

# Development of a rapid crosslinking preceramic polymer system

M. Scheffler<sup>a,\*</sup>, R. Bordia<sup>a</sup>, N. Travitzky<sup>b</sup>, P. Greil<sup>b</sup>

<sup>a</sup> Department of Materials Science and Engineering, University of Washington, Box 352120, Seattle, WA 98195-2120, USA

<sup>b</sup> Department of Materials Science, Glass and Ceramics, University of Erlangen-Nuernberg, Martensstrasse 5, D-91058 Erlangen, Germany

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## Abstract

A low-viscosity, fast crosslinking preceramic polymer system was developed as a base for liquid state processing. The system consists of a water-crosslinkable silicone polymer, a latent water source for in situ water generation, and a tin catalyst. While the silicone polymer and the water source can be mixed in any proportion, the catalyst must be added separately to achieve crosslinking at room temperature within a short time. By pyrolysis in inert atmosphere at 1000 °C the system was shown to have a high ceramic yield of ~54 wt.%. The base system is compatible with alkanes, which makes it suitable for viscosity control when the system is filler-loaded for tailoring of properties. Due to its low viscosity one possible use of the system is in inkjet printing. Further since the crosslinking is rapid it can also be used in the layer by layer manufacturing of ceramic parts.

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**Keywords:** Preceramic polymers; Polymer-derived ceramic; Crosslinking

## 1. Introduction

Thermal transformation of preceramic polymers to ceramic materials has become a matter of intensive research during the past 20 years.<sup>1–3</sup> The poly(siloxane) resins [RSiO<sub>1.5</sub>]<sub>n</sub> with R = –CH<sub>3</sub> (methyl), –C<sub>6</sub>H<sub>5</sub> (phenyl), –C<sub>2</sub>H<sub>3</sub> (vinyl), –C<sub>3</sub>H<sub>7</sub> (propyl) have been converted into various ceramic products: ceramic foams,<sup>4,5</sup> bulk composite components,<sup>3</sup> planar tapes<sup>6</sup> and tubes,<sup>7</sup> or engineering materials with high temperature and oxidation stability.<sup>8,9</sup> Processing of preceramic polymers into ceramic products involves shaping of a polymer precursor, subsequent curing and pyrolysis at temperatures above 800 °C. Due to the pronounced density differences between the polymer (1–1.2 g/cm<sup>3</sup>) and the ceramic phases (2–3 g/cm<sup>3</sup>) shrinkage of up to 70 vol.% may occur which gives rise to extensive porosity or cracking in the pyrolysed ceramic residue. Manufacturing of ceramic parts from preceramic polymers, however, is facilitated when the polymer is loaded with a filler powder. *Inert filler powders* such as Al<sub>2</sub>O<sub>3</sub>, SiC, B<sub>4</sub>C, Si<sub>3</sub>N<sub>4</sub>, etc., as well as *reactive fillers* like Ti, Cr, Mo, B,

MoSi<sub>2</sub>, etc., which may react with the pyrolysis atmosphere and/or with the solid and gaseous decomposition products of the polymer precursor to form carbides, oxides, etc., have been successfully used to reduce the polymer-to-ceramic conversion shrinkage and to improve the mechanical properties of non-oxide as well as oxide based polymer-derived ceramics.<sup>10–12</sup> In addition to these “macro part” manufacturing technologies the fabrication of micro parts by layer-wise production by so-called rapid prototyping (RP) techniques<sup>13</sup> and their adjustment to ceramic manufacturing for the making of small parts is of growing interest in ceramic processing technology. A promising and widely used technique for the fabrication of small parts of different materials with specific optical, electrical, chemical, biological or structural functionalities into well-defined locations is the inkjet printing technology.<sup>14</sup> With this technology a wide field of materials systems can be processed. Examples include specific polymers into thin-film transistor circuits<sup>15</sup> and light-emitting polymer displays,<sup>16</sup> biomolecules into biochips,<sup>17</sup> 3D scaffolds as templates for biomedical applications,<sup>18</sup> conductive gold tracks on substrates,<sup>19</sup> cobalt nanoparticles for catalytic growth of carbon nanotubes,<sup>20</sup> and for combinatorial materials research.<sup>21</sup> Ceramic particle-loaded inks have been developed containing ZrO<sub>2</sub> or

\* Corresponding author. Tel.: +1 206 543 2870; fax: +1 206 543 3100.  
E-mail address: [mscheff@u.washington.edu](mailto:mscheff@u.washington.edu) (M. Scheffler).

ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub><sup>22</sup> and PZT-powders.<sup>23</sup> The filler amount in the dispersant liquid which is used as a transportation vehicle for the inkjet printing process, however, is limited. Recently, details of the inkjet printing process with respect to the flow process and the operating parameters of the printhead were modeled, and alumina suspensions with a volume fraction of up to 0.4 were used for ceramic green part manufacturing.<sup>24</sup> An alternative route to increase the solid content is the use of a slurry consisting of a poly(carbosilane) preceramic polymer and a ceramic powder dispersed in a solvent as demonstrated by Mott and Evans.<sup>25</sup>

The system described in this work is based on a low-viscosity poly(siloxane) preceramic polymer, a latent water source and a catalyst for fast crosslinking at room temperature. Rheological measurements were carried out with respect to the crosslinking behaviour at room temperature and Fourier Transformed Infrared Spectroscopy (FTIR) was performed in order to investigate the crosslinking mechanism. Thermal analysis was used to investigate the polymer-to-ceramic conversion and to obtain the ceramic yield which is compared to the ceramic yield of a commercial silicone resin. Because of its low viscosity, rapid crosslinking, high ceramic yield after thermal conversion and the compatibility with organic solvents for viscosity tailoring it is suitable as a basic binder system for the use in liquid processing, especially for inkjet printing of filler-loaded preceramic polymers.

## 2. Experimental procedure

A poly(methoxymethylsiloxane) (MSE-100, Wacker Silicone AG, Muenchen, Germany), a hydroxy-terminated linear poly(dimethylsiloxane) (DMS-S12, Gelest Inc., Morrisville, PA, USA) and a crosslinking catalyst operating at room temperature ([bis(2-ethylhexanoate)tin] dissolved in 50 wt.% poly(dimethylsiloxane); SNB-1101, Gelest Inc.) were used in the formulation of the base system in this study. The amount of catalyst such that tin ions were 1 wt.% of the system. The chemical compounds used in this work are listed in Table 1.

The crosslinking reaction was studied by FTIR spectroscopy (Nicolet DBX-5; ThermoNicolet, Madison, WI, USA). In a first step, the single components (DMS-S12, MSE-100, Sn-catalyst in poly(dimethylsiloxane)) were investigated individually from 400 to 4000 cm<sup>-1</sup> (on a Si-wafer). In a second step, the reaction mixture MSE-100/DMS-S12 with a weight fraction of  $M_{\text{MSE-100}} = 0.7$  was investigated, and finally the reaction mixture with the

catalyst was studied as a function of time from 1 to 200 min. The identification of the vibrational modes was carried out according to Anderson and Bellamy.<sup>26,27</sup>

Viscosity measurements of the sample mixture with  $M_{\text{MSE-100}} = 0.7$  during crosslinking were carried out with a rotational rheometer (Haake VT 550, Thermo Electron GmbH, Karlsruhe, Germany) at 20 °C with shear rates of 10 and 100 s<sup>-1</sup> at 20 °C. Further viscosity adjustment was accomplished with *n*-hexane, which was added to the MSE-100/DMS-S12 sample in order to demonstrate the compatibility of the solvent with the base system. The *n*-hexane volume fraction was varied from 0 to 0.26, related to the total volume fraction of the MSE-100/DMS-S12 mixture. One of the overall goals of this research is to formulate a low-viscosity, particle loaded preceramic ink for inkjet printing. Therefore, a compatible solvent is necessary.

For thermal transformation and ceramic yield analysis the two liquid components were mixed in a test tube with a weight fraction of the MSE-100,  $M_{\text{MSE}} = m_{\text{MSE}}/(m_{\text{MSE}} + m_{\text{DMS}})$ , ranging from 0.37 to 1.0. The liquid was poured into a polyethylene mold with a diameter of 10 mm and a height of 8 mm for crosslinking and the catalyst was added under vigorous stirring within 60 s. These samples were held at room temperature for 12 h and at 110 °C for another 12 h.

The thermal transformation behaviour was monitored by thermal analysis (TGA and DTA) with a simultaneously operating thermobalance (STA 409A; Netzsch GmbH, Selb, Germany). About 50 mg of the dried samples was placed in an alumina crucible and heated to 1000 °C in argon atmosphere at a heating rate of 10 °C/min.

Pyrolysis was carried out in argon atmosphere in a tube furnace with a dwell time at 1000 °C of 2 h and at two different heating rates of 3 and 10 °C/min. From the pyrolysed samples the ceramic yield was calculated.

## 3. Results and discussion

### 3.1. Crosslinking mechanism of the poly(methoxymethylsiloxane)

When the catalyst was added to the DMS-S12 only, within a few seconds a cloudy precipitate appeared. This effect was not observed when the catalyst was added to the MSE-100/DMS-S12 mixture, which remained clear and colorless even after the viscosity increased. FTIR spectra of the catalyst-containing MSE-100/DMS-S12 mixture have shown, that the peak intensity of the stretching

Table 1  
Components of the rapid crosslinking preceramic polymer system

Brand	Chemical compound	Formula
MSE-100 (Wacker AG)	Poly(methoxymethylsiloxane)	CH <sub>3</sub> Si(O) <sub>1.1</sub> (OCH <sub>3</sub> ) <sub>0.9</sub>
DMS-S12 (Gelest Inc.)	Poly(dimethylsiloxane), hydroxyterminated	(OHSiCH <sub>3</sub> ) <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub><i>n</i></sub> (with 15 < <i>n</i> < 30)
<i>n</i> -Hexane (Merck)	Alkane	<i>n</i> -C <sub>6</sub> H <sub>14</sub>
SNB-1101 (Gelest Inc.)	Bis(2-ethylhexanoate) tin in 50 wt.% poly(dimethylsiloxane)	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub> Sn

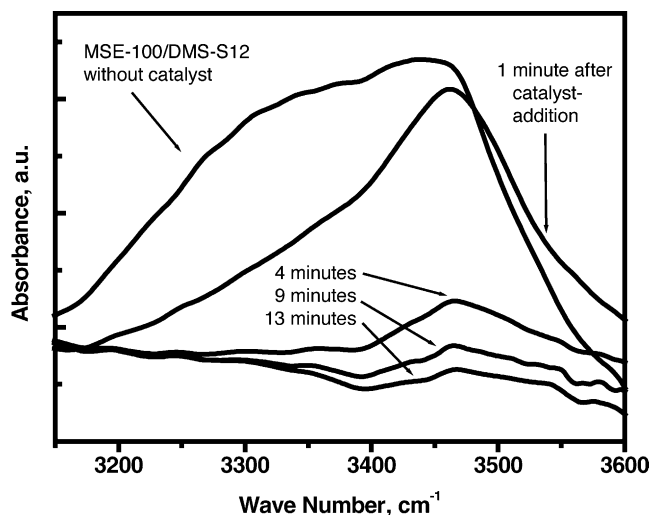


Fig. 1. FTIR spectra (time dependent) of the  $-OH$  region from  $3200$  to  $3600\text{ cm}^{-1}$ .

vibrations of the bonded and associated  $-OH$  groups of the poly(dimethylsiloxane) which are located between  $3200$  and  $3600\text{ cm}^{-1}$ , decreased drastically within a few minutes (Fig. 1). This effect may be caused by condensation reactions of the DMS-S12 hydroxy-terminated poly(dimethylsiloxane) resulting in water formation. From the average molecular weight of  $400$  to  $700\text{ g mol}^{-1}$  (manufacturer's data) an average latent water content of  $3.4\text{ wt.}\%$  (related to pure DMS-S12) was calculated which was assumed to be liberated completely by condensation reactions after catalyst addition.

In the fingerprint region of the preceramic polymer compounds, the vibrational modes at  $1190$ ,  $780$  and  $1080\text{ cm}^{-1}$  are related to the  $\text{Si}-\text{O}-\text{CH}_3$  units. The region from  $1000$  to  $1130\text{ cm}^{-1}$  is associated with the asymmetric stretching modes of  $\text{Si}-\text{O}-\text{Si}$  and  $\text{Si}-\text{O}-\text{C}$  bonds.<sup>26,27</sup> A set of FTIR spectra of the fingerprint region of the catalyst-free MSE-100/DMS-S12 mixture and after catalyst addition from  $1$  to  $42\text{ min}$  is presented in Fig. 2.

While after the catalyst addition the band at  $\sim 900\text{ cm}^{-1}$  disappeared caused by the condensation of silanol groups a major change in the spectra was observed after  $\sim 33\text{--}42\text{ min}$  of reaction time (cf. spectrum taken after  $42\text{ min}$ ; Fig. 2). The vibrational mode at  $780\text{ cm}^{-1}$  decreased, and an increase in intensity of the band at  $1030\text{ cm}^{-1}$  was found. While the first mode is related to the  $\text{Si}-\text{O}-\text{CH}_3$  unit, the mode at  $1030\text{ cm}^{-1}$  represents the stretching vibrations of the  $\text{Si}-\text{O}-\text{Si}$  bonds. Major changes after crosslinking times  $>42\text{ min}$  up to  $200\text{ min}$ , however, were not observed. Based on this preliminary results, we propose a tentative crosslinking mechanism illustrated in Fig. 3.

In the first step, water was generated within minutes from the condensation reaction of the poly(siloxane)-terminating hydroxy groups (step I). The water, however, associated with the methoxy groups of the MSE-100, caused hydrolysis of these units and the subsequent bond formation/condensation of the afore generated siliconether-bonded silanol groups

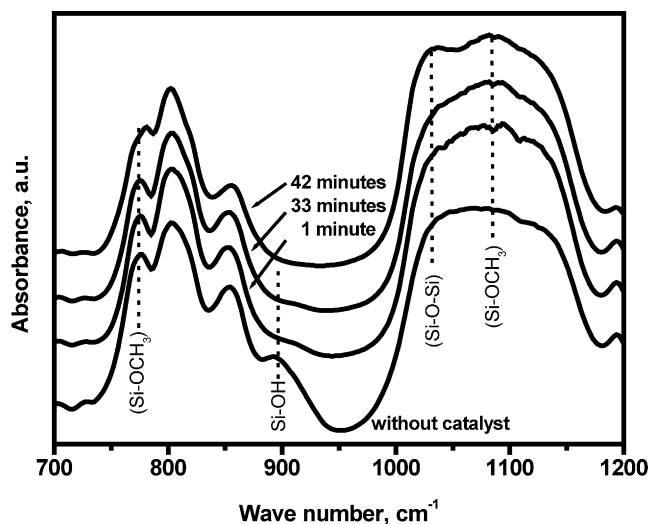


Fig. 2. FTIR spectra (time dependent) of the fingerprint region from  $700$  to  $1200\text{ cm}^{-1}$  after different crosslinking times.

(step II). This crosslinking mechanism may be more complex and is still under investigation.

### 3.2. Viscosity measurements and viscosity control

Fig. 4 shows the viscosity at  $20^\circ\text{C}$  as a function of time of a MSE-100/DMS-S12 (MSE-100 weight fraction,  $M_{\text{MSE-100}} = 0.7$ ) mixture after catalyst addition. As can be seen on this half-logarithmic scale, the viscosity increased linearly over a period of  $\sim 35\text{ min}$ , and then increased sharply. This effect may be caused by the formation of the  $-\text{Si}-\text{O}-\text{Si}-$  bonds, which is in good agreement with the FTIR results. When the temperature was increased to  $60^\circ\text{C}$  prior to catalyst addition, the crosslinking time could be reduced to  $\sim 3.3\text{ min}$ .

The viscosity of the starting system with a weight fraction of the poly(methoxymethylsiloxane)  $M_{\text{MSE-100}} = 0.7$  was found to be  $22.5\text{ mPa s}$  at  $20^\circ\text{C}$ . When fillers are introduced in the system, the viscosity is expected to increase. In order to keep the systems' viscosity below  $30\text{ mPa s}$ , which was shown to be the upper limit for inkjet printing,<sup>28</sup> *n*-hexane was used for viscosity adjustment. The *n*-hexane shows no miscibility gap when mixed with the MSE-100/DMS-S12 system, has a viscosity of  $0.31\text{ mPa s}$  at room temperature and a boiling point of  $69^\circ\text{C}$ , and thus allows rapid evaporation after printing. These physical properties make it a suitable modifier for the base system to be a preceramic ink. The resulting viscosity as a function of the *n*-hexane volume fraction is shown in Fig. 5.

An *n*-hexane volume fraction of only  $0.05$  reduced the viscosity to  $<20\text{ mPa s}$ , and the sample with a *n*-hexane volume fraction of  $0.2$  showed a viscosity less than  $10\text{ mPa s}$ .

### 3.3. Weight loss and ceramic yield

The TG curves (top) and first derivatives of the TG curves (bottom) of MSE-100/DMS-S12 mixtures



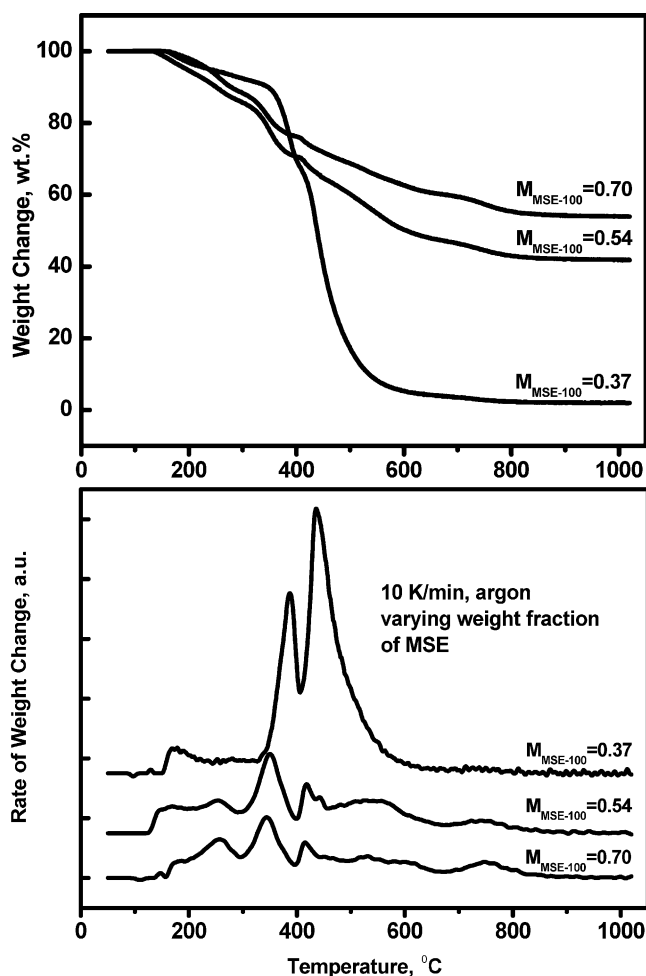


Fig. 6. TG curves (top) and their first derivatives (bottom) of MSE-100/DMS-S12 mixtures of different weight fraction.

The residue after holding at 110 °C and the overall ceramic yield after holding at 110 °C and pyrolysis at 1000 °C with a heating rate of 3 and 10 °C/min in argon atmosphere is shown in Fig. 7. Moreover, the expected overall ceramic yield from theoretical calculations (dotted line with circles) is shown based on a linear combination of the ceramic yield of the linear polydimethylsiloxane DMS-S12 (zero) and ceramic yield of pure, crosslinked MSE-100 (52 wt.% for pure MSE-100). The thermal decomposition behaviour of linear poly(dimethylsiloxanes) was described by Schiavon et al.<sup>29</sup> resulting in a total loss after pyrolysis at 600 °C.

No significant differences in the ceramic yield after pyrolysis at different heating rates of 3 and 10 °C/min were observed. A significant ceramic yield after pyrolysis at 1000 °C in the MSE-100/DMS-S12 system was measured at a MSE-100 weight fraction of  $\geq 0.37$ . With an increasing MSE-100 weight fraction the ceramic yield increased and showed a maximum of 54 wt.% at  $M_{\text{MSE-100}} = 0.7$ . It should be noted that the ceramic yield is significantly higher in the MSE-100 weight fraction range from  $0.45 \leq M_{\text{MSE-100}} \leq 0.95$  as compared to the expected (calculated) ceramic yield in this range. The reasons for this are under investigation. Possible mech-

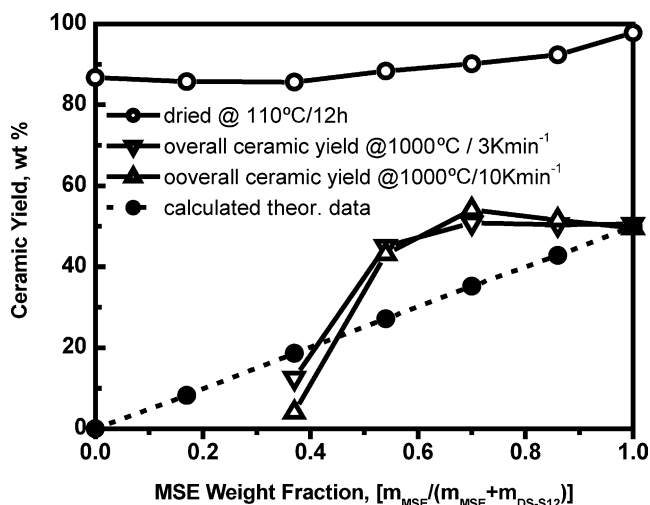


Fig. 7. Yield of the MSE-100/DMS-S12 samples with different MSE-100 weight fractions after drying at 100 °C, overall ceramic yield after drying and pyrolysis at 1000 °C in argon atmosphere and theoretical (calculated) ceramic yield.

anisms included, are the degree of crosslinking (expected to be higher around a MSE-100 weight fraction of 0.7); or copolymerisation leading to a less volatile structure. For comparison: A commonly used, pure poly(methylsilsequioxane) (MK, Wacker Siltronic AG, Muenchen, Germany) which is often used in preceramic polymer processing<sup>4,6,7,30</sup> resulted in an overall ceramic yield of  $\sim 80$  wt.% (which translates to 56 wt.% at a weight fraction of 0.7).

#### 4. Conclusions

A high-yield low-viscosity base system based on a poly(methoxymethylsiloxane) as a preceramic polymer and a hydroxy-terminated poly(dimethylsiloxane) as a latent water source for crosslinking was developed. The crosslinking reaction of the preceramic polymer was initiated by the water formation by condensation reactions of the poly(dimethylsiloxane) after catalyst addition and the reaction of the water with the methoxy groups of the preceramic polymer. The crosslinking reaction occurred at room temperature after  $\sim 35$  min. The system was shown to be compatible with alkanes for a further viscosity adjustment. After pyrolysis at 1000 °C in argon atmosphere a ceramic yield of  $\sim 54$  wt.% was measured. The low viscosity of  $\sim 22.5$  mPa s at room temperature, the compatibility with alkanes for viscosity adjustment (which is necessary for a filler-loaded system) and the short crosslinking time make this preceramic polymer system a suitable candidate for inkjet printing and layer-by-layer processing of 3D parts.

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## References

1. Wynne, K. J. and Rice, R. W., *Annu. Rev. Mater. Sci.*, 1984, **14**, 297.
2. Peuckert, M., Vaahs, T. and Brück, M., *Adv. Mater.*, 1990, **2**, 398.
3. Greil, P., *Adv. Eng. Mater.*, 2000, **2**, 339.
4. Colombo, P. and Hellmann, J. R., *Mater. Res. Innovations*, 2002, **6**, 260.
5. Zeschky, J., Goetz-Neunhoeffler, F., Neubauer, J., Lo, J. S. H., Kummer, B., Scheffler, M. et al., *Compos. Sci. Technol.*, 2003, **63**, 2361.
6. Cromme, P., Scheffler, M. and Greil, P., *Adv. Eng. Mater.*, 2002, **4**, 873.
7. Melcher, R., Cromme, P., Scheffler, M. and Greil, P., *J. Am. Ceram. Soc.*, 2003, **86**, 1211.
8. Hurwitz, F. I. and Meador, M. A. B., *J. Sol-Gel Sci. Technol.*, 1999, **14**, 75.
9. Soraru, G. D. and Suttor, D., *J. Sol-Gel Sci. Technol.*, 1999, **14**, 69.
10. Seyferth, D., Bryson, N., Workman, D. P. and Sobon, C. A., *J. Am. Ceram. Soc.*, 1991, **74**, 2687.
11. Greil, P., *J. Am. Ceram. Soc.*, 1995, **78**, 835.
12. Stackpoole, M. and Bordia, R. K., *Ceram. Trans.*, 2000, **108**, 111.
13. Pham, D. T. and Gault, R. S., *Intl. J. Machine Tools Manufacture*, 1998, **38**, 1257.
14. Siringhaus, H. and Shimoda, T., *MRS Bull.*, November 2003, 802.
15. Zaugg, F. G. and Wagner, P., *MRS Bull.*, November 2003, 837.
16. Shimoda, T., Morii, K., Seki, S. and Kiguchi, H., *MRS Bull.*, November 2003, 821.
17. Burns, S. E., Cain, P., Mills, J., Wang, J. and Siringhaus, H., *MRS Bull.*, November 2003, 829.
18. Lam, C. X. F., Mo, X. M., Teoh, S. H. and Huttmacher, D. W., *Mater. Sci. Eng.*, 2000, **C20**, 49.
19. Nur, H. M., Song, J. H., Evans, J. R. G. and Edirisinghe, M. J., *J. Mater. Sci. Mater. Electron.*, 2002, **13**, 213.
20. Ago, H., Qi, J., Tsukagoshi, K., Murata, K., Ohshima, S., Aoyagi, Y. et al., *J. Electroanal. Chem.*, 2003, **559**, 25.
21. Evans, J. R. G., Edirisinghe, M. J., Coveney, P. V. and Eames, J., *J. Eur. Ceram. Soc.*, 2001, **21**, 2291.
22. Zhao, X., Evans, J. R. G., Edirisinghe, M. J. and Song, J. H., *J. Mater. Sci.*, 2002, **37**, 1987.
23. Bhatti, A. R., Mott, M., Evans, J. R. G. and Edirisinghe, M. J., *J. Mater. Sci. Lett.*, 2001, **20**, 1245.
24. Seerden, K. A. M., Reis, N., Evans, J. R. G., Grant, P. S., Halloran, J. W. and Derby, B., *J. Am. Ceram. Soc.*, 2001, **84**, 2514.
25. Mott, M. and Evans, J. R. G., *J. Am. Ceram. Soc.*, 2001, **84**, 307.
26. Anderson, D. R., *Analysis of Silicones*. Wiley Interscience, New York, 1974 [chapter 10].
27. Bellamy, L. J., *The Infrared Spectra of Complex Molecules (3rd ed.)*. Chapman and Hall, 1975 [chapter 20].
28. Lee, D. H. and Derby, B., *J. Eur. Ceram. Soc.*, 2004, **24**, 1069.
29. Schiavon, M. A., Redondo, S. U. A., Pina, S. R. O. and Yoshida, I. V. P., *J. Non-Cryst. Solids*, 2002, **304**, 92.
30. Wei, Q., Pippel, E., Woltersdorf, J., Scheffler, M. and Greil, P., *Mater. Chem. Phys.*, 2002, **73**, 281.