-assembly process requires a rather long equilibration time in the presence of aqueous solvents, rendering this method incompatible with conventional rapid spin-coating manufacturing methods which have been developed to obtain uniform film thicknesses over the entire 8-in. silicon wafers. Moreover, the silica surfaces as formed in the sol-gel processes are hydrophilic and absorb moisture which increases the dielectric values and causes corrosion of the metallurgy.

Another way of incorporating porosity is to take advantage of microphase-separated block copolymers comprising a dispersed phase of thermally labile polymers in a high-temperature polymer matrix.⁶⁻⁹ For example, to obtain nanoporous polyimide films, the soluble precursor polymers are first spin-coated to yield uniform thin films and then converted into the phase-separated copolymers by thermally induced chemical changes (imidization) at 250–300 °C, and subsequently foamed by decomposing the dispersed thermally labile component at a higher temperature (330–350 °C). While low-dielectric ($k = 2.3$) films with closed-cell pores have been obtained by this method, the polyimide films absorb moisture and the pores collapse above 370 °C due to the creep of the matrix polymer below its glass transition temperature.

One class of promising low- k materials are organosilicate poly(silsesquioxanes), having empirical formula $(R-SiO_{1.5})_n$ where R is hydrogen or an organic substituent. Currently, spin-on poly(hydridosilsesquioxane) (PHSSQ) along with CVD-deposited and spin-on poly(methylsilsesquioxane) (PMSSQ) are either in use or under development for near-term applications, owing to their attractive properties.¹⁰ For example, fully cured PMSSQ shows intrinsic dielectric constants between 2.7 and 2.9 and low moisture absorption and exhibits good thermal stability to 500 °C and high mechanical hardness.^{11,12} Following a general strategy for lowering dielectric constants by incorporation of air voids into the insulating materials, increasing the porosity of poly(silsesquioxanes) can decrease their dielectric constants, while maintaining the other desired properties. (A major advantage of employing the same dielectric material in more than one device generation is the extension of the lifetime of tools and processes used in manufacturing, an attractive option in terms of cost savings.)

Here we present a detailed description of a new process for preparing low-dielectric nanoporous poly(methylsilsesquioxane) (PMSSQ) films via inorganic/organic polymer hybrid templates, together with the experimental results on the structures and properties

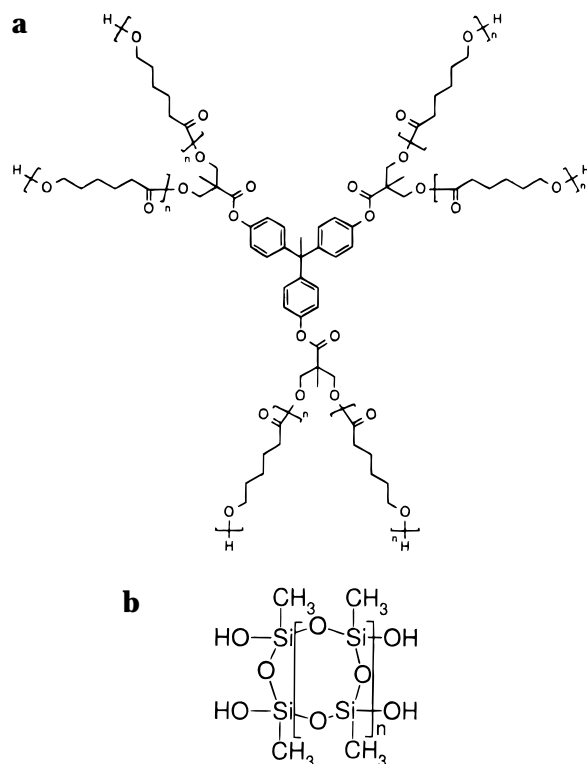


Figure 1. Schematics of the star-shaped 6-arm poly(caprolactone) (PCL) (a) and an idealized structure of the methylsilsesquioxane (MSSQ) prepolymer (b).

of the hybrid precursors and the final porous films. Porous PMSSQ films are obtained by thermally decomposing organic poly(ϵ -caprolactone) (PCL) components (porogens) of the inorganic/organic polymer hybrid films, which are formed in situ during the thermal curing of spin-coated thin films of mixtures of methylsilsesquioxane (MSSQ) prepolymers and star-shaped PCL polymers, as preliminarily described elsewhere.^{8,13} The development and characterization of phase-separated PCL domains and the final morphology and dielectric constants of porous PMSSQ films of varying porosity have been investigated as function of the porogen molecular structures. Also studied is the water absorption characteristics of the nanoporous PMSSQ films. In addition, experimental results on the breakdown voltages of porous PMSSQ films are presented along with conductance measurements on unfoamed PMSSQ/PCL polymer hybrids. The conductance method offers a novel means of investigating the interconnectivity of dispersed PCL domains in hybrid films and hence the final pores in the porous PMSSQ films.

Experimental Section

The star-shaped PCL derivatives used in this study were synthesized by the procedures described in detail elsewhere^{14,15} and the MSSQ prepolymer ($M_n \sim 1000$ g/mol) with hydroxy chain ends was commercially available (see Figure 1). Electronic-grade propylene glycol monomethyl ether methyl acetate

(6) Hedrick, J. L.; Labadie, J.; Russell, T. P.; Hofer, D.; Wakharker, V. *Polymer* **1993**, *34*, 4717.

(7) Cha, H. J.; Hedrick, J. L.; DiPietro, R.; Blum, T.; Beyers, R.; Yoon, D. Y. *Appl. Phys. Lett.* **1996**, *68*, 1930.

(8) Hedrick, J. L.; Miller, R. D.; Hawker, C. J.; Carter, K. R.; Volksen, W.; Yoon, D. Y.; Trollsås, M. *Adv. Mater.* **1998**, *10*, 1049.

(9) Hedrick, J. L.; Carter, K. R.; Labadie, J. W.; Miller, R. D.; Volksen, W.; Hawker, C. J.; Yoon, D. Y.; Russell, T. P.; McGrath, J. E.; Breiber, R. M. *Adv. Polym. Sci.* **1999**, *141*, 1.

(10) See, for example: *Semicond. Intl.* **1998**, *21* (September), 63.

(11) Kim, S. M.; Yoon, D. Y.; Nguyen, C. V.; Han, J.; Jaffe, R. L. *Mater. Res. Soc. Symp. Proc.* **1998**, *511*, 39.

(12) Cook, R. F.; Liniger, E. G.; Klaus, D. P.; Simonyi, E. E.; Cohen, S. A. *Mater. Res. Soc. Symp. Proc.* **1998**, *511*, 33.

(13) Remenar, J. F.; Hawker, C. J.; Hedrick, J. L.; Kim, S. M.; Miller, R. D.; Nguyen, C. V.; Trollsås, M.; Yoon, D. Y. *Mater. Res. Soc. Symp. Proc.* **1998**, *511*, 69.

(14) Trollsås, M.; Hedrick, J. L.; Mecerreyes, D.; Dubois, Ph.; Jerome, R.; Ihre, H.; Hult, A. *Macromolecules* **1997**, *30*, 8508. Trollsås, M.; Hedrick, J. L.; Mecerreyes, D.; Dubois, Ph.; Jerome, R.; Ihre, H.; Hult, A. *Macromolecules* **1998**, *31*, 2756.

(15) Trollsås, M.; Hedrick, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 4644.

(PMA) was used as the solvent. The PMSSQ/PCL hybrids and porous PMSSQ films were prepared as follows. Homogeneous solutions of MSSQ and PCL in PMA at 30 wt % solids were loaded into a disposable syringe and passed through a 0.2- μm Acrodisc CR PTFE filter directly onto a sample substrate. The coated substrate was spun at 2500 rpm for 30 s and placed directly onto a hot plate at 50 °C under nitrogen. The sample was then heated at 2 °C/min to a desired set temperature of 250 °C for the hybrids and 430 °C for the porous films, respectively, and held for 2 h before cooling. The final film thickness is $\sim 1 \mu\text{m}$.

The change in mechanical moduli during thermal curing of MSSQ was monitored by Dynamic Mechanical Analyzer (DMA) measurements using glass fabric samples coated with MSSQ prepolymer. The development of phase-separated hybrid morphology during thermal curing was followed with synchrotron small-angle X-ray scattering (SAXS) experiments at the National Synchrotron Light Source (Brookhaven National Laboratory), performed on sample films prepared on 0.1-mm thin silicon wafers. The morphology of the final porous PMSSQ films was determined by bright-field TEM imaging (Topcon 002B microscope operating at 180 kV) of very thin sections, ~ 50 nm, fabricated with a focused ion beam (FIB) as described in detail elsewhere.¹⁶ The porosity of the final samples was estimated from the change in electron density as determined from the critical angle in the X-ray reflectivity profile.¹⁷

Dielectric constants, dielectric loss tangent δ s, and conduction measurements were carried out with a Hewlett-Packard multifrequency LCR meter Model 4275A interfaced with a personal computer using LABSPC software to collect data. Electrodes were attached via HP 16048A test leads. The polymer mixture samples were spin-coated on glass substrates with patterned (bottom) Al electrodes and the patterned top Al electrodes were evaporated via a shadow mask after the samples had undergone thermal treatment. All samples were placed in a brass testing cell that included a thermocouple mounted at the sample and were heated by convection in a nitrogen atmosphere using a Eurotherm temperature controller assembly. The heating rate in all cases was 5 °C/min, and data were collected while heating from -100 °C to 150 °C. Dielectric breakdown measurements were carried out using the same configuration of electrodes and sample setups. The current-voltage curves were measured using a Keithley 237 Source Measurement Unit.

Results and Discussion

Figure 1a shows a schematic of the 6-arm PCL employed as a domain-forming, thermally degradable polymer (porogen) to generate the pores. In this study, two porogen structural parameters were varied, namely, the length and the number of arms. The MSSQ prepolymer (shown as an idealized structure in Figure 1b) undergoes chain extension and cross-linking reactions of the OH groups beginning around 150 °C, and MSSQ samples heated for 2 h at 250 °C showed practically no detectable OH groups by IR. In comparison, the PCL component heated for 2 h at 250 °C showed no change in the chemical structure as seen by ¹H NMR and GPC analysis.

Qualitative features of the variation of the dynamic mechanical modulus of MSSQ prepolymer versus temperature during the initial heating to 430 °C and subsequent cooling are shown by the DMA traces in Figure 2. The experimental results indicate that the MSSQ resin initially softens and becomes liquidlike

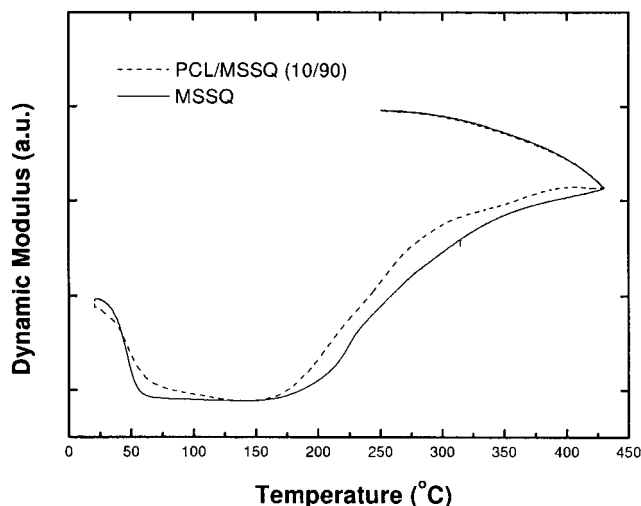


Figure 2. The variation of the dynamic mechanical modulus (a.u.) of MSSQ-coated glass fabric with temperature during the first heating and cooling (2 °C/min). Also shown for comparison is the plot for the MSSQ/6-arm PCL (DP = 5.8/arm) mixture with 10 wt % PCL.

around 70 °C but begins to solidify around 200 °C as significant chain extension and cross-linking reactions of the hydroxyl functionalities occur. Further chemical reactions appear to proceed in the solid state as seen by the continuing increase in mechanical modulus with increasing temperature until the sample temperature reaches 430 °C (at the heating rate of 2 °C/min). As the sample is cooled, the modulus of the fully cured PMSSQ continues to increase as expected. The DMA results for the MSSQ/PCL mixture (10 wt % 6-arm PCL with DP = 5.8/arm), also shown in Figure 2, exhibit practically the same characteristics. Therefore, it is seen that the intermolecular cross-linking chemical reactions of MSSQ occurring in the glassy state further increase the modulus or stiffness of the PMSSQ component. The nature of the chemical reactions will be discussed in detail elsewhere.¹⁸

Figure 3 shows small-angle X-ray scattering (SAXS) results from the MSSQ mixture with 6-arm PCL with DP = 5.8/arm at 25 wt % as a function of curing temperature. These data show that at 200 °C the material exhibits a phase-separated morphology, indicating that as the MSSQ begins to chain extend and cross-link, the PCL-based porogen starts to phase separate. For a 250 °C cure, the shape of the SAXS profile does not change but the overall scattering intensity increases significantly. Thus, there is an increase in the electron density contrast between the PMSSQ-rich matrix and PCL-rich dispersed phase.

The composition in the unfoamed, but phase-separated PMSSQ/PCL mixtures cured to 250 °C may be probed by the dielectric relaxation characteristics of the PCL-rich phase, as seen by the loss tangent δ results in Figure 4, since PMSSQ exhibits practically no dielectric loss. The loss peaks at -40 °C and at -60 °C for pure 6-arm PCL porogen represent the glass (or α -) relaxation and subglass (or β -) relaxation, respectively. The temperatures of these loss maxima show only minor shifts in the PMSSQ/porogen mixtures of varying po-

(16) FIB TEM Sample Preparation, Technical Notes, FEI Company: Hillsboro, OR, 1997.

(17) Findeisen, E.; Feidenhans'l, R.; Vigild, M. E.; Clausen, K. N.; Hansen, J. B.; Bentzen, M. D.; Goff, J. P. *J. Appl. Phys.* **1994**, *76*, 4636.

(18) Nguyen, C. V.; Jaffe, R. L.; Chung, K.; Moyer, E.; Yeakle, C.; Kim, S. M.; Yoon, D. Y. *Chem. Mater.*, in preparation.

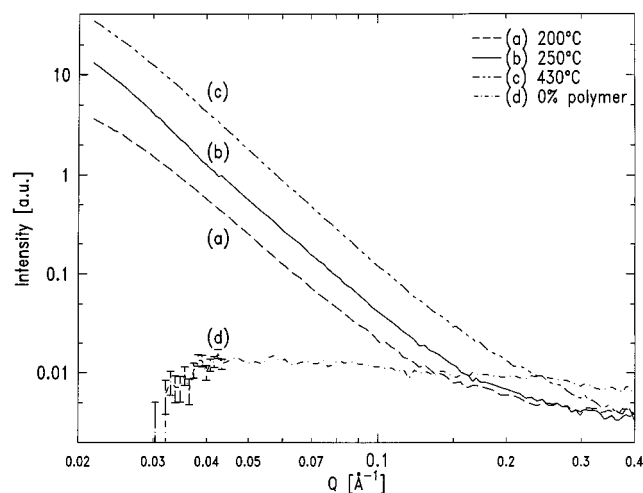


Figure 3. The small-angle X-ray scattering (SAXS) profile plotted against the scattering vector q for PMSSQ/PCL hybrid (75/25 by wt) films cured for 2 h at 200 °C (a), 250 °C (b), and the nanoporous sample prepared by heating for 2 h at 430 °C (c). The porogen was the 6-arm PCL derivative with DP = 5.8/arm; see Figure 1a. The results for PMSSQ matrix itself are also shown in the figure (d).

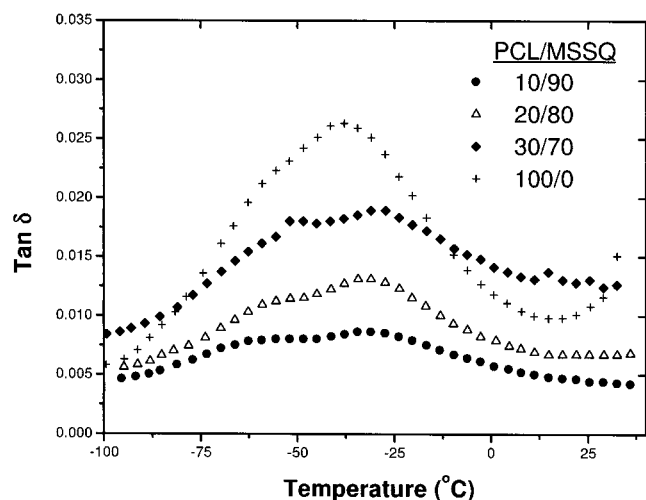


Figure 4. The dielectric loss tangent delta (100 kHz) versus temperature for the PMSSQ/PCL hybrid films prepared by heating the spin-coated mixtures of varying porogen loading levels for 2 h at 250 °C. The porogen was the 6-arm PCL derivative with DP = 5.8/arm and the porogen weight % is indicated in the figure.

rogen contents, indicating that the dispersed phase comprises a nearly pure porogen component. The slight increase in the temperature of α -relaxation maxima for the mixtures may be due to a very small amount of dissolved PMSSQ or alternatively to the effects of confinements into very small domains by the solid PMSSQ matrix. Regardless of the origin of this observation, the experimental result demonstrates that due to the highly cross-linked nature of the PMSSQ matrix, the phase separation leads to the formation of nearly pure PCL domains dispersed in a PMSSQ matrix. Hence, the phase-separated structures may be described as inorganic/organic polymer hybrids.

The PCL porogen decomposes and volatilizes between 260 and 370 °C according to the TGA weight loss data (2 °C/min heating rate) in Figure 5. In comparison, the TGA data for the MSSQ/PCL mixture with 10 wt % PCL show an apparent increase, by ~ 50 °C, in the temper-

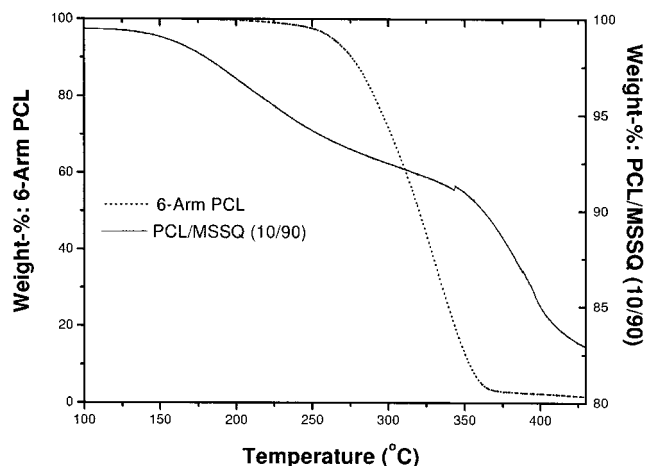


Figure 5. The change in the weight of the 6-arm PCL (DP = 5.8/arm) and PMSSQ/PCL (90/10 by wt) hybrid, respectively, versus temperature at a heating rate of 2 °C/min.

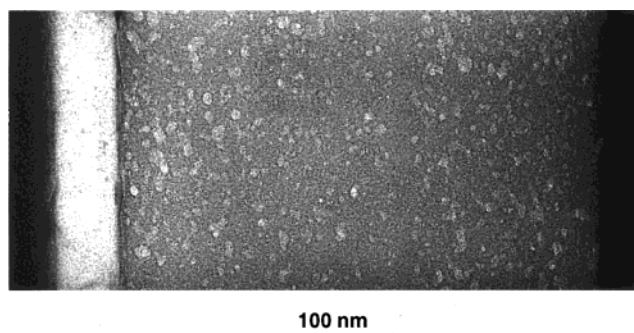


Figure 6. Transmission electron micrographs for the final porous PMSSQ films prepared from 10 wt % loading level of the 6-arm PCL with DP = 5.8/arm, prepared on an aluminum layer of 100-nm thickness.

ature range of the PCL porogen decomposition, possibly reflecting the slow diffusion of decomposed PCL fragments through the PMSSQ matrix. In this regard, the SAXS pattern of the porous sample fully foamed at 430 °C (see Figure 3c) appears to be nearly identical to that of the sample cured to 250 °C, except for the increase in the overall scattering intensity. This indicates that the phase-separated morphology is already fixed around 200–250 °C without any discernible changes occurring at higher temperatures, most likely due to the vitrification of the PMSSQ matrix which prevents any large-scale movement of PCL porogens. Moreover, the pores generated upon thermal decomposition of PCL do not appear to undergo any significant collapse even at temperatures as high as 430 °C. Furthermore, these SAXS patterns indicate a pore diameter of ~ 20 nm, consistent with the TEM results (see below), which will be discussed in detail in a separate publication.¹⁹

Figure 6 shows a TEM micrograph of a porous PMSSQ film prepared from a 10 wt % mixture of the 6-arm PCL with a degree of polymerization (DP) of 5.8 for each arm. Randomly distributed pores of ~ 5 –20 nm in diameter are seen. Similar TEM results are seen for a 20% mixture but beyond a composition of 30%, significantly larger pores and large-scale phase separations were observed for mixtures containing either the

(19) Toney, M. F.; Nguyen, C. V.; Yoon, D. Y. *Chem. Mater.*, in preparation.

4- or 6-arm star PCLs. The 4- and 6-arm star PCLs of higher molecular weights also showed severe aggregation in the PMSSQ matrix. Films of the 12-, 24-, and 48-arm PCLs (see ref 15 for their synthesis) prepared at 10 wt % loading levels in the MSSQ resin remained optically clear even after complete foaming. In general, PMSSQ/PCL mixtures containing more than 10 wt % of the 12-, 24-, or 48-arm PCLs exhibited severe phase separation and aggregation in spin-coated films. Also, mixtures containing 10 wt % of low molecular weight linear PCLs initially gave optically clear films but severely phase-separated during the thermal curing process as indicated by the appearance of cloudiness in the films.

The morphological results discussed above show that the morphology of the PMSSQ/PCL hybrids is entirely controlled by the onset and the growth of phase separation process before the matrix becomes sufficiently vitrified around 200 °C due to significant cross-linking reactions of the PMSSQ matrix. Therefore, there is no evidence of any chemical reaction between the porogen and the matrix polymer below ~200 °C, which would have had a significant effect on the phase-separated morphology. An important consequence of this is that the better the miscibility between the PCL porogens and the PMSSQ matrix, the shorter will be the time interval for the growth of PCL-rich domains, resulting in smaller final pores (assuming that the chain mobility is the same). Another important factor is the mobility of polymer chains after the onset of phase separation. More detailed experiments are necessary to separate the respective roles of the thermodynamic miscibility factor and the dynamic mobility issue. In this regard, it is reasonable to assume that increasing the molecular weight/arm and/or the number of arms of PCL porogens will decrease the miscibility, while the dynamic mobility will decrease significantly with the number of arms and molecular weight/arm. Hence, one may minimize the pore size at a certain molecular weight and a given number of arms. In fact, for the 6-arm PCL porogen at 20 wt % loadings the maximum pore size is ~80 nm for a DP/arm = 4.8, ~20 nm for DP/arm = 5.8, 30 nm for DP/arm = 7, and >100 nm for DP/arm = 9.5, showing the interplay of different contributing factors.

Data for the dielectric constants (100 kHz at 100 °C) versus the PCL loading levels are shown in Figure 7 for smooth, optically clear, porous PMSSQ films generated from mixtures containing different molecular weight PCLs with varying number of arms. The plot shows an apparent universal relationship between dielectric constants and PCL content, indicating that the final porosity is not dependent on the molecular size and structure of PCLs, provided that the initial mixtures and hybrids do not show severe aggregation. The widest range of acceptable quality samples was obtained for the relatively low molecular weight 4- and 6-arm PCLs. Dielectric constants ranging from 2.4 to 1.9 were measured for porous PMSSQ films prepared from 10% to 30% (by weight) of the 4- and 6-arm star-shaped PCLs.

Also plotted in Figure 7 is the porosity estimated using the electron density measured with low-angle X-ray reflectivity (assuming a constant density of the PMSSQ). The porosity closely matches the initial PCL weight fraction and shows little dependence on the molecular structure of PCL in agreement with the

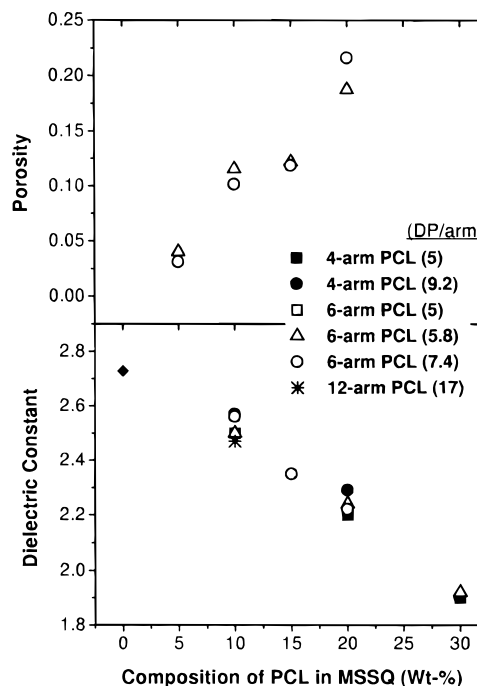


Figure 7. Dielectric constants (100 kHz at 100 °C) and porosities of the final porous PMSSQ films as function of the initial weight percent in MSSQ prepolymer of the PCL-based porogens with various molecular structures as indicated in the figure.

conclusion drawn from the dielectric results. This is consistent with the formation of nearly pure PCL domains in all the PMSSQ/PCL mixtures and the absence of any collapse of the pores in the PMSSQ matrix upon decomposition of PCL porogens.

One serious concern for nanoporous dielectric materials is water adsorption on the pore surfaces. Indeed, porous silicate aerogels and xerogels suffer from severe water adsorption and must be subjected to chemical hydrophobic modification of pore surfaces to minimize this effect.²⁰ In this regard, quartz crystal microbalance experiments (see ref 21 for experimental details) show that porous PMSSQ films with ~25% porosity absorb 1.09% water at 95% relative humidity, as compared with 0.85% for PMSSQ film itself. These results indicate that the pore surfaces of the nanoporous PMSSQ films are strongly hydrophobic and not contaminated with the polar thermal degradation fragments of the PCL porogens.

Breakdown voltages of 2–3 MV/cm were measured for both nonporous PMSSQ films and porous PMSSQ films generated from the MSSQ mixtures containing up to 20 wt % of the 6-arm PCL. These breakdown voltages for porous PMSSQ are close to that of conventional SiO₂ insulators (5 MV/cm). The possible interconnectivity of the pores was also investigated by ac electrical conductance measurements on PMSSQ/PCL hybrids prepared by heating the spin-coated mixtures to 250 °C. Figure 8 shows an initial linear increase in conductance (1 kHz at 25 °C) as the PCL content in the hybrid films

(20) Ramos, T.; Rhoderick, K.; Roth, R.; Wallace, S.; Drage, J.; Dunne, J.; Endisch, D.; Katsanes, R.; Viernes, N.; Smith, D. M. *Proc. 4th Intl. Dielectric for ULSI Multilevel Interconnection Conf*; VMIC: Tampa, FL, 1998; p 211.

(21) Moylan, C. R.; Best, M. E.; Rhee, M. *J. Polym. Sci. Part B: Polym. Phys.* **1991**, *29*, 87.

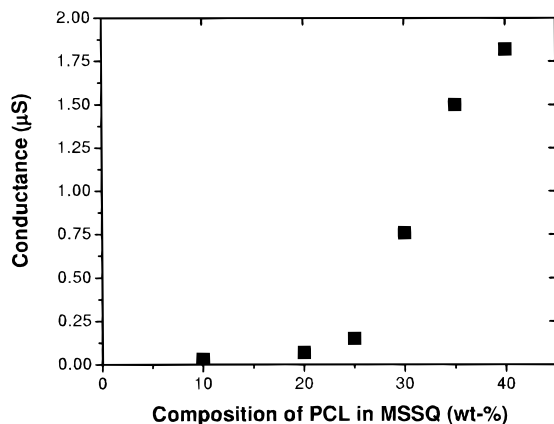


Figure 8. Conductance (1 kHz at 25 °C) of the PMSSQ/PCL polymer hybrids cured at 250 °C for 2 h as function of the initial weight percent of the 6-arm PCL (DP = 5.8/arm) in MSSQ prepolymer.

increases. However, an abrupt increase in conductance was observed as the PCL composition was increased from 25 wt % to 30 wt %. Appearance of interconnected PCL domains, which are liquidlike at a temperature well above the glass transition (ca. -35 °C according to Figure 4), is most likely to be responsible for the dramatic increase in ac conductivity, occurring at compositions above 25 wt % PCL. In agreement with this conductance result, the corresponding breakdown voltages for porous PMSSQ films obtained from mixtures with PCL loading levels greater than 25 wt % were always considerably lower than 1 MV/cm.

Therefore, the upper limit of closed-cell porosity in these systems seems to be about 25%, which places the practical lower limit of the dielectric constant for closed-cell porous PMSSQ films prepared in this manner to be ~2.1 according to the results presented in this paper. In this regard, our work represents a significant progress, but it also points out an urgent need for novel materials and processes for producing closed-cell porous films with a significantly higher porosity if the requirements for low dielectric-constant materials with k approaching 1.5 are to be realized by year 2003 as targeted by the *National Technology Roadmap*.

Conclusions

We have obtained the experimental results for the structures and dielectric properties of nanoporous poly-

(methylsilsesquioxane) (PMSSQ) films prepared via thermal decomposition of star-shaped poly(ϵ -caprolactone) (PCL) porogens in PMSSQ/PCL hybrids. The nanoscale polymer hybrids are generated in situ by heating homogeneous mixtures of methylsilsesquioxanes (MSSQ) prepolymers with star-shaped hydroxy-terminated PCLs to ~250 °C. Experimental results show that chain extension and cross-linking of MSSQ during this initial heating causes the phase separation of pure PCL domains and sufficient vitrification of PMSSQ matrix. Subsequent heating to 430 °C causes thermal decomposition of the PCL porogens and volatilization of the fragments from the glassy PMSSQ matrix, generating nanoporous PMSSQ films with little change from the hybrid morphology. The number of arms and molecular weight/arm of the star-shaped PCLs strongly influence the phase-separation behavior of the mixtures and hence the morphology of the porous PMSSQ films. The dielectric constants, however, show a continuous decrease with increasing amounts of the PCL porogens with little dependence on their molecular structure, provided that the hybrids do not show severe aggregation. Porous PMSSQ films containing desired closed-cell pores, which are smaller than ~20 nm in size and exhibit hydrophobic surfaces, were successfully obtained with dielectric constants as low as 2.1 and a high breakdown strength which is close to that of SiO₂. Moreover, results from ac conductance measurements on PMSSQ/PCL hybrid samples offer insight into the interconnectivity of PCL domains (and hence the pores). A large jump in ac conductance for the hybrids above a porogen loading level of 25 wt %, coupled with the substantially lower breakdown fields observed for the porous PMSSQ films generated from these hybrids, suggests some interconnectivity of the PCL domains in the hybrids and the resulting pores at such high porogen loading levels.

Acknowledgment. This work was supported in part by the NSF Materials Science and Engineering Grant DMR-9400354 for the Center for Polymer Interfaces and Macromolecular Assemblies (CPIMA). C.V.N. was supported by NASA Contract NAS2-14031 to ELORET Inc. D.Y.Y. was supported in part by Korean Collaborative Project for Excellence in Basic System IC Technology (98-B4-C0-00-01-00).

CM990114D