



## Polycyclic siloxanes: Base resins for novel high temperature resistant platinum curing transparent silicone adhesives



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### ABSTRACT

There is increasing demand for polymers having optical transparency along with high thermal stability for specific applications. Herein, the synthesis of high performance, mainly ethylene bridged, polycyclic silicones possessing multiple functionalities like optical clarity, high temperature stability and inherent flame retardancy is reported which is formulated further as high temperature resistant polymeric adhesive. These specialty silicones were synthesized from cyclic siloxanes through hydrosilylation reactions. The reaction conditions were optimized to synthesise the polycyclic silicone system with varying 2,4,6,8-tetramethyl-2,4,6,8-tetra-vinylcyclotetrasiloxane (D<sub>4</sub>V): 1,3,5,7-tetramethylcyclotetrasiloxane (D<sub>4</sub>H) ratio and the effect of cyclomer ratios on various physical, thermal, dynamic mechanical characteristics were explored. Among different cyclomer feed ratios, the ratio of 1:1 resulted in effective hydrosilylation with improved thermal stability. High temperature resistant adhesive formulations were made with a polycyclic silicone polymer as base resin, which showed improved strength at 350 °C than at RT, and retained 25% of its strength at 450 °C. All conventional silicone polymeric adhesives fail catastrophically at this temperature. The network formation in the polymer resulted in higher decomposition temperature and increased flame retardancy, which are essential requirements for high temperature resistant adhesives.

### 1. Introduction

Silicone based adhesives are known for good adhesion to low energy surfaces and outstanding thermal stability. Most commonly used silicone polymers are resins containing dimethylsiloxy and diphenylsiloxy groups along with a vinyl or acrylic functionality for crosslinking reactions. In spite of several advantages, these adhesives fail for applications necessitating elevated temperatures. The thermal stability of the silicones can be improved by the insertion of rigid groups into the chain backbone, where the rigid structures hinder the intra-chain rearrangements that cause polymer degradation at higher temperatures [1–7]. Another way to improve the thermal stability is through close-packed polymer network formation. Similar to the previous case, the usual thermal degradation mechanisms are minimized in polymer networks, due to higher restriction of the rearrangements and suppression of reactive end blocks [8].

The development of different polycyclic silicones by hydrosilylation

reactions from tetrafunctional siloxane cyclics have been reported [9–12]. The membrane obtained from 1,3,5,7-tetra vinyl, 1,3,5,7-tetramethylcyclotetrasiloxane (D<sub>4</sub>V) and 1,4-bis(dimethylsilyl)benzene has been reported to possess good permeability coupled with ideal selectivity relationships, especially for CO<sub>2</sub>/CH<sub>4</sub> [9]. In this hybrid system, the introduction of the rigid 1,4-silphenylene group between the siloxane cyclics, in stoichiometric amounts, increased the T<sub>g</sub> value in relation to silicone membranes. On the other hand, polymeric networks obtained by free radical polymerization of divinylbenzene, DVB, are densely crosslinked and brittle materials, with residual non-reacted double bonds, particularly with higher DVB contents [13]. In addition, DVB-based networks obtained by the introduction of dimethylsiloxane of different chain lengths, showed clear boundaries between the soft and hard phases in the material [14]. The product of platinum-catalyzed hydrosilylation reaction between 1,3,5,7-tetramethylcyclotetrasiloxane (D<sub>4</sub>H) and D<sub>4</sub>V has been reported as a “hard transparent glass” and the materials prepared from 1:1 and 1:2 M ratios

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of D<sub>4</sub>V and D<sub>4</sub>H were found to be significantly more thermally stable than PDMS; this was attributed to the absence of a pathway to form the cyclic trimer, which is the major thermal decomposition product of PDMS [8]. The networks prepared from 1:2 and 2:1 M ratios of D<sub>4</sub>V and D<sub>4</sub>H were reported to be amorphous by XRD [10]. The hydrosilylation reaction between D<sub>4</sub>H and D<sub>4</sub>V was reported to be highly exothermic in one case and burst into flames [10]. In another case, the exotherm and reaction rate were controlled easily by adjusting the platinum concentration and reaction temperature and extremely cross-linked D<sub>4</sub>V/D<sub>4</sub>H based polymers with good optical, mechanical and surface properties were obtained [12]. However, from the survey of literature reports available, it became evident that the multiple qualities, properties and potentials of both the reaction and the product have not been fully explored so far by researchers.

Though it has been reported that the polycyclic silicone (with 1:2 ratio of D<sub>4</sub>V:D<sub>4</sub>H) exhibits good thermal stability along with high UV-visible transparency [12], detailed investigations on the influence of reaction time, temperature and mole ratios of D<sub>4</sub>V: D<sub>4</sub>H on the properties of the products have not been reported so far. Also, the effect of cyclomer mole ratios on characteristics such as thermal, solvent resistance and flame retardancy were not studied till now. Hence, herein an attempt is made to optimise the reaction conditions to synthesise the polycyclic silicone system with 1:2 M ratio of D<sub>4</sub>V: D<sub>4</sub>H and to employ the optimised conditions for the synthesis of polycyclic silicones with varying D<sub>4</sub>V: D<sub>4</sub>H ratios. Further, the effect of cyclomer ratios on various physical, thermal, dynamic mechanical and flame retardancy characteristics were explored. A high temperature resistant adhesive system also was developed based on the optimised polymer; and to the best of our knowledge, this is the first time that a polycyclic silicone based adhesive system is reported which possesses the capability of withstanding very high temperatures, ~ 450 °C.

## 2. Experimental

### 2.1. Materials

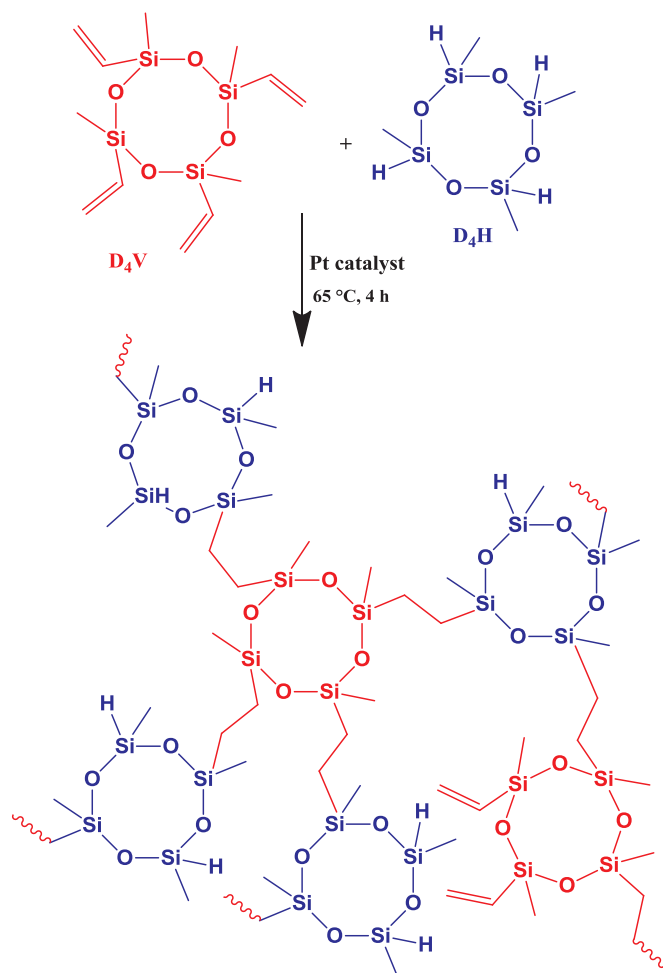
The precursors used were 2,4,6,8-tetramethyl-2,4,6,8-tetra-vinylcyclotetrasiloxane (D<sub>4</sub>V) and 1,3,5,7-tetramethylcyclotetrasiloxane (D<sub>4</sub>H), procured from Alfa Aesar. 0.05 M Pt (0) 1,3-divinyl 1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) in vinyl terminated polydimethylsiloxane (V-PDMS) purchased from Aldrich was diluted to 0.01 M with V-PDMS, procured from Anabond, Chennai and used as catalyst. Boron nitride (BN) with particle size < 10 μm purchased from CDH and ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) (assay: 90%) procured from Fischer Scientific, silica with Particle size < 20 μm purchased from CMET, Kerala and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, fused, – 325 mesh) from CDH were used as the filler materials.

### 2.2. Synthesis of polycyclic silicones

Polycyclic silicones, T1, T2 and T3 were synthesized following the method reported by Zheng *et al.* [12]. The synthesis of T3 with 1:2 M ratio of D<sub>4</sub>V and D<sub>4</sub>H is described here as a typical example. The tetrafunctional oligomers, D<sub>4</sub>V [0.03 mol, 10.36 ml], D<sub>4</sub>H [0.06 mol, 14.56 ml], and 0.01 M Pt (0) 1,3-divinyl 1,1,3,3-tetramethyldisiloxane complex in V-PDMS [0.07 wt. % of total reactants/ 0.018 g] were charged into a three necked, round bottom flask equipped with condenser, stirrer and thermometer. Reaction was carried out at 65 °C with vigorous stirring at 500 rpm for 4 h. The reaction pathway is depicted in Scheme 1. The same procedure was adopted for the synthesis of other copolymers with varying ratios of D<sub>4</sub>V and D<sub>4</sub>H.

### 2.3. Cure procedure

The cure procedure adopted for the composites in the study includes one day cure under ambient conditions followed by a second stage



Scheme 1. Synthesis of polycyclic silicones from tetrafunctional oligomers.

crosslinking with Pt catalyst. For this, the polymer was mixed thoroughly with 2 wt. % Pt catalyst for 2–3 min and cured under ambient conditions for 7 days.

### 2.4. Characterization

The viscosity of the polymers was measured at 25 °C using a Brookfield Viscometer. FTIR spectra were taken using a Perkin Elmer Spectrum GX A FTIR spectrophotometer. <sup>1</sup>H NMR and <sup>29</sup>Si NMR spectra were recorded using a 400 MHz BRUKER nuclear magnetic resonance spectrometer (Bruker, Germany), using CDCl<sub>3</sub> as the solvent. Chemical shifts (δ) are expressed in ppm, downfield using tetramethylsilane (TMS) as an internal standard. Refractive indices were determined using an Abbe refractometer (make: Atago/Japan, Model: DR-A1). Perkin Elmer Lambda 950 UV/Vis spectrometer was employed for the determination of UV-visible transparency of the samples.

The cure reaction of the polymeric system was studied using TA instruments Q-20 differential scanning calorimeter (DSC). About 10 ± 1 mg of sample was taken in aluminium pans and was heated from room temperature to 200 °C at heating rate of 10 °C/min in an ultra-pure nitrogen (99.999%) atmosphere at a flow rate of 50 mL/min. The thermal decomposition behavior of the cross-linked polymeric systems was studied using a TA instruments SDT Q-600 simultaneous thermogravimetric–differential scanning calorimetric analyzer (TG-DSC). About 10 ± 1 mg of sample was taken in alumina crucible and the TG analysis was carried out from room temperature to 900 °C at a heating rate of 10 °C/min in an ultra-pure nitrogen atmosphere at a flow rate of 100 mL/min. The glass transition temperature (T<sub>g</sub>) of the cured

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