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Dendrimeric organosiloxane with thermopolymerizable –OCF═CF$_2$ groups as the arms: synthesis and transformation to the polymer with both ultra-low *k* and low water uptake†

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A novel fluoro-containing dendrimeric macromolecule with cyclic siloxane as the core and aryl-trifluorovinyl-ether (–OCF═CF$_2$) units as the arms was reported. The macromolecule was easily converted to a cross-linked structure showing an ultra-low *k* value and low water uptake. In particular, the network also exhibited high thermostability and excellent transparency.

Introduction

One of the important applications of polysiloxanes is their use as low dielectric constant (*k*) materials in the electronics industry.[1–5] For this application, polymers need to be converted to insoluble and infusible cross-linked networks to meet the rising requirements of electronic devices.[6–13] In order to realize cross-linking, two routes have been widely used. One is catalyzed-crosslinking (platinum salts are used) and the other is radiated-crosslinking (peroxides are used as initiators).[14–17] Nevertheless, residues of catalysts or initiators may have negative effects on the dielectric properties of the materials. Thus, the development of polysiloxanes having directly thermo-crosslinkable groups is required. To date, although a series of thermo-crosslinking polysiloxanes have been reported,[6,10] their expensive cost and complicated synthetic procedures may hinder applications of the polymers in broader areas. Furthermore, the *k* values of organosiloxane-based materials which have been reported with a low dielectric constant are still larger than 2.8.[10] So it is necessary to further decrease the *k* value to meet the requirements of the electrical/electronics industry.

Previously, our group reported a new kind of linear polysiloxane functionalized with trifluorovinyl ether (TFVE) groups on side chains, which can be thermally transformed to a cross-linked network showing a low dielectric constant and high thermostability.[18] To overcome the synthetic difficulty of the polymer on a large scale, we designed and synthesized a new fluoro-containing dendrimeric macromolecule with cyclic siloxane as the core and TFVE units as the arms. Such a macromolecule was easily synthesized and purified. When heated to a high temperature, it can convert to a cross-linked structure, which showed an ultra-low *k* and very low water uptake. Moreover, the cross-linked network exhibited high transparency with a transmittance of higher than 91% ranging from 400 to 1100 nm. These characteristics of the new TFVE-containing dendrimeric macromolecule indicated that it could be used as a matrix for the production of high-frequency printed circuit boards, as well as encapsulation resins in the microelectronics industry. Furthermore, this work is of considerable industrial importance because it provides a new way for the cross-linking of organosiloxanes to replace the general routes which usually require catalysts or initiators (platinum or peroxides).

Results and discussion

The new dendrimeric macromolecule (**D$_4$-TFVE**) was synthesized by the platinum-catalyzed hydrosilylation reaction between compound **1**[19] and a commercial cyclotetrasiloxane (D_4^V) in the absence of a solvent. The crude **D$_4$-TFVE** was easily purified. The pure product, showing a purity of 99.46% (HPLC), was a colorless liquid with low viscosity, suggesting its good processability. GPC data showed (Fig. S6 in the ESI†) that the number-average molecular weight (M_n) of **D$_4$-TFVE** was 1398 with a PDI of 1.01, which was consistent with the result of MALDI-TOF-MS in the range of allowable error (see the Experimental section and Fig. S7†). Moreover, the monodispersed M_n also reflected that no polymerization occurred during the hydrosilylation reaction. The chemical structure of **D$_4$-TFVE** was also characterized by NMR spectra. Fig. 1 shows ^{13}C NMR and ^{29}Si NMR spectra of **D$_4$-TFVE**. As shown in Fig. 1, there were only two kinds of signals in ^{29}Si NMR spectra. The signal at −0.42 ppm referred to the Si atoms

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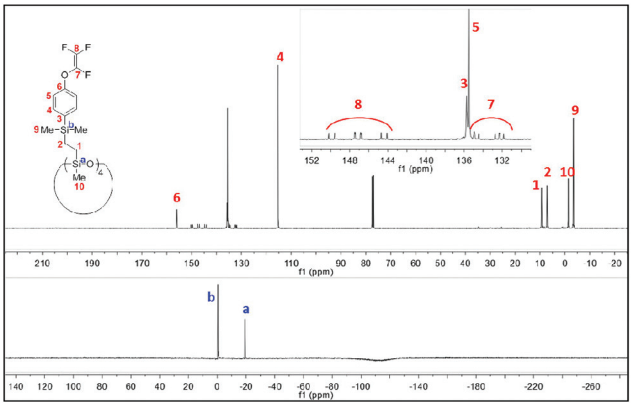
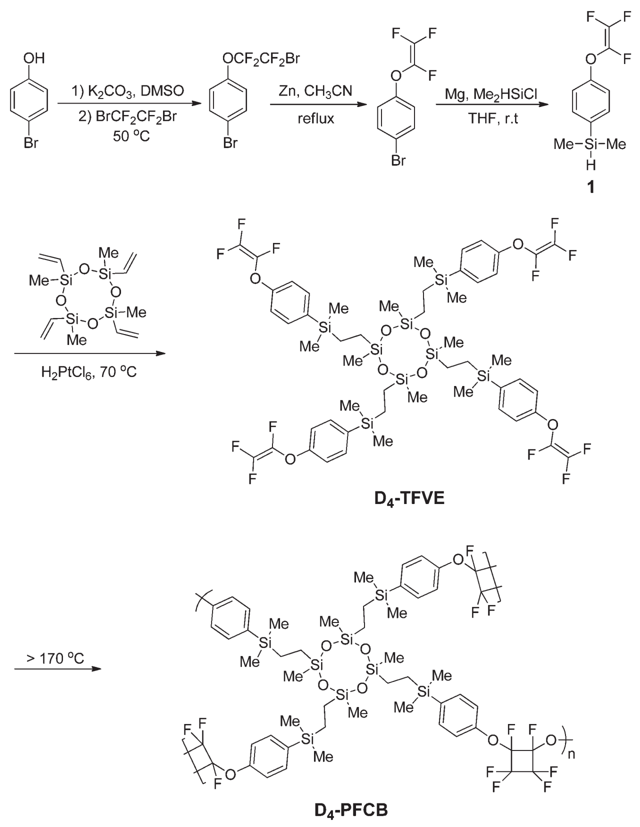


Fig. 1 ^{13}C NMR (up) and ^{29}Si NMR (down) spectra of **D_4-TFVE**.

connecting to the benzene while −19.26 ppm was attributed to the Si atoms on the ring of cyclotetrasiloxane. The NMR data indicate that the vinyl groups have been totally transformed, and TFVE groups are successfully introduced into the cyclic organosiloxane as the four arms in **D_4-TFVE**.

TFVE groups can be transformed into perfluorocyclobutane (PFCB) units *via* a [2π + 2π] reaction at high temperature (Scheme 1) without the release of volatiles.[9,20–22] In our case, such a transformation of **D_4-TFVE** was evaluated by differential scanning calorimetry (DSC). As can be seen from Fig. 2, **D_4-TFVE** showed a wide curing temperature ranging from 170 °C to 330 °C, giving a peak temperature of 250 °C with an enthalpy (Δ*H*) of 176.8 J g^{-1}. No exothermic peak was observed at the second scan, indicating that the cross-linking reaction was close to completion and the PFCB-containing siloxane network (**D_4-PFCB**) was formed.



Scheme 1 Procedure for the synthesis of **D_4-TFVE** and **D_4-PFCB**.

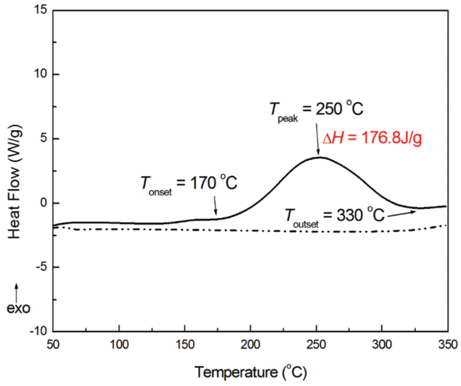


Fig. 2 DSC trace of **D_4-TFVE** at a heating rate of 10 °C min^{-1} in an N_2 atmosphere. The solid line and dash line represent the first and second scan, respectively.

The thermo-crosslinking degree of **D_4-TFVE** was monitored by Fourier transform infrared (FT-IR) spectra. Fig. 3 shows the FTIR spectra of the dendrimeric siloxane before and after the thermo-crosslinking reaction. As depicted in Fig. 3, the characteristic peak centered at 962 cm^{-1}, attributed to the perfluorocyclobutane groups, appeared in the spectrum of **D_4-PFCB** while the peak of trifluorovinyl-ether groups centered at 1830 cm^{-1} disappeared when cross-linked, further indicating that TFVE groups in the macromolecule have completely converted to PFCB units.

In order to investigate whether the eight-membered-ring on **D_4-TFVE** was opened or not during the thermo-crosslinking procedure, a model compound (**D_4-Ph**) was synthesized (Scheme 2). It was observed that both of the freshly prepared **D_4-Ph** and **D_4-TFVE** were colorless with good fluidity (Fig. S8 in the ESI†). When treated at high temperature (170 °C for 2 h

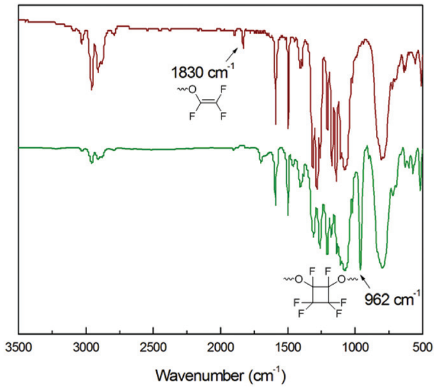
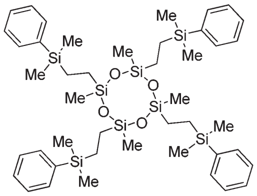


Fig. 3 FT-IR spectra of **D_4-TFVE** and **D_4-PFCB**.



D$_4$-Ph

Scheme 2 Model molecule used to prove the stability of the cyclotetrasiloxane.

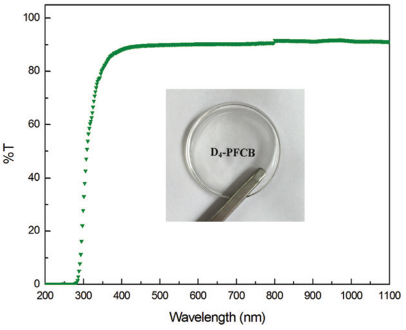


Fig. 5 UV-vis-NIR spectrum of **D$_4$-PFCB** sheet with an average thickness of 1.2 mm. The insert is an image of the **D$_4$-PFCB** sheet.

and 180 °C for 6 h, respectively) in an argon atmosphere, **D$_4$-TFVE** converted into a solid (Fig. S8d†), while **D$_4$-Ph** was still a liquid (Fig. S8b in the ESI†). Moreover, **D$_4$-Ph** showed no difference between its MALDI-TOF-MS data before and after heating at high temperature. In addition, no obvious change was found from the ^{29}Si NMR spectra of **D$_4$-Ph** before and after the heating treatment (Fig. S9 in the ESI†). These data implied that the eight-membered-ring on **D$_4$-TFVE** was highly stable during the period of the [2π + 2π] reaction.

Cross-linking procedures have been widely applied to improve the heat-resistance of polymer materials.[17,23–25] In this work, the cross-linked structure **D$_4$-PFCB** also shows high thermal stability. As shown in Fig. 4, the 5 wt% loss temperature of **D$_4$-PFCB** occurred at 441 °C, which was consistent with the previously reported PFCB-functionalized polymers.[20,21,26] Such a high thermal stability suggests that **D$_4$-PFCB** can be used as heat-resistant materials.

D$_4$-PFCB was colorless and highly transparent. Fig. 5 (see the insert) shows a top view of a **D$_4$-PFCB** sheet. The letters under the sheet could be clearly observed, indicating the excellent transmittance of **D$_4$-PFCB**. The UV-vis-NIR spectrum of the **D$_4$-PFCB** sheet with an average thickness of 1.2 mm showed that it possessed transmittances of higher than 91% at a range of wavelengths from 400 to 1100 nm (Fig. 5). Usually, polymers with high transmittance do not have high thermal stability.[27] For example, PMMA shows high transmittance, whereas its thermal stability is not satisfactory. In our case, **D$_4$-PFCB** exhibits both high transmittance and good thermal stability, suggesting that it can be used as a heat-resistant optical material.

Polyorganosiloxanes usually show *k* values of more than 2.8, which need to be further decreased to meet the requirements from the electrical/electronics industry.[10] It is found that the introduction of fluoro-containing units into the side chain of organic polysiloxanes can efficiently decrease the *k* values of the polymers.[18] In our case, the cross-linking of **D$_4$-TFVE** gives the silicon-containing polymer with perfluorocyclobutane (PFCB) units. Previously, we found that the PFCB units could endow the polymers with good dielectric properties.[9] In this work, **D$_4$-PFCB** shows constant *k* values at frequencies ranging from 40 Hz to 30 MHz, as shown in Fig. 6. For example, it shows a *k* value of 2.38 at 1 MHz and 2.35 at 30 MHz, respectively. These data are lower than most organosiloxanes, indicating that introducing PFCB groups into organosiloxanes can also improve the dielectric properties of the materials.

Water uptake of **D$_4$-PFCB** was measured by immersing it into boiling water (near 98 °C), and maintaining it at this boiling temperature for an appropriate time. Table 1 shows the water absorption of the **D$_4$-PFCB** sheet at a certain period of time. As can be seen from Table 1, **D$_4$-PFCB** exhibits very low water absorption of about 0.11% even after immersing in boiling water for 100 h. Both the good dielectric properties

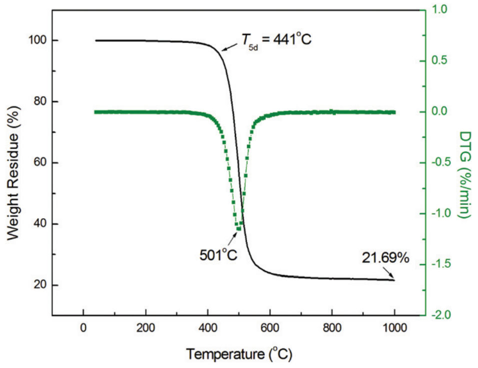


Fig. 4 TGA curves of the cross-linked **D$_4$-PFCB**.

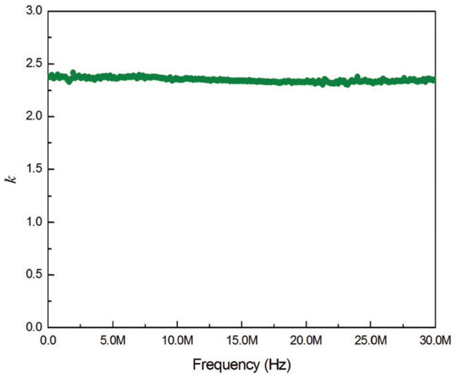


Fig. 6 Dielectric constants (*k*) of **D$_4$-PFCB** depending on the frequencies.

Table 1 Water absorption of D_4-PFCB measured in boiling water[a]

Time (h)	5	18	24	48	72	100
Water uptake (%)	0.11	0.13	0.13	0.11	0.11	0.11

[a] The data were obtained according to the procedure previously reported.[9] The thickness of the sample was 0.8 mm with a diameter of 20 mm.

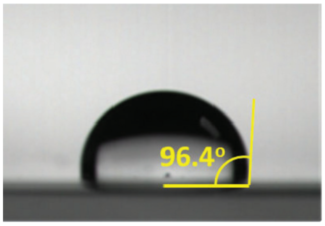


Fig. 7 Contact angle of water on the D_4-PFCB film.

and low water absorption imply the wide potential applications of **D_4-PFCB** while polymers having both ultra-low *k* and water uptake are rare.

The contact angle of water on the polymer film was measured to investigate the reason why **D_4-PFCB** showed such low water absorption. As can be seen from Fig. 7, the cross-linked **D_4-PFCB** film shows an average contact angle of about 96.4°, indicating high hydrophobicity of **D_4-PFCB**. Such good hydrophobicity renders the polymer with low water absorption, ensuring its reliability while working under moist conditions.

Conclusions

A new fluoro-containing dendrimeric macromolecule (**D_4-TFVE**) with cyclic organosiloxane as the core and trifluorovinyl-aryl-ether ($Ar–OCF{=}CF_2$) as the arms was successfully prepared. Through a heat-induced polymerization procedure, **D_4-TFVE** changed to a cross-linked network (**D_4-PFCB**), which exhibited good thermostability, ultra-low dielectric constant, as well as low water uptake. In particular, **D_4-PFCB** also showed high transparency. The good properties of the polymer suggests that it may have potential application in the microelectronics industry as the encapsulation resin for integrated circuit (IC) dies, as well as the laminated matrix utilized for production of high-frequency printed circuit boards in the electrical industry. Importantly, the directly thermocrosslinking procedure is of considerable industrial importance, which provides a new route for the cross-linking of organosiloxanes to replace the general routes using catalysts or initiators.

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