

# Synthesis of $\sigma$ – $\pi$ conjugated oligo(silylene-vinylene)s by metathesis of divinylsilanes over $\text{Re}_2\text{O}_7$ – $\text{Al}_2\text{O}_3$ catalyst

Tadashi Kawai\*, Keiichiro Shiga, Tomokazu Iyoda

*Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji-shi, Tokyo 192-0397, Japan*

## Abstract

Tetravinylsilane and divinylsilanes have been successfully metathesized over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst promoted with tetra-*n*-butyltin ( $\text{SnBu}_4$ ) under very mild reaction conditions. The addition of  $\text{SnBu}_4$  is essential to the acyclic diene metathesis (ADMET). A series of new oligo(silylenevinylene)s with  $\sigma$ – $\pi$  conjugation has been produced. Grubbs, Schrock catalysts and  $\text{WCl}_6$ – $\text{SnMe}_4$  were, however, inactive for the ADMET. All of the products were acyclic oligomers and the cyclic products were not formed. The reactivity of divinylsilanes is attributed to the bulkiness of substituent at silicon atom and the existence of silicon atom instead of carbon atom decreases the reactivity greatly. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Tetravinylsilane; Vinylsilanes; Metathesis; Acyclic diene metathesis (ADMET); Silylene-vinylene; Rhenia–alumina catalyst ( $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst);  $\sigma$ – $\pi$  conjugated oligo(silylenevinylene)s

## 1. Introduction

We have reported that  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst is one of the best metathesis catalysts due to its high activity and selectivity > 94% for various kinds of simple alkenes at low temperatures [1–10]. The catalyst promoted with alkyltin as a cocatalyst also showed high activity and selectivity for the metathesis of halogen-containing olefin [11].

Various kinds of monoallylsilanes and diallylsilanes have been metathesized with good

yields in the presence of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  [12,13] and Schrock catalysts [12,14–17]. However, it has been reported that dimethyldivinylsilane was practically inactive over both  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst promoted with tetra-*n*-butyltin ( $\text{SnBu}_4$ ) [13] and Schrock catalyst [12,15,18], although trimethylvinylsilane was metathesized with conversion of 3%–13% [12,13,16,17]. On the other hand, Marciniec et al. [12,19–29] have succeeded in getting silylene-vinylene oligomers via polycondensation of dimethyldivinylsilane and divinyltetramethyldisiloxane in the presence of a variety of ruthenium and rhodium catalysts. However, a fair amount of products, which essentially differs from the structures expected by metathesis reaction, was accompanied and thus the reaction has been understood as a non-metallacarbene mechanism.

\* Corresponding author. Tel.: +81-426-77-2837; fax: +81-426-77-2821.

E-mail address: kawai-tadashi@c.metro-u.ac.jp (T. Kawai).

The poly(silylenevinylene) and spiro compounds with  $\sigma$ – $\pi$  conjugation are of growing interest and importance as partly conjugated optical material with high transparency and relatively high second and third hyperpolarizability predicted by the ab initio molecular orbital calculation [30]. We have succeeded for the first time to synthesize oligo(silylenevinylene)s by the ADMET reaction of tetravinylsilane and divinylsilanes over a  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst and a part of the results has been earlier reported [31]. Here, we report the additional results on the synthesis of oligo(silylenevinylene)s by ADMET of tetravinylsilane and divinylsilanes over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalysts promoted with  $\text{SnBu}_4$  and over homogeneous metathesis catalysts,  $\text{WCl}_6$ – $\text{SnMe}_4$ , Grubbs, and Schrock catalysts. The reaction conditions, reactivities of divinylsilanes have been investigated in detail. The resulting oligomers were structurally characterized.

## 2. Experimental

$\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst ( $\text{Re}_2\text{O}_7$  content: 18.1 wt.%) was prepared by using impregnation technique described in previous papers [1,3,30]. Bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Grubbs catalyst) generously provided by Prof. Grubbs and 2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(hexafluoro-*t*-butoxide) (Schrock catalyst) (Strem Chemicals) were used without further purification.  $\text{WCl}_6$  was purified by sublimation under vacuum at  $110^\circ\text{C}$ .  $\text{SnBu}_4$  was dried over molecular sieves 5 Å and used without further purification. Tetravinylsilane, dimethyldivinylsilane, diphenyldivinylsilane, diethoxydivinylsilane, trimethylvinylsilane and 3,3-dimethyl-1-butene are commercially available from Shinetsu silicon company. The silanes and *n*-dodecane as an internal standard were dried over molecular sieves 5 Å. Benzene, 1,2-dimethoxyethane, *n*-decane and monochlorobenzene (PhCl) used as a solvent were dried over  $\text{P}_2\text{O}_5$  and distilled.

In a batch system, the reactions were carried out in nitrogen gas at atmospheric pressure in a Schlenk-type glass reactor with stirring. The activation conditions of the catalyst and the experimental procedures were essentially identical to those described in the previous paper [31]. In a flow system, the reactions were carried out at atmosphere pressure in a single path continuous-flow system with a fixed catalyst bed in a tubular Pyrex glass reactor. The activated catalyst was pretreated with  $\text{SnBu}_4$  before the reaction. Typical reaction conditions were as follows; catalyst: 1 g; reactant concentration: 0.06 M; flow rate: 2.5 ml/h.

Homogeneous metathesis reactions were carried out using three kinds of catalysts under the following reaction conditions: reactant/catalyst molar ratio: 50–100; temperature:  $20^\circ\text{C}$ – $60^\circ\text{C}$ ; reaction time: 18 h; and solvent: benzene or 1,2-dimethoxyethane.

Metathesis products were analyzed by GC, GC-MS and  $^1\text{H}$  and  $^{13}\text{C}$  NMR [31]. Each oligomer separated by using gel permeation chromatography (GPC) on a Shodex SD-4 was used for the identification and characterization of reaction products.

## 3. Results and discussion

### 3.1. Screening of metathesis catalysts

The activity of three kinds of homogeneous catalysts,  $\text{WCl}_6$ – $\text{SnMe}_4$ , bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride and 2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(hexafluoro-*t*-butoxide) was investigated using tetravinylsilane, dimethyldivinylsilane and diethoxydivinylsilane as substrates. However, it was found that the three kinds of catalysts were all inactive for the metathesis. A small amount of by-product formed with reactant and catalyst was determined. Only the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst promoted with  $\text{SnBu}_4$  appeared to be active for the ADMET reactions.

### 3.2. Reaction conditions

It was found that dimethyldivinylsilane, diphenyldivinylsilane and diethoxydivinylsilane underwent the ADMET reactions selectively over the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalysts in analogy with tetravinylsilane [30]. The ratio of higher oligomers increased with an increase in conversion, suggesting that the intermolecular metathesis proceeds with successive reaction. By-products were virtually not formed within the reaction temperatures (25°C–110°C) investigated. However, in the case of diphenyldivinylsilane a product with two constitutional repeating units was formed selectively and this might be attributed to the poor solubility of the product formed.

The effects of the amount of  $\text{SnBu}_4$  were examined using a batch and flow system. The activity increased greatly by the addition of small amount of  $\text{SnBu}_4$  and became constant for the catalyst treated with more than 0.07 Sn/Re molar ratio as shown in Fig. 1. No apparent differences were found in the product distributions by changing the ratio.

As the catalytic activity in the absence of  $\text{SnBu}_4$  was nearly 0%, the use of alkyltin is essential. The effective amount of  $\text{SnBu}_4$  for

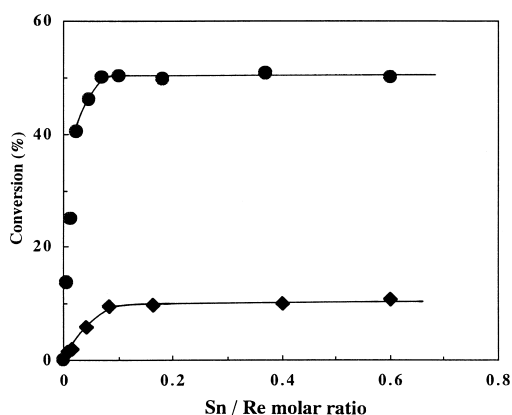


Fig. 1. Effects of the amount of cocatalyst on catalytic activity. Reaction conditions: substrate: tetravinylsilane; catalyst ( $\text{Re}_2\text{O}_7-\text{Al}_2\text{O}_3$ ): 1.0 g; reaction temperature: 50°C; reaction time: 12 h. ● Batch system; solvent: *n*-decane (4 ml). ◆ Flow system; substrate concentration in PhCl solvent: 0.06 M; W/F: 40.7 g cat h mol<sup>-1</sup>.

the catalyst has been reported to be 0.09 [11], in fairly good agreement with 0.07 in this study.

Two solvents, monochlorobenzene and *n*-decane, were used to see the solvent effects and to make sure there was no duplication of the solvents and reaction products in the analysis of GLC. The solvent effects were not found.

### 3.3. Identification of reaction products

Oligomers of tetravinylsilane and divinylsilanes, which are new compounds, were isolated by GPC and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra. The <sup>1</sup>H and <sup>13</sup>C NMR spectral data for a series of oligo(silylenevinylene)s with  $\sigma-\pi$  conjugation are summarized in Table 1.

Not only in Table 1, but also in this paper, e.g. dimer and hexamer mean that they have the constitutional repeating units 2 and 6, respectively.

The isomer ratio of tetramer to hexamer produced in the metathesis of tetravinylsilane were determined from GC and NMR data. In the case of tetramer, for example, the  $\delta$  and integrated values of outer  $-\text{CH}=\text{CH}_2$  and inner  $-\text{CH}=\text{CH}_2$  were 5.79 (dd, 9H) and 5.78 (dd, 5H), respectively, as shown in Fig. 2. The theoretical ratios of outer and inner  $-\text{CH}=\text{CH}_2$  is 6:4 for the straight chain compound and 9:1 for the branched compound. When we assume the ratio of the straight and the branched compound as  $x$  and  $y$ , respectively, the equation,  $(6x + 9y)/(4x + 1y) = 9/5$ , can be obtained, resulting in  $x = 85\%$ ,  $y = 15\%$ . The ratio agreed with the area ratio of GC. The other oligomer ratio determined in the same manner has already been reported [31].

In the case of the metathesis of tetravinylsilane, the formation of cyclic compounds and/or spiro compounds are expected, but they were not found in the reaction products of each divinylsilane. In the metathesis of 1,4-alkadiene over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst, 1,4-cyclohexadiene was formed by the intramolecular metathesis of trienes with fairly high selectivity

Table 1

<sup>1</sup>H and <sup>13</sup>C NMR data of oligo(silylene-vinylene)s with σ–π conjugation

## 1. Tetravinylsilane

## Dimer

<sup>1</sup>H NMR: δ = 6.14 (d, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.16 (d, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, CH = CH<sub>2</sub>), 5.79 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.75 (s, CH = CH), <sup>13</sup>C NMR: δ = 133.85 (s, CH = CH<sub>2</sub>), 135.31 (s, CH = CH<sub>2</sub>), 149.07 (s, CH = CH)

## Trimer

<sup>1</sup>H NMR: δ = 6.14 (d, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.16 (d, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, outer-CH = CH<sub>2</sub>), 5.79 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.74 (s, CH = CH), 5.78 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, inner-CH = CH<sub>2</sub>), <sup>13</sup>C NMR: δ = 133.85 (s, outer-CH = CH<sub>2</sub>), 135.31 (s, outer-CH = CH<sub>2</sub>), 149.04 (s, CH = CH), 149.07 (s, CH = CH), 135.42 (s, inner-CH = CH<sub>2</sub>)

## Tetramer

<sup>1</sup>H NMR: δ = 6.14 (d, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.16 (d, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, CH = CH<sub>2</sub>), 5.79 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, outer-CH = CH<sub>2</sub>), 6.74 (d, <sup>3</sup>J(H,H) = 0.7 Hz, CH = CH), 5.78 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, inner-CH = CH<sub>2</sub>), <sup>13</sup>C NMR: δ = 133.87 (s, outer-CH = CH<sub>2</sub>), 135.31 (s, outer-CH = CH<sub>2</sub>), 149.06 (s, CH = CH), 149.16 (s, CH = CH), 135.42 (s, inner-CH = CH<sub>2</sub>), 149.25 (s, CH = CH)

## Pentamer

<sup>1</sup>H NMR: δ = 6.14 (d, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.16 (d, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, outer-CH = CH<sub>2</sub>), 5.78 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.73 (t, <sup>3</sup>J(H,H) = 0 Hz, CH = CH), 5.77 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, inner-CH = CH<sub>2</sub>), <sup>13</sup>C-CH = CH<sub>2</sub>, 149.25 (s, CH = CH)

## Hexamer

<sup>1</sup>H NMR: δ = 6.14 (d, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.16 (d, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, outer-CH = CH<sub>2</sub>), 5.78 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, CH = CH<sub>2</sub>), 6.73 (t, <sup>3</sup>J(H,H) = 0 Hz, CH = CH), 5.77 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 16.2 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 7.9 Hz, inner-CH = CH<sub>2</sub>)

## 2. Dimethyldivinylsilane

## Dimer

<sup>1</sup>H NMR: δ = 5.69 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, trans-CH = CH<sub>2</sub>), 5.98 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, cis-CH = CH<sub>2</sub>), 6.23 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, CH = CH<sub>2</sub>), 0.14 (s, C<sub>2</sub>H<sub>5</sub>), 6.62 (s, CH = CH)

## Trimer

<sup>1</sup>H NMR: δ = 5.69 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, trans-CH = CH<sub>2</sub>), 5.98 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, cis-CH = CH<sub>2</sub>), 6.16 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, CH = CH<sub>2</sub>), 0.13 (s, inner-CH<sub>3</sub>), 0.14 (s, outer-CH<sub>3</sub>), 6.60 (s, CH = CH)

## Tetramer

<sup>1</sup>H NMR: δ = 5.69 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, trans-CH = CH<sub>2</sub>), 5.98 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, cis-CH = CH<sub>2</sub>), 6.16 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, CH = CH<sub>2</sub>), 0.13 (s, inner-CH<sub>3</sub>), 0.14 (s, outer-CH<sub>3</sub>), 6.61 (d, <sup>3</sup>J(H,H<sup>trans</sup>) = 1.4 Hz, CH = CH), 6.59 (s, CH = CH)

## Pentamer

<sup>1</sup>H NMR: δ = 5.69 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, trans-CH = CH<sub>2</sub>), 5.98 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, cis-CH = CH<sub>2</sub>), 6.16 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, CH = CH<sub>2</sub>), 0.13 (s, inner-CH<sub>3</sub>), 0.14 (s, outer-CH<sub>3</sub>), 6.61 (d, <sup>3</sup>J(H,H<sup>trans</sup>) = 1.4 Hz, CH = CH), 6.60 (s, CH = CH)

## 3. Diphenyldivinylsilane

## Dimer

<sup>1</sup>H NMR: δ = 5.69 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, trans-CH = CH<sub>2</sub>), 5.98 (dd, <sup>2</sup>J(H,H) = 4.3 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, cis-CH = CH<sub>2</sub>), 6.23 (dd, <sup>3</sup>J(H,H<sup>trans</sup>) = 19.8 Hz, <sup>3</sup>J(H,H<sup>cis</sup>) = 14.9 Hz, CH = CH<sub>2</sub>), 0.14 (s, C<sub>6</sub>H<sub>5</sub>), 6.62 (s, CH = CH), <sup>13</sup>C NMR: δ = 127.83 (s, CH = CH<sub>2</sub>), 129.49 (s, CH = CH<sub>2</sub>), 133.69–136.71 (m, C<sub>6</sub>H<sub>5</sub>), 150.11 (s, CH = CH)

and increased with increasing conversion, e.g. the selectivity was 42% at 40% conversion in the metathesis of 1,4-pentadiene, and 50% at 90% conversion from 1,4-hexadiene and 1,4-octadiene [5,6]. On the other hand, in the metathesis of 3-methyl-1,4-pentadiene over Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, main reaction products were

linear oligomer and the selectivity of cyclic compounds was only 3% at 60% conversion level [32]. The *cis* conformation of the inner olefin is essential to form cyclohexadiene via an intramolecular metathesis. The much lower formation of 3,6-dimethyl-1,4-cyclohexadiene from 3-methyl-1,4-pentadiene compared with cyclo-

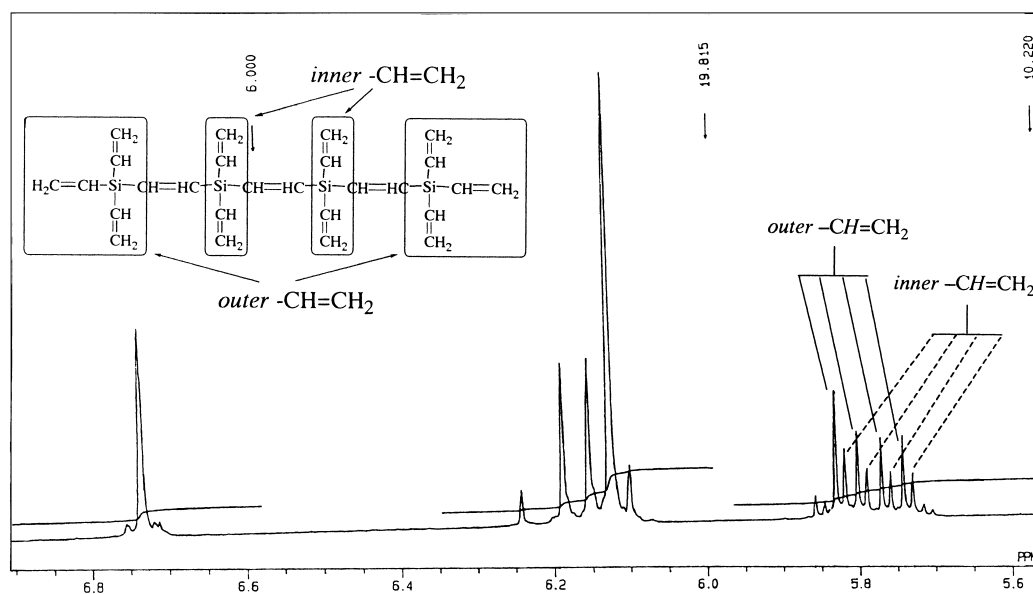


Fig. 2.  $^1\text{H}$  NMR spectrum of tetramer of tetravinylsilane.

hexadiene from 1,4-alkadiene could be attributed to the steric hindrance between methyl substituents at *cis* conformation of the inner olefin. In the case of tetravinylsilane, there are much larger steric strains; bulkiness of the vinyl substituent is larger than that of methyl group and two vinyl groups at silicon atom makes *cis* conformation much difficult. These could be the reasons why spiro compounds from tetravinylsilane were not formed. In the same manner, *cis* conformation at the inner olefin is essential to form the cyclic compounds from oligomers of tetravinylsilane and disubstituted divinylsilane. This makes ring-closing metathesis reaction more difficult, leading to no cyclic compound formation.

### 3.4. Reactivity of divinylsilanes

The relative reactivity of a series of methyl-1-hexene ( $\text{Me-1-C}_6$ ) is as follows:  $3\text{-Me-1-C}_6$  (0.08) <  $4\text{-Me-1-C}_6$  (0.72) <  $5\text{-Me-1-C}_6$  (1.00) [7]. The data show that the nearer the methyl substituent to the double bond, the lower the reactivity, and that the reactivity of divinylsilanes would be extremely low. The effect of the

catalyst quantity was examined and the data are shown in Fig. 3. The catalytic activities were directly proportional to the catalyst amount.

It was found that a larger amount of catalyst is needed to give reasonable conversion compared with the case of alkene metathesis. The degenerative metathesis due to the large steric

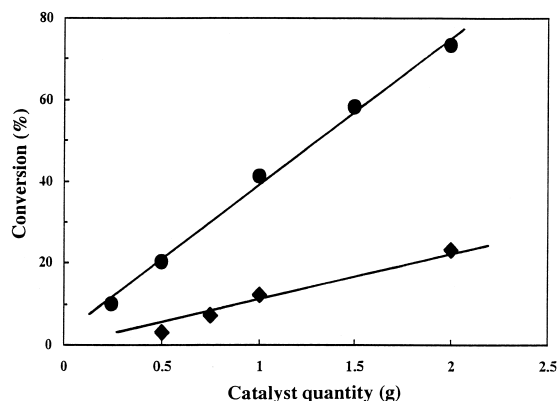


Fig. 3. Effects of catalyst quantity. Reaction conditions: substrate: tetravinylsilane; catalyst ( $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ ): 1.0 g; reaction temperature:  $50^\circ\text{C}$ ; reaction time: 12 h. ● Batch system: substrate: 0.4 g; Sn/Re molar ratio: 0.37; solvent: *n*-decane (4 ml). ◆ Flow system: Sn/Re molar ratio: 0.082; substrate concentration in PhCl solvent: 0.06 M; W/F: 20.3–81.4 g cat h mol $^{-1}$ .

Table 2  
Effect of substituent group on reactivity

	Tetravinyl- silane	Dimethyl- divinylsilane	Diethoxy- divinylsilane	Diphenyl- divinylsilane
Conversion (%)	10.5	7.1	5.0	3.0
Conversion normalized by vinyl group	2.6	3.6	2.5	1.5
Product distribution (%)				
dimer	90.4	82.5	86.8	100
trimer	8.6	13.3	10.6	trace
tetramer	1.0	4.2	2.6	0

Reaction conditions; catalyst ( $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ ): 1 g, Sn/Re molar ratio: 0.082, reaction temperature: 50°C, substrate concentration in PhCl solvent: 0.06 M, W/F: 40.7 g cat h mol<sup>-1</sup>, reaction time: 10 h.

hindrance by two substituents at silicon atom occurs more easily by the repulsive interaction at the coordination step between a reactant and carbenes, resulting in the lower reactivity [7].

The effects of substituent at silicon atom on the reactivity were investigated using a flow system under the same reaction conditions (Table 2).

The following order of increasing reactivity was determined when the reactivity was normalized by the number of vinyl groups: diphenyldivinylsilane < diethoxydivinylsilane < tetravinylsilane < dimethyldivinylsilane. This order corresponds to the order of bulkiness of the substituents.

### 3.5. Effect of silicon atom on reactivity

The reactivities of two olefin with a similar structure, trimethylvinylsilane and 3,3-dimethyl-

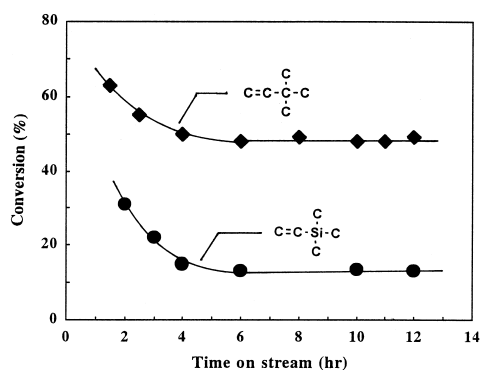


Fig. 4. Effects of silicon atom on reactivity. Reaction conditions: catalyst ( $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ ): 2 g; Sn/Re molar ratio: 0.082; reaction temperature: 50°C; substrate concentration in solvent (*n*-decane): 0.06 M; W/F: 155 g cat h mol<sup>-1</sup>.

1-butene, were investigated using a flow system and the result is shown in Fig. 4.

The rapid decrease in activity at the early stage of the reaction shows the adsorption of reactant [11]. The reactivity of trimethylsilylvinylene was much slower than that of 3,3-dimethyl-1-butene and the relative reactivity was about 1/4.

## 4. Summary

The ADMET reaction of tetravinylsilane and acyclic divinylsilanes over various kinds of metathesis catalysts has been carried out to synthesize new oligo(silylenevinylene)s with  $\sigma$ - $\pi$  conjugation. The results will be summarized as follows:

1.  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst promoted with  $\text{SnBu}_4$  is the only active catalyst for the metathesis of tetravinylsilane and divinylsilanes and new oligo(silylenevinylene)s with  $\sigma$ - $\pi$  conjugation were synthesized with high selectivity.  $\text{WCl}_6\text{-SnMe}_4$ , Grubbs and Schrock catalysts were found to be inactive.
2. The structures of all oligomers were identified by <sup>1</sup>H and <sup>13</sup>C NMR spectra. The oligomers were found to be  $\sigma$ - $\pi$  conjugated compounds of acyclic type and no cyclic compounds were formed.
3. The reactivity normalized by the number of vinyl groups increased in the following order: diphenyldivinylsilane < diethoxydivinylsilane < tetravinylsilane < dimethyldivinyl-

silane. This order agrees essentially with the steric hindrance of substituents.

4. The compound containing silicone atom lowered the reactivity greatly.

## Acknowledgements

This work was supported by Grant-in-Aid for Science Research from the Ministry of Education, Science, Sports and Culture, Japan (No. 10650773). T.K. thanks Prof. R.H. Grubbs for generously providing the Grubbs catalyst.

## References

- [1] T. Kawai, Y. Yamazaki, A. Tokumura, *Sekiyu Gakkai Shi* 26 (1983) 332.
- [2] T. Kawai, H. Goto, Y. Yamazaki, T. Ishikawa, *J. Mol. Catal.* 46 (1988) 157.
- [3] T. Kawai, Y. Yamazaki, T. Taoka, K. Kobayashi, *J. Catal.* 89 (1984) 452.
- [4] T. Kawai, Y. Yamazaki, M. Nishikawa, *Sekiyu Gakkai Shi* 27 (1984) 378.
- [5] T. Kawai, H. Goto, T. Ishikawa, Y. Yamazaki, *J. Mol. Catal.* 39 (1987) 369.
- [6] T. Kawai, H. Goto, Y. Yamazaki, *Sekiyu Gakkai Shi* 29 (1986) 212.
- [7] T. Kawai, N. Maruoka, M. Goke, T. Ishikawa, *J. Mol. Catal.* 49 (1989) 261.
- [8] T. Kawai, N. Maruoka, T. Ishikawa, *J. Mol. Catal.* 60 (1990) 209.
- [9] T. Kawai, T. Okada, T. Ishikawa, *J. Mol. Catal.* 76 (1992) 249.
- [10] T. Kawai, M. Furuki, T. Ishikawa, *J. Mol. Catal.* 90 (1994) 1.
- [11] T. Kawai, S. Uejima, T. Suzuki, T. Iyoda, *J. Mol. Catal.* 133 (1998) 51.
- [12] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997.
- [13] E.Sh. Finkel'shtein, N.V. Ushakov, E.B. Portnykh, *J. Mol. Catal.* 76 (1992) 133.
- [14] J.T. Anhaus, V.C. Gibson, W. Clegg, S.P. Collingwood, *Organometallics* 12 (1993) 1780.
- [15] K.B. Wagener, D.W. Smith Jr., *Macromolecules* 24 (1991) 6073.
- [16] R.A. Fridman, S.M. Nosakova, J.B. Krukov, A.N. Bashkirov, N.S. Nametkin, V.M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 20 (1971) 2100.
- [17] R.A. Fridman, L.G. Liberov, S.M. Nosakova, *Izv. Akad. Nauk SSSR, Ser. Khim.* 26 (1977) 678.
- [18] K.B. Wagener, D.W. Smith Jr., *Macromolecules* 26 (1993) 1633.
- [19] B. Marciniak, J. Galinski, *J. Organomet. Chem.* 266 (1984) C19.
- [20] B. Marciniak, L. Rzejak, J. Gulinski, Z. Foltynowicz, W. Urbaniak, *J. Mol. Catal.* 46 (1988) 329.
- [21] B. Marciniak, H. Maciejewski, J. Gulinski, L. Rzejak, *J. Organomet. Chem.* 362 (1989) 273.
- [22] B. Marciniak, C. Pietraszuk, *J. Organomet. Chem.* 412 (1991) C1.
- [23] B. Marciniak, Z. Foltynowicz, C. Pietraszuk, J. Gulinski, H. Maciejewski, *J. Mol. Catal.* 90 (1994) 213.
- [24] B. Marciniak, C. Pietraszuk, Z. Foltynowicz, *J. Organomet. Chem.* 474 (1994) 83.
- [25] B. Marciniak, C. Pietraszuk, *J. Chem. Soc., Chem. Commun.* (1995) 2003.
- [26] B. Marciniak, Z. Foltynowicz, M. Lewandowski, *J. Mol. Catal.* 90 (1994) 125.
- [27] B. Marciniak, M. Lewandowski, *J. Polym. Sci., Part A: Polym. Chem.* 34 (1996) 1443.
- [28] B. Marciniak, M. Lewandowski, *Tetrahedron Lett.* 38 (1997) 3777.
- [29] Y. Seki, K. Takeshita, K. Kawamoto, *J. Organomet. Chem.* 369 (1989) 117.
- [30] J. Abe, Y. Shirai, N. Nemoto, Y. Nagase, T. Iyoda, *J. Phys. Chem. B* 101 (1997) 145.
- [31] T. Kawai, K. Shiga, T. Suzuki, T. Iyoda, *J. Mol. Catal.* 140 (1999) 287.
- [32] T. Kawai et al., unpublished data.