Synthesis and dynamic mechanical behaviour of inorganic–organic hybrids containing various inorganic components

Noriko Yamada,* Ikuko Yoshinaga and Shingo Katayama

Advanced Technology Research Laboratories, Nippon Steel Corporation, 3-35-1 Ida, Nakahara-Ku, Kawasaki 211, Japan

Inorganic–organic hybrids containing various inorganic components have been successfully synthesized from silanol-terminated poly(dimethylsiloxane) (PDMS) and three different inorganic sources, $Al(OBu^s)_3$, $Ti(OEt)_4$ and $Ta(OEt)_5$, by using a sol–gel process. Inorganic components as well as the process conditions were found to affect the structure and properties of metal-O-PDMS hybrids from dynamic mechanical measurements and FTIR studies. The storage modulus increased and the peak height of the tan δ curve decreased in the order of Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS hybrids, which may result from the difference in valence and atomic mass of the metallic element constituting the inorganic component.

Since the preparation of organically modified silicates *via* the sol–gel method was reported in the middle of the 1980s,[1–3] there has been an increasing interest in hybrid materials combining inorganic components with organic components at a molecular scale. These materials not only provide both properties of organic and inorganic components but also have the possibility of providing novel properties which have been unknown in conventional materials. They promise new applications in many fields such as optics, electronics, mechanics and biology.[4–9]

One way of preparing inorganic–organic hybrids is to incorporate functionalized polymers into an inorganic network derived from metal alkoxides. Wilkes *et al.* have reported hybrid materials termed 'Ceramers' which have been prepared by the incorporation of silanol-terminated poly(dimethylsiloxane) (PDMS) into a siloxane network derived from tetraethoxysilane (TEOS).[3] These hybrids include only a siloxane network as an inorganic component. The TEOS–PDMS hybrids have been intensively studied and it has become clear that the structure and mechanical properties of the hybrids are strongly influenced by the process conditions such as acid content, TEOS content and molecular mass of the PDMS.[3,9–11] However, it is also expected that the chemical and physical properties of the hybrid are altered by incorporating inorganics other than silicon. The incorporation of inorganics can vary the structure of the hybrid reflecting the difference in nature such as reactivity and valence between TEOS and other metal alkoxides. By controlling the change of the hybrid structure, desired mechanical properties can be attained. In addition, the metallic element in the inorganic component shows its own particular electronic polarization which affects the relative permittivity and refractive index of the material. Thus, the introduction of inorganic components other than silicon has the potential of forming new hybrids because these inorganic components can alter the electrical and optical properties of the hybrid.

A few studies have been attempted to introduce inorganic components other than silicon into PDMS-based hybrids. Previously, titanium alkoxides were examined and incorporated into the hybrid structure. Mechanical, thermal and optical properties of hybrids incorporating titanium species have been reported.[12–14] However, there has been no investigation on differences in structure and properties among PDMS-based hybrids incorporating various inorganics.

In the present study, the inorganic sources $Al(OBu^s)_3$, $Ti(OEt)_4$ and $Ta(OEt)_5$ were used to synthesize metal-O-PDMS (M-O-PDMS) hybrids. The effect of inorganic components derived from metal alkoxides on the structure and mechanical properties of the M-O-PDMS hybrids was investigated after clarifying the effect of the processing conditions, *i.e* the molecular mass of the PDMS and the heat treatment.

Experimental

The reagents $Al(OBu^s)_3$, $Ti(OEt)_4$ and $Ta(OEt)_5$ were obtained from Kanto Chemical Co., Tokyo Chemical Industry Co., and Kojundo Chemical Laboratory Co., respectively. Silanol-terminated poly(dimethylsiloxane) (PDMS) with average molecular masses of 1500 and 3000 was obtained from Shin-Etsu Chemical Co. and are denoted PDMS(1500) and PDMS(3000), respectively. Ethyl acetoacetate (EAcAc) was used as a chemical modifier of metal alkoxides in order to retard hydrolysis since the metal alkoxides used in this study were reactive towards water.[15] The molar ratio of metal alkoxide, PDMS, EAcAc and H_2O was 1:0.25:2:2. A flow chart showing the processing procedure is shown in Fig. 1. For $Ti(OEt)_4$ and $Ta(OEt)_5$, the metal alkoxide and EAcAc were stirred in ethanol for 30 min. On the other hand, $Al(OBu^s)_3$ and EAcAc were stirred for 30 min in the absence of ethanol in order to prevent the formation of insoluble $Al(OEt)_3$ by reaction of $Al(OBu^s)_3$ with ethanol. With vigorous stirring, an ethanol solution of PDMS was added to the mixture of the metal alkoxide and EAcAc. After 30 min, water diluted with ethanol was added to the solution, which after stirring for 30 min, was allowed to gel at 70 °C for 48 h to yield a hybrid.

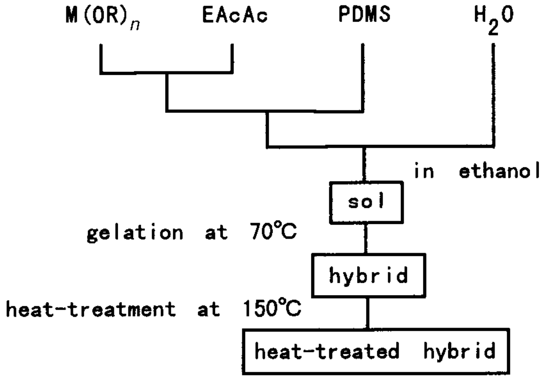

Fig. 1 Procedure for the synthesis of M-O-PDMS hybrids

The hybrid was heat treated at 150 °C for 72 h in order to complete hydrolysis and condensation reactions.

The microstructure of the hybrids was examined by transmission electron microscopy (TEM) using a Hitachi H-800 instrument with an acceleration voltage of 200 kV. FTIR spectra of the hybrids were recorded on a Perkin-Elmer System 2000 FTIR spectrometer. Dynamic mechanical data were obtained with a Rheology DVE-V4 dynamic viscoelastic analyzer with a specimen size of *ca.* $5 \times 25 \times 1$ mm. Most samples were tested within the temperature range -150 to $+300$ °C at a heating rate of 3 °C min^{-1}. A frequency of 110 Hz was selected for all the experiments.

Results and Discussion

Description of samples

The processing conditions and the appearance of the samples are summarized in Table 1. The samples prepared from Al(OBu^s)$_3$, Ti(OEt)$_4$ and Ta(OEt)$_5$ are denoted Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS, respectively. These hybrids were formed by the reaction of the hydrolysed metal alkoxide with silanol groups of PDMS.[15] All the hybrids were transparent, indicating that no visible precipitate was formed. Observation by TEM at a magnification of 75 000 also revealed that the hybrids were homogeneous and contained no inorganic particles such as oxide or hydroxide. If aggregates or clusters of metal oxide are formed from excess metal alkoxide, they must be smaller than the detection limit of TEM analyses, *ca.* 10 nm in our experiment.

As shown in Table 1, while the as-prepared M-O-PDMS hybrids synthesized from PDMS(1500) were soft and fragile, the heat-treated hybrids were brittle and glassy. Both the as-prepared and heat-treated hybrids with PDMS(1500) showed low toughness. The as-prepared hybrids synthesized from PDMS(3000) were also fragile with low toughness; however, after heat-treatment at 150 °C, they showed excellent flexibility and toughness. They could be bent as shown in Fig. 2. This feature was commonly observed in M-O-PDMS hybrids independent of the nature of inorganic components.

Effect of molecular mass of the PDMS on dynamic mechanical properties

Ta-O-PDMS hybrids were chosen as a representative of M-O-PDMS hybrids in order to observe the effect of molecular mass of the PDMS on dynamic mechanical properties. The dynamic mechanical properties of the as-prepared Ta-O-PDMS hybrids with PDMS(1500) and PDMS(3000) are shown in Fig. 3. The storage modulus exhibited a plateau with a magnitude of 10^9 Pa below -120 °C. As the temperature rose, both hybrids exhibited a glass transition region showing a gradually decreasing modulus and finally reached another plateau. In this low-modulus region, the hybrids prepared from

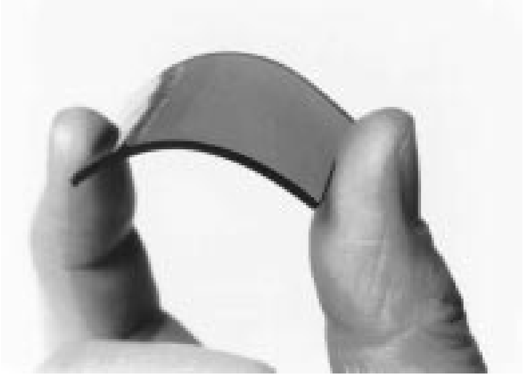

Fig. 2 Photograph of a Ti-O-PDMS hybrid. The molecular mass of PDMS was 3000. Heat treatment was performed at 150 °C for 72 h.

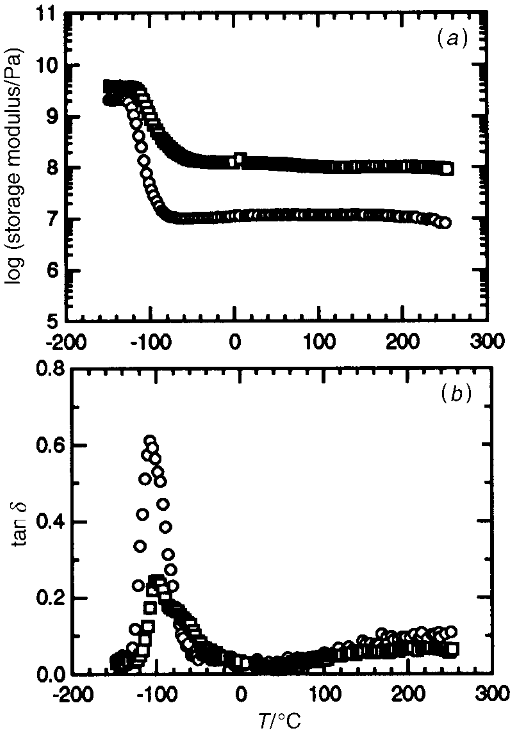

Fig. 3 Dynamic mechanical behaviour of the as-prepared Ta-O-PDMS hybrids with PDMS(1500, □) and PDMS(3000, ○): (*a*) storage modulus, (*b*) tan δ

Table 1 Effect of molecular mass (M_w) of PDMS and heat treatment on sample appearance

inorganic source	M_w	heat treatment	colour	appearance of bulk sample	dynamic mechanical measurement
Al(OBu^s)$_3$	1500	none	yellow	soft, fragile	impossible
Al(OBu^s)$_3$	1500	150 °C	yellow–brown	brittle, glassy	impossible
Al(OBu^s)$_3$	3000	none	yellow	soft, fragile	impossible
Al(OBu^s)$_3$	3000	150 °C	yellow–brown	flexible	measured
Ti(OEt)$_4$	1500	none	yellow	soft, fragile	impossible
Ti(OEt)$_4$	1500	150 °C	dark brown	brittle, glassy	impossible
Ti(OEt)$_4$	3000	none	yellow	soft, fragile	impossible
Ti(OEt)$_4$	3000	150 °C	dark brown	flexible, rubbery	measured
Ta(OEt)$_5$	1500	none	yellow	soft, fragile	measured
Ta(OEt)$_5$	1500	150 °C	brown	brittle, glassy	impossible
Ta(OEt)$_5$	3000	none	yellow	soft, fragile	measured
Ta(OEt)$_5$	3000	150 °C	brown	flexible, rubbery	measured

PDMS(3000) showed one order of magnitude lower storage modulus than those prepared from PDMS(1500). The amount of siloxane chain is considered to affect the storage modulus because the Si—O bond in the PDMS chain has high dynamic mobility owing to its low rotational barrier.[16]

The tan δ curves of the Ta-O-PDMS hybrids showed a peak in the glass transition region. The hybrids prepared from PDMS(3000) and PDMS(1500) had a tan δ peak at -108 and -99 °C, respectively. The glass transition temperature, T_g, of linear PDMS is expressed by

$$T_g = T_{g\infty} - (6500/M_w) \qquad (1)$$

where M_w is the molecular mass of the PDMS and $T_{g\infty}$ represents the glass transition temperature at infinite molecular mass which is estimated to be -123 °C.[17] The calculated T_g of PDMS(3000) and PDMS(1500) by use of eqn. (1) are -125 and -127 °C, respectively. Therefore, it is seen that T_g of the hybrid was shifted to a considerably higher temperature as compared to that of pure PDMS. Since T_g is estimated to be -123 °C for PDMS with infinite molecular mass, the large T_g shift cannot be explained by self-condensation of PDMS. It is considered that the ends of PDMS are connected to the inorganic component by the reaction of $Ta(OEt)_5$ with PDMS, resulting in restriction of the motion of the PDMS. This restriction may increase the energy for PDMS to cause the glass transition and shift T_g to a higher temperature in the Ta-O-PDMS hybrids. In the TEOS–PDMS system, it has been pointed out that PDMS connected to a TEOS species shifts T_g to higher temperature.[11]

The hybrid with PDMS(1500) showed the larger T_g shift and the broader peak of the tan δ curve than that with PDMS(3000), as shown in Fig. 3. The micro-Brownian motion of PDMS is restricted by the interaction between the ends of the PDMS chain and the inorganic component derived from the metal alkoxide. The region where the restraining effect of the inorganic component ranges may be independent of the chain length of PDMS. Thus, PDMS(1500), with a shorter chain length, is considered to be affected more significantly by the inorganic component and show wider variety in its restricted motion. This may be the reason for the larger T_g shift and the broader peak of the hybrid with PDMS(1500).

An increase in molecular mass of PDMS was found to lower the storage modulus at temperatures above T_g and to reduce the restraining effect of the inorganic component on the motion of PDMS.

Effect of heat treatment

Fig. 4 shows a comparison of dynamic mechanical properties of the as-prepared and heat-treated Ta-O-PDMS(3000) hybrids. There was a significant difference in the storage modulus above -80 °C between the two hybrids. The storage modulus increased upon heat-treatment at 150 °C. The high storage modulus means that the motion of PDMS was restricted as a result of the progress in the reaction between PDMS and the inorganic component derived from $Ta(OEt)_5$.

Heat treatment at 150 °C broadened the tan δ peak at *ca.* -108 °C attributed to the glass transition toward a higher temperature, indicating that part of the PDMS interacting with the inorganic component requires higher energy to cause the transition. It is likely that the heat treatment increased the reaction between PDMS and the inorganic component, leading to strong interaction between them. As a result, such PDMS has tight restriction imposed on its motion and requires higher energy to cause a transition.

FTIR spectra of the as-prepared and heat-treated Ta-O-PDMS hybrids are shown in Fig. 5. Absorption peaks at 1615 and 1538 cm^{-1} ascribed to EAcAc chelating to tantalum were observed for the as-prepared hybrid and disappeared after heat treatment at 150 °C. The release of EAcAc from tantalum leads

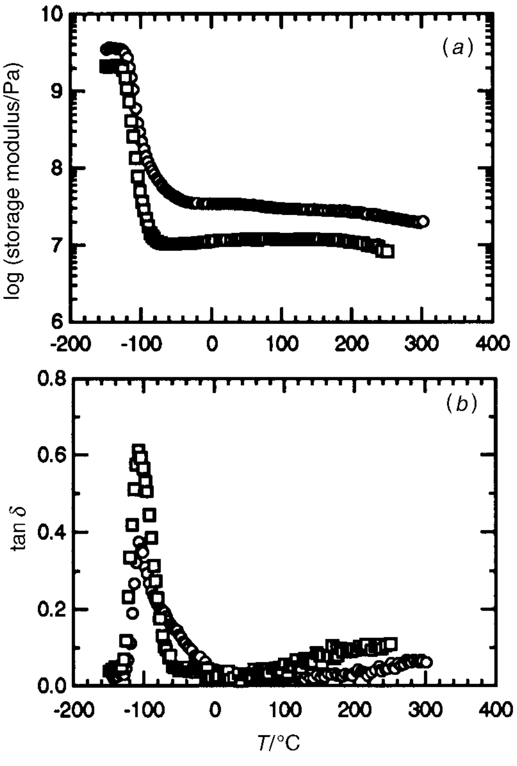

Fig. 4 Dynamic mechanical behaviour of the as-prepared (□) and heat-treated (○) Ta-O-PDMS hybrids with PDMS (3000): (*a*) storage modulus, (*b*) tan δ

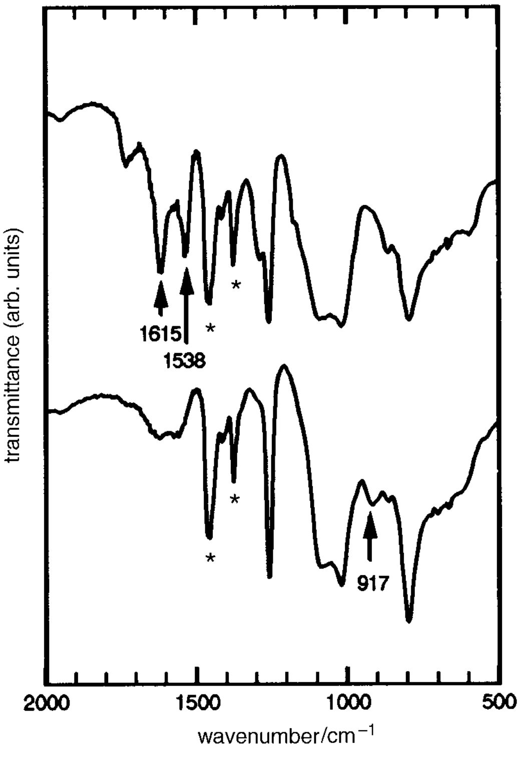

Fig. 5 FTIR spectra of (*a*) as-prepared and (*b*) heat-treated Ta-O-PDMS hybrids with PDMS(3000) (asterisks indicate bands due to liquid paraffin)

to further formation of Ta—O—Ta and Ta—O—Si bonds. An absorption peak corresponding to the Ta—O—Si bond was observed at 917 cm^{-1} after heat-treatment while the as-prepared hybrid did not clearly show this peak. This indicates that considerable amounts of chemical bonds were formed between PDMS and the inorganic component derived from Ta(OEt)$_5$ during heat treatment.

Comparison between the as-prepared and heat-treated Ta-O-PDMS hybrids with PDMS(3000) has established that heat treatment increased the number of Ta—O—Si bonds between PDMS and the inorganic component and led to a stronger interaction between them. The structure change upon heat treatment and use of the longer siloxane chain may be the reason for the flexible and rubbery properties of heat-treated hybrids with PDMS(3000).

The heat-treated hybrids with PDMS(1500) were brittle and glassy materials, as shown in Table 1. For the shorter siloxane chain, the effect of restriction on both its terminals by the inorganic component becomes larger. Upon increased interaction between PDMS(1500) and the inorganic component, the dynamic mobility of the Si—O bond was lost so as to yield a glassy material.

Effects of inorganic components

While as-prepared Ti-O-PDMS and Al-O-PDMS hybrids were too fragile to measure their mechanical properties, Ta-O-PDMS hybrids were strong enough for dynamic mechanical measurements. This indicates that mechanical properties of M-O-PDMS hybrids are influenced by the inorganic components. Heat treatment at 150 °C made it possible to measure the dynamic mechanical properties of Ti-O-PDMS and Al-O-PDMS hybrids. FTIR studies of Ti-O-PDMS and Al-O-PDMS hybrids showed that EAcAc chelating to titanium and aluminium in these hybrids was released by the heat-treatment, as discussed in the Ta-O-PDMS hybrid system. This suggests that heat treatment promoted the formation of bonds between PDMS and the inorganic component in Ti-O-PDMS and Al-O-PDMS hybrids as well as in the Ta-O-PDMS hybrid.

Transparent and flexible M-O-PDMS hybrids were synthesized using PDMS(3000) after heat treatment at 150 °C. Comparisons in dynamic mechanical properties among heat-treated Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS hybrids are shown in Fig. 6. In the glassy region below -120 °C, all of these hybrids showed a storage modulus of the order of 10^9 Pa. Above 80 °C the storage modulus became higher in the order Al-O-PDMS, Ti-O-PDMS, Ta-O-PDMS, suggesting that the structure of the hybrid becomes more rigid in this order. From the results of the FTIR study, it is seen that the alkoxy groups and EAcAc belonging to the modified metal alkoxide are all removed in the heat-treated hybrids. Tantalum, with a higher valence than titanium or aluminium bonds with a larger number of silanol groups of PDMS, leading to the formation of a denser three-dimensional inorganic–organic network, and as a consequence a higher storage modulus.

No significant difference was found between samples in the peak temperature of the tan δ curves. It is expected that the restraining effect of the inorganic component on the micro-Brownian motion of PDMS depends on the inorganic species. However, the difference is too small to be detected by dynamic mechanical measurements.

The peak height of the tan δ curve decreased in the order Al-O-PDMS, Ti-O-PDMS, Ta-O-PDMS. A decrease of the peak height implies that energy loss accompanying the glass transition is lowered in this order. The origin of the energy loss is friction between polymers constituting the inorganic–organic network. As the atomic mass of metallic element in the inorganic component becomes larger, its restraining effect on the motion of PDMS becomes larger. This results in low friction between the PDMS chains and, therefore, low energy loss associated with the glass transition.

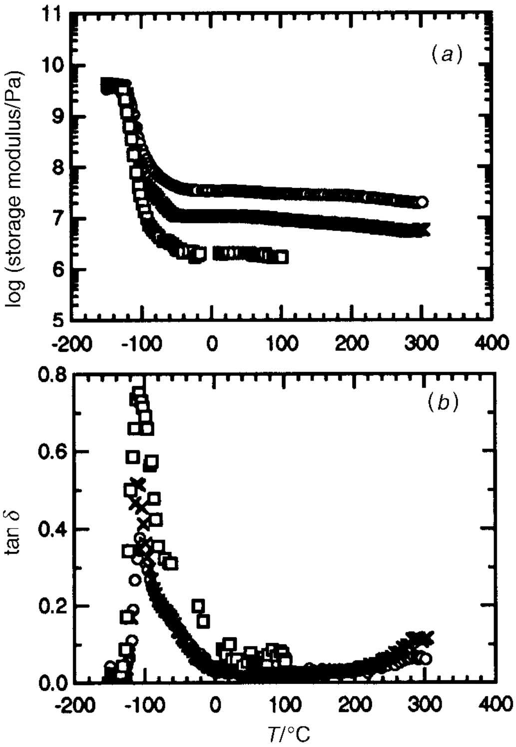

Fig. 6 Dynamic mechanical behaviour of the heat-treated Al-O-PDMS (□), Ti-O-PDMS (×) and Ta-O-PDMS (○) hybrids: (*a*) storage modulus, (*b*) tan δ

The effects of the inorganic components of M-O-PDMS hybrids on the structure and dynamic mechanical properties were clarified from dynamic mechanical measurements. The valence and atomic mass of the metallic element within the inorganic component were found to be important in modifying the structure and properties of the hybrids.

Conclusions

1. Transparent inorganic–organic hybrids containing various inorganic components have been synthesized from silanol-terminated PDMS and the metal alkoxides Al(OBu^s)$_3$, Ti(OEt)$_4$ and Ta(OEt)$_5$ by a sol–gel process.

2. The hybrids synthesized from PDMS(3000) with higher molecular mass showed a lower storage modulus above the glass transition temperature and a smaller restraining effect of the inorganic component on the motion of PDMS. Heat treatment at 150 °C led to the formation of M—O—Si bonds which were detected by FTIR.

3. Inorganic components were found to affect the structure and dynamic mechanical properties. The storage modulus increased and the peak height of the tan δ curve decreased in the order Al-O-PDMS, Ti-O-PDMS, Ta-O-PDMS. This may result from the difference in valence and atomic mass of the metallic element in the inorganic component.

This work was supported by NEDO as part of the Synergy Ceramics Project under the Industrial Science and Technology Frontier (ISTF) Program promoted by AIST, MITI, Japan. The authors are members of the Joint Research Consortium of Synergy Ceramics.

References

1 G. Philipp and H. Schmidt, *J. Non-Cryst. Solids*, 1984, **63**, 283.
2 H. Schmidt, *J. Non-Cryst. Solids*, 1985, **73**, 681.

3 G. L. Wilkes, B. Orler and H. Huang, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* 1985, **26**, 300.

4 B. Lintner, N. Arfsten and H. Dislich, *J. Non-Cryst. Solids*, 1988, **100**, 378.

5 H. Schmidt and M. Popall, in *Sol-Gel Optics I*, ed. J. D. Mackenzie and D. R. Ulrich, Proc. SPIE, Washington, 1990, vol. 1328, p. 249.

6 H. Schmidt and H. Wolter, *J. Non-Cryst. Solids*, 1990, **121**, 428.

7 R. Collino, J. Therasse, F. Chaput, J-P. Boilot, Y. Levy, in *Better Ceramics through Chemistry VI*, ed. A. K. Cheetham, C. J. Brinker, M. L. Mecartney and C. Sanchez, *Mater. Res. Soc. Symp. Proc.* Pittsburgh, PA, 1994, vol. 346, p. 1033.

8 D. Levy and L. Esquivias, *Adv. Mater.*, 1995, **7**, 120.

9 J. D. Mackenzie, Y. J. Chung and Y. Hu, *J. Non-Cryst. Solids*, 1992, **147–148**, 271.

10 H. Huang, B. Orler and G. L. Wilkes, *Polym. Bull.*, 1985, **14**, 557.

11 H. Huang, B. Orler and G. L. Wilkes, *Macromolecules*, 1987, **20**, 1322.

12 C. S. Parkhurst, W. F. Doyle, L. A. Silverman, S. Singh, M. P. Andersen, D. McClurg, G. E. Wnek and D. R. Uhlmann in *Better Ceramics through Chemistry II,* ed. C. J. Brinker, D. E. Clarke and D. R. Ulrich, Pittsburg, PA, *Mater. Res. Soc. Symp. Proc.*, 1986, vol. 73, p. 769.

13 R. H. Glaser and G. L. Wilkes, *Polym. Bull.*, 1988, **19**, 51.

14 S. S. Joardar, M. A. Jones and T. C. Ward, *Polym. Mater. Sci. Eng.*, 1992, **67**, 254.

15 S. Katayama, I. Yoshinaga and N. Yamada, in *Better Ceramics through Chemistry VII*, ed. B. K. Coltrain, C. Sanchez, D. W. Schaefer and G. L. Wilkes, *Mater. Res. Soc. Symp. Proc.*, Pittsburgh, PA, 1996, vol. 435, p. 321.

16 R. F. T. Stepto, in *Siloxane Polymers*, ed. S. J. Clarson and J. A. Semlyen, PTR Prentice Hall, Englewood Cliff, NJ, 1993, p. 373.

17 S. J. Clarson, in *Siloxane Polymers*, ed. S. J. Clarson and J. A. Semlyen, PTR Prentice Hall, Englewood Cliff, NJ, 1993, p. 216.

Paper 7/00793K; *Received* 4*th February*, 1997