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**REVIEW**

# Some Applications of the Diels–Alder Reaction in Organosilicon Chemistry

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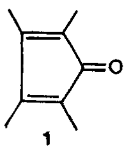
**A review of advances in the applications of the Diels–Alder reaction in organosilicon chemistry in our laboratory is presented. Using this reaction, we have synthesized a series of organosilicon monomers and polymers with polyphenyl groups and condensed rings and established a novel vulcanization system for silicone rubber. In addition, we discuss the influences of the large aromatic groups on the properties of the polymers.**

**Keywords: Diels–Alder reaction; organosilicon chemistry; polymers; vulcanization**

## INTRODUCTION

The Diels–Alder reaction is important in organic chemistry and much work has been done on it. A number of facts have demonstrated that the reaction is a [4 + 2] *cis*-cycloaddition with high stereospecificity. It is usually reversible and the reaction products of dienes with dienophiles can be pyrolyzed at higher temperature to give the initial reagents. However, some dienes with special structures, such as **1** and **2**, can liberate small molecules (CO, $CO_2$, $H_2$, etc.) in the Diels–Alder reaction, so the reaction becomes irreversible and the cycloadducts become stable.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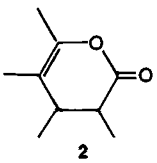
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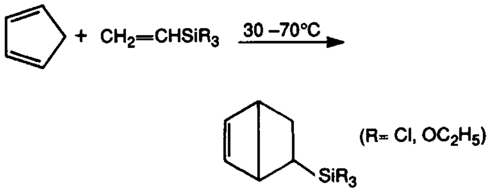
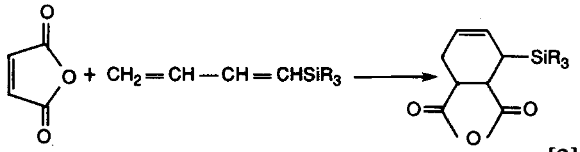
Dienophiles are usually unsaturated organic compounds such as alkenes or alkynes. Wagner *et al.* have found that the similar organosilicon compounds are also good dienophiles and can readily react with dienes in the Diels–Alder reaction,[1] for example according to Eqn [1].



[1]

Of course organosilicon compounds with dienyl groups can also be made to react with various monoenes[2] (Eqn [2]).



[2]

If there is a monoenyl group and a conjugated dienyl group in one molecule, a continuous intermolecular reaction will probably occur to form a polymer. In addition, if there are two monoenyl groups in one molecule and two conjugated dienyl groups in another molecule, a reaction between the two kinds of molecules can also form a polymer. There are a number of instances of Diels–Alder polymerization in organic synthesis, but little has been found concerning silicon compounds.[3] Equation [3] gives one example.

In recent years we have carried out work on the applications of the Diels–Alder reaction in organosilicon polymers. First we synthesized several dienes (**3–8**), and then we synthesized numerous organosilicon monomers, oligomers and polymers as heat-resistant additives, crosslinking agents or functional polymers by the Diels–Alder reaction

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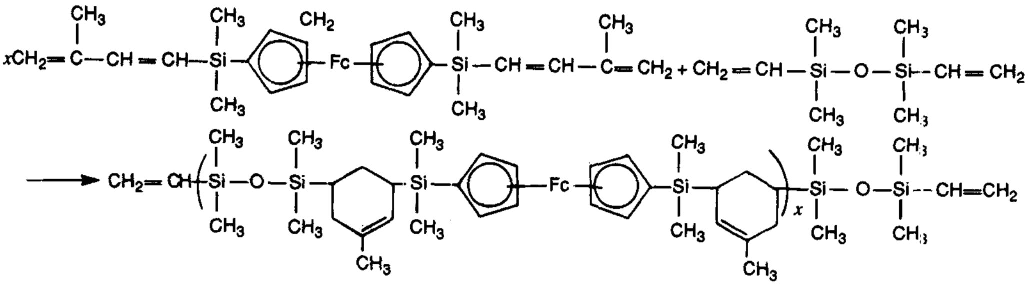

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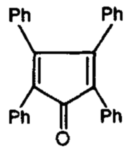

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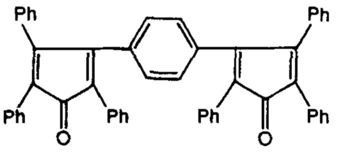

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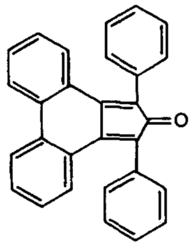

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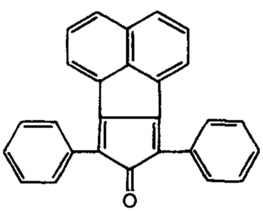

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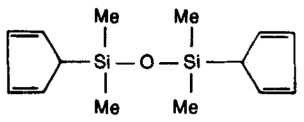


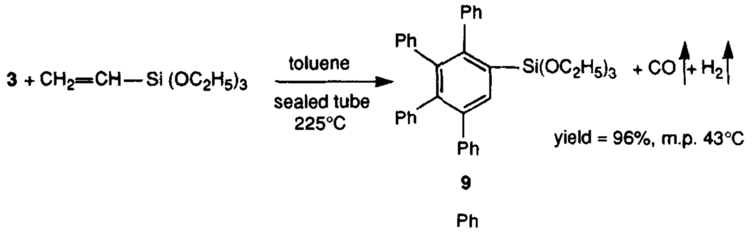
**8**

of these dienes with organosilicon compounds containing unsaturated bonds. In addition, we have established a novel vulcanization system for silicone rubber by the reaction.

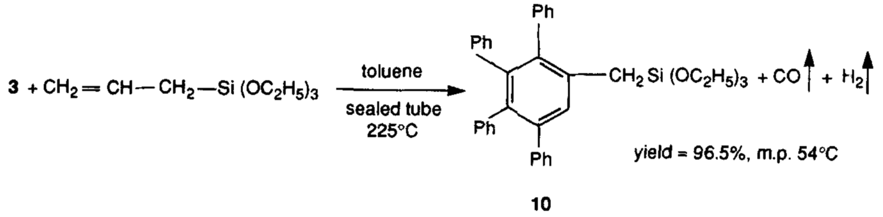
## SYNTHESIS AND APPLICATIONS OF TETRAPHENYLARYLTRIETHOXYSILANE[4]

Vinyltriethoxysilane or allyltriethoxysilane undergoes the Diels–Alder reaction with tetraphenylcyclopentadienone (**3**) to give tetraphenylphenyltriethoxysilane (**9**) and tetraphenylbenzyltriethoxysilane (**10**), respectively:

Both **9** and **10** can be used as heat-resistant additives for high-temperature-vulcanized (HTV) silicone rubber and exhibit good properties (see Table 1). However, the properties of **10** are not as good as those of **9**, because the $-CH_2-$ between the phenyl group and the silicon atom in **10** breaks up the $d_\pi$–$p_\pi$ conjugation between the



[4]



[5]

**Table 1** Influence of **9** and **10** on the ageing resistance of two kinds of silicone rubber

| Silicone rubber ageing condition | Heat-resistant additive | Tensile strength (MPa) | |
|---|---|---|---|
| | | Before ageing | After ageing |
| Methylvinyl rubber (0.15% vinyl), 280 °C, 24 h | 10% **9** | 11.9 | 11.9 |
| | 10% **10** | 12.8 | 10.1 |
| | None | 11.7 | 3.7 |
| Phenyl rubber (14.2% phenyl), 300 °C, 24 h | 10% **10** | | 5.0 |
| | None | | 3.9 |

**Table 2** Influence of **10** at various contents on the thermal weight loss of room-temperature-vulcanized silicone rubber

| Content of **10** (wt %) | Temperature of pyrolysis (°C) | Temperature of 50% weight loss at 400 °C (°C) | Weight loss (wt %) |
|---|---|---|---|
| 10 | 380 | 430 | 24 |
| 14 | 380 | 440 | 13 |
| 18 | 385 | 440 | 38 |
| 18 (+5% $SiO_2$)[a] | 385 | 465 | 24 |

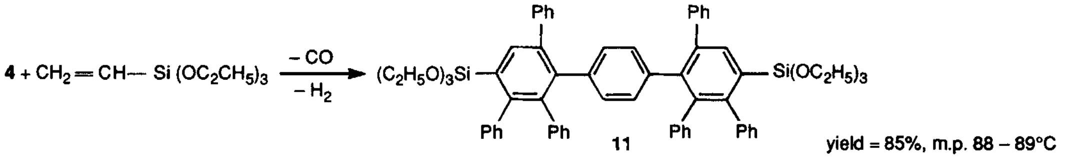
[a] Retained elasticity after ageing for 24 h at 350 °C, much better than normal RTV silicone rubber.

phenyl group and the silicon atom; the phenyl group in **9** is linked to the silicon atom directly.

By forming **9** and **10** into a silicone rubber, the temperature of initial weight loss was increased, usually to between 370 and 375 °C. The thermal weight loss was 6% at 400 °C. Both **9** and **10** contain three ethoxy groups, so they can be used as crosslinking agents in room-temperature-vulcanized (RTV) silicone rubber in place of ethyl silicate. Table 2 shows the thermal weight loss of silicone rubber vulcanized by **10**.

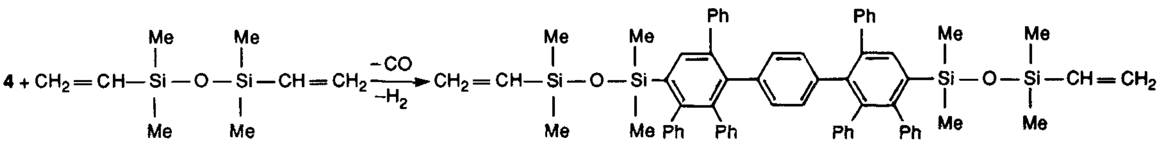
## REACTION OF BISCYCLOPENTADIENONE (4) WITH VINYLORGANOSILICON COMPOUNDS[5]

This type of reaction is interesting and the reaction products contain triethoxy and polyfunctional groups, so they exhibit very good heat resistance and high reactivity with other compounds. The synthesis reactions are introduced simply as Eqns [6] and [7].



yield = 85%, m.p. 88 – 89°C

[6]



**12**

yield = 80%, m.p. 119°C

[7]

**Table 3** Influence of the use of X on ageing resistance in silicone rubber (containing 3% $Fe_2O_3$)

| | Tensile strength (MPa) | | Elongation ratio (%) | | Permanent transformation (%) | | Hardness (Shore A) | |
|---|---|---|---|---|---|---|---|---|
| Content of X (%) | 250 °C 24 h | 320 °C 72 h | 250 °C 24 h | 320 °C 72 h | 250 °C 24 h | 320 °C 72 h | 250 °C 24 h | 320 °C 72 h |
| 0.5 | 13.2 | 5.9 | 611 | 238 | 6 | 2 | 51 | 63 |
| 1 | 12.2 | 5.7 | 685 | 150 | 6 | 2 | 50 | 66 |
| 3 | 11.9 | 5.2 | 866 | 90 | 12 | 2 | 48 | 74 |
| 5 | 5.1 | 5.1 | 1156 | 89 | 28 | 2 | 40 | 74 |
| 0.2 | 14.1 | 5.7 | 507 | 166 | 6 | 5.6 | 56 | 72 |
| 0 | 10.6 | 3.8 | 684 | 150 | 6 | 0 | 52 | 69 |

Compound **11** exhibits good effects as a crosslinking agent for RTV silicone rubber: the weight loss of the rubber was only 4.9% at 400 °C, and the rubber retained good elasticity after ageing at 300 °C for 48 h; ordinary RTV silicone rubber becomes brittle after the same process.

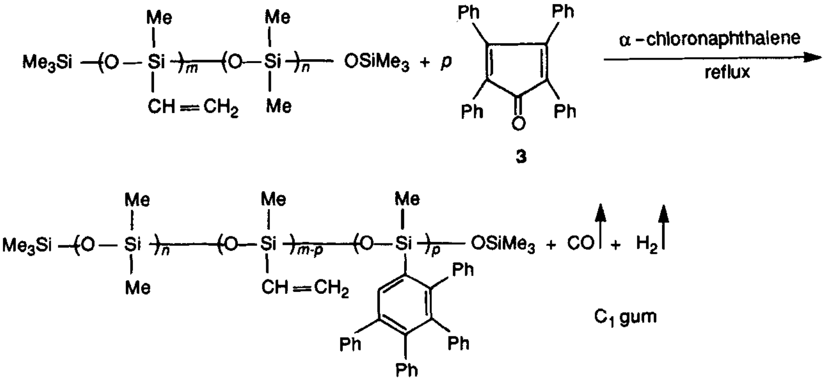
Compound **12** exhibits very good effects as a heat-resistant additive for HTV silicone rubber. When taken with auxiliary agents such as $Fe_2O_3$, its heat-resistant properties are excellent. For example, if ratios of X = 0.5, $Fe_2O_3$ = 2, and methylvinyl silicone raw gum = 100, are mixed and vulcanized in a standard procedure, the ageing resistance mechanical property of the resulting rubber is affected as follows:

| | |
|---|---|
| Aged at 250 °C for 24 h | Tensile strength 10.3 MPa |
| Aged at 320 °C for 72 h | Tensile strength 6.2 MPa |

The influence of X with $Fe_2O_3$ on the ageing resistance properties of methylvinyl silicone rubber is shown in Table 3, from which it can be observed that tensile strength is decreased dramatically if $Fe_2O_3$ only is used; it will be little vulcanized if the use level of X is much higher; heat-resistant properties are not good if X only is used. Experiments showed that the suitable use level of X is 0.2–0.5%.

## SYNTHESIS AND APPLICATION OF POLYPHENYLPHENYLPOLYSILOXANE[6]

Polyvinylsilicone oil is called C gum because of its use as a concentrated crosslinking agent in the working-up of HTV silicone rubber.[7] The vinyl groups in C gum can undergo Diels–Alder reaction with cyclopentadienone, partly converting the vinyl groups to polyphenylphenyl groups, and the residual vinyl groups act as a concentrated crosslinking agent. Heat-resistant properties and strength of the rubber are increased by introduc-



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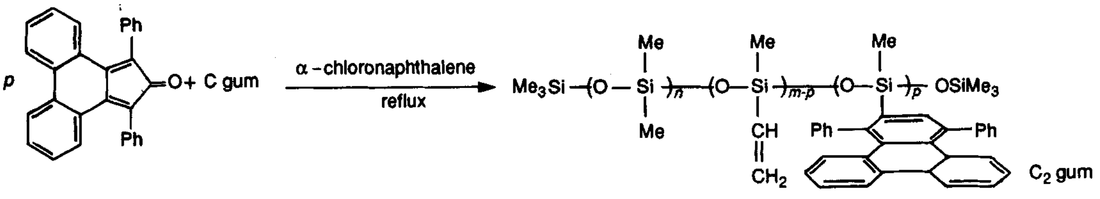
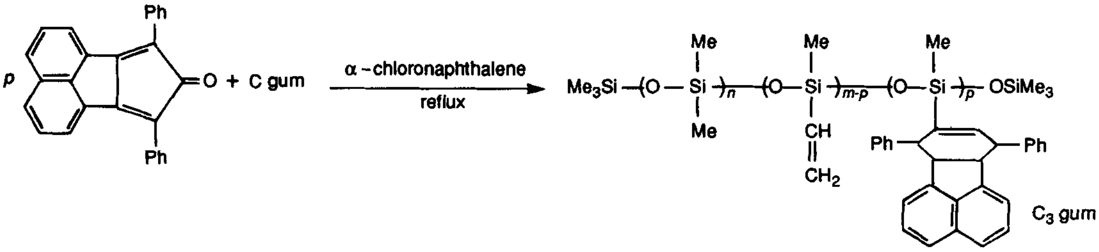


[9]



[10]

ing the polyphenylphenyl groups because they increase intermolecular attractive forces.

We have used the substituted cyclopentadienones **3**, **5** and **6** as dienes to react with C gum by the Diels–Alder reaction and obtained three kinds of polyphenyl aromatic C gum: $C_1$, $C_2$ and $C_3$ gum (Eqns [8], [9] and [10], respectively). First, we discuss the $C_1$ gum: $C_1$ gum containing tetraphenylphenyl groups is a viscous liquid and can be used as a concentrated crosslinking agent in peroxide-type and addition-type HTV silicon rubber. We have studied its influence on the nature of vulcanized rubber and compared it with C gum. The results are listed in Tables 4 and 5. In addition, we also have done ageing experiments at 280 °C for 12 h and 280 °C for 24 h and have found that the tensile strength of the rubber containing $C_1$ gum holds at 5–7 MPa, but that containing C gum became brittle. Although some of the data mentioned above have not been very clear, it can also be concluded that the ageing resistance properties of $C_1$ gum are better than those of C gum. In order to improve further the properties of addition-type silicone rubbers, we have synthesized $C_1$ gum terminated with vinyl groups, which much improved various properties of the rubber.[9]

In order to assess the influence of tetraphenylphenyl groups on thermal ageing, we performed experiments as shown in Table 6: it can be observed in Table 6 that the greater the content of tetraphenylphenyl groups in $C_1$ gum, the better are its heat-resistant properties.

In order to further increase heat-resistance and the intermolecular attractive forces, we configured the vinyl groups in the C gum reacting by the Diels–Alder reaction to become condensed rings. First, we synthesized two kinds of substituted cyclopentadienones: **5** and **6**, which were then reacted with C gum to obtain two kinds of

**Table 4** Influence of content of tetraphenylphenyl groups in $C_1$ gum on the properties of peroxide-type vulcanized silicone rubber[8]

| Content of tetraphenylphenyl groups (mol %) | Tensile strength (MPa) | | Tearing strength (kN m$^{-1}$) | | Elongation ratio (%) | |
|---|---|---|---|---|---|---|
| | Before ageing[b] | After ageing | Before ageing | After ageing | Before ageing | After ageing |
| 0.15 | 8.94 | 8.82 | 26.5 | 29.4 | 462 | 387 |
| 0.28 | 9.3 | 8.04 | 29.4 | 51.9 | 549 | 396 |
| 0.49 | 9.6 | 8.53 | 49.0 | 46.1 | 643 | 552 |
| 0.74 | 10.4 | 7.7 | 42.0 | 44.1 | 612 | 490 |
| 1.14 | 10.4 | 5.5 | 35.3 | 30.4 | 858 | 550 |
| 0[a] | 8.0 | 6.76 | 20.6 | 14.7 | 430 | 309 |

[a] C gum only, not containing any compounds with tetraphenylphenyl groups.
[b] The ageing conditions were 250 °C for 24 h.

**Table 5** Influence of content of tetraphenylphenyl groups in $C_1$ gum on the properties of addition-type vulcanized silicone rubber[9]

| Content of tetraphenylphenyl groups (mol %) | Tensile strength (MPa) | | Tearing strength (kN $m^{-1}$) | | Elongation ratio (%) | |
|---|---|---|---|---|---|---|
| | Before ageing[b] | After ageing | Before ageing | After ageing | Before ageing | After ageing |
| 0.13 | 10.3 | 3.7 | 50 | | 680 | 32 |
| 0.28 | 11.3 | 4.5 | 24 | | 557 | 48 |
| 0.49 | 10.2 | 4.9 | 45 | | 563 | 100 |
| 0.74 | 10.6 | 5.1 | 25 | | 636 | 107 |
| 1.14 | 11.1 | 4.8 | 53 | | 695 | 174 |
| 0[a] | 10.1 | 3.5 | 49 | | 680 | 41 |

[a] C gum only, not containing any compounds with tetraphenylphenyl groups.
[b] The ageing conditions were 250 °C for 24 h.

**Table 6** Influence of content of tetraphenylphenyl groups in $C_1$ gum on thermal-ageing stability[6]

| Content of tetraphenylphenyl group (mol %) | 250 °C for 24 h: State/weight loss (wt %) | 280 °C for 24 h: State/weight loss (wt %) | 350 °C for 24 h: State/weight loss (wt %) |
|---|---|---|---|
| 0 | Brittle, brown/19.0 | | — |
| 1.29 | Brittle, red–orange/11.0 | | — |
| 2.79 | Slightly brittle, orange/10.5 | | — |
| 4.12 | A little brittle, yellow-orange/10.6 | | — |
| 5.75 | Elastic solid, yellow/9.4 | | — |
| 6.93 | Elastic solid, yellow/8.0 | | — |
| 11.00 | Noncrosslinked liquid, yellow/— | Noncrosslinked liquid, slightly viscous/— | Crosslinked, elastic, yellow/5 |

**Table 7** Comparison of thermal weight loss of $C_2$, $C_3$ and C gums

| Polysiloxane | Content of condensed ring (mol %) | Weight loss (wt %) | |
|---|---|---|---|
| | | 200 °C for 24 h | 250 °C for 24 h |
| C gum | 0 | 5.12 | 21.5 |
| $C_2$ gum | 1.09 | 1.89 | 12.6 |
| $C_3$ gum | 2.43 | 2.21 | 13.2 |

gums containing condensed rings, i.e. $C_2$ and $C_3$ gum.[10]

$C_2$ gum contains substituted phenanthrene, $C_3$ gum contains substituted acenaphthylene and both of the condensed rings are planar conjugated systems. To study the thermal stability of these two polysiloxanes containing condensed rings we compared the thermal weight loss of $C_1$, $C_2$ and $C_3$ gums. The results are listed in Table 7.

The data in Table 7 show that the thermal-oxidant stability of C gum is much worse than for $C_2$ and $C_3$ gums, and the heat-resistance of the $C_3$ gum is a little worse than that of $C_2$ gum although it contains more condensed rings than the $C_2$ gum. This is reasonable on structural grounds, for phenanthrene is more stable than acenaphthylene. To investigate the practical application of $C_2$ and $C_3$ gums, we used them as concentrated crosslink-

**Table 8** The mechanical properties of thermally aged addition-type silicone rubber

| Type of gum[a] | wt % | Tensile strength (MPa) | Tearing strength (kN m$^{-1}$) | Elongation ratio (%) | Hardness Shore A | Permanent deformation (%) | Ageing conditions |
|---|---|---|---|---|---|---|---|
| C | 2 | 11.2 | 30.8 | 412 | 71 | <8 | 210 °C for 24 h |
| | 4 | 11.0 | 33.6 | 485 | 70 | <8 | |
| | 8 | 10.3 | 28.6 | 560 | 70 | <8 | |
| $C_2$ | 2 | 13.6 | 26.3 | 432 | 70 | <8 | 210 °C for 24 h |
| | 4 | 10.2 | 54.6 | 515 | 71 | <8 | |
| | 8 | 10.9 | 43.8 | 600 | 70 | <8 | |
| $C_3$ | 2 | 10.7 | 29.8 | 470 | 71 | <8 | 210 °C for 24 h |
| | 4 | 10.1 | 53.8 | 495 | 70 | <8 | |
| | 8 | 9.8 | 44.8 | 550 | 70 | <8 | |
| C | 2 | 7.4 | 9.8 | 215 | 74 | <5 | 250 °C for 10 h |
| $C_2$ | 2 | 9.2 | 21.3 | 323 | 72 | <5 | |
| $C_3$ | 2 | 8.1 | 15.5 | 280 | 73 | <5 | |

[a] The content of condensed rings in $C_2$ gum was 1.09 mol %, $C_3$ 2.43 mol %.

ing agents in methylvinylsilicone rubber and obtained the physical and mechanical properties shown in Table 8. The data listed in Table 8 are ageing data only. It can be observed from this table that the thermal-oxidant stability of $C_2$ gum is better than that of $C_3$ gum, as mentioned above. The tearing strength is considerably improved by adding $C_2$ or $C_3$ gum.

## VULCANIZING METHYLVINYLSILICONE RUBBER BY THE DIELS–ALDER REACTION

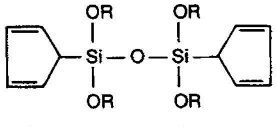
It is well known that there are only two vulcanizing systems to produce HTV silicone rubber: one is the peroxide system and the other is the addition system catalysed by rare metals. The cost of the two systems is high and there are residues which harm the vulcanized silicone rubber. To improve the shortcomings of the two systems, we established a novel vulcanizing system, which proceeds by a Diels–Alder reaction of organosilicone dienes with vinyl groups in the raw gum to give cycloaddition crosslinks.[11] Four kinds of biscyclopentadienone alkoxysiloxane were synthesized and all of them could vulcanize silicone rubber by heating with silicone raw gum. The strength of the vulcanized rubber obtained was the same as that of traditional vulcanized rubber. We now give two examples to illustrate the vulcanizing mechanism.

### Vulcanizing mechanism using vinylsilicone rubber with compound 8

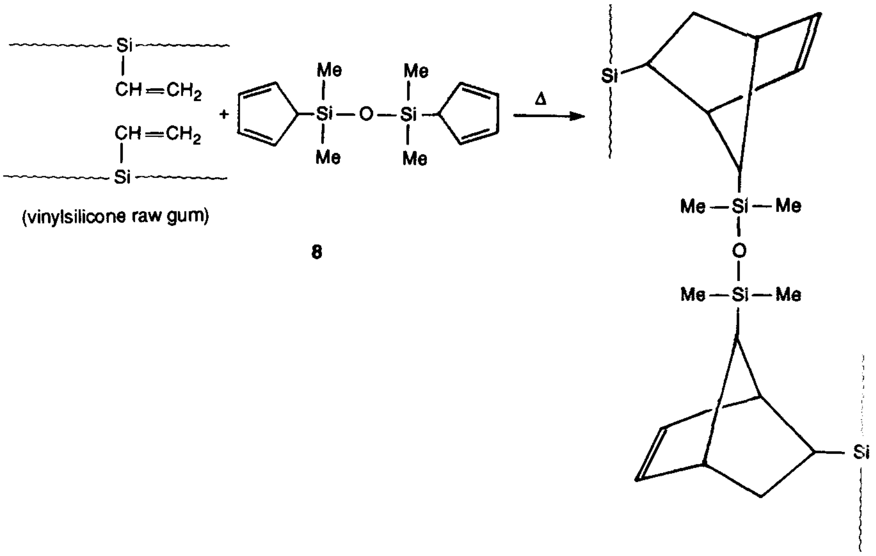
Two products were obtained when compound **8** reacted with vinyl groups; therefore the raw gum was crosslinked to give a vulcanized rubber (Eqn [11]).

### Vulcanizing mechanism of vinylsilicone rubber with compound 7

Compound **8** contains two cyclopentadiene groups and both of them can react by heat; therefore crosslinking occurs. Why compound **7** can vulcanize raw gum although it contains only one cyclopentadiene group and does so more readily when white carbon-black is added to raw gum is not apparent. We assume that there are two reasons. First, compound **7** is readily hydrolysed to give



and therefore it can vulcanize raw gum by two additional reactions. Second, many hydroxyl groups on the additive molecule react with Si—OR easily, so many cyclopentadiene groups

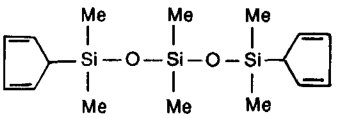


[11]

**Table 9** Mechanical properties of silicone rubber vulcanized by the novel system

| No. | Molecular weight | Content of **8** (mol %) | Diene type (wt %) | Tensile strength (MPa) | Tearing strength ($kN\,m^{-1}$) | Elongation ratio (%) | Hardness: Shore A | Permanent deformation (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 40 | 1.39 | vinyl (5) | 10.5 | 30 | 510 | 60 | 10 |
| 2 | 53 | 3.10 | vinyl (3) | 13.0 | 56 | 560 | 56 | 2 |
| 3 | 81.9 | 1.02 | **13**[a] (3) | 11.7 | 43 | 812 | 46 | 12 |
| 4 | 55 | 2 | **7** (5) | 11.9 | 38 | 500 | 50 | 4 |

[a] **13** stands for



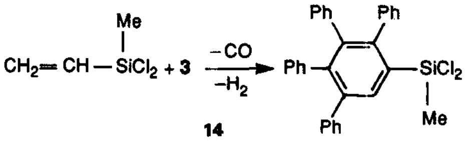
are linked to the additive and therefore vulcanization occurs.

It is better if the R group of compound **7** is small, e.g. Me or Et. If the R group is i-$C_3H_7$, reaction is not easy and vulcanization is difficult, for steric hindrance makes hydrolyses or ester exchange less active. For this novel vulcanizing system, the content of vinyl groups in raw gum is above 0.6% and the vulcanizing conditions are 180 °C for 1 h. The physical and mechanical properties of the vulcanized rubber are shown in Table 9.

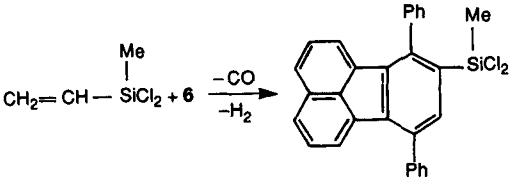
The data in Table 9 indicate that overall properties are good, reaching the level of high-strength silicone rubber. This novel system could be exploited.

## SYNTHESIS OF POLYPHENYLARYLPOLYSILANE

Most of the above mentioned polyphenylaryl groups are linked to the silicon atom in the polysilane; in this section polymers which have large groups on the polysilane chain will be discussed. The monomers of these polymers are synthesized by Diels–Alder reaction, also. Some examples are shown in Eqns [12] and [13].[12, 13]



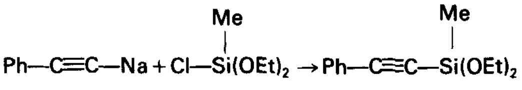
[12]



**15** [13]

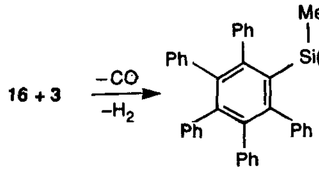
The reaction was carried out in a sealed tube as the boiling point of methylvinyldichlorosilane is low and the reaction temperature is up to 230 °C.

Pentaphenylphenylsilane can be obtained only when the dienophile contains a phenylethyl group, for example by reactions [14] and [15].[14, 15]



$$\mathrm{Ph{-}C{\equiv}C{-}Na + Cl{-}\overset{Me}{\overset{|}{Si}}(OEt)_2 \rightarrow Ph{-}C{\equiv}C{-}\overset{Me}{\overset{|}{Si}}(OEt)_2} \quad [14]$$

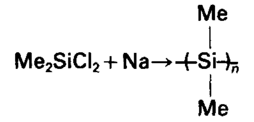
**16**



**17** [15]

Compounds **18–20** were synthesized by the same procedure.

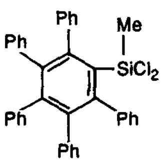
It is known that dichlorosilane containing small groups on the silicon atom can undergo a Wurtz-type reaction to give polysilanes of high molecular weight, for example by Eqn (16).



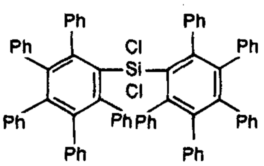
$$\mathrm{Me_2SiCl_2 + Na \rightarrow {-}\!\!(\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}})\!\!{-}_n}$$

(linear type or cyclomer) [16]

We did not find any linear polymer but obtained cyclomers (usually three or four) by the

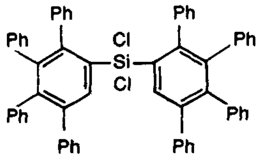


**18**

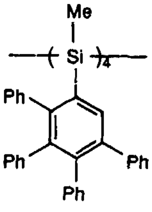


**19**

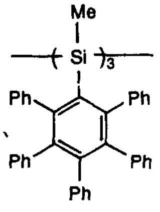
Wurtz reaction of polyphenyldichlorosilane by the same procedure, for example products such as **21–23**.[14, 15]



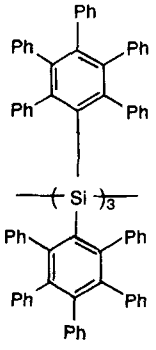
**20**



**21**



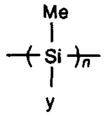
**22**



**23**

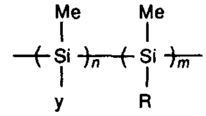
To produce a linear polyphenylphenyl polymer, the only way was to copolymerize with dichlorosilanes which have small groups. We synthesized some homo- and co-polymers **24–27**, where Y is the polyphenylaryl group and R is the methyl, vinyl or phenyl group. The copolymers synthesized exist as soluble castings and melts etc.

Polysilane has the property of semiconductivity; its UV absorption wavelength is near the visible light zone, and it can form charge-transfer complexes with electron receptors.[16, 17] We have found that polyphenylarylpolysilane shifts to longer-wavelength UV absorption, especially after formation of charge-transfer complexes with tetracyanoethene (TENE), tetrachloroquinone, iodine and $SbCl_5$, etc. Their conductivities are much increased. The molecular weight of the



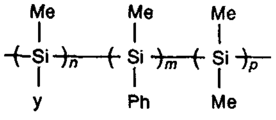
$$\mathrm{{-}(\underset{\underset{Y}{|}}{\overset{\overset{Me}{|}}{Si}})_n{-}}$$

**24**



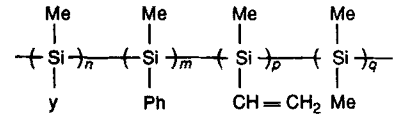
$$\mathrm{{-}(\underset{\underset{Y}{|}}{\overset{\overset{Me}{|}}{Si}})_n{-}(\underset{\underset{R}{|}}{\overset{\overset{Me}{|}}{Si}})_m{-}}$$

**25**



$$\mathrm{{-}(\underset{\underset{Y}{|}}{\overset{\overset{Me}{|}}{Si}})_n{-}(\underset{\underset{Ph}{|}}{\overset{\overset{Me}{|}}{Si}})_m{-}(\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}})_p{-}}$$

**26**



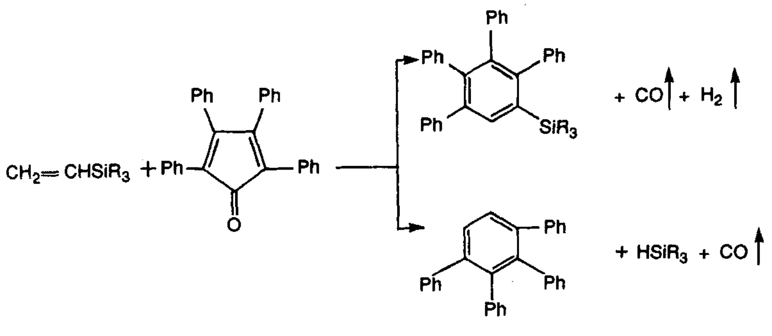
$$\mathrm{{-}(\underset{\underset{Y}{|}}{\overset{\overset{Me}{|}}{Si}})_n{-}(\underset{\underset{Ph}{|}}{\overset{\overset{Me}{|}}{Si}})_m{-}(\underset{\underset{CH=CH_2}{|}}{\overset{\overset{Me}{|}}{Si}})_p{-}(\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}})_q{-}}$$

**27**

**Table 10** UV absorption wavelength ($\lambda$) and electrical resistivity ($\rho$) of charge-transfer (CT) complexes of some polysilanes[a]

| CT complex | $\lambda$ (nm) | $\rho$ ($\Omega$ cm) | CT complex | $\lambda$ (nm) | $\rho$ ($\Omega$ cm) |
|---|---|---|---|---|---|
| **26**–TENE | 710.8, 325.8,<br>562.8, 270.8,<br>424, 375 (sh) | $8.5\times10^4$ | **24**–TENE | 710.8, 45.8,<br>698.5, 270.8,<br>415 (sh), 375 (sh) | $6\times10^3$ |
| **25**–tetrachloroquinone | 720, 344.2,<br>420, 267.5 | $1.0\times10^8$ | **24**–$I_2$ | — | $8.0\times10^2$ |
| **26**–$SbCl_5$ | 710, 330.8,<br>430, 267.5 | $1.5\times10^5$ | **27**–$I_2$ | 710, 309, 498<br>241.7, 358 | $1.3\times10^3$ |

[a] The $\rho$ of normal polysilane is $10^8$–$10^{12}$ $\Omega$ cm and the $\lambda_{max}$ is 370–390 nm.



[17a]

[17b]

copolymer is 3000–5000, and that of the homopolymer is below 2000, down to the tetramer. Table 10 shows the UV absorption wavelength ($\lambda$) and electrical resistivity ($\rho$) of some polysilanes. There are large changes in $\rho$ and $\lambda_{max}$ of polysilanes on introducing the tetraphenyl group, because the electrons in the conjugated $\pi$-bond are easily delocalized. There are similar influences on $\rho$ and $\lambda_{max}$ by introducing the pentaphenylphenyl group. We synthesized polysilane which contained substituted acenaphthylene, too, and its UV absorption spectrum exhibited an obvious red shift.[18]

## THE DIRECTION OF REACTION OF TETRAPHENYLCYCLOPENTADIENONE WITH VINYLORGANOSILICON COMPOUNDS

The reaction of tetraphenylcyclopentadienone with ethynyl silicon compounds liberates only CO, not $H_2$, so there is not a problem with reaction direction. However, when it reacts with vinyl silicon compounds there are two reactions, found by analysing the products of reactions [17a] and [17b].

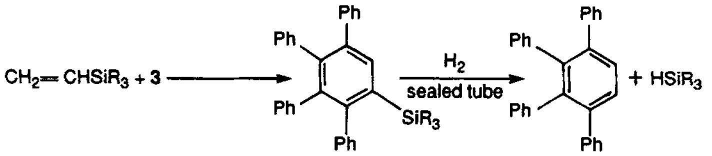
This indicates that there is another direction of reaction which liberates CO and $HSiR_3$ besides the route involving liberation of CO and $H_2$. The products mainly consist of those shown in [17a] or [17b], under different conditions. The reaction has been studied and is summarized in Table 11.[19]

It can be observed from Table 11 that if there are more electrophobic groups (such as Me) linked to the silicon atom, reaction [17b] predominates and if there are more electrophilic groups (such as Cl) linked to the silicon atom, reaction [17a] predominates at high reaction rate and good yield. The authors assume that this is the result of an induction effect. A positive group favours electrophilic attack on the phenyl group, so the products are mainly tetraphenylbenzene; a negative group favours enhancement of the $p_\pi$–$d_\pi$ conjugated effect of the phenyl group and the silicon atom, so the phenyl group is not easily attacked, therefore the products are mainly tetraphenylphenylsilicon compounds. In addition, the authors assume that another reason for reaction [17b] to occur is hydrogenolysis. In order

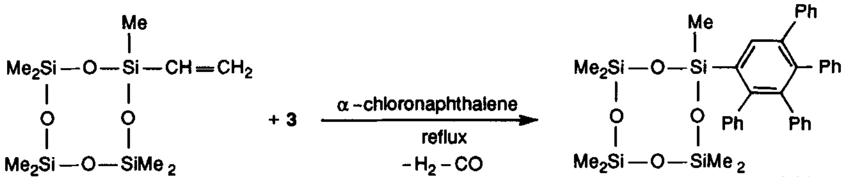
**Table 11** Influence of the substituent group on the silicon atom on the cycloaddition reaction[a]

| $CH_2{=}CHSiR_1R_2R_3$ | | | Total yield | $Ph_4C_6H_2$ | $Ph_4C_6HSiR_1R_2R_3$ |
|---|---|---|---|---|---|
| $R_1$ | $R_2$ | $R_3$ | (%) | (%) | (%) |
| Me | Me | Me | 93 | 88 | 12 |
| Me | Me | OEt | 90 | 78 | 22 |
| Me | OEt | OEt | 88 | 69 | 31 |
| OEt | OEt | OEt | 81 | 19 | 81 |
| Me | Me | H | — | 100 | 0 |
| Me | Me | $OSiMe_2Vi$ | 99.1 | 47 | 53 |
| Me | Cl | Cl | 95 | 0 | 100 |

[a] Data for the table were obtained by reaction in sealed tube.



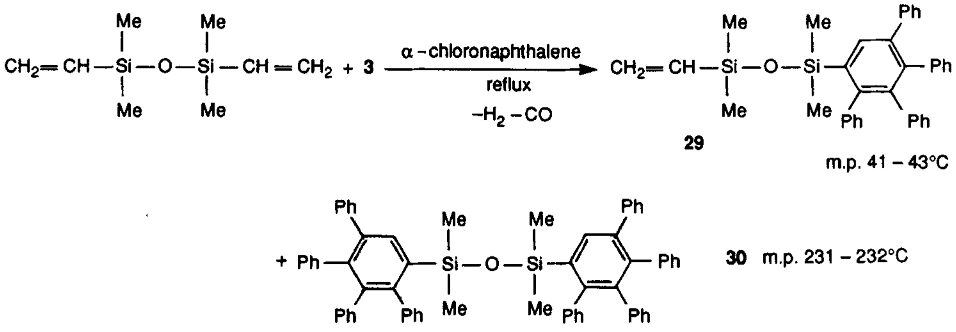
[18]



28

yield = 95.1%, m.p. 56 – 58°C

[19]



29

m.p. 41 – 43°C

30 m.p. 231 – 232°C

[20]

to prove this, we carried out the reaction in an open flask at the reflux temperature of a high-boiling-point solvent, so that the $H_2$ and CO could disappear over time to prevent hydrogenolysis. The result proved our surmise.

Therefore, we can be certain that reaction [17b] occurs as eqn [18].

This side-reaction will not exist if there is no $H_2$ in the system. Compounds **28–30** were synthesized by the same method.[20]

Compound **28** can be used as an intermediate for the synthesis of silicone rubber. The total yield of **29** and **30** was 95% and **29** comprised more than 60%. There was no tetraphenylbenzene because of use of an open flask, the reaction differing markedly from the sealed-tube reaction (see Table 11).

Compound **30** is an effective stationary phase for gas chromatography to separate normal alkanes. It can be used to separate $C_{32}$ alkanes cleanly and has a good heat resistance.

$C_1$, $C_2$ and $C_3$ gums were also synthesized by the above method.

## CONCLUSION

The Diels–Alder reaction is very useful in organosilicon chemistry. It can be used not only in synthesizing special monomers which may be difficult to obtain by other methods, but also for condensing, polymerizing, grafting and vulcanizing (crosslinking), etc. Various polar groups, functional groups or heat-resistant groups can be introduced to a molecule by the reaction and give rise to electrical optical, thermal or other properties in the products which produce useful materials.

According to molecular orbital and frontier orbital theory, we know that if the number of $\pi$-electrons of the diene obey the Hückel rule ($m+n=4q+2$, $q=1, 2, 3 \ldots$), the only energy required to promote the reaction is heat, and no catalysis is necessary. This is a characteristic of the Diels–Alder reaction. Overall then, the Diels–Alder reaction can be used to synthesize new materials and to create new applications in various respects.

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