

## **Structure-property behavior of new hybrid materials incorporating oligomeric poly(tetramethylene oxide) with inorganic silicates by a sol-gel process**

### **3. Effect of oligomeric molecular weight**

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#### **ABSTRACT**

Novel transparent hybrid materials incorporating triethoxysilane endcapped poly(tetramethylene oxide) with tetramethoxysilane have been successfully prepared by a sol-gel process. The molecular weight of PTMO has been varied to study its effect on the structure-property behavior of these hybrid materials. Mechanical properties and dynamic mechanical behavior have been measured; small angle X-ray scattering (SAXS) has been utilized to obtain structural information. Based on the experimental results, a simplified morphological model has been suggested to describe these new hybrid systems.

#### **INTRODUCTION**

It has been reported in earlier publications [1-3] that novel systems incorporating organic oligomers into inorganic silica glasses can be prepared through sol-gel processes. Tetraethoxysilane (TEOS) has been the inorganic component of these new systems, and silanol terminated poly(dimethyl siloxane) (PDMS) was initially chosen as the oligomeric species for the incorporation. The hybrid materials produced possess some characteristics of inorganic glasses and also display some flexibility. The success of this "combination" offers a new approach in bridging organic and inorganic compounds. Furthermore, it demonstrates that hybrid materials with tailor-made properties can be prepared by choosing appropriate organic and/or inorganic components.

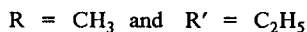
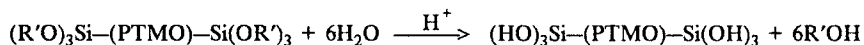
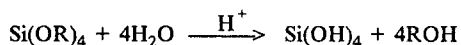
With the experience of combining PDMS into TEOS based silica gel, other types of oligomers have been considered so that materials with various properties can be produced. In addition, the inorganic component has also been varied to study its effect on the final structure and properties of these hybrid materials [4]. As a result, systems incorporating poly(tetramethylene oxide) (PTMO) into tetramethoxysilane (TMOS) based networks have been prepared and studied. It is expected that the hybrid materials made with PTMO should show different mechanical properties from the PDMS systems. Also, by changing the inorganic component from TEOS to TMOS, the weight loss due to the hydrolysis reaction will decrease and the shrinkage problem may be reduced. To further assure the intimate combination of the inorganic and organic components, hydroxyl terminated PTMO oligomers were endcapped with triethoxysilane. That is, the higher functionality of the triethoxysilane relative to silanol endcapping would improve the mechanical strength and, at the same time, serve to promote higher compatibility between the oligomer and the sol-gel environment at the start of the reaction. In this paper, initial results concerning the effect of the molecular weight of PTMO on the structure-property behavior of the hybrid materials produced are reported.

## EXPERIMENTAL

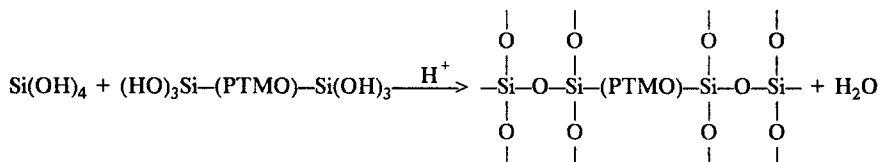
**Materials.** High purity tetramethoxysilane was obtained from the Fluka company; triethoxysilane endcapped poly(tetramethylene oxide) with four different molecular weight -- 650, 1000, 2000, and 2900 (before the endcapping reaction) -- were generously supplied by Dr. J. Carlson of the 3M company. All components were used without further purification. Hydrochloric acid (10N) obtained from Fisher Scientific Inc. was employed as a catalyst for the sol-gel reaction. Tetrahydrofuran and isopropanol were used as cosolvents to insure homogeneous solutions.

**Reaction Scheme.** Although the exact stepwise reaction mechanisms are still unknown, the overall sol-gel reaction of the present TMOS-PTMO system can be illustrated by the simplified reaction scheme shown below:

HYDROLYSIS (complete hydrolysis is indicated for simplicity)



POLYCONDENSATION (not stoichiometrically balanced)



Both the TMOS and endcapping triethoxysilane groups will undergo hydrolysis with the added water to generate silanol groups; these can then condense to form Si-O-Si linkages. However, hydrolysis and condensation can and most likely will take place simultaneously [5,6]. Depending on the catalyst used, the reactivities of the ethoxy and methoxy groups will also change with the number of hydrolyzable groups remaining on the silicon atom [7]. As a result, the actual network-forming process will be much more complicated than shown in the above reaction scheme. Furthermore, the completion of the hydrolysis reaction will be limited due to the entrapment of some ethoxy or methoxy groups. These reactive groups can undergo further reaction even after the gelation and initial "vitrification" -- this latter feature resulting in an "aging" process. The influence of aging on the structure and properties of the hybrid materials will be discussed in a future publication [8]. Moreover, the usage of different reaction media can also affect the extent of reaction due to chemical equilibrium. In most of the pure sol-gel systems being studied, alcohol is often used as the solvent. However, as shown in the reaction scheme, alcohol is always a by-product of the hydrolysis reaction. Therefore, its presence can limit the reaction according to LeChatelier's principle and limit the extent of hydrolysis. It has been shown by McGrath et al. [9] that using a non-alcoholic solvent such as DMF can increase the hydrolysis rate considerably. Experiments are currently underway to study the effect of using different solvents, particularly non-alcohols.

**Example Procedure.** In this study, all the reaction conditions were kept constant except for the PTMO molecular weight. The initial weight ratio of the TMOS and the endcapped PTMO was 50:50; the amount of water added to initiate the hydrolysis reaction was in exact stoichiometry; the molar ratio of HCl to TMOS was 0.04:1. An example of the reaction procedure is shown below:

eight milliliters of isopropanol and 2 ml of THF were first added to a 100 ml flask, then 10 ml of TMOS and an appropriate amount of PTMO were added and mixed thoroughly until the solution appeared to be homogeneous. Then, a mixture of HCl and deionized water were added to the base solution under rapid agitation. The reaction usually proceeded rapidly at ambient temperature, and the system quickly turned into a viscous liquid. After approximately 30 seconds, the clear liquid was cast into Teflon coated petri dishes and covered with parafilm. After 1-2 days, the parafilm was removed and the gel was dried under ambient conditions for another week prior to testing.

Although the initial weight ratios of the TMOS and the endcapped PTMO were the same in all cases, the silicate content should be higher for the system with lower molecular weight of PTMO due to the finite size of the endcapping group. However, such difference should become less significant as the molecular weight of PTMO increases. The two oligomers with higher molecular weight (2000 and 2900) were in crystalline form prior to the reactions, therefore, both of these species were heated under mild temperature (ca. 60°C) before dissolving into the solution. Prior to the addition of water and acid, all systems appeared to be homogeneous. This indicated that both components -- organic and inorganic -- were well dispersed into the reaction media. Since the refractive indices of the components are not the same, such homogeneity would be crucial in terms of making transparent materials. The rate of reaction was extremely high and the system usually became very viscous within a few minutes with a mild exotherm occurring in all cases. Warping and shrinking problems have often been observed by previous investigators in preparing sol-gel systems. The former can be attributed to the different evaporating rates of the volatiles from the top and the bottom surfaces of the sample, while the latter is due to the large weight loss in the hydrolysis step of the sol-gel process. In the present systems, these problems became increasingly severe as the PTMO molecular weight decreased, however, it was still possible to cut samples for various tests. One interesting point to mention is that these problems can be significantly reduced by casting the film onto a plastic petri dish. Since the sample adheres to the plastic surface, it does not warp in the first few days of the drying process. After the sample is relatively dry, one can easily remove the film and let it undergo further drying. Another advantage for this method is that highly transparent films can easily be prepared due to the smooth surface of the plastic petri dish, whereas the film cast on a Teflon coated dish was usually turbid due to surface scattering.

**Characterization Methods.** Structural information of the present systems was obtained by utilizing the technique of small angle X-ray scattering (SAXS). A Siemens Kratky camera system in conjunction with an M. Braun position sensitive detector was employed for all the SAXS measurements. The width of the entrance slit on the camera was fixed at 100 microns, and the X-ray generator was operated at 40 kV and 20 mA. Wide angle X-ray diffraction results were obtained utilizing a Philips table-top X-ray generator and a Warhus camera system.

Mechanical properties were measured by an Instron model 1122. Dogbone samples of 10 mm in length were used, and the crosshead speed was fixed at 2 mm/min.. Dynamic mechanical data were obtained utilizing a DDV-IIC Rheovibron dynamic viscoelastometer with an automated system developed by Imass company. Most samples were tested within the temperature range of -100°C to 150°C with a heating rate of 1-2°C/min.. Dynamic mechanical properties measured at 11 Hz were reported.

## **RESULTS AND DISCUSSION**

The thickness of most cast films was in the range of 10 to 20 mils, though making thicker films was possible. Film cracking problems were hardly observed for most samples, however, the films made with PTMO(mw = 650) did show some level of cracking but this problem was far from severe. As mentioned earlier, some of the oligomers used -- MW = 2000 and 2900 -- can crystallize under ambient conditions. Therefore, wide angle X-ray scattering (WAXS) was utilized to determine the possible existence of crystallinity in these samples. The resulting pattern (not shown in this paper) displayed an amorphous halo only; this clearly indicated the absence of crystallization. A sample made with TMOS-PTMO(2900) was strained to 50% elongation and the WAXD experiment rerun still

Table 1. Mechanical Properties of TMOS-PTMO-100-0.04-RT under ambient conditions

sample no.	wt% of TMOS	m.w. of PTMO	elongation at break (%)	ultimate strength (MPa)	Young's modulus (MPa)
1	50	650	9	18	490
			8	17	451
2	50	1000	28	14	102
			22	13	113
3	50	2000	34	12	58
			49	18	52
			43	18	65
4	50	2900	83	33	66
			73	27	70

showed no crystallization. Although crystallites might form at lower temperature, the dynamic mechanical results (presented shortly) did not support the presence of crystallinity. This result implies that the incorporation of the PTMO oligomeric chains into the network is successful and, therefore, no crystallites were formed due to the restrictions imposed.

The stress-strain properties of all the samples under ambient conditions are listed in Table 1. The elongation at break increases considerably as the molecular weight of PTMO changes from 650 to 2900, whereas the initial modulus decreases one order of magnitude. For the samples made with PTMO(650), the elongation at break is ca 8% and the modulus is ca  $5 \times 10^8$  Pa., which is close to the behavior of typical glassy polymers. While for the samples made with PTMO(2900), the modulus is ca 60 MPa., which is similar to some "stiff" rubbers. It is clear that a gradual change occurs in the structure with the variable of PTMO molecular weight. This speculation will become more convincing as the dynamic mechanical and SAXS results are presented. The tensile strength is between 12 and 18 MPa. for most of the materials, however, the sample with PTMO(2900) shows a strength as high as 33 MPa.. These quantities are much more impressive as compared to the earlier systems made with TEOS and silanol terminated PDMS. Furthermore, such improvement in mechanical properties are clearly of importance as one considers practical applications.

The results of the dynamic mechanical experiments are shown in Figure 1 a&b. The general behavior of the storage modulus is similar for all four samples: a glassy region which shows a magnitude of  $10^9$  Pa.; a transition region after which the modulus decreases to a plateau region with a modulus ca  $10^8$  Pa. and finally a rising trend at high temperatures. However, some features should still be noted. First, the temperature at which the modulus begins to drop from the glassy region decreases with increasing molecular weight of PTMO. This indicates that the incorporated PTMO chain has higher mobility as its molecular weight increases. In other words, the oligomeric chain of MW = 650 is more restrained than that of MW = 2900. Secondly, the modulus increases as the molecular weight of PTMO decreases. This general trend is true except an inversion is observed above ambient temperature for the two samples with PTMO(MW = 2000) and PTMO(MW = 2900). The reason for this inversion is still not clear, however, it is consistent with the stress-strain data shown earlier (see Table 1). To further understand the dynamic mechanical responses of these materials, one must examine the corresponding  $\tan\delta$  spectra shown in Figure 1b. For the sample made with PTMO(MW = 650), a single, broad peak at 50°C is observed. As the molecular weight of PTMO increases to 1000, the position of this peak shifts to 25°C. However, it seems that a second peak -- or a shoulder -- begins to appear and its position is near 50°C. As the molecular weight of PTMO increases further, this double-peak behavior becomes more distinct. The low temperature peak continues to shift toward lower temperatures -- 15 and 0°C for samples with PTMO(MW = 2000) and PTMO(MW = 2900), respectively. On the other hand, the position of the high temperature peak is relatively constant -- around 45°C. This bimodal type of behavior is important in interpreting the experimental results.

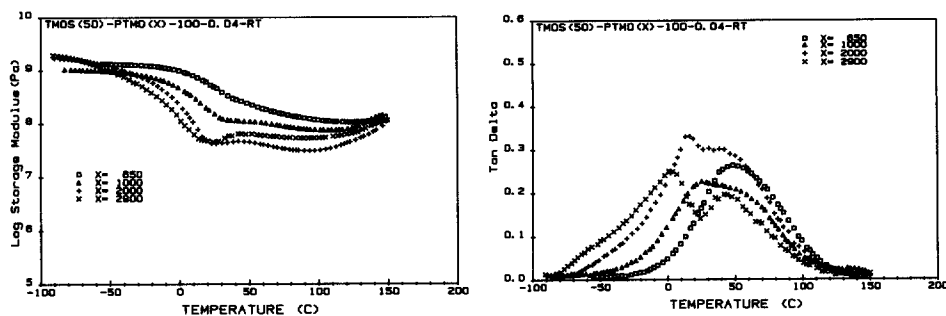


Figure 1. Dynamic mechanical spectra of materials made with 50 wt% TMOS and different molecular weight of PTMO. (a) storage modulus, (b)  $\tan\delta$ .

As the PTMO oligomer is incorporated into the silica network, several possible situations may exist. The first is that the oligomer may form a rich PTMO phase whose mobility will not be restrained too much by the network except through the end-linking effect. PTMO chains under this type of environment should show a  $T_g$  similar to that of the pure PTMO oligomer, which is reported to be near  $-80^\circ\text{C}$  from loss shear modulus ( $G''$ ) measurements and dilatometry [10,11]. However, if  $T_g$  is determined by the temperature where the maximum of  $\tan\delta$  occurs, then it will always be somewhat higher than that from the loss modulus measurement. The second type of situation is that the oligomer chain may form a mixed phase with partially condensed TMOS species. Due to the interaction between these two species, the mobility of the PTMO chain should be reduced and its  $T_g$  would rise. The third type of environment for the PTMO chain is that it may be encapsulated in a region formed by highly condensed TMOS species; the  $T_g$  for this type of oligomeric chain will be even higher than the previous ones. Most likely, all these regions will exist in the hybrid system under investigation. However, the relative amount of each region should depend significantly on the molecular weight of PTMO. For a short chain such as PTMO(MW=650), the chance of being encapsulated or forming a mixed phase with condensed TMOS species is higher. For a longer chain like PTMO(2900), the formation of an oligomer-rich phase is more likely. This is in line with the result that the low temperature  $\tan\delta$  peak shifts to lower temperatures as the molecular weight of PTMO increases. However, as shown by the existence of the high temperature  $\tan\delta$  peak, the encapsulation of PTMO is believed to occur in all materials. This kind of change in structure will, of course, influence the mechanical properties of these materials. For the sample made with PTMO(MW=2900), most of the tensile force will be taken by the oligomeric chains due to less encapsulation. As a result, the elongation is relatively high and the modulus is similar to that of a stiff rubber. This is in contrast to the sample made with PTMO(MW=650), where the elongation at break is lower and the modulus is considerably higher. This interpretation is, again, consistent with both the mechanical and dynamic mechanical results. However, another important point is that due to the finite molecular weight of the endcapping groups, the actual content of the glass component is higher for the system with lower molecular weight of PTMO. This factor will also contribute to changes in mechanical properties.

To obtain further insight of the structure of these hybrid systems, the technique of SAXS was utilized. The smeared SAXS profiles of all four materials under investigation are shown in Figure 2. The absolute scattering intensity of the sample is plotted against the scattering vector,  $s$ , which is defined as:

$$s = \frac{1}{d} = \frac{2\sin\theta}{\lambda}$$

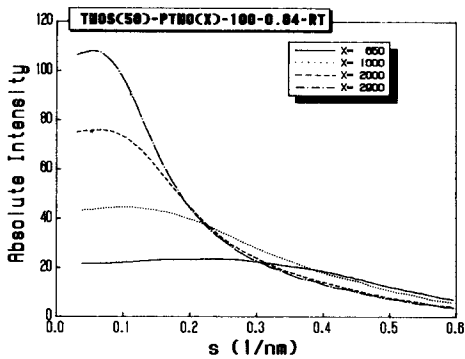


Figure 2. SAXS profiles of materials made with 50 wt% TMOS and different molecular weight of PTMO.

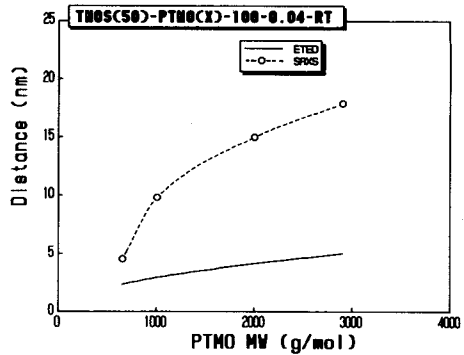


Figure 3. A comparison of the correlation distance from SAXS and the unperturbed end-to-end distance calculated by the Flory-Fox equation.

where  $d$  is the approximate correlation distance between two regions having the same electron density,  $\theta$  is one half of the radial scattering angle, and  $\lambda$  is the wavelength of the X-ray utilized (1.54 Å) Figure 2 shows a broad maximum exists for each sample and its position shifts toward smaller  $s$  values, or a larger correlation distance as the molecular weight of the PTMO oligomer increases. The shape of the maximum also becomes broader as the molecular weight of PTMO decreases. Figure 3 shows the dependence of the correlation distance,  $d$ , on the molecular weight of PTMO. This quantity is estimated by taking the inverse of  $s$  at which the maximum is observed. One can clearly see the increasing trend with PTMO molecular weight. Also shown in the figure is the unperturbed end-to-end distance (ETED) of the PTMO oligomer calculated as a first approximation by the Flory-Fox equation:

$$\langle r^2 \rangle^{1/2} = a(M_v)^{1/2}$$

where  $a = 0.093$  for the PTMO chain in isopropanol at 46°C (theta temperature) and  $M_v$  is the molecular weight measured by intrinsic viscosity [12]. Although the molecular weight of PTMO in this work is the number average molecular weight, this calculation should still be a reasonable approximation due to the narrow molecular weight distribution of PTMO oligomers. At lower molecular weight, these two quantities-- the correlation distance from SAXS and the value of the unperturbed end-to-end distance -- are close. However, as the molecular weight increases, the difference increases and reaches almost a constant value.

As mentioned in the experimental section, all of the PTMO oligomers used were first endcapped with triethoxysilane before carrying out the sol-gel reaction. Since the functionality is 3 at each end of the oligomer, it is most likely that both ends will be connected into the silica network. Moreover, besides the three types of regions mentioned above (i.e., PTMO-rich, mixed, and encapsulated PTMO), there are likely to be some highly condensed TMOS regions. Without getting into the details of the structure, the term "cluster" will be liberally used here to describe such regions. Based on the experimental results and all the speculations mentioned above, a model is suggested as schematically shown in Figure 4. Since the electron density of the highly condensed TMOS clusters should be different from that of PTMO, distinct small angle X-ray scattering will be observed if such fluctuations in electron density occur over suitable dimensions. As suggested above, the distance between two clusters would be expected to be of the order of the root-mean-square chain length of the PTMO oligomer, a correlation distance should be observed which is consistent with the SAXS results. If this is true, then this correlation distance should increase with the molecular weight of PTMO. However, this distance would be larger than the calculated end-to-end distance due to the finite size of the highly

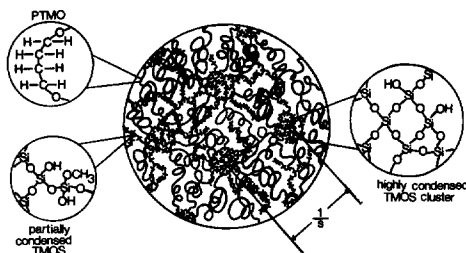


Figure 4. A simplified model suggested for the hybrid system made with TMOS and PTMO.  $s$  is the scattering vector of the SAXS experiment.

condensed TMOS clusters and the deviation of the PTMO molecular from the gaussian chain. Up to this point, all of the experimental results match well with the suggested model. For the sample made with PTMO(MW = 650), since the encapsulation of PTMO chains is more probable, the behavior of the oligomer chain may well deviate from gaussian chain behavior. In addition, the glass content of this material is close to 50 % by volume. Therefore, the model shown in Figure 4, which suggests a dispersion of highly condensed TMOS clusters within PTMO-rich matrix, may not truly illustrate the whole structure. As a result, the difference between the correlation distance from SAXS and the calculated unperturbed end-to-end distance is not as large as the other three samples. As the molecular weight of PTMO increases, the model should become a better simulation of the real structure. Therefore, the difference between the correlation distance and the unperturbed end-to-end distance becomes almost constant and can be related to the average size of the clusters. However, it should be noted that the oligomeric chain may be somewhat extended as the clusters shrink with further curing of the system. In addition, the scattering profiles from the SAXS experiments are slit-smearred data and, hence, the calculated correlation distance is always several Å larger than the actual value. Therefore, the difference mentioned above may not be directly equal to the size of the clusters but can only be used as an approximation. To further verify this model, experiments are currently underway to prepare samples with a fixed PTMO molecular weight but having different composition ratios of TMOS and PTMO. As the weight percent of the glass component approaches 0%, the correlation distance determined by SAXS should approach the end-to-end distance calculated theoretically. The results of these studies will be reported in the future.

## CONCLUSIONS

Transparent hybrid materials incorporating PTMO into TMOS based silica network were prepared through a sol-gel process. No PTMO crystallinity was observed in these samples which implied a successful incorporation of the oligomers. The mechanical properties showed a distinct dependency on the molecular weight of PTMO: the initial modulus increased while the elongation at break decreased with increasing PTMO molecular weight. Dynamic mechanical results showed a bimodal  $\tan\delta$  behavior which suggested two somewhat different environments for the PTMO chains. The encapsulation of PTMO chains became more significant as the molecular weight of PTMO decreased. SAXS results showed that a distinct correlation distance existed in all the samples, and the magnitude of this distance increased with the molecular weight of PTMO. The difference between this correlation distance and the unperturbed end-to-end distance calculated by Flory-Fox equation approached a constant value as the molecular weight of PTMO

increased. This resulted in the suggestion of a simplified model in which TMOS-rich clusters are dispersed within PTMO-rich areas.

### **ACKNOWLEDGMENT**

The authors would like to extend deep appreciation to Dr. Carlson of the 3M company for supplying the endcapped PTMO oligomers.

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Accepted September 28, 1987      K