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Sol-Gel Thin Films: Thermal and Corona-Field Accelerated Curing

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Greatly accelerated curing (30–45 min) at ambient temperature of spin-cast poly(methylsiloxane) (PMSO) thin films (10–25 μm) and similar siloxane resins prepared by a fast sol–gel process was obtained by exposure to an intense corona-discharge field (3–12 MV/cm) across the films. The progress of thermal and corona-accelerated curing of the sol–gel films were investigated by means of FTIR and by optical methods using chromophores embodied in the matrix. Using two-step thermal curing experiments, it was shown that only partial cross-linking takes place at low temperatures (25–110 °C) in the first curing stage due to microphase separation between hydrophilic (–OH-rich) and hydrophobic (–CH_3- and –OCH_3-rich) moieties. More complete cross-linking can proceed only at higher curing temperatures (150–175 °C). The corona-cured sol–gel films exhibited a more compact matrix as manifested by lower mobility of chromophores embodied in the matrix and a more hydrophilic surface than thermally-cured ones. These findings are discussed in terms of the competing processes of formation of cross-linking bonds and field-induced removal of condensate small molecules and solvents.

Introduction

Sol–gel techniques are gaining importance for the preparation of advanced glassy matrices.[1] In previous papers we have introduced a new "fast sol–gel" method for the preparation of supported crack-free thin films, which could be polymerized and cured within a few hours. Further, we demonstrated the capability to encage in these film matrices high concentrations of discrete guest molecules, aiming at various applications to nonlinear optics.[2]

Corona discharge has been widely investigated for use in surface treatment of polymeric and glassy materials.[3] Corona poling of poly-embodied donor–acceptor molecules has been reported for several years, aiming at a noncentrosymmetric assembly and second harmonic generation (SHG).[4-7] A few corona-poled chromophore-embodying sol–gel films have been recently reported.[8] We have previously reported incorporation of SHG molecules in fast sol–gel produced thin films and the correlation between the matrix-curing/poling procedure and the intensity of the resultant SHG.[9] During this research activity we have first noticed a substantial increase in the rate of curing of the sol–gel films.

In the present communication, we report the various features of thermal curing and the corona-discharge acceleration of the curing of sol–gel films. The findings are discussed in terms of competing processes of poling, drying, stress relaxation, and cross-linking.

Experimental Section

Materials. Methyltrimethoxysilane (MTMS), methyltriethoxysilane (MTES), and disperse orange 3 (DO3) were purchased from Aldrich Chemical Co. Phenyltrimethoxysilane (PTMS) was purchased from Hüls America. All silanes were used without further purification. Pyrene and perylene were purchased from Aldrich and purified via three recrystallizations from ethanol. Hydrochloric acid was purchased from Baker and used without further purification. DO3 was used as received and was added to the sol–gel reacting mixture as 5 wt % in reagent grade dimethylformamide solution. Pyrene and perylene were added to the reacting sol–gel in distilled tetrahydrofuran at concentrations of 10^{-4} and 10^{-5} M, respectively.

Sol–Gel Thin Films. Earlier publications have detailed the preparation of thin films using the fast sol–gel method.[2] The following is a synopsis of this procedure. Polysilasequioxane films were prepared using the fast sol–gel technique in an acid-catalyzed reaction. Near-stoichiometric amounts of water (where the water-to-silane ratio was 1.5–2.0) and hydrochloric acid were added as a dilute acid solution in a single step to the organotrialkoxysilane. Typically, a 0.01 M HCl solution was used for the polymerization of MTMS, while a 0.1 M HCl solution was used for the polymerization of PMTS and MTES. The precursors (and chromophore, if applicable) were combined in a small, disposable vial and heated, with constant stirring, in a water bath at 84 °C (±2 °C). Hydrolysis of alkoxides produces an alcohol which acts as a cosolvent for the monomer and water phases. As the monomer and water become more miscible, the

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(1) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic: San Diego, 1990.

(2) (a) Haruvy, Y.; Webber, S. E. *Chem. Mater.* **1991**, *3*, 501. (b) Haruvy, Y.; Heller, A.; Webber, S. E. In *Supermolecular Architecture: Synthetic Control in Thin Films and Solids*; Bein, T., Ed.; American Chemical Society: Washington, DC, 1991; p 405. (c) Haruvy, Y.; Webber, S. E. *Chem. Mater.* **1992**, *4*, 89.

(3) (a) *Electrets*; Sessler, G. M., Ed. *Topics in Applied Physics*; Springer-Verlag: Berlin, 1980; Vol. 33. (b) Tyler, R. W.; Webb, J.; York, C. C. *J. Appl. Phys.* **1955**, *26*, 61. (c) Ikezaki, K.; Fujita, I.; Wada, K. *J. Electrochem. Soc.: Solid State Sci. Technol.* **1974**, *121*, 591.

(4) (a) Singler, K. D.; Sohn, J. E.; Lalama, S. *J. Appl. Phys. Lett.* **1986**, *49*, 248. (b) Small, R. D.; Singer, K. D.; Sohn, J. E.; Kuzyk, M. G.; Lalama, S. J. *SPIE* **1986**, *682*, 160.

(5) Ye, C.; Minami, N.; Marks, T. J.; Yang, J.; Wong, G. K. In *Nonlinear Optical Effects in Organic Polymers*; Messier, J., et al., Eds.; Kluwer Academic: Dordrecht, 1989; p 713 and references therein.

(6) (a) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3640. (b) Hampsch, H. L.; Torkelson, J. M. *J. Appl. Phys.* **1990**, *67*, 1037.

(7) Yitschaik, S.; Berkovic, G.; Krongauz, V. *Macromolecules* **1990**, *23*, 3541.

(8) Kim, J.; Plawsky, J. L.; Van Wagenen, E.; Korenowski, G. M. *Chem. Mater.* **1992**, *4*, 249.

(9) Haruvy, Y.; Byers, J.; Webber, S. E. *ACS Polym. Prepr.* **1992**, *Ser. 32*, 134.

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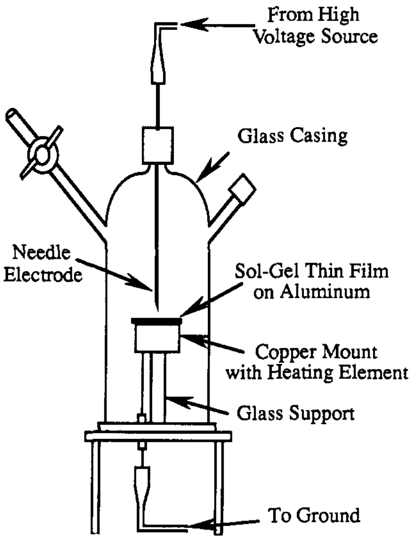

Figure 1. Schematic of the enclosed system used to corona-pole the films.

reaction, which is exothermic, becomes vigorous and care must be taken to prevent hazardous splashing or loss of product due to the rapid evaporation of the alcohol or alcohol/water azeotrope. Hence all reactions are started in capped vials, thus eliminating splashing and evaporation of reagents. The vials are carefully opened once the vigorous part of the reaction is completed (ca. 30 s) to allow for evaporation of alcohol. No water is believed to be present at this stage.

The viscous sol is cast on an aluminum or glass support and spun cast using a bench-top spin coater (Headway Research, Model 2-EC101-R485). Individual films were cured by storing at room temperature, storing at an elevated temperature (60 or 110 °C), or using a corona field. Following curing, film thicknesses were measured using a Fowler Digitrix II digital micrometer. Typical film thicknesses were 25 μm, but by controlling the spinning rate and the viscosity at the time of spinning one can achieve thicknesses between 2 and 55 μm.

Corona Field Generation. A corona discharge was generated using a tungsten electrode sharpened to a fine point and held approximately 2 cm above the sample film. The power supply was a Glassman High Voltage series MJ high voltage power supply delivering 0–20 kV dc, positive with respect to ground, and 0–100 μA to the electrode. The electrode was mounted in a modified glass flange capable of sealing the sample and corona discharge in a constantly flowing inert atmosphere (Figure 1). Typical conditions were a total voltage of 5–15 kV and total current of 2–10 μA. These sol–gel films have very high resistivity soon after casting such that arcing is easily avoided with care, usually by slowly increasing the applied voltage during the early states of the curing.

An infrared thermocouple (Omega, Model OS-1200) with a remote sensing head was used to measure the temperature of the film surface during corona curing. No elevation in temperature was observed on the surface of the samples evaluated.

Fluorescence Methods. Steady-state fluorescence spectra were obtained using a Spex Fluorolog 2 employing a 450-W xenon lamp for excitation and a Products for Research R928 photomultiplier tube (PMT) for emission detection.[10] Steady-state fluorescence anisotropy spectra were recorded using a Photon Technology International LS-100 luminescence spectrophotometer using Glan-Thompson polarizers at the exit of the excitation monochromator and entrance of the emission monochromator.

An enclosed sample holder was constructed to enable the LS-100 to measure front-face illumination (Figure 2). Measurements were performed with the sample oriented slightly off the 45° position to reduce reflected excitation light which was further rejected by the emission monochromator. The sample holder was equipped with argon purging and a controlled heating element. In a typical experiment fluorescence anisotropy growth in an argon atmosphere (see eq 1) was monitored as a function of temperature from ca. 25 to 150–175 °C, before allowing the sample to cool to room temperature. As will be discussed, this caused further curing in the film to occur.

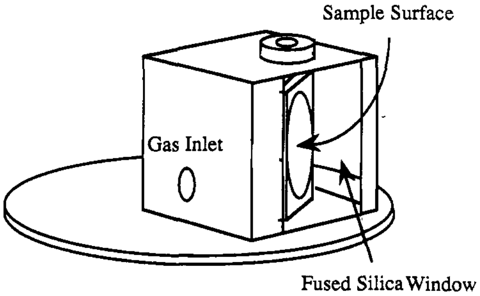

Figure 2. Sample holder designed to measure front-face illumination from a right-angle orientation. The emission beam enters through a fused silica window, reflects off the surface of the sample, and exits through a second fused silica window. The holder is also capable of degassing a sample in an inert environment.

The LS-100 provides the ability to continuously observe anisotropy changes in a sample over long time periods (minutes to hours) at set excitation and emission wavelengths and can also provide a steady-state anisotropy spectrum over an emission or excitation range. The anisotropy, r, is defined in eq 1,[11]

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \tag{1}$$

where I_{ij} is the measured intensity with the emission polarizer in the i position (V = vertical, H = horizontal) and the excitation polarizer in the j position. The instrumental anisotropy correction, called the G factor, is measured and applied on a point-by-point basis throughout the measured wavelength range:

$$G = I_{HV}/I_{HH} \tag{2}$$

FTIR Spectroscopy. Infrared spectrum were obtained on a Nicolet 730 FTIR spectrometer using 64 averaged scans at 4-cm^{-1} resolution. Data collection was performed using the Nicolet FTIR 630 workstation. Reflectance measurements were accomplished using a diffuse reflectance attachment (Harrick, DRA-2CR).

The standard units used in FTIR, i.e., percent transmittance and absorbance, are inappropriate in reflection measurements. For quantitative interpretations in diffuse reflection Kubelka–Munk (KM) units are used which are obtained from

$$\mathrm{KM} = (1 - R)^2/2R \tag{3}$$

in which R is the fraction of light reflected, and these values are linear with concentration. The reflectance spectra was converted to Kubelka–Munk units and band areas integrated using standard Nicolet software. Overlapping peaks were separated using iterative curve fitting based on spectral peaks having combined Lorentzian and Gaussian character.[12]

Gel Permeation Chromatography. Molecular weight distributions were characterized using gel permeation chromatography (GPC) on a Waters solvent delivery system (Model 510) employing a series of 500-, 10^3-, 10^4-, and 10^5-Å μ-Styragel columns and a Waters R401 differential refractometer. A calibration curve was established based on a series monodisperse polystyrene standards (Scientific Polymer Products). Molecular weights quoted later are in terms of these polystyrene standards.

PMSO samples for GPC analysis were prepared as mentioned previously. Each PMSO thin film was removed from the substrate with a razor blade, added to 5 mL of distilled THF and sonicated for 1 h to break up the sample as much as possible. Particulates were allowed to settle before the solution was removed. The solution (4 mL) was placed in a sample vial, dried under vacuum,

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(10) Sturtevant, J. L.; Webber, S. E. *Macromolecules* **1989**, *22*, 3564.

(11) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; Chapter 5.

(12) Seshadri, K. S.; Jones, R. N. *Spectrochim. Acta* **1963**, *19*, 1013.

and reweighed as part of a percent solids determination. The solution (1 mL) was filtered through a 0.2-μm filter for injection into the GPC column. Because of the small amount of PMSO present in the solution, each sample required a 150-μL injection.

UV–Visible Absorbance. DO3 is a chromphore that was introduced into these films primarily for SHG studies.[6] However, it was found that the absorption spectrum of DO3 is sensitive to its environment and provides clues as to the location of this molecule as a function of curing condition. The absorption spectra of DO3 in thin films of PMSO and poly(phenylsilasesquioxane) (PPSO) spun cast on glass was recorded using a Hewlett-Packard diode array spectrophotometer (HP8451A). The absorbance of DO3 in various solvent systems was also recorded using the diode array spectrophotometer. For films spun cast on aluminum a Varian UV–visible spectrophotometer (DMS 300) with a diffuse reflectance accessory was used to measure the absorbance of DO3.

Thermal Analysis. Differential scanning calorimetry and thermogravimetry measurements were carried out on a Perkin-Elmer 7 series DSC and TGA system. Heating conditions will be described in the discussion of the results.

Results

Thermal Curing of Fast Sol–Gel Thin Films. It is expected that much of the trialkoxysilane chemistry will be similar to that of tetraalkoxide systems. Both form three-dimensional networks but because the trialkoxides have a lower functionality linear polymers are more likely to be obtained. The non-alkoxide ligand will impart behavioral characteristics unique to that particular group.

Initially, a two-phase mixture of methyltrimethoxysilane (MTMS) and dilute acid are heated while stirring vigorously. The stirring creates an emulsion with an opaque appearance. As hydrolysis occurs on the surface interface of the emulsion, methanol is liberated and acts as a cosolvent:

$$CH_3Si(OCH_3)_3(l) + H_2O(l) \leftrightarrow CH_3Si(OCH_3)_2OH(l) + CH_3OH(g) \quad (4)$$

The solution becomes clear and uniform as enough methanol is liberated to solvate the system. The hydrolysis step is no longer limited to the relatively small surface at the interface and can proceed rapidly. At the elevated temperature employed condensation reactions start immediately, producing water and methanol as condensates.[13] While the water is rapidly consumed by the additional hydrolysis reactions, the methanol evaporates (bp 65.5 °C). Thus both hydrolysis and condensation reactions are being driven forward. As the molecular weight of the PMSO is increased by the condensation reaction, the viscosity of the sol increases rapidly.

With continued heating the sol thickens and can be spin-cast when a weight loss of approximately 40% is obtained in the sol. This weight loss is ascribed primarily to methanol, assuming that in the stage of the reaction carried out in a capped vial (see Experimental Section) the reaction has progressed until the water has completely reacted. The 40% weight loss corresponds to loss of approximately 70% of the available methoxy groups (there is some residual free methanol in the viscous sol). The entire process takes less than 5 min for a 1-g sample of MTMS reacted with a stoichiometric amount of water.

We have previously argued that the ability of a polymer of this type to form a crack-free film with a thickness in excess of 10 μm when spin-cast is a strong indication that it is composed primarily of linear segments.[2] This method is not limited to MTMS, and optically clear films have been spun using other precursors such as phenyltrimethoxysilane (PTMS), ethyltrimethoxysuilane (ETMS), methyltriethoxysilane (MTES), and even *N*-[3-(triethoxysilyl)propyl]-2,4-dinitrophenylamine (TDP) combined with MTES. The MTMS films do not fracture during heating or cooling on an aluminum or glass substrate and remain fracture-free after being heated to above 100 °C if cooled slowly. Films made from PTMS are even more forgiving.

Table 1. Average Weight Loss of Spin-Cast Film of Poly(methylsilasesquioxane) (PMSO) and Poly(phenylsilasesquioxane) (PPSO) for Given Curing/Drying Temperatures (All Cured for 24 h)

curing temp (°C)	av wt loss in PMSO (%)	av wt loss in PPSO (%)
25	8	2
60	11	3
110	15	10
corona at 25	13	

Evaporation during the spinning cycle cannot be monitored. Following film formation PMSO continues to lose 6–17 wt %, depending on curing temperature (see Table 1). This corresponds to a total loss of 75–90% of the methoxy ligands if one assumes that only methanol is evaporating.

In practice, we assume films to be cured when they have a hard, nontacky surface. This occurs after 1 day when cured at 60 °C and after 2–3 days when allowed to cure at room temperature. All films that are compared in the following were selected for the same degree of cure based on these surface properties.

Polymer Size Prior to Film Forming and Gelation. As mentioned previously, the ability to form thin films and to draw fibers indicates substantial linearity of the polysiloxanes. The ability of a polymer to swell without dissolving in a good solvent is a traditional test for cross-linking, while total dissolution would imply a non-cross-linked matrix. In our sol–gel reaction conditions the sol can be entirely dissolved in THF at any time prior to spin-casting but will continue to react within the solution and will, in time, form particulate matter which will precipitate out of the THF solution. Once cured, a PMSO film can be separated from its support in the presence of a good solvent such as THF or acetone. It can be partially dissolved in the solvent with the insoluble residue of the film settling to the bottom of the container. Films of PPSO entirely dissolve in THF leaving no discernible residue after curing at all temperatures up to 110 °C. These monomers are well-known to form ladder polymers.[14] To more fully characterize our materials, we determined the percent solids and the GPC properties of the soluble fraction. Several PMSO films cured at various temperatures were removed from their support, placed in THF, and sonicated for 1 h. Samples cured above 100 °C were extremely brittle and fractured readily. Samples cured below 60 °C were relatively easy to peel off supports in large pieces. Fragments of the room temperature cured film displayed some ductility and could be bent approximately 30° before fracturing. The solids that remained after sonication were allowed to settle before

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(13) Chambers, R. C.; Jones, W. E.; Haruvy, Y.; Webber, S. E.; Fox, M. A. *Chem. Mater.* **1993**, *5*, 1481.

(14) Munk, P. *Introduction to Macromolecular Science*; John Wiley & Sons: New York, 1989; p 124.

Table 2. Molecular Weights and Distribution from GPC and Percent Solids for PMSO Spin-Cast under Different Cure Conditions

cure condition	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% solids
room temperature 2–3 days	2500	970	2.5	82
24 h at 60 °C	3000	1400	2.1	90
24 h at 110 °C	4400	2900	1.5	95
24 h at 60 °C, 30 min at 150 °C	3800	2100	1.8	88
corona at 25 °C, 45 min	3600	2200	1.7	80

cautiously siphoning off the solution containing the non-cross-linked portion of the sol–gel material which was used for GPC and percent solids measurements. After drying, the insoluble solid portions were observed to have different appearances which correlated with the curing temperature. The films cured at room temperature appeared as white powders while the 60 °C cured films bore a similar appearance but with additional small glasslike shards mixed in the powder. Small glasslike plates were the predominant feature in the films cured over 100 °C. The percent solids correlated fairly well with the curing temperature (Table 2).

Gel permeation chromatography (GPC) results indicate that the soluble portion of the sol–gel material has a low molecular weight with a polydispersity value, $\bar{M}_w/\bar{M}_n$, typical of a condensation polymer (Table 2). Slight deviations inherent in the preparative methods cannot be ignored when comparing the relatively small differences in molecular weight obtained. It is assumed that these polymers did not continue to grow in the constricted environment of the thin film and the polymeric material evaluated by the GPC with an average molecular weight of 3000 is representative of the sizes that exist in the sol prior to spin-casting.

GPC was also used to evaluate the PPSO sol–gels cured at various temperatures. In the case of PPSO, GPC determinations represented the average molecular weight of the entire sample since it dissolves completely in THF. Three peaks were observed from a sample cured at 110 °C corresponding to molecular weights of 7200, 2500, and <1000. All other samples of PPSO resulted in one peak at a molecular weight of <1000. Thus, this material is composed entirely of small-chain oligomers.

Analysis of Cure Using FTIR Spectroscopy. As stated earlier, films are assumed to be cured when they have a hard, nontacky surface. Using this criterion, we compare films when cured at 60 °C for 24 h and after 2–3 days when allowed to cure at room temperature. Under these circumstances somewhat different results are obtained from analysis of the FTIR spectra. By using methyl group peak areas as a reference, the relative peak areas of the methoxy peaks and hydroxy peak can be compared. Two of the stronger peaks for methyl and methoxy, the symmetric CH_3–Si deformation at 1262 cm^{-1} and the asymmetric Si–O–C stretch at 1110 cm^{-1}, are unusable because of the extremely intense asymmetric Si–O–Si stretching vibration. The siloxane stretching band is strongly absorbing, and it distorts the region 1180–975 cm^{-1} in spectra obtained by diffuse reflectance measurements. The C–H stretching bands in the 2970–2840-cm^{-1} region can be easily observed. Peaks at 2972 and 2912 cm^{-1} can be attributed to the C–H stretching of the methyl attached to silicon, and peaks at 2947 and 2844 cm^{-1} are characteristic of the methoxy group.[15] The spectral shift between these peaks and the hydroxy peak allows for a good quantitative comparison. The effects of curing at room temperature and at 60 °C on these peaks can be seen in Figures 3 and 4, respectively, along with the relative changes in the hydroxy peak. Two differences are obvious: (1) the time scale for loss of methoxy is much shorter at 60 °C; (2) the fraction of OH loss is much greater for the 60 °C cure.

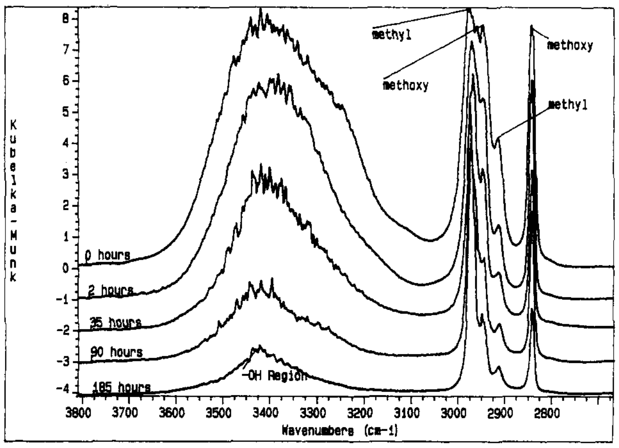

Figure 3. In situ FTIR spectra of PMSO while curing at 60 °C. Note the steady decrease of the peaks at 2947 and 2844 cm^{-1} and the large decrease in the area of the hydroxy peak.

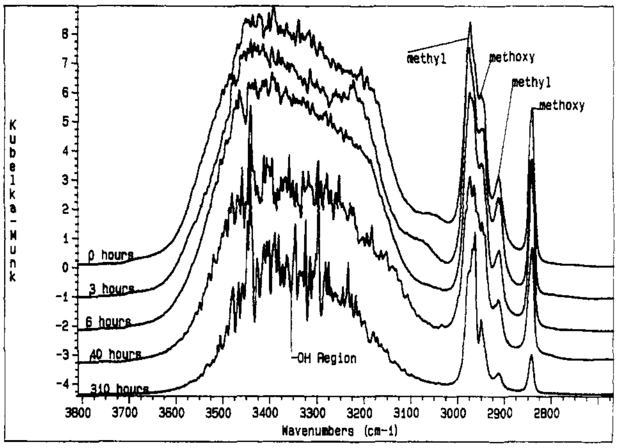

Figure 4. In situ FTIR spectra of PMSO while curing at room temperature (25 °C).

Deconvolution of the methyl peaks and the methoxy peak in the 2974–2912-cm^{-1} region was required in order to quantify the results. Deconvolution of the peak areas was accomplished using iterative methods, assuming a combined Lorentzian and Gaussian shape.[12] No change is noted in the area of the broad and strong hydroxy peak centered at ca. 3400 cm^{-1}, for the room-temperature cured sample while a 47% decrease is seen for the sample cured at 60 °C. The methoxy peaks behave similarly for the two curing temperatures with a peak area approximately 54% of the initial peak area after the 1–3-day curing period. This implies that the film is considered cured when approximately 83% of the methoxy groups have been removed from the system based on earlier assumptions and therefore half of the silicon atoms retain one unreacted methoxy ligand. The extent of unreacted hydroxy ligands remains unclear but the strength and breadth of the peak implies a significant amount of hydroxy groups present, while the absence of a peak at 1640 cm^{-1} implies that there

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(15) *The Analytical Chemistry of Silicones*; Smith, A. L., Ed.; John Wiley & Sons: New York, 1991; Chapter 11, pp 305–331 and references therein.

is negligible free water. The evidence indicates that the polymer matrix is only weakly branched at the spin-coating stage, and continues to undergo thermal polycondensation and thus cross-linking after spinning and curing. The peak area analysis carried out over longer periods revealed that a similar fraction of the initial methoxy groups was removed in both room temperature and 60 °C curing over 7–12 days, 69% and 66%, respectively. This demonstrates that hydrolysis has ceased after the spin casting, probably because of the complete consumption of water. For these longer time periods we also observed a strong dependence on the curing temperature of the fraction of hydroxy groups removed. In the sample allowed to cure at room temperature, there was only an 11% decrease in the area of the hydroxy peak, while an 80% decrease was observed in the sample cured at 60 °C.

Given the assumption that approximately 70% of the methoxy groups have been removed prior to spin-casting based on the weight loss and the observed decrease of about two-thirds in the area of the methoxy peaks upon subsequent curing, it is now reasonable to assume that methoxy groups remain intact on approximately 10% of the silicon atoms after prolonged curing (7–12 days). We are unable to estimate the fraction of hydroxy groups remaining after spin-casting. Since the initial water-to-silane ratio is near-stoichiometric, and significant water evaporation is not plausible under our fast hydrolysis conditions, an equal quantity of residual hydroxy groups also should be present in the gel. Theoretically, therefore, the cross-linking of the gel could be completed.

These two observations strongly suggest that in the advanced curing stage the primary condensation mechanism in the PMSO gel involves the reaction of two Si–OH groups rather than Si–OH and Si–OCH_3. This is in contrast to the sol where the latter predominates in light of the reaction stoichiometry. This suggests that a microphase separation may occur in the gel with separate hydrophobic and hydrophilic regions that are rich in Si–OH or Si–CH_3 and Si–OCH_3 groups respectively. This existence of such regions would have important implications for the entrapment of guest molecules (see later discussion).

Corona Field Acceleration of Curing. The term corona poling is used to describe a method of orienting molecular dipoles using an electric field. A needle electrode is used to generate a plasma to provide a carrier for charged ions of the ambient atmosphere.[3] The charged particles are deposited on the sample which was previously placed under the needle electrode and create a field through the sample due to the buildup of compensating charges under the tip of the needle electrode. To maximize the field through the thin film, an aluminum substrate was used to support the thin films. Other options include ITO glass, gold-plated glass slides, and uncoated glass slides. Ordinary glass microscope slides are typically used for studies in nonlinear optical methods. Our efforts to obtain second harmonic materials with these sol–gel systems will be described separately.[16]

The rapid curing while exposed to the corona discharge was a surprise when first observed. Curing of PMSO thin films had previously required approximately 24 h at 60 °C or 2–3 days at room temperature. Under a corona discharge, the films became hard and nontacky within 30–45 min at a water to silane ratio of 1.8. Sol–gels on both aluminum and copper supports were rapidly cured in this way, but the effect was much less evident on thin films spun-cast on glass. This is almost certainly an effect of the huge field developed across a thin insulating film on a conductor as contrasted with the same film on a relatively thick glass support.[17] In all cases, the spin-cast sample was prepared using the method described earlier. The sample was then placed in a corona field of ca. 8 kV dc and 4 μA for 30–45 min after which time the thin film appeared hard and nontacky.

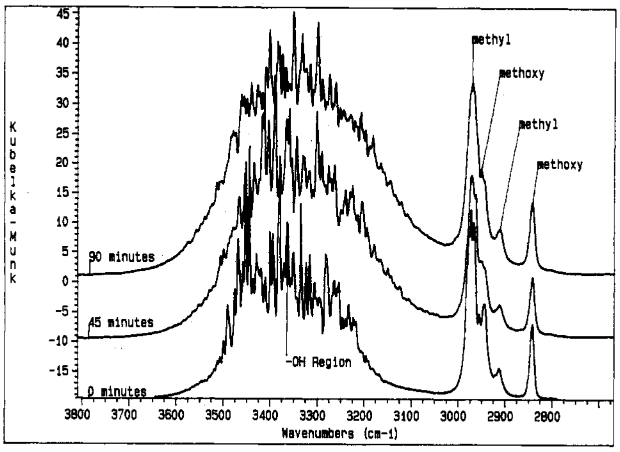

Figure 5. In situ FTIR spectra of PMSO while corona curing at room temperature (25 °C).

Most results revealed no differences between the sol-gels cured thermally and those cured via a corona discharge. A PMSO corona-cured thin film was removed from the aluminum support by a razor, dissolved in THF, and sonicated for 1 h. The thin film displayed surprising ductility when removed from the aluminum surface and could be bent into a small tube. The solid particles that remained after sonication were allowed to settle before siphoning off the solution for the GPC and percent solids determination. Upon drying the solid samples, small glasslike shards and platelets remained which were more like the residue of the 110 °C cured sample than the powdery residue remaining from the room-temperature-cured sample. The results of the GPC analysis and percent solids were similar to thermally cured samples (Table 2), but there was a higher weight loss during corona cure than a normal 25 °C cure for 2–3 days (see Table 1).

The FTIR spectra collected during corona curing revealed a decrease in the number of methoxy groups as evidenced by the decrease in the peaks at 2947 and 2844 cm^{-1}. Additionally, a continued increase in the hydroxy peak is observed throughout the corona-curing (Figure 5). The methoxy loss during the 90-min corona discharge was approximately 50% while the number of hydroxy groups doubled. It is conjectured that the additional hydroxy groups are brought to the surface under the corona field and this resulted in a significant effect on the FTIR diffuse reflectance spectra. The higher concentration of hydroxy groups observed via FTIR directly correlates to the increase in hydrophilicity of the surface. For example, the contact angle of water on a film cured at room temperature is typically 65–70°. In the region directly under the corona field tip the contact angle may be as low as ca. 30°.

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(16) Lu, E.; Hibben, Q.; Haruvy, Y.; Byers, J.; Webber, S. E., manuscript in preparation.

(17) A related discussion is presented by: Kim, J.; Plawsky, J. L.; Van Wagenen, E.; Korenowski, G. M. *Chem. Mater.* 1993, *5*, 1118.

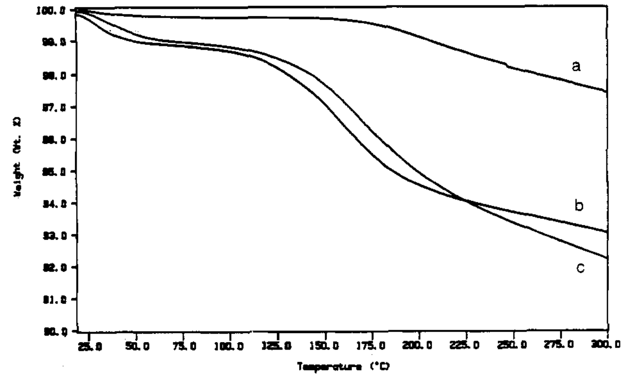

Figure 6. TGA curves for sol–gel film cured at 100 °C (curve a), room temperature (curve b), and at room temperature with the corona (curve c).

Table 3. TGA Analysis of PMSO Sample

	wt loss (%)		
cure condition	200 °C	400 °C	900 °C
25 °C (4 days)	5	8	13
corona (2 hr.)	5	10	15
60 °C (1 day)	2	5	11
110 °C (1 day)	1	4	9

Thermal Analysis of PMSO Films. Thermal analysis studies were performed on corona and thermal cured pure PMSO films with the objective of determining the T_g and the loss of volatiles either through continued reaction within the film or loss of entrapped solvent. The corona-cured film was spin-cast on an aluminum support and poled for 2.5 h at room temperature. The thermally cured films were cast on glass slides and cured at room temperature for 4 days, 60 °C for 1 day, or at 110 °C for 1 day.

The corona and thermal cured films were scraped from the supports with a razor blade. As mentioned above, the corona-cured film exhibits surprising ductility when removed from the aluminum substrate. The sample cured at room temperature is less ductile while the sample cured at 110 °C is brittle.

For DSC measurements the sample were heated from room temperature to 200 °C at a heating rate of 5 °C/min. No endo- or exothermic phase transition was observed within the temperature range for any sample. Thus we conclude that there is no glass transition in this temperature range.

TGA was performed at a heating rate of 10 °C/min within the temperature range 25–900 °C. Figure 6 shows the weight loss curves for these samples over the 25–300 °C range. The curves for the samples cured at room temperature show a small initial weight loss due to evaporation of residual solvent and further condensation, followed by a more rapid loss at ca. 150 and 130 °C for the sample with and without the corona treatment respectively. The TGA curve of the 110 °C cured sample is relatively flat between room temperature and 170 °C, indicating that condensation is almost completed in this sample. The TGA results are summarized in Table 3. The total weight loss percentage differs with the different samples because they are cured to different extents, as expected.

The smallest weight loss is observed for the 110 °C cured sample, indicating that 110 °C curing leads to a more condensed or more cross-linked matrix than other curing processes. The weight loss of the corona-cured sample is similar to that of the sample cured at room temperature for 4 days, showing that condensation and drying are indeed greatly accelerated under the corona field. At the highest temperature some of the weight loss for all samples can be ascribed to pyrolysis of the Si–CH_3. groups.

Table 4. Solution Absorbance Spectra of DO3 in Various Solvents and in the Monomers Methyltrimethoxysilane (MTMS) and Methyl Methacrylate (MMA)

solvent	λ_{max} (nm)	ϵ^a
$(CH_3)_4Si$	396	1.92
toluene	414	2.38
benzene	418	2.28
acetone	432	20.7
ethyl ether	432	4.34
methanol	440	32.6
THF	442	7.58
glycerol	460	42.5
DMF	468	36.7
water	insoluble	78.5
MTMS	432	
MMA	435	2.9

[a] Solvent dielectric constants have been included for comparison (*CRC Handbook of Chemistry and Physics*, 66th ed.; Weast, R. C., Ed.; Chemical Rubber: Boca Raton, FL 1985).

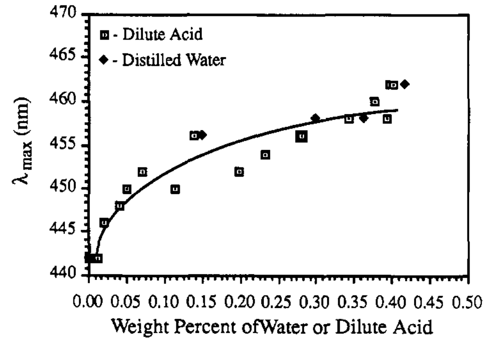

Figure 7. Dependence of absorbance on acid content as compared to water content. DO3 solution was 5.5 × 10^{-5} M in THF prior to either addition.

Absorption Spectra of Disperse Orange 3. Disperse orange 3 (DO3) is a typical dye that can be used for nonlinear optical studies.[6] As part of our efforts to orient DO3 in these sol–gel-derived matrices a dramatic effect on the DO3 UV–vis absorption spectrum was observed during curing of the DO3-loaded PMSO thin films. A blue shift of approximately 60 nm occurred during the first 48 h at elevated temperatures. As an example, the λ_{max} of a PMSO/DO3 film was observed to shift from 486 to 424 nm when cured at 110 °C. A similar trend was found with DO3 in thin films of PMMA, where a 15-nm blue shift was observed starting at 450 nm as a wet film and ending at 435 nm after drying. Further heating of the PMSO film induced an additional shift to shorter wavelengths. Absorption maxima for all PMSO samples were at 422 nm after heating to 150 °C for 1 h in a second curing step. A PPSO sample heated to 150 °C for a second curing phase showed no shift in the absorbance of DO3 which remained at 436 nm.

To establish the dependence of the DO3 absorption on polarity, DO3 in different solvents was studied. From the data in Table 4, the absorbance of DO3 is seen to red-shift with the increasing dielectric constant of the solvent. The effects of acid on the wavelength shift were shown to be negligible when we examined the effect of dropwise addition of 1 mL of 0.001 M HCl and distilled water into 2 mL of 5.5 × 10^{-5} M DO3 in THF (Figure 7). An additional two drops of 1 M HCl were added to the acidified solution without a change in absorbing wavelength. Thus we

Table 5. Thermal Curing Dependence of III:I Ratio of Pyrene in PMSO

sample	thermal history	III:I
A	cured at room temperature	1.16
A	second cure at 150 °C	1.20
B	cured at 60 °C	1.19
B	second cure at 150 °C	1.22
C	cured at 110 °C	1.30

conclude that protonation of DO3 is not an important contribution to the observed spectral shifts.

The UV-vis absorbance of DO3 shifted to a maximum at 391 nm when the film was corona cured. This shift is 30 nm greater than that observed in the thermally cured samples and indicates that DO3 molecules reside in very nonpolar regions, similar to DO3 in tetramethylsilane (see Table 4). The reason for this effect of the corona treatment is unclear but our SHG studies suggest that the corona field is orienting the PMSO polymer during early stages of poling.[16] Also there seems to be less freedom for molecular rotations in the corona-cured samples (see the fluorescence anisotropy discussion later).

The absorbance spectra of DO3 appears to be entirely related to the polarity of its environment. For DO3 in PMMA, the peak maximum in a freshly cast film is in a region that corresponds to a solvent more polar than THF and blue shifts upon curing to that expected for methyl methacrylate. Water, which has a much higher dielectric constant than any of the solvents that could be measured, should have provided an absorbance maximum to the red of 468 nm, but DO3 does not dissolve in water. Likewise, a highly hydrolyzed silanol could not be evaluated. It is suspected that a highly hydroxylated environment causes the initial red-shift of DO3. Upon curing, the hydrolyzed groups condense and the water diffuses away from the region, leaving a less polar environment for the DO3. It is unlikely that the DO3 is diffusing to any great extent within the film as the half-life for diffusive loss of the chromophore in a PMSO thin film was calculated to be 250 h at 110 °C and could not be measured at lower temperatures. As the sol-gel continues to cross-link, the DO3 becomes trapped in a predominantly nonpolar environment, possibly in a region rich in methyl groups (see later discussion).

Pyrene Fluorescence. Pyrene fluorescence measurements indicate that this chromophore also resides in an increasingly nonpolar environment as curing continues. The nature of the environment surrounding the pyrene molecule is characterized by comparing the dominant peak heights in the pyrene fluorescence. Thomas and Kalyanasundaram have reported that the ratio of the peaks at 383 nm (peak III) and 372 nm (peak I) give values in the 0.50-0.80 range for polar solvents, in the 0.80-1.00 range for aromatic solvents, and in the 1.65-1.75 range for hydrocarbon solvents.[18] This ratio for pyrene in PMSO films corresponds to a nonpolar environment with a slight dependence on the thermal history of the thin film (Table 5) where a slight increase in the III:I is observed in all samples as they are heated during the second curing phase.

PMSO Curing as Measured by Fluorescence Anisotropy. Fluorescence anisotropy can be used to determine the rotational mobility of a fluorescent probe in a particular environment. Polarized excitation light is absorbed only by those molecules with transition moments parallel to the polarization vector. If the molecule is able to rotate during the excited state lifetime the light emitted will have a different orientation than the light absorbed. The fluorescence anisotropy is defined by eq 1 given earlier. If a fluorophore is chosen so that the transition moments for excitation and emission are parallel, then an anisotropy value of unity is possible for a molecule that is unable to rotate during its fluorescent lifetime. For freely rotating molecules the emission fluorescence would be emitted equally at all angles of rotation causing a complete loss of anisotropy and r is equal to zero.

Perylene is an example of a molecule with parallel absorption and emission transition dipoles and a relatively short fluorescence lifetime (ca. 6 ns).[19] For perylene in a poly(methyl methacrylate) (PMMA) thin film excited at 410 nm and observed at 468 nm the anisotropy is unity even as PMMA is heated above its glass transition temperature of 109 °C.

Small amounts of perylene could be incorporated into the sol-gel prior to casting, yielding a homogeneously fluorescing film with the expected perylene fluorescence spectrum. Following initial anisotropy measurements (excitation and observation wavelengths as above), all samples were heated to 150-175 °C during a second curing phase while the anisotropy was observed. As temperature is increased, a slight decrease in anisotropy was observed in some samples at ca. 60 and ca. 110 °C which is interpreted as arising from segmental motion at these temperatures. This effect was dependent on the thermal history of the particular film, and the effect was observed only in films that were cured below the temperature associated with the anisotropy change. That is, for films cured at room temperature, an initial decrease in anisotropy was observed at ca. 60 °C with a second decrease observed at ca. 110 °C. Films cured at 60 °C exhibited a decrease in anisotropy at ca. 110 °C but not at any lower temperature. No appreciable decrease in anisotropy was observed in films cured at 110 °C.

Typical plots for anisotropy versus temperature are shown in Figure 8. The decrease in anisotropy can be seen in the samples initially cured at room temperature 25 and at 60 °C. Above 135 °C, anisotropy begins to rise, with a more rapid rise at ca. 150 °C. The temperature effect on the anisotropy can be qualitatively understood using the steady-state form of the Perrin equation:

$$r_0 = \frac{r}{1 + (\tau/\phi)} \qquad (5)$$

where r_0 is the observed anisotropy, r is the anisotropy for an infinite rotational diffusion time (ϕ), and τ is the fluorescence lifetime. The rotational diffusion in homogeneous solution is governed by viscosity (η), temperature (T), and the volume of the rotating fluorophore (V) according to

$$\phi = \eta V/RT \qquad (6)$$

While we did not measure the perylene lifetime as a function of temperature, one generally expects a decrease of τ, which will tend to increase r_0 if there is not a concomitant decrease in ϕ. However the very strong increase in r_0 at ≈150 °C for the 25 and 60 °C cured sample

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[18] Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.

[19] See ref 11, pp 134-138.

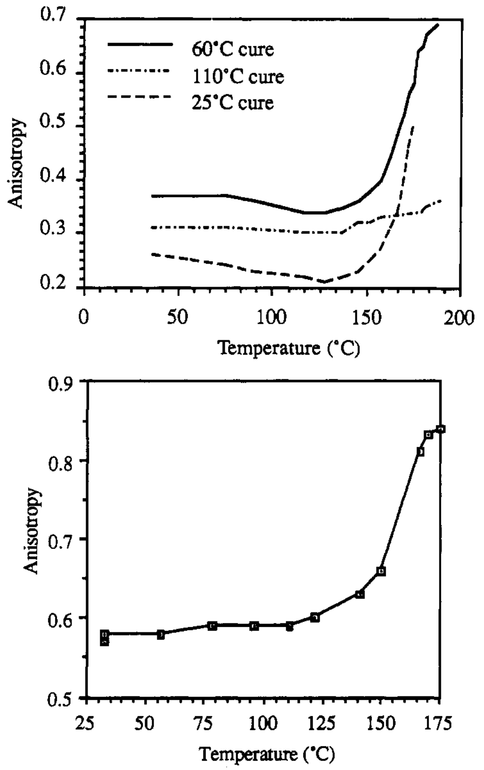


Figure 8. Plots of anisotropy vs temperature of a second cure for PMSO thin films. Upper panel, thermal curing; lower panel, corona curing.

Table 6. Dependence of Curing Temperature on the Fluorescence Anisotropy of Perylene in PMSO

PMSO sample	temp of first cure (°C)	anisotropy after first cure	anisotropy after second[b] cure
A	25	0.271	0.948
B	25	0.227	0.934
C	60	0.361	0.879
D	60	0.503	0.931
E	110	0.330	0.547
F	110	0.420	0.534
G	CP at 25	0.668	0.716
H	CP at 25	0.565	0.965
I	CP at 25	0.672	0.800

[a] Corona-poled sample. [b] The second curing phase was accomplished at 150–175 °C for 30 min. All measurements were taken at 33–36 °C, exciting at 410 nm, and observing at 468 nm.

is not observed for the 110 °C cured sample (Figure 8) and must be ascribed to a change in the film rather than the photophysics of the perylene itself. We note that this is the temperature range at which the sample displayed the onset of weight loss (see Figure 6). More importantly, the value of r_0 at 33–36 °C before and after the second thermal cycle is markedly different for the different cure conditions (see Table 6). In particular, there is a tendency for the initial value of r_0 to be lower for a film cured at 25 °C than 60 or 100 °C, although there are significant variations among different samples, presumably because of variations in the film preparation. The r_0 values after the second thermal cycle are higher for the films cured at lower temperatures. We interpret these results as a consequence of the larger densification that is possible for PMSO cured at lower temperatures because there is a greater fraction of linear polymers and concomitant segmental motion that ultimately results in a more rigid matrix, at least in the region occupied by the perylene probe. By comparison of anisotropy values for various curing methods, a trend can be observed (Table 6). The samples cured via corona poling have higher initial anisotropy values than samples cured thermally. Hence, it may be concluded that the perylene molecules are in a more constrained environment in the poled thin films on the average.

Coincident with the anisotropy increase was a significant decrease in fluorescence intensity in the samples cured at 25 and 60 °C. The final intensity observed in the lower temperature cured samples was only 15% of the initial intensity prior to the second cure. The drop in fluorescence intensity in the samples initially cured at 110 °C was not as significant, retaining ca. 85% of the initial intensity. We believe this loss represents sublimation of the chromophore from the film as oxidation is unlikely because the experiments were conducted in a nitrogen atmosphere. This loss is probably related the degree of cross-linking and hydrophobic chromophore entrapment in the film, which depends on curing conditions.

The anisotropy increase can be explained either by the preferential loss of weakly held fluorophores due to thermal diffusion or by an increase in cross-linking which increases the fraction of fluorophores held rigidly in place, or a combination of the two. In the case of the samples cured at 110 °C, the small amount of perylene fluorescence lost does not appear to be significant enough to be the sole cause of the increase seen in anisotropy. Using a very simple model in which it is assumed that there are two possible conditions in which the molecule is either free to rotate or is constrained to prevent rotation, the total anisotropy would be a weighted average of the fluorescence intensity from the two populations. The fluorescence intensity parallel to the excitation would be

$$I_\parallel = I_\parallel^{f} + I_\parallel^{r} \qquad (7)$$

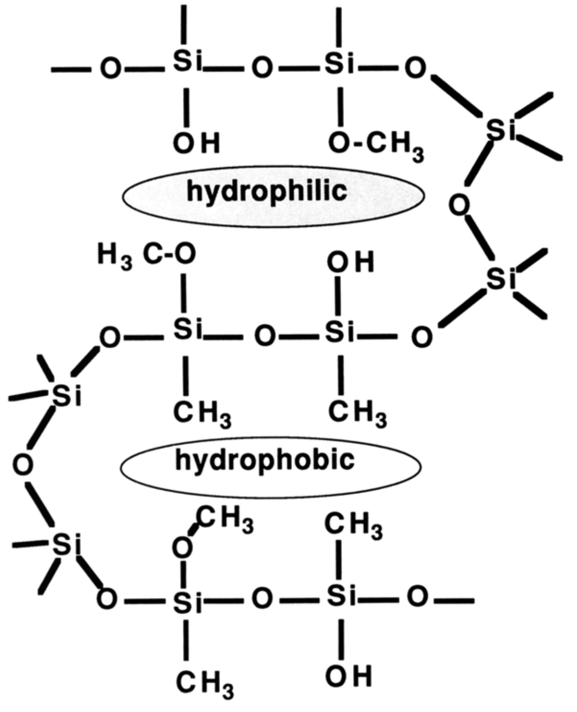
where the superscripts f and r stand for the freely rotating and rigid populations, respectively. The intensity of fluorescence perpendicular to the excitation is simply the intensity from the free rotating population only since the rigid population cannot contribute. Combining this with eq 1, we obtain

$$\frac{I_\parallel^{r}}{3I_\parallel^{f}} = \frac{r}{1-r} \qquad (8)$$

where the G factor has been taken to be unity. By assuming that all of the anisotropy increase can be attributed to the loss of the freely rotating species and that no other factors affect fluorescence intensities, the two 110 °C cured samples of PMSO in Table 6 would be required to lose 53% and 39%, respectively, of their initial fluorescent intensity rather than the 15% observed. Although these are crude calculations, it seems reasonable to regard cross-linking as the primary factor in increasing the anisotropy. Thermal cross-linking should apply to all films, not only to films cured at 110 °C.

For films cured at room temperature and at 60 °C, the interpretation is more complex. If segmental motion occurs during the second curing phase, many perylene molecules which were previously held tightly become free to rotate (thus the dip in anisotropy) and to diffuse out of the film. The ability of the segments to move also allows unreacted hydroxy ligands that are relatively close together to react and form cross-links. The continued condensation of the film traps the remaining perylenes, resulting in an anisotropy approaching unity. In addition to segmental

Chart 1



motion to permit further cross-linking reactions, transesterification can occur which permits the motion of reactive OH or $-OCH_3$ groups, i.e.

$$\text{Si–O–Si}' + \text{HO–Si}'' \rightarrow \text{Si–OH} + \text{Si}'\text{–O–Si}''. \quad (9)$$

In all these studies with hydrophobic chromophores we anticipate that the chromophores reside in hydrophobic pockets composed primarily of $Si–CH_3$ groups. Cross-linking reactions are expected to occur primarily in hydrophilic regions with a higher concentration of SiOH groups. These ideas are illustrated Chart 1, which is appropriate to the earlier curing stages. The nature of this microphase separation will undoubtedly depend on the precise condition of film curing. Thus one can anticipate some degree of empirical control over the film properties by a combination of thermal and corona curing protocols. The anisotropy results in Table 6 (right column) demonstrate that in the second curing phase a higher density of cross-links are formed, resulting in a more densely packed matrix around the fluorophores. Thus we conclude that a lower curing temperature in the first stage diminishes the microphase separation between the hydrophobic and hydrophilic regions such that these samples can reach a higher anisotropy level at the end of the second curing phase.

An important feature of the corona cured film results in Table 6 is the 2–3 times higher anisotropy than attained in the first curing compared to the samples cured without corona at 25 °C. Since the weight loss of thermally cured films is less than that of the corona cured (see Table 1), the anisotropy difference has to be attributed to the formation of additional cross-links or an increased degree of linear polymerization induced by the corona. Since the percent solids is similar in both room-temperature cases (Table 2), we favor the latter explanation. This additional matrix compactness is a consequence of the speed of curing induced by the corona. If the curing is faster than the microsphase separation, more SiOH groups have neighboring SiOMe groups that can form cross-links or continue linear polymerization. In the second curing stage the corona-cured PMSO matrices follow the same trend as the thermally cured ones: the more cross-linking in the first stage, the less in the second. That is to say, the higher the density of cross-links and/or degree of polymerization, the slower the intermoiety "diffusion" of reactive groups becomes. Work is continuing to correlate these processes that occur during the corona curing process and the SHG of entrapped chromphores.[16]

Initial fluorescence anisotropy studies of perylene in PPSO sol–gels also indicate the same trends as in PMSO sol–gels. It is interesting to note that samples of PPSO that received a second thermal curing to 175 °C were no longer soluble in THF and left a significant amount of solids, indicating extensive cross-linking.

Conclusions

In this paper we have described the curing of PMSO films cast using our "fast sol–gel process"[2] using a variety of techniques. We have also described a very marked acceleration of curing for a sol–gel film on a conducting substrate exposed to a dc corona discharge. This phenomenon has not been previously reported so far as we know. While the full mechanism of this process is not known to us, it seems clear that it involves the low-temperature removal of small molecules (e.g., H_2O, CH_3OH) that result from the hydrolysis and condensation reactions that occur during gelation and curing. The physical properties of a film thermally cured or cured by a combination of corona field and higher temperature postcure are also different. The latter films are more flexible than an equivalent thermally cured film and have a much smaller tendency to crack upon being heated to 175–200 °C and cooled to room temperature while remaining attached to the aluminum disk on which it was spin-cast. We believe that the properties of the PMSO glass are modified in part because of the strong orienting field that is present during the corona field exposure. This could affect the juxtaposition of SiOH groups which governs the final degree of cross-linking through formation of Si–O–Si bonds.

Our studies of both thermally and corona-cured PMSO sol–gel films imply the following reaction sequence: The initial reaction with a stoichiometric amount of water at high temperature yields primarily linear polymers with ca. 1 residual methoxy/Si atom at the time the viscous liquid is spin-cast. Cross-linking occurs primarily between the SiOH groups and this process is very slow at room temperature. Approximately 10–20% of the sol–gel can be extracted by a good organic solvent like THF unless the film has been heated above 150 °C for at least 30 min. Thus a film that is no longer tacky may contain very little cross-linking and ca. 10% of the original $SiOCH_3$ groups.

The use of the probe molecules DO3, pyrene, and perylene provides other insights of the curing process at the molecular level. The absorption spectrum of DO3 is sensitive to the polarity of its environment. If DO3 is incorporated into the spin-cast film, a steady blue shift in λ_{max} of its absorption spectrum is observed during curing, which corresponds to a less polar environment. This effect is particularly noticeable in corona-cured PMSO in which the final environment of the DO3 is similar to $Si(CH_3)_4$. We believe this illustrates how as curing progresses a kind of microphase separation occurs in which hydrophobic regions are created within the film. Pyrene, which is smaller and much more hydrophobic than DO3 appears to be in a fairly nonpolar region of the film at all curing stages. It was also found that aromatics like pyrene or perylene could be sublimed out of the film at the elevated curing temperatures (175–200 °C) which illustrates that there must be significant porposity in these films. Similar conclusions have been reached by Chambers et al. based on oxygen quenching studies.[20]

Fluorescence anisotropy measurements on perylene provides insights as to molecular rotational mobility on a short time scale (ca. 6 ns). These measurements demonstrate that these sol–gel films are much less constricting than PMMA unless it has been heated to 175–200 °C. The degree of anisotropy will depend on the cure history. In particular the lower temperature cured films display the highest anisotropy after this secondary heating, even though the anisotropy of the fresh film may be relatively low. The corona-cured film has a relatively high initial anisotropy implying more complete cross-linking and/or linear polymerization reactions than a film that has been thermally cured only. This illustrates that the detailed internal morphology of a film is the result of a complex series of events that determine its final extent and location of cross-link sites.

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(20) Work in progress: Chambers, C.