

Supercritical Carbon Dioxide Extraction of Porogens for the Preparation of Ultralow Dielectric Constant Films

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Abstract

Supercritical carbon dioxide (SCCO₂) extraction of a CO₂-soluble poly(propylene glycol) (PPG) porogen from poly(methylsilsesquioxane) (PMSSQ) cured to temperatures adequate to initiate matrix condensation, but still below the decomposition temperature of the porogen is demonstrated to produce nanoporous, ultralow dielectric constant thin films. Both closed and open cell porous structures were prepared simply by varying the porogen load in the organic/inorganic hybrid films. The porogen loads investigated in the present work ranged from 25 - 55 wt.%. Structural characterization of the samples conducted using transmission electron microscope (TEM), small angle X-ray scattering (SAXS) and Fourier transform infrared spectroscopy (FTIR) confirms the successful extraction of the porogen from the PMSSQ matrix at relatively low temperatures ($\leq 200^{\circ}\text{C}$). The standard thermal decomposition process is performed at much higher temperatures (typically in the range of 400°C - 450°C). The values of dielectric constants and refractive indices measured are in good agreement with the structural properties of these samples.

With the ever-growing demand for higher speed in computers, the feature dimensions of integrated circuits (IC) continue to shrink. As a consequence, narrower and thinner metal lines are being used in ICs and the spacing between the metal lines is also being reduced. The former increases the wiring resistance (R) whereas the latter increases the capacitance (C), resulting in an increase in the interconnect (RC) delay. In order to reduce R, copper is being used instead of aluminum for back-end-of-the-line (BEOL) wiring. In an effort to reduce the capacitance, the main focus of current research has been the development of suitable insulating materials with lower dielectric constants (k) than SiO₂. The International Technology Roadmap published by the semiconductor industry association (2001 Edition) indicates that there will be need for materials with extremely low $k = 1.5-1.9$ by year 2003.¹ The only viable approach to this goal is the incorporation of nanoporosity in the insulating matrix.²

One promising class of low- k candidates is spin-on glasses, such as the organosilicate poly(methylsilsequioxane) (PMSSQ), having an empirical formula (CH₃-SiO_{1.5})_n. This material has an inherently low value of k , low moisture uptake, and excellent thermal stability up to 500°C.³ The k value can be further lowered by introducing nanoporosity through the incorporation and subsequent thermal degradation of pore generating organic materials, termed porogens, into the PMSSQ matrix.⁴⁻⁶ However, there are some inherent disadvantages with the thermal degradation route to nanoporosity. The process window can be narrow since the porogen decomposition must occur below the glass transition (T_g) of the thermally stable phase (when plasticized with the porogen) so that the nanopores formed do not collapse. Since many organic polymers have relatively low T_gs compared to their degradation temperatures, this processing constraint can lead to incomplete porogen decomposition often resulting in char formation. Therefore, it is of interest to develop a lower temperature process for the introduction of porosity. Such a process could also be advantageous in the generation of patterned porous films since there is a tendency toward degraded resolution (resolution of what) in high temperature processes. A possible alternative to the purely thermal decomposition method is the use of supercritical carbon dioxide (SCCO₂) treatment to extract CO₂-soluble porogens from the PMSSQ matrix at lower process temperatures. Above its critical temperature (31°C) and critical pressure (1050 psi), CO₂ is supercritical. In this state, it has a very high

diffusivity due its gas-like viscosity coupled with a high solvent power due to its liquid-like density.⁷ Moreover it is a well-established fact that CO₂ in its supercritical state can be a good solvent for many low molecular weight molecules.^{7,8} Furthermore, CO₂ is inexpensive, nonflammable and environmentally benign. These properties of CO₂ in its supercritical state have motivated us to examine the feasibility of extracting porogens using SCCO₂ treatment to form nanopores.

Another key area of interest is the porous morphology in the low-*k* film, i.e., whether it is open or closed cell. The creation of closed pores in the matrix is desirable because pore interconnectivity can result in low mechanical strength and breakdown voltage.⁶ Highly interconnected pores may also allow contaminants to diffuse between structures, possibly resulting in electrical shorts.⁴ Thus, a key goal is the study of SCCO₂ processes to produce nanoporosity in thin films of the order of 1μm thick. This film thickness is compatible with integration requirements. Generation of nanoporosity in such thin films has not been achieved by SCCO₂ saturation techniques.^{9,10} In this investigation, two porogen compositions in PMSSQ were studied. The first composition (75/25, PMSSQ/porogen), is expected (WHY) to form nanohybrids with a dispersed porogen morphology while the second (45/55) **has been demonstrated to** (need a citation if demonstrated) produce an interconnected nanohybrid. For purely thermal processes, the final porous morphology is dictated by that of the nanohybrid. Here we report, for the first time, the successful extraction of phase separated porogens from each sample using SCCO₂. For simplicity, the two nanohybrid samples will be hereafter referred to as OS7525 and OS4555.

A solution containing appropriate quantities of the linear poly(propylene glycol) (PPG) porogen ($M_n = 20,000$ g/mol and PDI = 1.05) and low molecular weight PMSSQ dissolved in propylene glycol methyl ether acetate (PM acetate) were loaded into a disposable syringe and passed through a 0.2μm PTFE filter directly onto silicon substrates. The spin-coated samples were heated briefly to 50°C on a hot plate under nitrogen atmosphere to remove residual solvent before curing at 200°C to produce the organic/inorganic polymer hybrid. This curing temperature is still well below the thermal degradation temperature of the porogen in an inert atmosphere. During matrix curing, phase separation of the porogen occurs via a nucleation and growth process. The thermal

processes (baking/curing) were carried out under nitrogen as porogen decomposition begins as low as 150°C in the presence of trace amounts of oxygen. The experimental steps involved in the SCCO₂ extraction process are described here. The samples were placed inside a small cylindrical pressure vessel made of stainless steel with inner diameter of 2.5 cm, outer diameter of 6.3 cm, and depth of 12.7 cm. The ambient air was then pumped out using a roughing pump and the vessel backfilled with CO₂ at approximately 300 psi. The process temperature was then ramped slowly to achieve the desired temperature. The chamber was subsequently pressurized isothermally with CO₂ using a gas booster pump (Haskel) driven by air at 70 psi and the pressure of the chamber was maintained over the duration of the experiment. High purity (99.99%) CO₂ was used in these studies. At the completion of the experiment, the vessel was depressurized to 500 psi and the temperature was ramped down to room temperature. Depressurization was then completed at room temperature.

FTIR spectroscopy was used to quantify the degree of porogen extraction. FTIR spectra were recorded before and after extraction using a Perkin-Elmer Model 1600 spectrometer with a resolution of 8 cm⁻¹ in the range of 400 to 4000 cm⁻¹. The microstructure of the samples after extraction was examined using transmission electron microscopy (TEM, TopCon-002B) and small angle x-ray scattering (SAXS). Samples for TEM were prepared using a FEI 830XL dual beam focused ion beam (FIB) machine. A thin carbon layer less than 20 nm and a Pt layer of ~50 nm thick were deposited on the surface to minimize contamination. The pore size and size distribution were determined by SAXS. SAXS experiments were performed at the IMM-CAT at the Advanced Photon Source at Argonne National Laboratory. A detailed description of the experimental geometries has been reported elsewhere.¹¹ The thickness and refractive index of the samples were measured using ellipsometry after every SCCO₂ treatment. Porosity was estimated applying the Maxwell-Garnett effective medium approximation method.¹² For dielectric measurements, Ti electrodes with an area of $0.196 \times 10^{-6} \text{ m}^2$ were deposited by e-beam evaporation on the organic/inorganic hybrid films deposited on heavily doped silicon substrates.

In order to quantify the amount of porogen remaining after extraction in the films using FTIR, it is necessary to know which characteristic vibrational bands are assigned to

the PPG $(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_n$ and PMSSQ $(\text{CH}_3\text{-SiO}_{1.5})_n$ components. FTIR absorbance measurements for the PMSSQ and PPG, respectively, show many overlapping vibrational bands; prominent among these are the OH stretch at $3150\text{-}3700\text{ cm}^{-1}$ and CH_n stretch at $2800\text{-}3000\text{ cm}^{-1}$. However, in case of CH_n bands, the CH_3 asymmetric stretch at 2960 cm^{-1} is the only band observed in PMSSQ sample, whereas the CH_2 asymmetric stretch at 2915 cm^{-1} is observed in PPG in addition to CH_3 bands corresponding to symmetric and asymmetric stretch. Thus, in a hybrid film, the CH_2 contribution arises from PPG. A ratio of the area of this peak before and after extraction gives a reasonable quantitative estimate of porogen left in the sample after extraction.

The strongest vibrational bands for PMSSQ were observed from $1000\text{-}1200\text{ cm}^{-1}$. From the literature¹³⁻¹⁵, the peaks at 1120 cm^{-1} and 1030 cm^{-1} in the as-spun samples can be assigned to the cage and/or chains with non-bridging oxygen atoms and network structures of MSSQ, respectively.^{16,17} In the FTIR spectra of PPG films, we observe the strongest peak in the region of $1000\text{-}1200\text{ cm}^{-1}$. This band is assigned as the C-O stretching vibration as observed for alcohols and ethers.¹⁸ As a result, the region from $1000\text{-}1200\text{ cm}^{-1}$ in the FTIR spectrum of the organic/inorganic hybrid film contains overlapping bands for both PPG and PMSSQ and deconvolution of the bands in this region is not easy. In the present context of the SCCO₂ extraction of PPG from PMSSQ matrix, we monitor both the bands at $2800\text{-}3000\text{ cm}^{-1}$ and $1000\text{-}1200\text{ cm}^{-1}$. In addition, we also monitor changes in OH band intensity since it is important from the perspective of lowering the k value.

The procedure used for the analysis of FTIR data has been described elsewhere.¹⁹ Fig.1 (a) and Fig.1 (b) show plots of the absorption coefficient versus wave number for the two spectral regions of interest; $400\text{-}1800\text{ cm}^{-1}$ and $2700\text{-}4000\text{ cm}^{-1}$ of as-spun OS4555 and for OS4555 films treated with SCCO₂ at 7000psi for 14 hours at 160°C . The intensities of the CH and OH bands decreased significantly after SCCO₂ treatment; a feature consistent with extraction of the porogen. However, we still observe a small peak at 2915 cm^{-1} attributed to the asymmetric CH_2 stretching of the porogen signifying a small residue remaining in the sample after extraction. Careful analysis of the integrated intensities of the CH_2 bands before and after extraction yields a value of 8% for the amount of porogen remaining. The value of n measured for the extracted film is sharply

reduced (1.146) from 1.442 measured for the as-spun film. The reduction in the n value is attributed to the extraction of significant amounts of porogen and generation of porosity.

In case of sample OS7525 treated with SCCO₂ at 7000 psi for 14 hours at 160°C, the intensity of the band at 1000-1200 cm⁻¹ and that of the CH_n band does not show appreciable decrease after SCCO₂ treatment. There was also only a small reduction in the intensity of the OH band. The results indicate that SCCO₂ treatment is not able to effectively extract the porogen under these process conditions presumably due to the lack of interconnectivity of the PPG phase. A possible solution is to increase the temperature of the extraction process. Although increasing the temperature decreases the solubility of the porogen both in the SCCO₂ and in the matrix, it does increase the diffusivity of the porogen through the matrix. In addition, at higher temperatures, some limited bond breaking may occur resulting in a decrease in molecular weight, which would make the polymer easier to extract. When the OS75/25 as-spun samples were treated with SCCO₂ at 200°C we observed an appreciable decrease in the intensity of the bands at both 1000-1200 cm⁻¹ and 2800-3000 cm⁻¹ as shown in Fig.2 (b) after extraction in comparison to Fig.2 (a) for as-spun OS7525 films. The amount of porogen left in this sample after extraction is estimated to be ~15%. Thus for this example, the SCCO₂ process has not extracted the porogens completely even at the higher temperatures for non-interconnecting morphologies. We are currently trying to further optimize extraction process by tuning certain process parameters, e.g. the use of a suitable co-solvent along with SCCO₂. We are also in the process of building a flow-through system to facilitate complete removal of porogens.

The refractive index of the extracted OS7525 sample decreased substantially from 1.441 before extraction to 1.313. It is noteworthy that the treatment temperature is still, however, much lower than required for complete thermal decomposition of the porogen. As a control, a sample thermally annealed 14 hours at 200°C in nitrogen ambient showed no change in the IR absorbance spectra for either of the as-spun OS4555 and OS7525 samples. This confirms that the removal of the porogen is exclusively due to SCCO₂ extraction and was not simply due to thermal decomposition and volatilization of PPG. . The data confirm that extraction of porogens even from non-interconnecting hybrid morphologies can be accomplished with SCCO₂.

As mentioned earlier, in the conventional thermal decomposition process, the porogen is removed by heating to 400°C-450°C in a nitrogen atmosphere. In addition to the creation of nanopores, this thermal treatment also further cures and crosslinks the matrix, increasing the mechanical strength of the film. For this reason, after extraction of the porogen from our samples, we annealed the films under nitrogen at 430°C for two hours. The FTIR results for these samples shown in Fig.1(c) and Fig.2 (c) clearly indicate that there is an increase in the intensity of the peak at 1040 cm⁻¹ corresponding to network formation with simultaneous decrease in the intensity of the peak at 1140 cm⁻¹ corresponding to cage structure and/or nonbridging oxygen. In addition, the 430°C annealing treatment also removed the residual OH functionality completely, a critical issue for lowering the value of *k*. For comparison, Fig.1 (d) and Fig.2 (d) show FTIR absorption spectra for OS4555 and OS7525 films after only thermal treatment at 430°C for two hours (no SCCO₂). It is apparent that the thickness normalized intensity of the CH₃ signals at 2970 cm⁻¹ and 1270 cm⁻¹ is higher for the film first treated with SCCO₂ and then annealed at 430°C than for the film heated directly to 430°C. It is well known that the concentration of bonds is proportional to the area under the peak. The OS4555 sample first treated with SCCO₂ and then annealed showed ~7% higher concentration of CH₃ than the directly annealed sample. In case of the OS7525 sample, the concentration was ~ 18% higher. The relative porosity of the films can be calculated from the *n* values of the treated films.²⁰ Using the Lorentz-Lorenz equation, and relating that to the total volume of the pores, the porosity of the films can be evaluated using the following equation:

$$V = 1 - \left[\frac{(n_p^2 - 1)}{(n_p^2 + 2)} \right] / \left[\frac{(n_d^2 - 1)}{(n_d^2 + 2)} \right] \quad (1)$$

where *V* is the total pore volume, *n_p* is the refractive index for the film after porogen extraction and *n_d* is the refractive index of the dense matrix of the film (MSSQ matrix in this case).

The *n*-values for the samples first extracted with SCCO₂ followed by thermal annealing are 1.137 and 1.274 for the OS4555 and OS7525 samples, respectively. Porosity estimates for these samples are 62.5% and 27.5% respectively (XRR should be done to confirm these). The values of *n* and porosity for the samples which received only

thermal annealing were 1.143 and 1.257 and 60.9% and 31.7% respectively. From a practical point of view, annealing after extraction provides an ancillary benefit in that most of the porogen has already been removed by extraction minimizing mass transport issues and for interconnecting morphologies an efficacious path for expelling the thermalized fragments is provided.

The dielectric constant results for all of the samples studied are collected in Table I. The results include samples which (i) were only annealed at 430°C in N₂ atmosphere (ii) those which were treated with SCCO₂ only, and (iii) samples which were both treated with SCCO₂ and thermally annealed at 430°C in N₂ atmosphere. In the case of the OS4555 films, the measured k value was essentially the same for SCCO₂ extraction and annealing as for thermal annealing at 430°C alone (1.47). After only SCCO₂ extraction at 160°C, the value of k was 1.87. For the OS7525 sample, SCCO₂ treatment followed by annealing resulted in a value of k of 2.29, whereas thermal annealing alone at 430°C produced a k = 2.47. The film sample which received only the SCCO₂ treatment showed a measured k = 2.81. In the case of the samples with a dispersed morphology for the nanohybrids, the lowest values of k are obtained for films first treated with SCCO₂ and then annealed at 430°C. The decrease in the k -value after annealing to 430°C for both compositions is attributed to the completed removal of the porogens and also to further curing of the MSSQ matrix

The cross-sectional TEM images of the nanoporous thin films prepared with only SCCO₂ treatments are shown in Fig. 3. The images suggest that pore structure is strongly dependent on the porogen loading. Uniformly distributed small pores throughout the entire thickness of the film are observed for OS7525 while increase in pore size with localized pore distribution is observed for OS4555. Although TEM provides useful information regarding the pore structure, the extraction of quantitative values for pore size and size distribution from these images is difficult due to several factors including overlapped pore structure in the specimen and TEM resolution limitation.

SAXS was used to quantify the porous structure. Fig. 4a shows the background subtracted, circularly averaged, and transmitted beam intensity normalized SAXS profiles (was the MSSQ subtracted?). The open and closed symbols correspond to the porous films prepared by SCCO₂ and thermal method, respectively. The scattering intensities

increase and profiles shift to a lower scattering angle with increasing porogen loading. It is noted that no significant differences in SAXS profile were observed between two pore generation methods for both OS7525 and OS4555 (I disagree! The two lower curves are different! Also see caption). To determine the pore distribution, we have quantitatively modeled the SAXS data based on Pedersen's approach.²¹ The scattered intensity, $I(q)$, is written as,

$$I = c \int_0^{\infty} n(r) f(qr) S(qr) dr \quad (2)$$

where c is a constant, $n(r)$ is the pore size distribution, $f(qr)$ is the spherical form factor, and $S(qr)$ is the structure factor for the monodisperse hard sphere model.^{11,21} The best fit of the data was obtained using log-normal pore size distributions as shown in Fig. 4b. The size distributions in Fig. 4b show that the average pore size increases and the size distribution broadens with increasing porosity. This is in good qualitative agreement with the images obtained by TEM.

In summary, supercritical CO₂ extraction of a PPG porogen has been demonstrated to lower k by creating nanoporosity in both connecting and non-interconnecting hybrid compositions of thin MSSQ films with thicknesses ranging from 0.6 to 1 μm . It is quite remarkable that SCCO₂ treatment is able to extract the porogen from the MSSQ matrix even in a sample with an initial non-interconnecting hybrid morphology. These extractions were performed using SCCO₂ at much lower temperatures (160°C for the interconnecting and 200°C for dispersed nanohybrid compositions) compared to the conventional thermal sacrificial porogen removal process. For the dispersed morphology, the dielectric constant is lower for films undergoing SCCO₂ extraction followed by annealing at 430°C compared to those directly annealed at 430°C without SCCO₂ treatment. For interconnected hybrid compositions, both processes (extraction plus annealing and only annealing) resulted in the same value of k .

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Figure Captions

Fig.1 FTIR absorption spectra of OS4555 films (a) as spun, (b) SCCO₂ treated at 7000psi, 160°C, 14hours, (c) first SCCO₂ treated at 7000psi, 160°C, 14 hours and then thermally annealed at 430°C for two hours and (d) only thermally annealed at 430°C for two hours.

Fig.2 FTIR absorption spectra of OS4555 films (a) as spun, (b) SCCO₂ treated at 7000psi, 200°C, 14hours, (c) first SCCO₂ treated at 7000psi, 200°C, 14 hours and then thermally annealed at 430°C for two hours and (d) only thermally annealed at 430°C for two hours.

Fig.3 Cross-sectional TEM images of nanoporous PMSSQ films, (a) OS7525, (b) OS4555. Scale bar=150nm.

Fig.4 Small angle x-ray scattering (SAXS) profiles of nanoporous poly(methylsilsesquioxane) films. (a) closed and open symbols present thermal and SCCO₂ processes, respectively. (b) pore size distribution obtained from the best fits (solid line in (a)). This figure is hard to follow. Edit out the superions and plot with lines.

List of Tables

Table I	Measured values of refractive index, estimated values of porosity and dielectric constant for OS4555 and OS7525 as-spun, SCCO ₂ treated and SCCO ₂ treated + annealed and only thermally annealed films.
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Table I Measured values of refractive index, estimated values of porosity and dielectric constant for as-spun, SCCO2 treated, SCCO2 treated + annealed and only annealed OS4555 and OS7525 films

Sample Name	Treatment	Thickness (μm)	Refractive index	Percent Porosity	<i>k</i> value ± 0.1
MSSQ	As-spun pure organosilicate MSSQ film cured at 200°C	0.4799 ±0.0042	1.4099 ±0.0004		3.1
OS4555 As-spun	As spun sample cured at 200°C	0.9205 ±0.013	1.4423 ±0.0006
OS4555 Press.	SCCO2 treated at 7000psi 160°C for 14 h	0.9119 ±0.0011	1.146 ±0.003	1.87
OS4555 Press.& ann	SCCO2 treated first + Annealed at 430°C in 600mTorr N ₂ for 4h	0.6051 ±0.0009	1.137 ±0.003	62.5 0.005	1.47
OS4555 Ann	Only annealed at 430°C in 600mTorr N ₂ for 4h	0.6310 ±0.0011	1.143 ±0.003	60.9 ±0.005	1.47
OS7525 As-spun	As-spun sample cured at 200°C	0.5779 ±0.0037	1.441 ±0.0008
OS7525 Press.	SCCO2 treated at 7000psi 200°C for 14 h	0.5690 ±0.0014	1.313 ±0.003	2.81
OS7525 Press. & Ann	SCCO2 Treated first + Annealed at 430°C in 600mTorr N ₂ for 4h	0.4435 ±0.0009	1.274 ±0.003	27.5 0.002	2.29
OS7525 Ann	Only annealed at 430°C in 600mTorr N ₂ for 4h	0.4502 ±0.0011	1.257 ±0.003	31.7 ±0.002	2.47

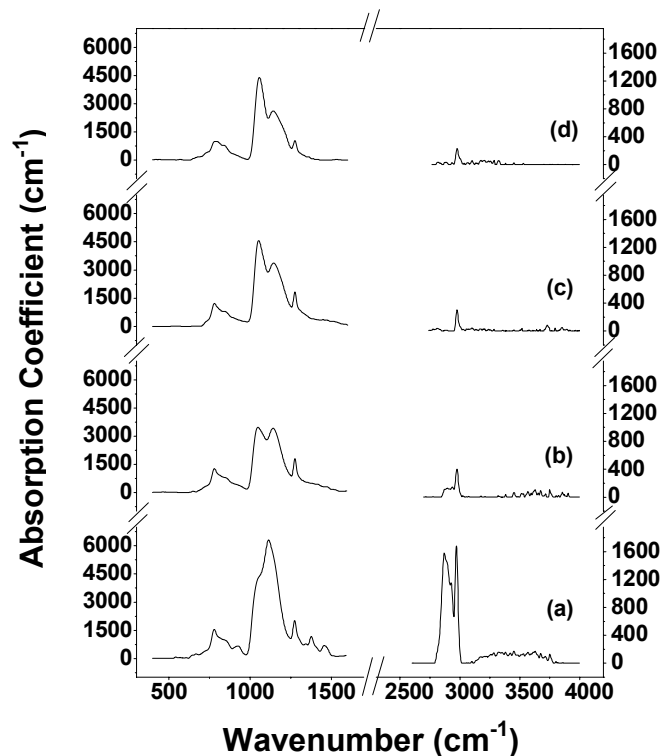


Fig.1 FTIR absorption spectra of OS4555 films (a) as spun, (b) SCCO₂ treated at 7000psi, 160°C, 14hours, (c) first SCCO₂ treated at 7000psi, 160°C, 14 hours and then thermally annealed at 430°C for two hours and (d) only thermally annealed at 430°C for two hours.

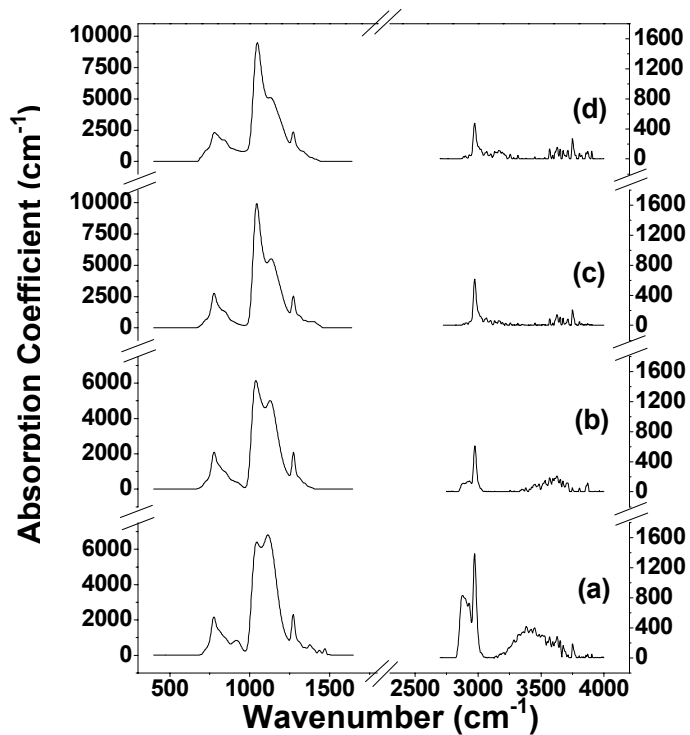


Fig.2 FTIR spectra of OS7525 films (a) as spun, (b) SCCO₂ treated at 7000psi, 200°C, 14 hours, (c) first SCCO₂ treated at 7000psi, 200°C, 14 hours and then thermally annealed at 430°C for two hours and (d) Only thermally annealed at 430°C for two hours.

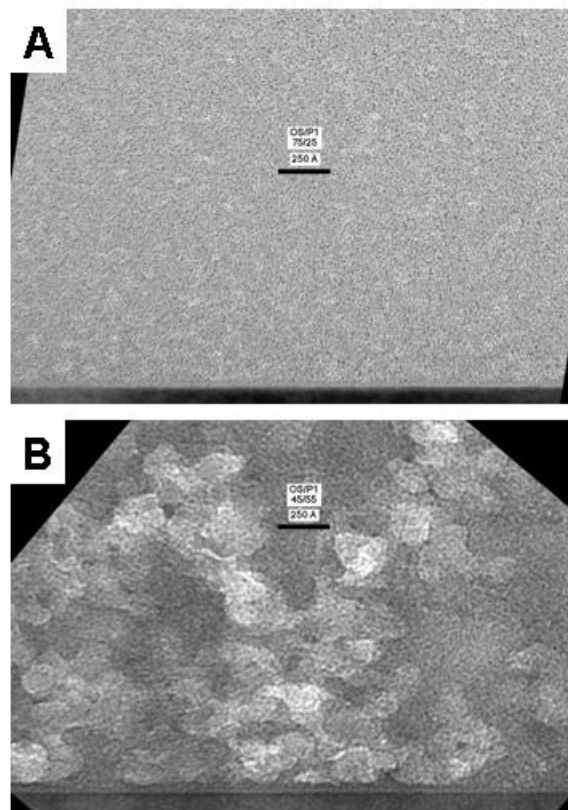


Fig.3 Cross-sectional TEM images of nanoporous PMSSQ films, (a) OS7525, (b) OS4555. Scale bar=25nm.

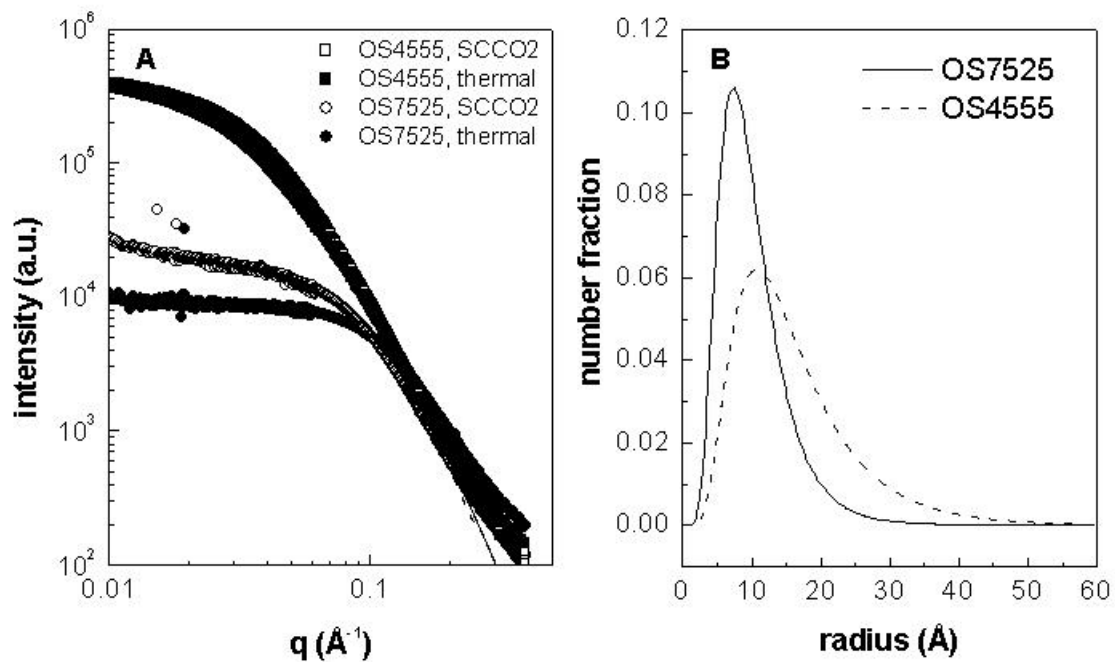


Fig.4 Small angle x-ray scattering (SAXS) profiles of nanoporous poly(methylsilsesquioxane) films. (a) closed and open symbols present thermal and SCCO2 processes, respectively. (b) pore size distribution obtained from the best fits (solid line in (a)).