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Dendrimeric Organosiloxane with Thermopolymerizable -OCF=CF₂ Groups as the Arms: Synthesis and Transformation to the Polymer with both Ultra-low *k* and low Water Uptake

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Jiajia Wang, Kaikai Jin, Jing Sun, Qiang Fang*

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A novel fluoro-containing dendrimeric macromolecule with cyclic siloxane as a core and aryl-trifluorovinyl-ether (-OCF=CF₂) 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 the low dielectric constants (*k*) materials in electronic industries.¹⁻⁵ For this application, polymers need to be converted to insoluble and infusible cross-linked networks to meet the rising requirements of the electronic devices.⁶⁻¹³ In order to realize cross-linking, two ways 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 dielectric properties of the materials. Thus, development of polysiloxanes having directly thermo-crosslinkable groups is required. Up to date, although a series of thermo-crosslinking polysiloxanes have been reported,^{6, 10} their expensive cost and complicated synthetic procedure may hinder applications of the polymers in broader areas. Furthermore, the *k* values of organosiloxanes-based materials which have been reported with 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 electrical/electronic industries.

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 low dielectric constant and high thermostability.¹⁸ To overcome the synthetic difficulty of the

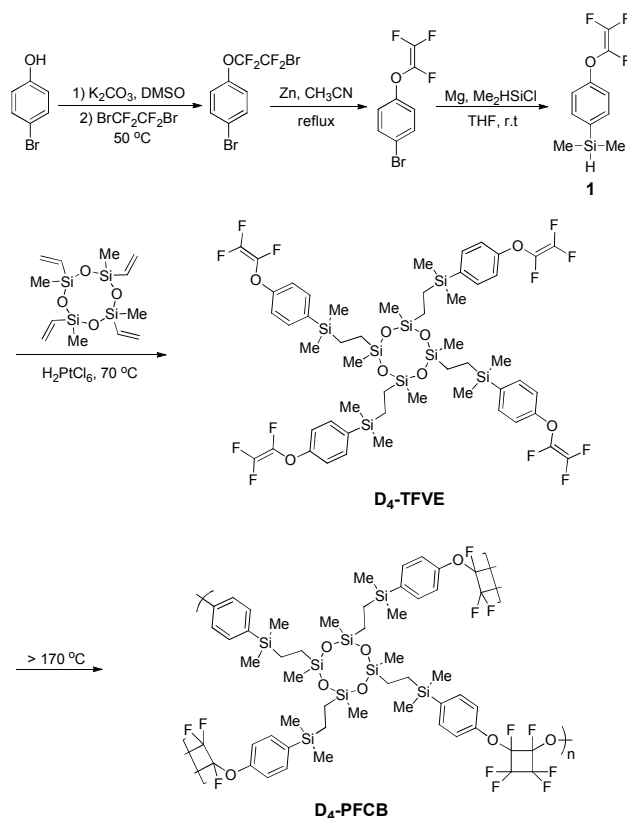
polymer on a large scale, we designed and synthesized a new fluoro-containing dendrimeric macromolecule with cyclic siloxane as a core and TFVE units as the arms. Such macromolecule was easily synthesized and purified. When heated to a high temperature, it can convert to a cross-linked structure, which showed an ultra-low *k* and very low water uptake. Moreover, the cross-linked network exhibited high transparency with the 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 matrix for the production of high-frequency printed circuit boards, as well as the encapsulation resins in the microelectronic industries. 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 (**D₄-TFVE**) was synthesized by the platinum-catalyzed hydrosilylation reaction between compound **1**¹⁹ and a commercial cyclotetrasiloxane (D₄^V) in the absence of solvent. The crude **D₄-TFVE** was easily purified. The pure product, showing a purity of 99.46% (HPLC), was a colorless liquid with low viscosity, suggesting its good process ability. GPC data showed (Fig. S6 in Supplementary Information) that the number-average molecular weight (*M_n*) of **D₄-TFVE** was 1,398 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 mono-dispersed *M_n* also reflected that no polymerization occurred during the hydrosilylation reaction. The chemical structure of **D₄-TFVE** was also characterized by NMR spectra. Fig. 1 showed ¹³C NMR and ²⁹Si NMR spectra of **D₄-TFVE**. As shown in Fig. 1, there were only two kinds of signals in ²⁹Si NMR spectra. The signal at -0.42 ppm referred to the Si atoms connecting to the benzene while -19.26 ppm was attributed to the Si atoms on the ring of cyclotetrasiloxane. The NMR data indicate that vinyl groups have been totally transformed, and TFVE groups are

Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China. E-mail: qiangfang@mail.sioc.ac.cn. Electronic Supplementary Information (ESI) available: Experimental routes, characterizations of the organosiloxanes. See DOI: 10.1039/x0xx00000x

successfully introduced into the cyclic organosiloxane as the four arms in **D₄-TFVE**.



Scheme 1 Procedure for the synthesis of **D₄-TFVE** and **D₄-PFCB**.

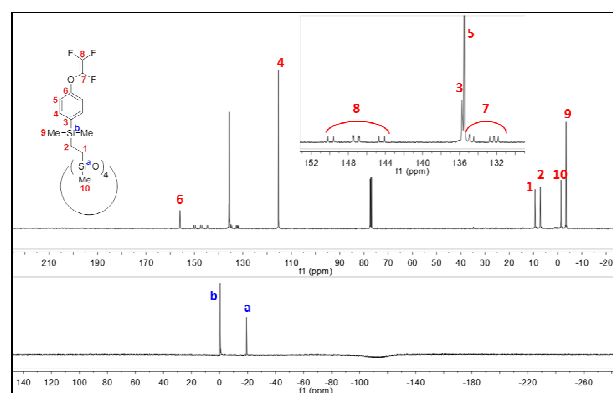


Fig. 1 ^{13}C NMR (up) and ^{29}Si NMR (down) spectra of **D₄-TFVE**.

TFVE groups can be transformed into perfluorocyclobutane (PFCB) units via a [2 π +2 π] reaction at high temperature (Scheme 1) without release of volatiles.^{9, 20–22} In our case, such transformation of **D₄-TFVE** was evaluated by differential scanning calorimetry (DSC). As can be seen from Fig. 2, **D₄-TFVE** showed a wide curing temperature ranging from 170°C to 330°C , giving a peak temperature of 250°C with an enthalpy (ΔH) of 176.8 J/g . 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 (**D₄-PFCB**) was formed.

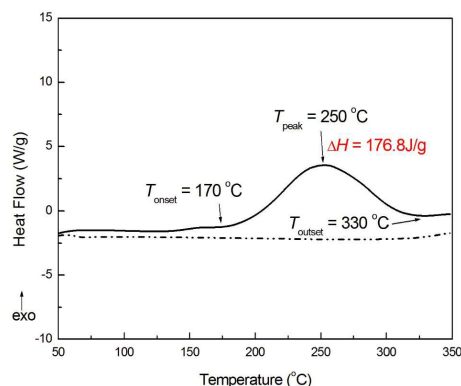


Fig. 2 DSC trace of **D₄-TFVE** at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere. The solid line and dash line represent the first and second scan, respectively.

The thermo-crosslinking degree of **D₄-TFVE** was monitored by Fourier transform infrared (FT-IR) spectra. Fig. 3 showed the FTIR spectra of the dendrimeric siloxane before and after thermo-crosslinking reaction. As depicted in Fig. 3, the characteristic peak centered at 962 cm^{-1} , attributed to the perfluorocyclobutane groups, was appeared in the spectrum of **D₄-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.

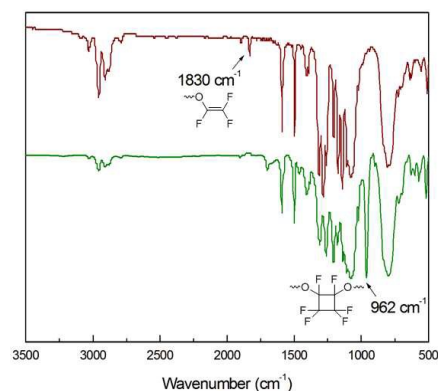
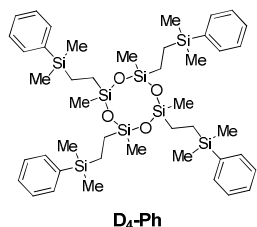


Fig. 3 FT-IR spectra of **D₄-TFVE** and **D₄-PFCB**.

In order to investigate whether the eight-membered-ring on **D₄-TFVE** was opened or not during the thermo-crosslinking procedure, a model compound (**D₄-Ph**) was synthesized (Scheme 2). It was observed that both of the freshly prepared **D₄-Ph** and **D₄-TFVE** were colorless with good fluidity (Fig. S8 in Supplementary Information). When treated at high temperature (170°C for 2 h and 180°C for 6 h, respectively) in argon atmosphere, **D₄-TFVE** converted into a solid

(Fig. S8, d), while **D₄-Ph** was still a liquid (Fig. S8, b in Supplementary Information). Moreover, **D₄-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 ²⁹Si NMR spectra of **D₄-Ph** before and after the heating treatment (Fig. S9 in Supplementary Information). These data implied the eight-membered-ring on **D₄-TFVE** was highly stable during the period of the [2π+2π] reaction.



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

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 **D₄-PFCB** also shows high thermal stability. As shown in Fig. 4, the 5 wt% loss temperature of **D₄-PFCB** occurred at 441 °C, which was consistent with the previously reported PFCB-functionalized polymers.^{20, 21, 26} Such high thermal stability suggests that **D₄-PFCB** can be used as the heat-resistant materials.

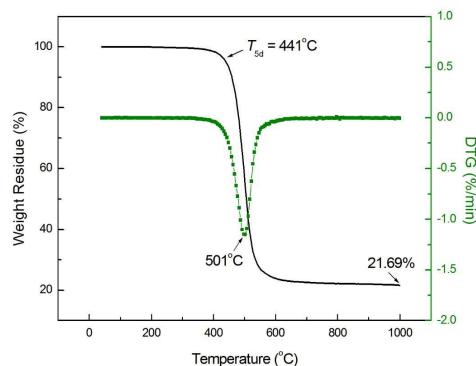


Fig. 4 TGA curves of the cross-linked **D₄-PFCB**.

D₄-PFCB was colorless and highly transparent. Fig. 5 (see the insert) showed a top view of a **D₄-PFCB** sheet. The letters under the sheet could be clearly observed, indicating the excellent transmittance of **D₄-PFCB**. UV-vis-NIR spectrum of a **D₄-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, **D₄-PFCB** exhibits both high transmittance and good

thermal stability, suggesting that it can be used as the heat-resistant optical materials.

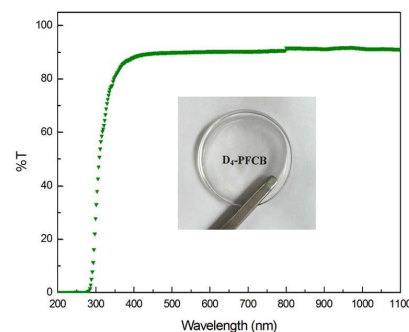


Fig. 5 UV-vis-NIR spectrum of **D₄-PFCB** sheet with an average thickness of 1.2 mm. The insert is an image of the **D₄-PFCB** sheet.

Polyorganosiloxanes usually show *k* values of more than 2.8, which need to be further decreased to meet the requirements from electrical/electronic industries.¹⁰ It is found that the introducing 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 **D₄-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, **D₄-PFCB** shows constant *k* values at the frequencies ranging from 40 Hz to 30 MHz, as shown in Fig. 6. For example, it shows *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.

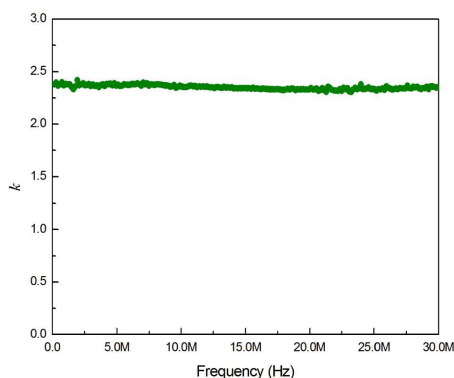


Fig. 6 Dielectric constants (*k*) of **D₄-PFCB** depending on the frequencies.

Water uptake of **D₄-PFCB** was measured by immersing it into boiling water (near 98 °C), and maintaining at this boiling temperature for proper time. Table 1 showed the water absorption of **D₄-PFCB** sheet in a certain period of time. As can be seen from Table 1, **D₄-PFCB** exhibits very low water absorption of about

0.11 % even after immersing in boiling water for 100 h. Both the good dielectric properties and low water absorption imply the wide potential applications of **D₄-PFCB** while the polymers having both ultra-low *k* and water uptake are rare.

Table 1 Water absorption of **D₄-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.

Contact angle of water on polymer film was measured to investigate the reason why **D₄-PFCB** showed such low water absorption. As can be seen from Fig. 7, cross-linked **D₄-PFCB** film shows an average contact angle of about 96.4°, indicating high hydrophobicity of **D₄-PFCB**. Such good hydrophobicity offers the polymer with low water absorption, ensuring its reliability while working at moisture.

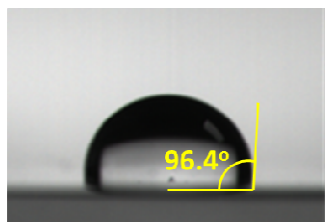


Fig. 7 Contact angle of water on the **D₄-PFCB** film.

Conclusions

A new fluoro-containing dendrimeric macromolecule (**D₄-TFVE**) with cyclic organosiloxane as the core and trifluorovinyl-aryl-ether (Ar-OCF=CF₂) as the arms was successfully prepared. Through a heat-induced polymerization procedure, **D₄-TFVE** changed to a cross-linked network (**D₄-PFCB**), which exhibited good thermostability, ultra-low dielectric constant, as well as low water uptake. In particular, **D₄-PFCB** also showed high transparency. The good properties of the polymer suggests that it may have potential application in microelectronics industry as the encapsulation resins for integrated circuit (IC) dies, as well as the laminated matrix utilized for production of high-frequency printed circuit boards in electrical industry. Importantly, the directly thermocrosslinking procedure is of considerable industrial importance, which provides a new way for the cross-linking of organosiloxanes to replace the general routes using catalysts or initiators.

Acknowledgements

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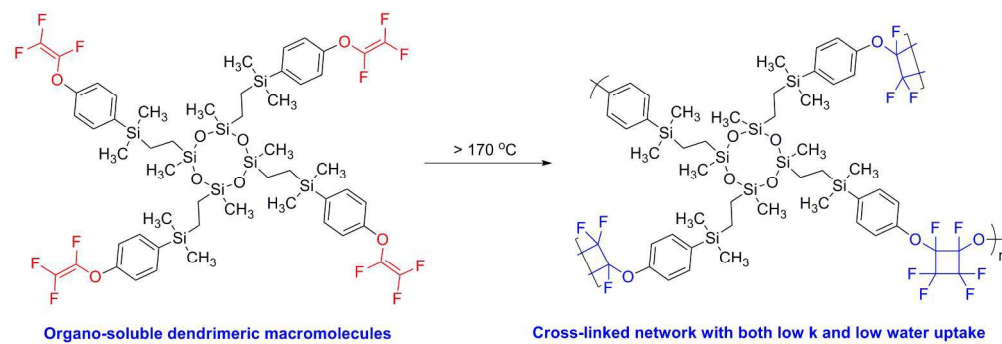
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