

Synthesis of Phosphorus-Containing Polyhedral Oligomeric Silsesquioxanes via Hydrolytic Condensation of a Modified Silane

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ABSTRACT: A simple route to synthesize a new type of phosphorus-containing polyhedral oligomeric silsesquioxanes (DOPO-POSS) in high yield, by the hydrolytic condensation of a modified silane, is reported. The starting material was a phosphorus-containing triethoxy silane (DOPO-VTES), which was synthesized by addition reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and vinyl triethoxy silane (VTES). This product was subjected to hydrolytic condensation using an HCl catalyst in methanol. The new types of phospho-

rus-containing POSS were obtained and characterized using ^1H , ^{13}C , ^{29}Si -NMR, MALDI-TOF MS, XRD, DSC, and FTIR. All of these results suggested that the DOPO-POSS were amorphous mixtures of T_8 , $T_9(\text{OH})$, and TGA curve of DOPO-POSS shows that the cage-like compound has high thermal stability. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3383–3389, 2011

Key words: organic-inorganic hybrid; polyhedral oligomeric silsesquioxanes; phosphorus

INTRODUCTION

Hydrolytic condensation of the organotrialkoxysilanes, $\text{RSi}(\text{OR}'_3)$, performed in the presence of water and an acid or base as catalysts, leads to oligomeric or polymeric products that are generically called silsesquioxanes.¹ These polymers have acquired increasing importance for the synthesis of functionalized organic-inorganic hybrid materials.² Species present in a silsesquioxanes may vary from perfect polyhedra of formula $(\text{RSiO}_{1.5})_n$ or T_n , where n is an even number ($n \geq 6$), and R is hydrogen or any alkyl, alkylene, aryl, arylene, or organofunctional derivatives of alkyl, alkylene, aryl, arylene groups, denoted as polyhedral oligomeric silsesquioxanes (POSS), to partially condensed (but completely hydrolyzed) products of generic formula $T_n(\text{OH})_m$, where $T = \text{RSiO}_{1.5-m/2n}$.³⁻⁵ These organic-inorganic hybrid materials have attracted great interest in recent years, because of the combination of properties derived from the organic and inorganic components.⁶ POSS molecules with a nanosized cage-shaped three-

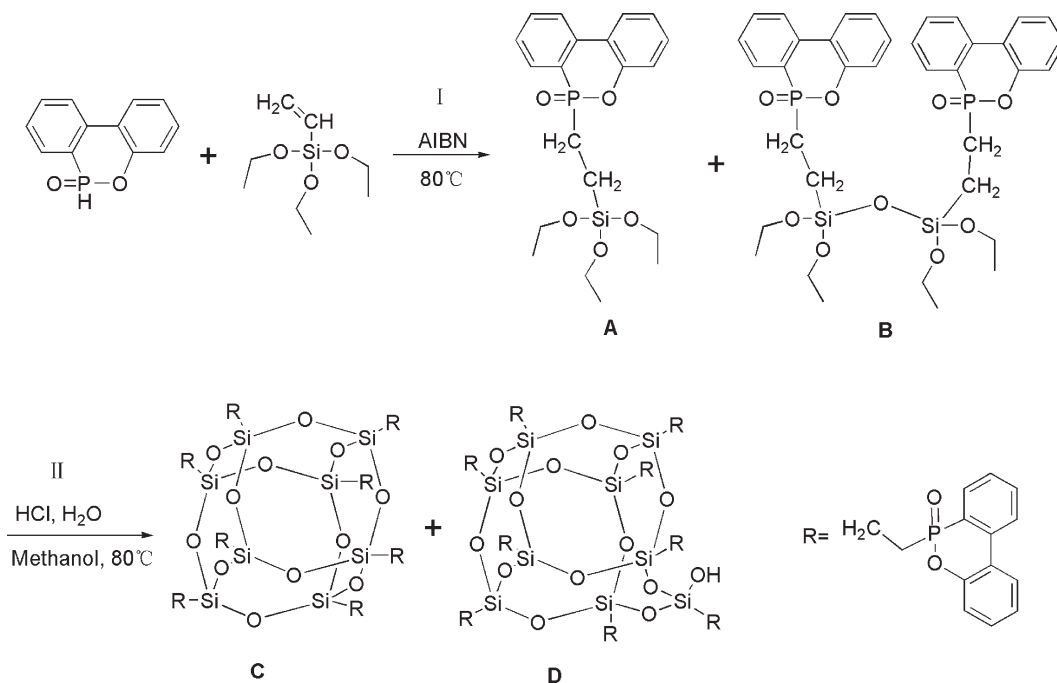
dimensional structure can be incorporated into almost all kinds of thermoplastic or thermosetting polymers by blending, grafting, crosslinking, or copolymerization to improve their mechanical and thermal properties, oxidation resistance, and reduced flammability.^{6,7}

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a kind of cyclic phosphate, whose P-H group shows high reactivity toward the double C=C bond group. Furthermore, DOPO has high thermal stability, oxidation resistance, and good water resistance. DOPO and its derivatives have been widely incorporated into polymers, such as the epoxy resin, for improving their flame-retardant properties and thermal stability.^{8,9} Our current studies aim at preparing a new type of caged phosphorus-containing silsesquioxanes by introducing DOPO to a silsesquioxanes molecules.

To the best of our knowledge, most of the works reported on phosphorus-containing silsesquioxanes have been one-pot synthesis, where silsesquioxanes monomers and phosphorus-containing monomers were mixed together prior to the reaction process.¹⁰⁻¹² Preparation of a series of phosphorus-containing silsesquioxanes by Arbuzov reaction has been published by Feher et al.¹³ Moreover, using simple organic/inorganic reactions (nucleophilic substitution and radical addition) researchers have introduced different phosphorus substituents (PR_2 , $\text{R} = \text{Et}, \text{Me}, \text{Ph}$) on the periphery of silsesquioxanes.¹⁴⁻¹⁷ However, synthesis of

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Scheme 1 Schematic illustration for the preparation of DOPO-VTES and DOPO-POSS.

these phosphorus-containing POSS were restricted by absence of the $\text{RSi}(\text{OR}'_3)$ or RSiCl_3 silane, which has phosphorus-containing group R, and by long time spending and low yield in preparation of functional

POSS monomers, such as $(\text{ClCH}_2\text{CH}_2\text{CH}_2)_8\text{Si}_8\text{O}_{12}$ and $(\text{CH}_2=\text{CH})_8\text{Si}_8\text{O}_{12}$.^{18,19}

In this article, we report a new approach to the synthesis of phosphorus-containing POSS and

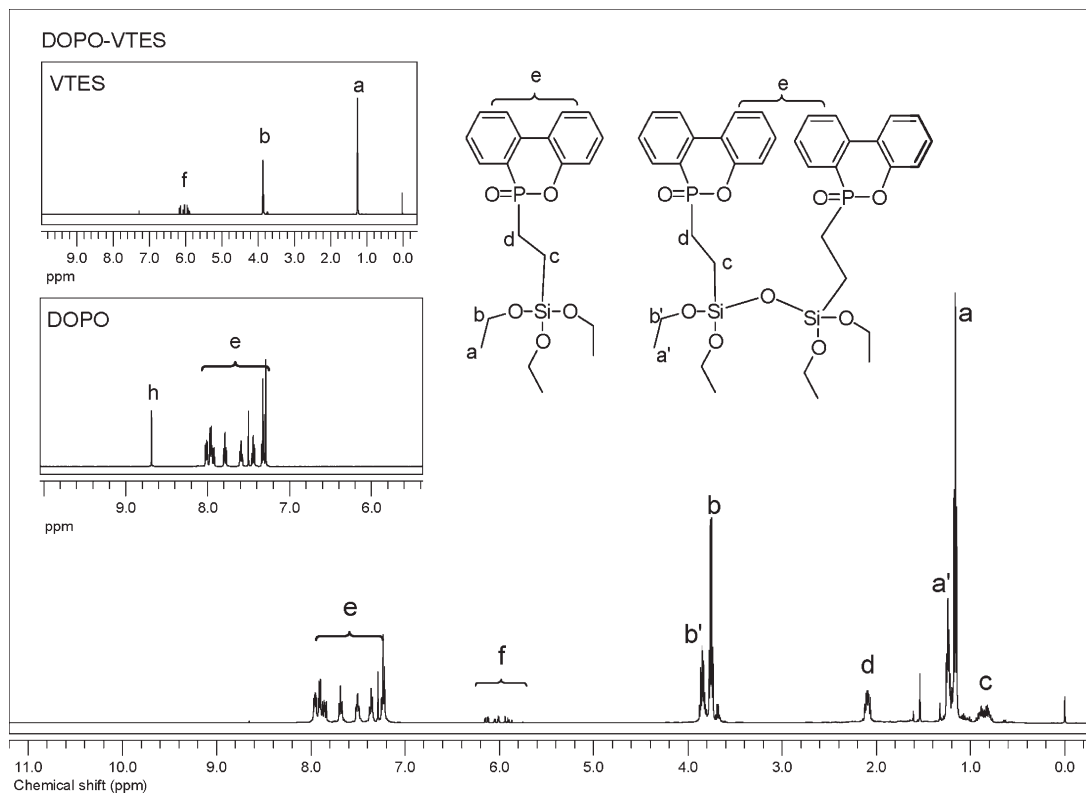


Figure 1 ^1H -NMR spectra obtained for VTES, DOPO, and DOPO-VTES.

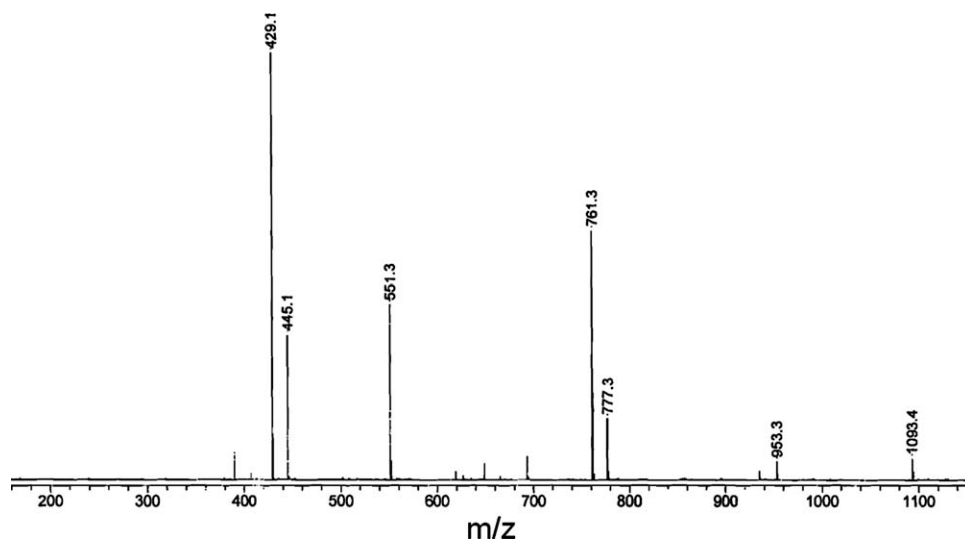


Figure 2 Mass spectra of DOPO-VTES.

provide characterization results of these new type silsesquioxanes. First, addition reaction between the P-H group of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and the C=C bond of vinyl triethoxy silane (VTES) was used to synthesize a new DOPO-containing triethoxy silanes (DOPO-VTES); second, DOPO-containing polyhedral oligomeric silsesquioxanes (DOPO-POSS) were synthesized in high yield through hydrolytic condensation of the DOPO-VTES. The pathway of the synthesis of DOPO-containing polyhedral oligomeric silsesquioxanes can be presented in Scheme 1.

EXPERIMENTAL

Materials

Methanol (99.7%), concentrated hydrochloric acid (HCl, 36.5%), and azobisisobutyronitrile (AIBN, 99.5%) were purchased from Beijing Chemical Works. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was

purchased from Eutec Trading (Shanghai) Co. Vinyl triethoxy silane (VTES) was purchased from Ark (Fogang) Chemicals Industry Co. All materials were used without further purification.

Sample preparation

DOPO-VTES Synthesis: The addition reaction between VTES (10 g) and DOPO (10.8 g) was catalyzed by azobisisobutyronitrile (0.164 g). Temperature was held at 80°C for 10 h, leading to the DOPO-containing triethoxy silanes (DOPO-VTES) (19.6 g, yield: 97%). DOPO-VTES was a light yellow liquid.

DOPO-POSS Synthesis: The hydrolytic condensation of the DOPO-VTES (10 g) was performed in methanol (50 mL) solution, using HCl (3 mL) as a catalyst. Temperature was held at 80°C for 24 h. The leading DOPO-POSS mixtures were obtained as a white powder after suction filtration and rinsing with deionized water (5.9 g, yield: 81%).

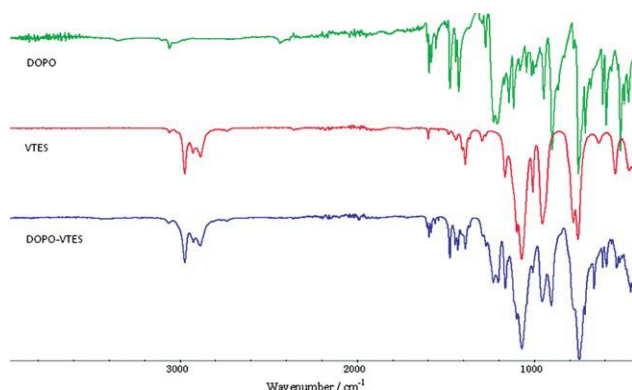


Figure 3 FTIR spectra obtained for DOPO, VTES, and DOPO-VTES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Measurements

Nuclear Magnetic Resonance (NMR) Spectroscopy: ^1H - and ^{13}C -NMR spectra were recorded on Bruker Avance 500 NMR spectrometer operated in the Fourier transform mode. CDCl_3 was used as the solvent, and the solution was measured with tetramethylsilane (TMS) as an internal reference. ^{29}Si -NMR spectra were recorded on Bruker Avance 600 NMR spectrometer, and CDCl_3 was used as the solvent.

Fourier Transform Infrared (FTIR) Spectroscopy: FTIR spectra were recorded on a NICOLET 6700 IR spectrometer. The spectra were collected at 32 scans with a spectral resolution of 4 cm^{-1} .

Mass Spectrometry: Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

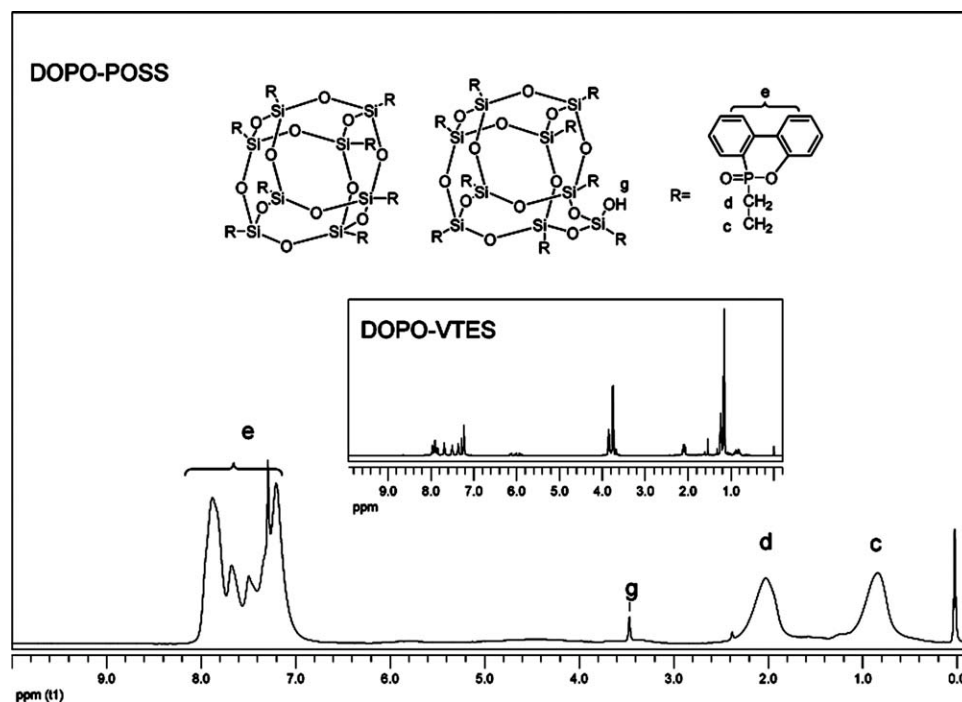


Figure 4 $^1\text{H-NMR}$ spectra of DOPO-VTES and DOPO-POSS.

(MALDI-TOF MS) was performed using a Bruker BIFLEX III device. It was equipped with a pulsed nitrogen laser ($\lambda = 337$ nm, pulse width = 3 ns, and average power = 5 mW at 20 Hz). The extraction voltage in TOF analyzers was 20 kV, and ions were obtained by irradiation just above the threshold laser power (about 1/3 of the average laser power). Samples were measured in positive ion modes. Usually 50 spectra were accumulated. The MALDI mass spectrum using α -Cyano-4-hydroxycinnamic acid matrix and the salts are the mixture of NaCl and KCl.

The thermal gravimetric analysis (TGA) was performed with a NETZSCH 209 F1 thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere, and the temperature ranged from room temperature to 800°C .

RESULTS AND DISCUSSION

DOPO-VTES

DOPO-VTES was prepared by addition reaction between vinyl triethoxy silane (VTES) and 9,10-dihydro-

9-oxa-10-phosphaphenanthrene-10-oxide (DOPO); its schematic illustration is shown in Scheme 1 (I). FTIR (KBr, cm^{-1}): 3037–3100 (biphenyl), 2876–2988, 1391, 959 ($-\text{CH}_2-\text{CH}_3$), 1477 (P-biphenyl), 1207 (P=O), 1069 (Si–O), 909 (P–O–biphenyl). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm, TMS): 0.74–0.88 (2H, Si– CH_2 –), 1.07–1.25 (9H, $-\text{CH}_3$), 2.05–2.11 (2H, P– CH_2 –), 3.65–3.88 (6H, O– CH_2 –), 7.00–7.88 (6H, H in biphenyl group).

$^1\text{H-NMR}$ spectra of the DOPO-VTES, VTES, and DOPO were shown in Figure 1. Compared with those of the two precursors, the new signals observed at 0.86 and 2.1 ppm (peaks c, and d) for the DOPO-VTES are ascribed to methylene protons in Si– CH_2 and P– CH_2 , respectively. Furthermore, signal of P–H at 8.68 ppm (peak h) for the DOPO almost completely disappeared, and very small amount of the unreacted vinyl group at 5.9–6.2 ppm (peaks f) for the VTES were observed, in the spectra of the DOPO-VTES. The split signals of methylene (b and b') and methyl (a and a') protons may correspond to the DOPO-VTES dimer.

MALDI-TOF MS analysis for the DOPO-VTES (Fig. 2) exhibited another evidence of the DOPO-VTES dimer. The theoretical m/z values for the compounds A and B as shown in Scheme 1 should be 406.1 and 738.2 (m/z), respectively. The detected molecular ions corresponding to the ionization with Na^+ and K^+ are 429.1 [A + Na^+] $^+$, 445.1 [A + K^+] $^+$, 761.3 [B + Na^+] $^+$, and 777.3 [B + K^+] $^+$ (m/z).

FTIR spectra analysis for the products of addition reaction between DOPO and VTES (Fig. 3) implied disappearance of the absorbance peak in the region

TABLE I

Assignment of MALDI-TOF MS Peaks of DOPO-POSS

Assignment ^a	Calcd. m/z	Exptl. m/z
C	2383.2(+ Na^+)	2384.7
C	2361.2(+ H^+)	2361.7
D	2687.2(+ Na^+)	2688.7
D-OH	2647.2(+ H^+)	2647.7

^a Molecular structures of C and D are shown in Scheme 1.

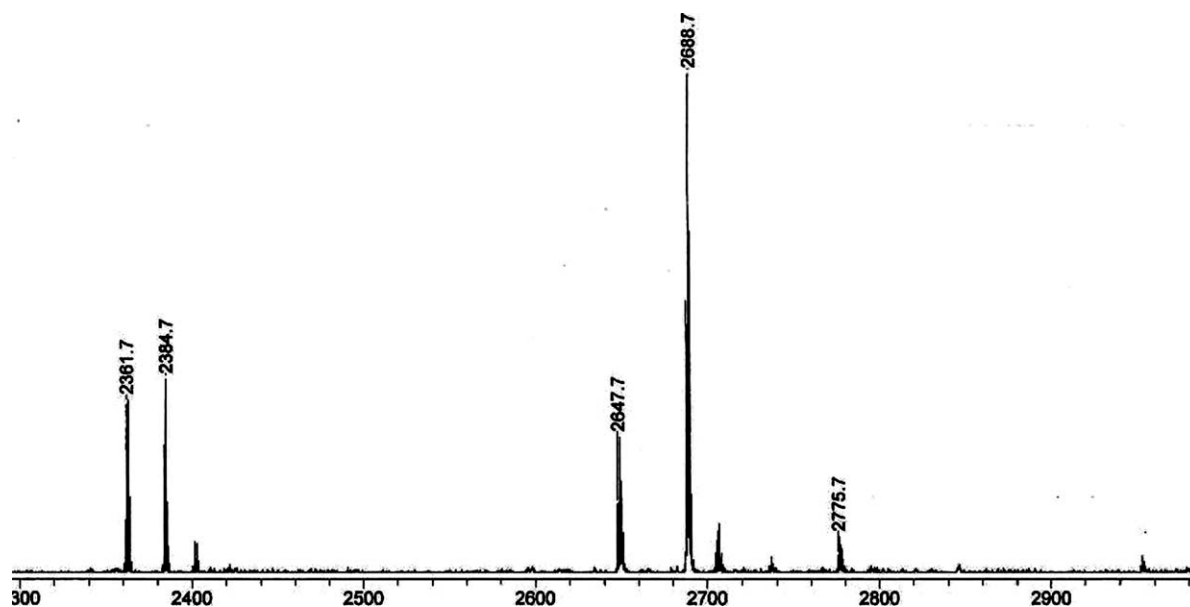


Figure 5 Mass spectra of DOPO-POSS.

around 2436 cm^{-1} , which is characteristic of P—H group of DOPO, and existence of the characteristic P—O—C, P=O, and P—phenyl absorbance peaks at 909, 1206, and 1477 cm^{-1} , for DOPO-VTES, as compared to VTES and DOPO, respectively.

DOPO-POSS

DOPO-containing polyhedral oligomeric silsesquioxanes (DOPO-POSS) were obtained from DOPO-VTES via hydrolytic condensation using an HCl catalyst under mild conditions (Scheme 1 II). FTIR (KBr, cm^{-1}): 3200–3250 (Si—OH), 3017–3080 (biphenyl), 2863–2954 ($\text{CH}_2\text{—CH}_2$), 1477 (P—biphenyl), 1207 (P=O), 1085 (Si—O—Si), 909 (P—O—biphenyl). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm, TMS): 0.74–0.88 (2H, Si— $\text{CH}_2\text{—}$), 1.20–1.26 (2H, P— $\text{CH}_2\text{—}$), 3.46 (1H, Si—OH), 7.00–7.88 (6H, H in biphenyl group). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm, TMS): 3.8 (Si— $\text{CH}_2\text{—}$), 21.8 (P— $\text{CH}_2\text{—}$), 120.4–149.0 (C in the biphenyl group and

vinyl). $^{29}\text{Si-NMR}$ (CDCl_3 , δ , ppm): 59.4 (Si—OH), 67.9 and 69.7 (Si atoms of completely condensation).

Figure 4 shows $^1\text{H-NMR}$ spectra of the DOPO-VTES and DOPO-POSS. It is observed that the signals at 1.2–1.26 ppm and 3.83–3.88 ppm ascribed to methyl and methylene protons in O— $\text{CH}_2\text{—CH}_3$ of DOPO-VTES disappear in the spectra of DOPO-POSS. In addition, a new signal at 3.46 ppm (peak g) for the DOPO-POSS is ascribed to hydroxyl proton in Si—OH in DOPO-VTES.

Results of MALDI-TOF MS analysis for the DOPO-POSS were listed in Table I and Figure 5. Molecular ions identified are corresponding to the ionization with Na^+ or H^+ . It is verified that the hydrolytic condensation products of the DOPO-VTES were a mixtures of T_8 , $\text{T}_9(\text{OH})$, including main two kinds of structures shown in Scheme 1 (C and D).

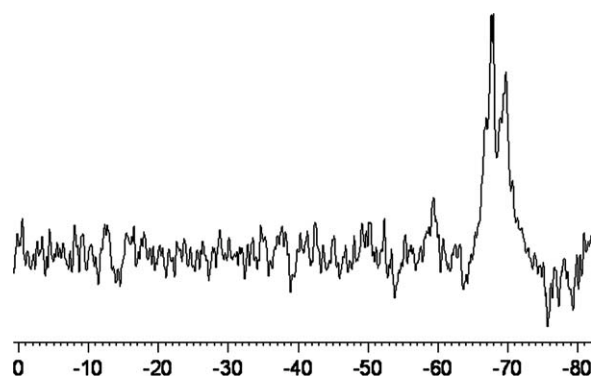


Figure 6 $^{29}\text{Si-NMR}$ spectra of DOPO-POSS (ppm).

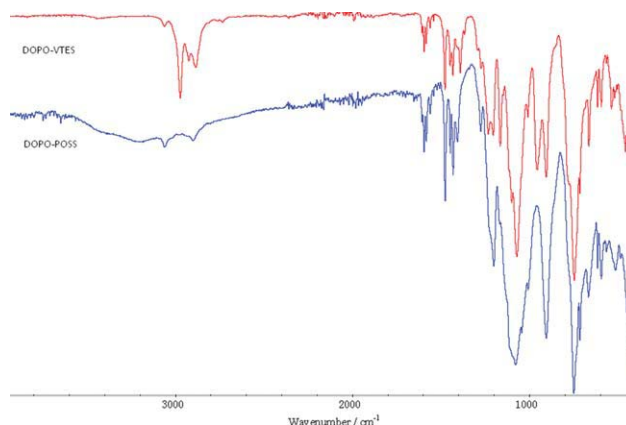


Figure 7 FTIR spectra obtained for DOPO-VTES and DOPO-POSS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

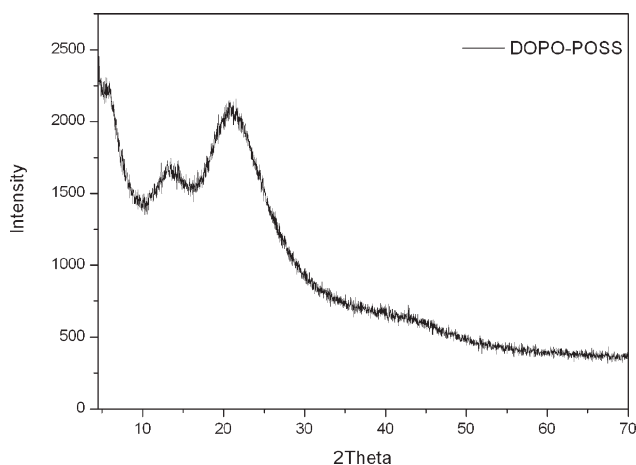


Figure 8 XRD pattern of DOPO-POSS.

^{29}Si -NMR spectra of the DOPO-POSS were shown in Figure 6. Main peaks were observed around 59.4, 67.9, and 69.7 ppm. Si-OH groups were reported in the region -57 to -61 ppm,³ and Si atoms in perfect or imperfect caged POSS structures were found in the region -65 to -80 ppm for different R substituents.^{3,20,21} Therefore, the signal at 59.4 ppm implied that there is very small amount of Si-OH. The split signals at 67.9 and 69.7 ppm indicated main Si atoms of completely condensation connected to DOPO groups, and those groups belong to T_8 and $T_9(\text{OH})$, respectively.

In FTIR spectra of the DOPO-POSS (Fig. 7), the characteristic absorbance of $-\text{O}-\text{CH}_2-\text{CH}_3$ groups at 959, 1391, 2888, 2925, and 2975 cm^{-1} completely disappear, as compared to that of DOPO-VTES. FTIR spectra of the DOPO-POSS showed a strong absorbance band at 1085 cm^{-1} , ascribed to formation of the Si-O-Si bonds. Moreover, characteristic Si-OH absorbance at 3218 cm^{-1} could be observed as well.

The earlier mentioned results from ^1H -NMR, ^{29}Si -NMR spectra, MALDI-TOF MS, and FTIR spectra

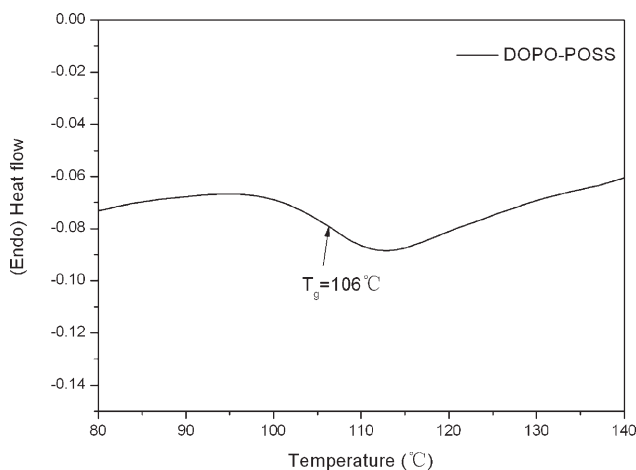


Figure 9 DSC curve of DOPO-POSS.

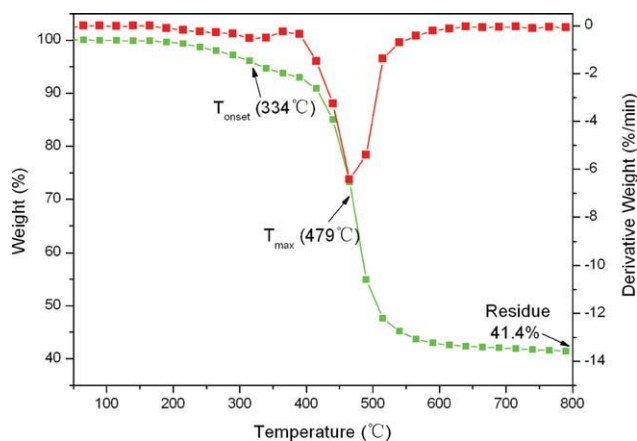


Figure 10 TGA and DTG curves of DOPO-POSS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

supplied evidences from complete hydrolytion of the DOPO-VTES to complete and partial condensation leading to the POSS mixtures of T_8 and $T_9(\text{OH})$, which were shown in Scheme 1 ($T_8 = \text{C}$ and $T_9(\text{OH}) = \text{D}$).

Amorphous DOPO-POSS

The microstructure of the DOPO-POSS was of further interest to be studied by the wide-angle X-ray diffraction (XRD) measurements. XRD profile of DOPO-POSS in Figure 8 indicates that DOPO-POSS is an amorphous composite. Moreover, we can observe a glass transition temperature in DSC curve of DOPO-POSS in Figure 9, which also indicates DOPO-POSS is an amorphous composite. The presence of T_g of DOPO-POSS may be attributed to that the conformation of huge functional groups would change under heating. These movements of huge functional groups induce the irregular arrangement of organic groups in the DOPO-POSS. It is the reason that two broad peaks were observed in XRD measurement, which indicates that the DOPO-POSS is an amorphous composite.

Thermal gravimetric analysis of DOPO-POSS

TGA and DTG curves of DOPO-POSS are presented in Figure 10. We can observe thermal decomposition data, the T_{onset} (334°C), which is defined as the temperature at which 5% weight loss occurs, the T_{max} (479°C), which is defined as the temperature at maximum weight loss rate and the char residue at 800°C in Figure 10. It can be seen that the weight loss in the temperature range of 250–400°C is slow, probably caused by the residual silanol in the DOPO-POSS. A rapid weight loss between 400 and 550°C is also observed, which corresponds to the degradation of silsesquioxane, especially for the degradation of the organic corner groups. Moreover, the residue of

DOPO-POSS at 800°C is 41.4%. As we observed from Figure 10, DOPO-POSS possesses superior thermal stability to common polymeric material; it shows great potential as modifier to thermal properties of plastics.

CONCLUSIONS

A triethoxysilane containing a bulky quinquivalence phosphorus substituent, DOPO-VTES, was synthesized by addition reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and vinyl triethoxy silane (VTES). Polyhedral oligomeric silsesquioxanes of the $T_8 \sim T_9$ caged structures with the DOPO groups (DOPO-POSS) were synthesized by hydrolytic condensation of the DOPO-VTES using HCl as catalyst. MALDI-TOF MS, $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$, XRD, DSC, and FTIR analysis confirmed that the DOPO-POSS products were amorphous mixtures of T_8 and $T_9(\text{OH})$. Thermal gravimetric analysis showed that the cage compound had superior thermal stability to common polymeric materials. This kind of the POSS combining phosphorus with silicon will be useful in flame retardant polymer materials.

References

1. Fasce, D. P.; Williams, R. J. J.; Erra-Balsells, R.; Ishikawa, Y.; Nonami, H. *Macromolecules* 2001, 34, 3534.
2. Unno, M.; Alias, S. B.; Saito, H.; Matsumoto, H. *Organometallics* 1996, 15, 2413.
3. Fasce, D. P.; Williams, R. J. J.; Méchin, F.; Pascault, J. P.; Llauro, M. F.; Pétiaud, R. *Macromolecules* 1999, 32, 4757.
4. Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem Rev* 1995, 95, 1409.
5. dell'Erba, I. E.; Fasce, D. P.; Williams, R. J. J.; Erra-Balsells, R.; Fukuyama, Y.; Nonami, H. *J Organomet Chem* 2003, 686, 42.
6. Zhang, W. A.; Fang, B.; Walther, A.; Müller, A. H. E. *Macromolecules* 2009, 42, 2563.
7. Zhang, Z. P.; Liang, G. Z.; Lu, T. L. *J Appl Polym Sci* 2007, 103, 2608.
8. Zhong, H. F.; Wei, P.; Jiang, P. K.; Wang, G. L. *Fire Mater* 2007, 31, 411.
9. Lin, C. H.; Feng, C. C.; Hwang, T. Y. *Eur Polym Mater* 2007, 43, 725.
10. Fei, Z. F.; Schmutzler, R.; Edelman, F. T. Z. *Anorg Allg Chem* 2003, 629, 353.
11. Lee, A.; Xiao, J.; Feher, F. J. *Macromolecules* 2005, 38, 438.
12. Hong, B.; Thoms, T. P. S.; Murfee, H. J.; Lebrum, M. *J Inorg Chem* 1997, 36, 6146.
13. Feher, F. J.; Schwab, J. J.; Phillips, S. H.; Eklund, A.; Martinez, E. *Organometallics* 1995, 14, 4452.
14. Ropartz, L.; Morris, R. E.; Foster, D. F.; Cole-Hamilton, D. J. *Chem Commun* 2001, 4, 361.
15. Ropartz, L.; Morris, R. E.; Foster, D. F.; Cole-Hamilton, D. J. *J Mol Catal A-Chem* 2002, 182, 99.
16. Ropartz, L.; Morris, R. E.; Schwarz, G. P.; Foster, D. F.; Cole-Hamilton, D. J. *J Inorg Chem Commun* 2000, 3, 714.
17. Lücke, S.; Stoppek-Langner, K.; Kuchinke, J.; Krebs, B. *J Organomet Chem* 1999, 584, 11.
18. Ge, Z. S.; Wang, D.; Zhou, Y. M.; Liu, H. W.; Liu, S. Y. *Macromolecules* 2009, 42, 2903.
19. Yang, B. H.; Li, J. R.; Wang, J. F.; Xu, H. Y.; Guang, S. Y.; Li, C. *J Appl Polym Sci* 2009, 111, 2963.
20. Tanabe, M.; Mutou, K.; Mintcheva, N.; Osakada, K. *Organometallics* 2008, 27, 519.
21. Kim, S. G.; Choi, J.; Tamaki, R.; Laine, R. M. *Polymer* 2005, 46, 4514.