Solid-State Proton NMR Characterization of Ethylene Oxide and Propylene Oxide Random and Block Copolymer Composites with Poly(methyl silsesquioxanes)

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Solid-state proton NMR with fast magic-angle sample spinning has been used to study the structure and dynamics of block and random ethylene oxide/propylene oxide copolymers in the bulk and as 30 wt % composites with poly(methyl silsesquioxane) which are precursors to nanoporous ultralow dielectric constant films. The NMR results for the bulk diblock copolymer show that the propylene oxide block is relatively mobile and the proton line widths are effectively narrowed with 12 kHz magic-angle sample spinning, while most of the signals for the semicrystalline ethylene oxide block are too broad to be observed under these conditions. Both the ethylene oxide and propylene oxide signals are observed in the 30 wt % composite, demonstrating that the formation of crystalline domains in the ethylene oxide block is inhibited in the composite. Dipolar filter NMR experiments show that the propylene oxide is less mobile than the ethylene oxide in the block copolymer composites, suggesting that the propylene oxide is near the methyl silsesquioxane interface. The results from proton spin diffusion studies show that the polymer domain sizes in the composites are on the order of 5−7 nm, the size range of most interest for the formation of ultralow dielectric constant materials.

Introduction

Advances in the design and production of integrated circuits has led to microprocessors with small feature sizes and an increased density of devices. As the feature size shrinks, the distance between wires is decreased and the performance is limited by the circuit delays, power consumption, and cross talk between multilevel interconnects.[1] The performance can be improved by using packaging materials with low dielectric constants (k). Silicon dioxide is the current material of choice, but it has a dielectric constant of 4, and it will not be suitable for the next generation of integrated circuits as the feature size shrinks below 0.1 μm.

A number of materials are currently under consideration for the next generation of low-k films, including organic and inorganic materials as well as organic/inorganic hybrids. Since the dielectric constants of most materials are greater than 3, it is difficult to produce ultralow dielectric constant materials ($k < 2$) without taking advantage of the low dielectric constant of air ($k = 1$). Dielectric constants less than 2 have recently been reported by introducing porosity into thin films.[2,3] The pores must be small and isolated to achieve the lowest possible dielectric constant while limiting metal diffusion through the films. In addition to a low dielectric constant, these films must have a high breakdown voltage, low moisture uptake, good thermal stability, and the mechanical integrity to withstand the chemical−mechanical processing used in the production of integrated circuits.

One very promising approach to the design of ultralow-k materials is to introduce sacrificial materials such as polymers,[3] high boiling point liquids,[4] or organic spacers into organic/inorganic hybrids. Among the candidates for the matrix materials are the silsesquioxanes, which have the molecular formula $R-SiO_{1.5}$. Poly(methyl silsesquioxane) is of particular interest as the bulk material has a low dielectric constant ($k = 2.6-2.8$), good thermal stability, and a low moisture uptake. IBM researchers have reported that ultralow-k materials can be made with hyperbranched poly(ϵ-caprolactone) as the sacrificial material and that only 30% porosity is required to reach the ultralow-k regime.[3] The pore structure for the composites was reported to depend on the molecular weight and number of arms in the hyperbranched poly(ϵ-caprolactone).

Another approach to the design of ultralow-k materials is to use the templated self-assembly of block copolymers to control the pore size and distribution.[5] Block copolymers can adopt a variety of morphologies, and well-ordered block copolymer composites have been reported in spherical, cylindrical, and lamellar morphologies.[6] Block copolymers are available with a vari-

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ety of monomers that make it possible to tune the interactions between the blocks and the matrix. This should make it possible to choose block copolymers to control the aggregation and structure formation in the methyl silsesquioxane composites so that the pore size and distribution can be also be controlled.

Solid-state NMR is a powerful method for the study of polymers and composites, since it provides information about the structure and dynamics over a wide range of time scales and length scales.[7,8] Solid-state NMR, for example, has been used to study the structure and dynamics of both the polymer and the matrix in organic/inorganic composites.[9,10] In the present studies, we have used solid-state proton NMR with fast magic-angle spinning to study the structure and dynamics of ethylene oxide/propylene oxide diblock and random copolymers in the bulk and in methyl silsesquioxane composites. The purpose of these studies is to understand how the polymer architecture affects the formation of polymer domains in the composites, which ultimately affects the pore size and distribution. The results show that the propylene oxide block preferentially interacts with the methyl silsesquioxane matrix and affects how the polymer domains are organized. Proton spin diffusion studies show that the polymer domain sizes are in the range most useful for the formation of ultralow-*k* materials.

Materials and Methods

The random ethylene oxide/propylene oxide copolymer containing 75 wt % ethylene oxide with a molecular weight of 12 000 g mol^{-1} was obtained from Aldrich. The ethylene oxide/propylene oxide diblock copolymer with block molecular weights of 5500 and 1100 g mol^{-1} for the ethylene oxide and propylene oxide blocks was obtained from Polymer Source, Inc. The methyl silsesquioxane precursor was obtained from Techneglass as a 30 wt % solution in a mixture in *n*-butanol and ethyl alcohol. The methyl silsesquioxane has a number average molecular weight of 1668 and polydispersity of 3.2 as measured by GPC.

The copolymers and methyl silsesquioxanes were dissolved in *n*-butanol and passed though 0.45 μm PTFE filters. The solutions were cast as films under vacuum for 12 h at 120 °C. This treatment partially cures the methyl silsesquioxane into a relatively rigid, clear material. The final concentration of polymer in the composite is 30 wt %.

The solid-state proton NMR experiments were performed at 400 MHz by using a Varian Unity NMR spectrometer with a 4 mm magic-angle spinning probe and spinning speed regulation at 12 kHz. The proton pulse widths were 3.5 μs, and the dipolar filter pulse sequence[11] was used to measure the chain dynamics and for the spin diffusion experiments. All experiments were performed at ambient temperature.

Results

Solid-state proton NMR with fast magic-angle sample spinning has been used to study the structure and dynamics of random and block ethylene oxide/propylene oxide copolymers in the bulk and as composites with poly(methyl silsesquioxane). Solid-state proton NMR is not often used to study the structure of polymers because the lines are broadened by the combination of dipolar interactions and chemical shift anisotropy.[7,8] It is possible to use solid-state proton NMR to study the structure and dynamics of polymers in the cases where the spinning speed is greater than the magnitude of the dipolar couplings. Since the dipolar couplings are on the order of 30−50 kHz for rigid materials, very fast spinning is required to obtain a high-resolution spectrum.[12] If the dipolar couplings are partially averaged by chain motion, as for polymers above T_g, then a high-resolution spectrum can be obtained with moderate magic-angle sample spinning.[13,14] In these studies, we have used 12 kHz magic-angle spinning to study the copolymers and the composites; this spinning speed is fast enough for line narrowing in polymers above T_g but insufficient to narrow the lines in the crystalline phases. The glass transition temperatures for poly(ethylene oxide) and poly(propylene oxide) (−70 and −75 °C)[15] are well below the ambient temperature, so these lines will be effectively narrowed with fast magic-angle sample spinning. Figure 1 shows the 400 MHz solid-state proton NMR spectra for the poly(ethylene oxide-*b*-propylene oxide) block copolymer and the 30 wt % composite with poly(methyl silsesquioxane) acquired with 12 kHz magic-angle sample spinning. The polymer peaks of interest are the signals at 3.5 ppm that arise from the methylene protons of ethylene oxide and the methine and methylene protons of propylene oxide and the signal at 1 ppm from the propylene oxide methyl protons. The peak at 0 ppm is assigned to the methyl silsesquioxane methyl protons.

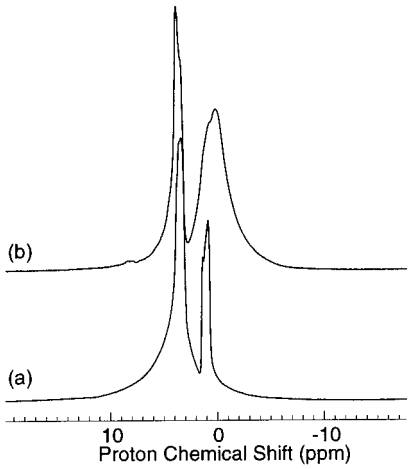
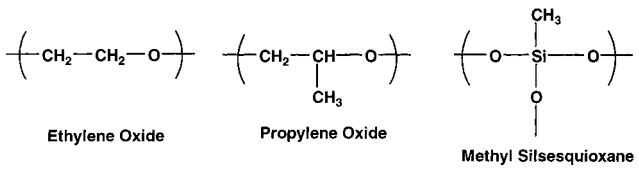


Figure 1. The 400 MHz solid-state proton NMR spectra of (a) poly(ethylene oxide-*b*-propylene oxide) and (b) the 30 wt % methyl silsesquioxane/poly(ethylene oxide-*b*-propylene oxide) composite. The spectrum was obtained with 12 kHz magic-angle sample spinning at ambient temperature.



The solid-state proton spectra with 12 kHz magic-angle spinning provides information about the structure

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of the poly(ethylene oxide-*b*-propylene oxide) block copolymer, since a high-resolution spectrum is only obtained for the mobile segments where the dipolar couplings are partially averaged by chain motion. The expected peak intensity ratios for the peaks at 3.5 and 1.0 ppm can be directly calculated from the chemical structures and the block molecular weights for the $PEO_{125}-PPO_{19}$ copolymer. If all of the polymer protons were observed, the intensity ratio would be 9.7:1. The data in Figure 1a shows that the intensity ratio for the block copolymer is on the order of 2:1. This shows that a significant fraction of the intensity at 3.5 ppm is missing from the spectra. We believe that this is due to a large fraction of the ethylene oxide being in a rigid crystalline conformation, since a 1:1 intensity ratio is expected from the propylene oxide block alone. The peak at 3.5 ppm is therefore due to the methine and methylene protons of propylene oxide and some mobile ethylene oxide methylene protons, presumably those at the ethylene oxide−propylene oxide interface. The conclusion that the ethylene oxide blocks are partially crystalline is consistent with DSC studies of the diblock and triblock copolymers showing sharp melting transitions in the range of 30−61 °C, depending on the length of the ethylene oxide block (not shown).

Figure 1b shows the solid-state proton spectrum for the 30 wt % diblock copolymer composite. The features to note in this spectrum are the polymer signals at 3.5 and 1 ppm and the broad peak at 0 ppm from the methyl silsesquioxane. The poly(methyl silsesquioxane) methyl peak is sharper than expected for a rigid solid with 12 kHz magic-angle sample spinning, demonstrating that the dipolar interactions are partially averaged by molecular motion. This is most likely due to averaging of the dipolar interactions by methyl group rotation and the low density of protons in poly(methyl silsesquioxane) relative to most organic materials.

As with the bulk block copolymer, the relative signal intensities in the composite provide information about the structure and dynamics. The relative intensities of the ethylene oxide methylene protons and the methyl silsesquioxane methyl peak are expected to be about 1:1 for the 30 wt % composite. We have not attempted to accurately measure the relative peak intensities because of peak overlap, but a rough comparison shows that the peak intensity ratios for the peaks at 3.5 and 0 ppm are about 1:1. In contrast to the observations with the bulk copolymer, this result shows that nearly all of the ethylene oxide in the block copolymer can be observed with moderate magic-angle sample spinning, demonstrating that the ethylene oxide block is not semicrystalline as it is in the bulk diblock copolymer. These data show that the block copolymer adopts a very different conformation in the composite relative to the bulk material.

Figure 2 shows the solid-state proton spectrum for the 30 wt % random copolymer composite with methyl silsesquioxane. The poly(ethylene oxide-*co*-propylene oxide) is a liquidlike material at ambient temperature,

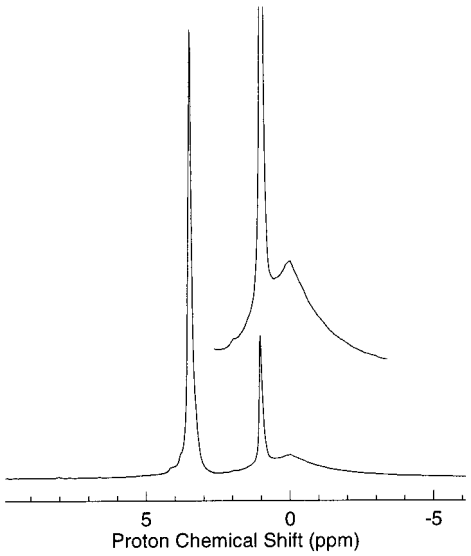

Figure 2. The 400 MHz proton NMR spectrum of the methyl silsesquioxane/poly(ethylene oxide-*co*-propylene oxide) composite at ambient temperature. The inset plot shows the methyl peak from the matrix at 0 ppm.

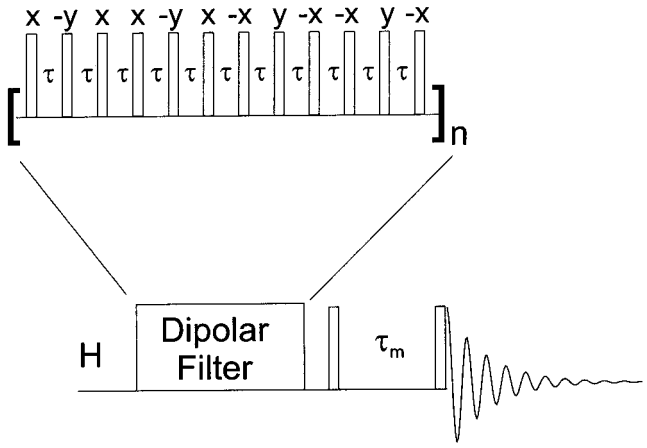

Figure 3. Pulse sequence diagram for the dipolar filter pulse sequence.

and we have not studied its properties using solid-state NMR. The spectra for the random copolymer composite shows some differences relative to the diblock copolymer composite, including sharper lines for the polymer peaks and a broader signal for the matrix. The inset plot shows the broad peak at 0 ppm from the methyl silsesquioxane.

The relative intensities of the polymer peaks at 3.5 and 1.0 ppm were also compared with the values calculated from the composition of the random copolymer. The random copolymer contains 75% ethylene oxide and the relative ratio of the peaks should be about 6:1. Again, it is difficult to accurately measure the peak intensities, but the ratio appears to be about 5:1 based on the peak heights and line widths. Thus, it appears that nearly all of the polymer signals are visible in the magic-angle spinning experiments in the random copolymer composite.

The molecular dynamics of the polymer and the length scale of phase separation in the copolymers and the composites have been investigated by using the dipolar filter pulse sequence[11] shown in Figure 3. This experiment is used to create a polarization gradient across the sample based on differences in the dynamics

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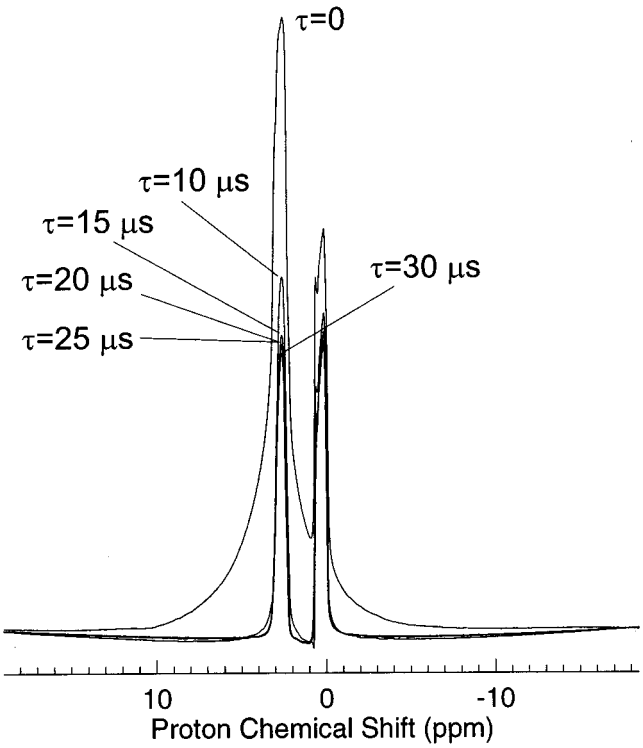

Figure 4. Effect of the dipolar filter strength on the appearance of the proton spectra for the poly(ethylene oxide-*b*-propylene oxide) block copolymer. The filter strength is increased by lengthening the delay time τ between pulses in the dipolar filter.

and the relaxation times.[16] The peak intensities as a function of the dipolar filter strength provide information about the molecular dynamics, and the domain sizes can be measured using proton spin diffusion as the polarization gradient is relaxed.

The dipolar filter pulse sequence begins with the application of several cycles of a 12-pulse decoupling sequence to the protons. The phases of the pulses are chosen such that this sequence provides effective decoupling when the delay between the pulses τ is short. When τ becomes comparable to the spin−spin relaxation times, the decoupling is inefficient and the signals are saturated rather than decoupled. In samples with strong and weak dipolar couplings, the dipolar filter creates a polarization gradient by saturating the protons with strong dipolar couplings while retaining the magnetization from the more weakly coupled ones. This pulse sequence is used to investigate the domain structure of the composite by choosing a delay time such that the signals from the matrix are saturated while those from the polymer are retained.

Figure 4 shows the effect of increasing dipolar filter strength on the spectra of the bulk poly(ethylene oxide-*b*-propylene oxide) block copolymer. The equilibrium spectrum ($\tau = 0$ μs) shows both broad and narrow components. The broad component is suppressed by using a dipolar filter with a 10 μs delay time, and the intensity of the peak at 3.5 ppm is significantly reduced.

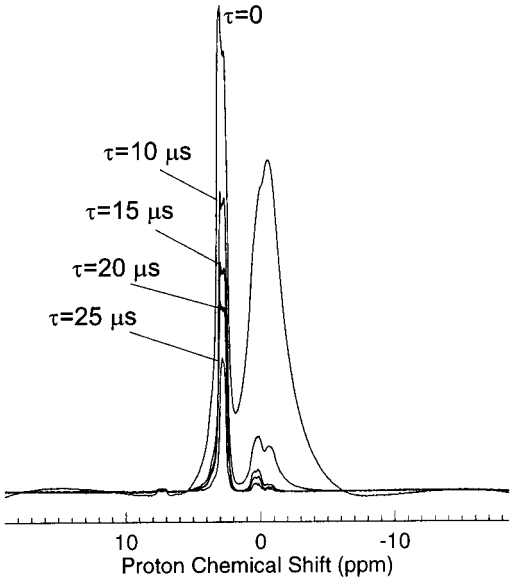

Figure 5. Effect of increasing the dipolar filter strength on the spectra for the methyl silsesquioxane/poly(ethylene oxide-*b*-propylene oxide) composite.

An increase in the delay time to 25 μs (a strong dipolar filter) produces relatively small changes in either the intensity or the line width of the remaining signals. Furthermore, the relative intensities of the peaks at 3.5 and 1 ppm after the dipolar filter are approximately 1:1, the value expected from the propylene oxide block alone. This suggests that the broad component arise from ethylene oxide protons.

Figure 5 shows that the dipolar filter has a fundamentally different effect on the solid-state proton NMR spectra of the poly(methyl silsesquioxane)/poly(ethylene oxide-*b*-propylene oxide) composite. The largest effect is the decrease in intensity of the peak at 0 ppm from the poly(methyl silsesquioxane) methyl protons with a weak ($\tau = 10$ μs) dipolar filter. In addition, the peak at 3.5 decreases in intensity but the line shape does not change significantly. A further increase in the filter strength leads to a complete suppression of the poly(methyl silsesquioxane) methyl signal, a systematic decrease in the peak intensity at 3.5 ppm and a very strong decrease in signal intensity for the propylene oxide methyl peak at 1 ppm. It is important to note that the propylene oxide methyl peak has a very different dependence on the dipolar filter strength in the bulk block copolymer and the composite. This shows that the propylene oxide block is restricted in the composite, most likely from interactions with the methyl silsesquioxane. The propylene oxide units are either dissolved in the methyl silsesquioxane or at the interface. In the random copolymer composite, the dipolar filter has only a small effect on the polymer peaks but efficiently suppresses the methyl silsesquioxane signal at 0 ppm (not shown).

The domain sizes in phase-separated mixtures can be determined by measuring the rate of proton spin diffusion following the dipolar filter.[11,16−18] The characteristic length scale of spin diffusion L depends on the proton

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Table 1. Volume Fraction, Static Spin−Spin Relaxation Rates, and the Diffusion Coefficients Used To Calculate the Domain Sizes in the Ethylene Oxide/ Propylene Oxide Diblock Copolymer and Composites with Methyl Silsesquioxane

sample	f_A[a]	T_2 (s)[b]	D (nm^2 (ms)$^{-1}$)[c]
poly(ethylene oxide-*b*-propylene oxide)	0.17	0.010	0.015
poly(ethylene oxide-*b*-propylene oxide)/ methyl silsesquioxane	0.30	0.002	0.098
poly(ethylene oxide-*co*-propylene oxide)/ methyl silsesquioxane	0.30	0.005	0.028

[a] f_A is the volume fraction of the minority phase, the propylene oxide in the diblock copolymer and the polymer volume fraction in the composites. [b] Multiexponential T_2 recovery was observed in all samples, and the longest T_2 is used to calculate the diffusion coefficient for the mobile phase. [c] The diffusion coefficients were calculated from the static T_2's by using the reported correlation.[16] The diffusion coefficient for crystalline ethylene oxide in the diblock copolymer was taken as 0.8 nm^2 (ms)$^{-1}$.[13] The diffusion coefficient for methyl silsesquioxane in the composites (0.4 nm^2 (ms)$^{-1}$) was calculated from the static T_2 for the most rapidly relaxing component.

spin diffusion constants (D_A and D_B), the proton densities (ρ_A^H and ρ_B^H), the volume fractions (f_A and f_B), and the characteristic spin diffusion time constant $(t_{sd})^{1/2}$ that is determined experimentally. This length scale is related to the characteristic spin diffusion time by[16]

$$L = \frac{4\sqrt{t_{sd}}\sqrt{D_A D_B}(\rho_A^H f_A + \rho_B^H f_B)}{f_A f_B \sqrt{\pi}(\rho_A^H \sqrt{D_A} + \rho_B^H \sqrt{D_B})} \quad (1)$$

This length scale L can then be used to calculate the distance d across the minor phase and the overall repeat distance, or long period d_{lp}. For a two-dimensional (cylindrical) morphology, d is the rod diameter and d_{lp} is the rod spacing, and the domain sizes are related to the spin diffusion length scale as[16]

$$d = 2f_A L \quad (2)$$

and

$$d_{lp} = 1.9 f_A^{1/2} L \quad (3)$$

For a three-dimensional morphology, d is the sphere diameter and d_{lp} is the center-to-center spacing between the spheres, and the L is related to the domain sizes by

$$d = 3f_A L \quad (4)$$

and

$$d_{lp} = 2.6 f_A^{2/3} L \quad (5)$$

Several of the parameters required for interpretation of the spin diffusion data can be directly calculated from the chemical structure and the composition of the polymers and composites. The spin diffusion coefficients have been measured for crystalline and rigid glassy polymers,[17] and a correlation has been reported between the diffusion coefficients of polymers above T_g and the static spin−spin relaxation rate.[19] Since the spin diffusion coefficients can be strongly affected by magic-angle spinning,[8] we measured the rate of spin diffusion in nonspinning experiments. The parameters used for the spin diffusion calculations are listed in Table 1.

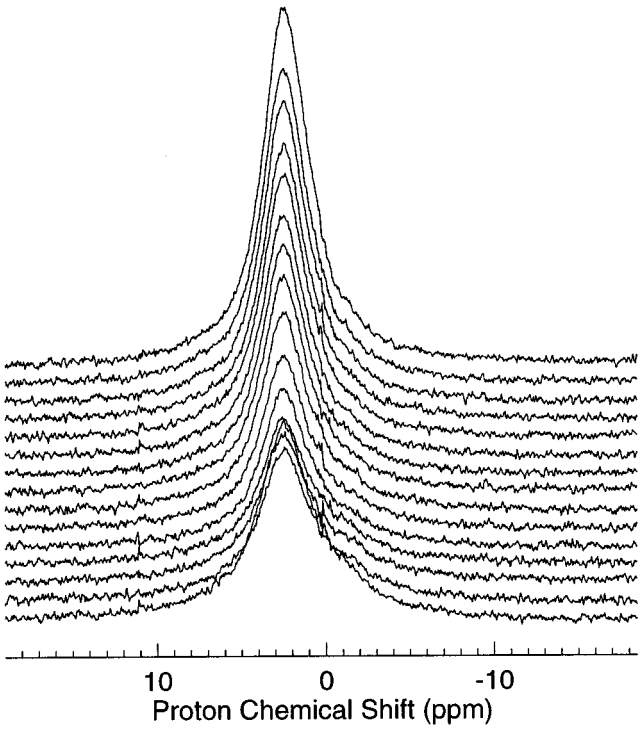

Figure 6. Static spin diffusion data for the methyl silsesquioxane/poly(ethylene oxide-*b*-propylene oxide) composite at ambient temperature. The data show the decrease in signal intensity from spin diffusion as the delay time between the dipolar filter, and acquisition is increased from 1 to 200 ms.

Figure 6 shows the static spin diffusion data for the poly(methyl silsesquioxane)/poly(ethylene oxide-*b*-propylene oxide) composite. The resolution is much lower in the static experiment because the lines are not narrowed by magic-angle spinning. The polarization gradient was established at the start of the experiment by using 10 cycles of the dipolar filter with a 25 μs delay for τ. The signals that remained, after the dipolar filter but before spin diffusion proceeded, are primarily those from the ethylene oxide segments. We can monitor the decrease in intensity as the magnetization diffuses from the ethylene oxide to the parts of the sample that were saturated with the dipolar filter to make the spin diffusion plot. The data are plotted as $\Delta M(t)$ vs $(t)^{1/2}$ where $\Delta M(t)$ is given by[16]

$$\Delta M(t) = \frac{M(t) - \bar{M}}{M_0 - \bar{M}} \quad (6)$$

where $M(t)$ is the measured intensity as a function of the spin diffusion delay time, M_0 is the intensity after the application of a polarization gradient, and $\bar{M}$ is the intensity after sample-wide spin equilibrium has been attained. The value of $(t_{sd})^{1/2}$ required to calculate L is obtained by extrapolating the initial linear part of the decay to the $(t)^{1/2}$ axis. The data are corrected for spin−lattice relaxation at longer spin diffusion delay times by using standard procedures.[17,19,20]

Figure 7 shows the spin diffusion plot for bulk poly(ethylene oxide-*b*-propylene oxide). The initial linear portion of the curve is extrapolated to give a value of

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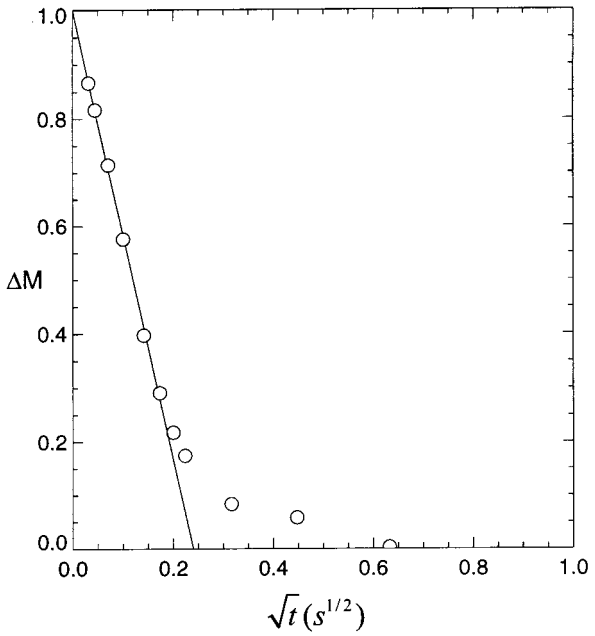

Figure 7. Spin diffusion plots for the poly(ethylene oxide-*b*-propylene oxide) diblock copolymer. The intercept is used to calculate the domain size.

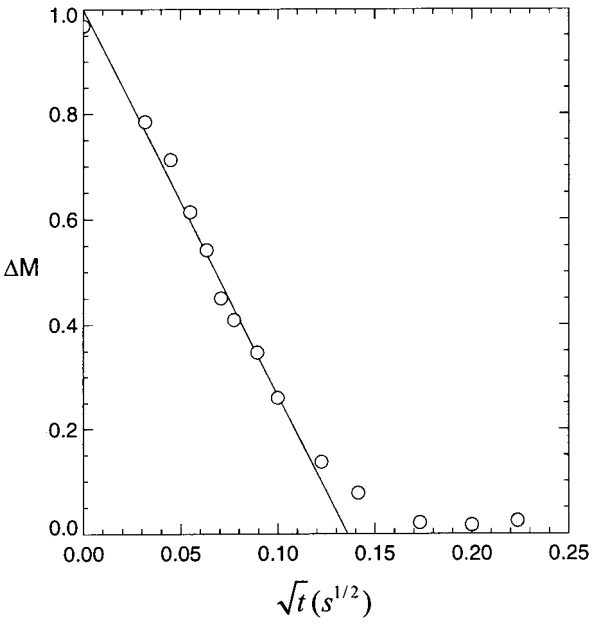

Figure 8. Spin diffusion plot for the methyl silsesquioxane/poly(ethylene oxide-*b*-propylene oxide) composite.

0.24 $s^{1/2}$ for $(t_{sd})^{1/2}$. Figure 8 shows a similar plot for the poly(methyl silsesquioxane) composite, where a value of 0.13 $s^{1/2}$ was obtained for $(t_{sd})^{1/2}$. These values are used to calculate the length scale of spin diffusion, the domain sizes, and the long periods, and the results are listed in Table 2 for the block copolymer and the methyl silsesquioxane composites with the random and block copolymers. The dimensionality of the system (2D or 3D) was chosen based on previously reported positron annihilation lifetime spectroscopy data.[5] The domain size for the propylene oxide in the bulk block copolymer is 6.6 nm and the long period is 10.5 nm. The polymer domain sizes for the block and random copolymers composites are 4.8 and 7.3 nm, and the long periods are 8.4 and 12.7 nm. The NMR results show that the domain sizes are in the range to be very useful in ultralow-*k* dielectric materials.

Table 2. Domain Sizes and Long Periods for the Diblock Copolymer and Methyl Silsesquioxane Composites Measured by Proton Spin Diffusion

sample	ϵ^a	d (nm)	d_{lp} (nm)
poly(ethylene oxide-*b*-propylene oxide)	3	6.6	10.5
poly(ethylene oxide-*b*-propylene oxide)/ methyl silsesquioxane	2	4.8	8.4
poly(ethylene oxide-*co*-propylene oxide)/ methyl silsesquioxane	2	7.3	12.7

[a] The dimensionality for the bulk diblock copolymers was chosen based on the expected phase diagram with a low volume fraction (0.17) of the minority component. The dimensionality for the 30 wt % composites were based on positron annihilation loss spectroscopy that showed a two-dimensional morphology with loading levels above 20 wt %.[5]

Discussion

The methyl silsesquioxane composites are of interest as candidate materials for the next generation of ultralow-*k* dielectrics. Methyl silsesquioxane films have a number of favorable properties, including a low dielectric constant ($k = 2.6-2.8$) for the bulk material, which can be further reduced by incorporating sacrificial polymers that can be removed with heating at 400−500 °C. The best low-*k* films are expected to be those that contain isolated nanometer-sized pores at high loading levels, and the challenge is to discover the sacrificial materials that can enable us to achieve this goal. Block copolymers are of interest as sacrificial materials, since they are available with well-defined block lengths for a wide variety of monomers, and they have a rich phase structure. The goal of our studies is to understand how copolymer architecture and molecular weight affect phase separation and pore formation in the composites. Additional studies are required to determine how the polymer domain sizes compare with the pore sizes after the sacrificial polymer has been removed. Studies of mesoporous silicas have shown that the pore structure is retained after cancination, but there is usually some shrinkage resulting from the high-temperature treatment.[21−24]

In the present studies, we have used solid-state proton NMR to study the structure and dynamics of the polymers and the methyl silsesquioxane in the block copolymer and the composites. Proton NMR is used for these studies because it has a high sensitivity and provides a unique window into the structure and dynamics of the polymers and the matrix. The 12 kHz spinning speeds used in these studies are sufficient to narrow the lines for polymers above their glass transition temperatures but insufficient to narrow the lines for polymers in a crystalline environment. This enables us to derive information about the conformation and

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dynamics of the block copolymer by comparing the line intensities for the ethylene oxide and propylene oxide peaks. The results show that the conformation is fundamentally different for the bulk block copolymer and the methyl silsesquioxane composite. The ethylene oxide is semicrystalline in the bulk $PEO_{125}-PPO_{19}$ diblock copolymer but not in the composite, showing that the formation of phase-separated domains in the composite inhibits the formation of crystallinity in the poly(ethylene oxide) domains. We also observe a phase-separated morphology for the random copolymer composite, and the data show that the random copolymer is very mobile in the composite.

The dipolar filter NMR studies are used both to monitor the dynamics of the block copolymer and the matrix and to create a polarization gradient that is used to measure the domain sizes by using proton spin diffusion. The results for the bulk diblock copolymer show that the propylene oxide block is very mobile and is not strongly affected by the dipolar filter. Very different behavior is observed for the block copolymer in the poly(methyl silsesquioxane) composite, where the ethylene oxide appears to be more mobile than the propylene oxide. Propylene oxide is not a crystalline polymer, so the decrease in chain mobility must be due to the association of the propylene oxide segments with the methyl silsesquioxane. Additional experiments are required to determine if the propylene oxide is at the interface or is dissolved in the methyl silsesquioxane matrix. The signals for both the ethylene oxide and propylene oxide in the random copolymer composite are very sharp and not strongly affected by the dipolar filter, demonstrating that the polymer is phase separated and very mobile.

The dipolar filter can also be used to measure the length scale of phase separation in the diblock copolymer and the poly(methyl silsesquioxane) composites. The propylene oxide has a volume fraction of 0.17 in the bulk block copolymer, and the spin diffusion data show a domain size of 6.6 nm and a long period of 10.5 nm.

The methyl silsesquioxane composites were made with 30 wt % polymer, so the polymer constitutes the minority phase, and the NMR studies show that the polymer is phase separated from the methyl silsesquioxane. The domain sizes measured for the diblock and random copolymer composite were 4.8 and 7.3 nm, and the long periods were 8.4 and 12.7 nm. The results for the random and diblock copolymers show that the ethylene oxide/propylene oxide copolymers form phase-separated domains in the poly(methyl silsesquioxane) matrix but that the domain sizes and the nature of the polymer−silsesquioxane interface depend on the polymer architecture and molecular weight. This suggests that varying the block copolymer architecture to control the pore size and distribution is an effective means to develop ultralow-*k* dielectric films.

It is of interest to compare the results for the poly(methyl silsesquioxane) composites with those reported for polymer−silica composites made by using a sol−gel process. Mesoporous silicas with a variety of pore sizes and morphologies have been made by using ethylene oxide/propylene oxide triblock copolymers to template pore formation in mesoporous silica.[21−24] In one study, it was reported that highly ordered monolithic composites could be made by using high concentrations of ethylene oxide/propylene oxide triblock copolymers as the templating material.[9] Composites with hexagonal order were observed with polymer concentrations above 52 wt %. The NMR analysis of these composites showed phase separation between the silica and the polymer, and that the ethylene oxide block was located at the silica interface. At lower concentrations, the composites are homogeneous, as judged by NMR and X-ray diffraction. This is in contrast to the composites with poly(methyl silsesquioxane), where the polymer is phase separated from the matrix in the 30 wt % composites. Clear phase separation was also observed in composites with 5 wt % polymer (not shown).

Polymer−silica composites have also been made by using sol−gel components to swell polyisoprene-*b*-poly(ethylene oxide) diblock copolymers.[10] Composites and mesoporous structures were obtained for a variety of morphologies, including spheres, cylinders, and lamellae. In this case, the polyisoprene was phase separated from the inorganic phase that was intimately mixed with the poly(ethylene oxide) block.

In summary, we have used solid-state proton NMR to study the structure and dynamics of methyl silsesquioxane composites for ultralow-*k* applications. Our goal is to understand how the structure of the polymer influences the domain sizes of the precursor material and to identify any interactions between the polymer and the methyl silsesquioxane that may affect structure formation. The results show that the block and random ethylene oxide/propylene oxide copolymers form phase-separated domains in the methyl silsesquioxane matrix, and the domain sizes are on the order of 5−7 nm. The polymers are mobile in the methyl silsesquioxane, and the signals can be observed with solid-state proton NMR with the use of 12 kHz magic-angle sample spinning. The domain sizes are in the range to be extremely useful for ultralow-*k* materials. Other studies on the random and diblock copolymers as well as the poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymers show that the porous films are promising materials for low-*k* dielectrics with low dielectric constants, high breakdown voltages, good thermal and mechanical stability, and low moisture uptake.[5]

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