

Acyclic diene metathesis (ADMET) of vinylsilanes over $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ catalyst

Tadashi Kawai^{*}, Keiichiro Shiga, Takehiko Suzuki, Tomokazu Iyoda

Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, Tokyo 192-0397, Japan

Received 23 April 1998; accepted 13 July 1998

Abstract

Tetravinylsilane and divinylsilanes have been successfully metathesized for the first time over $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst promoted with tetrabutyltin under mild reaction conditions. All of the products were acyclic oligomers via intermolecular metathesis; the cyclic products via intramolecular metathesis were not formed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Tetravinylsilane; Vinylsilanes; Acyclic diene metathesis (ADMET); Metathesis; Nonlinear optical material; Silylenevinylene; Rhenia–alumina catalyst ($\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst)

1. Introduction

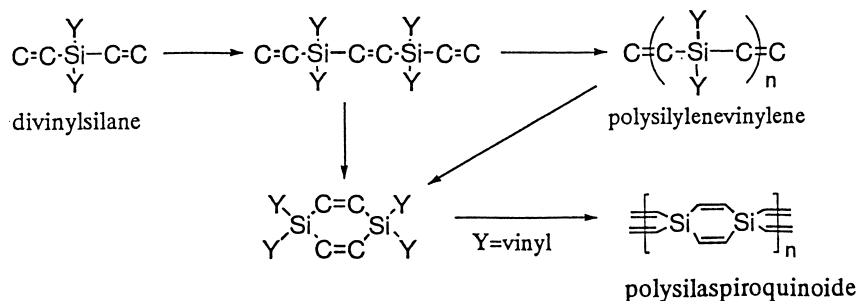
$\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst is one of the best metathesis catalysts due to its high activity and selectivity for various kinds of simple alkenes at low temperatures. Indeed, we have shown that *n*-alkenes [1,2], alkadienes [3–6], and alkyl-substituted alkenes [7,8], except alkyl-substituted vinylene compounds [9,10], were metathesized with high activity and selectivity of > 94% over $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts. Numerous studies on metathesis of various kinds of functionalized alkenes have also been reported [11].

Various kinds of alkenylsilanes [11] have been metathesized in the presence of several different metathesis catalysts. $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and Schrock catalysts appeared to exhibit high activity for alkenylsilanes [11]. Only a few study can be seen on the metathesis of vinyltrisubstituted silanes [12–14] and divinyl-disubstituted silanes [15]. It has been reported that the metathesis of vinyltrimethylsilane proceeded over $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst promoted with tetrabutyltin (SnBu_4) [12–14] and Schrock catalyst was inactive for the acyclic diene metathesis (ADMET) of divinyl-dimethylsilanes [15]. Thus, there is actually no paper on the ADMET of divinyl-disubstituted silanes over $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. On the other hand, a variety of ruthenium and rhodium catalysts work well for both reactants [16–24]. Recently, Marciniec and Lewandowski [25,26] have succeeded to get silylene–vinylene oligomers via polycondensation of divinyl-dimethylsilane and divinyl-tetramethyldisiloxane in the

^{*} Corresponding author. Tel.: +81-426-77-2837; Fax: +81-426-77-2821; E-mail: kawai-tadashi@c.metro-u.ac.jp

presence of $\text{RuCl}_2(\text{PPh}_3)_3$ and $[\text{RhCl}(\text{cod})]_2$, but the reaction has been interpreted in terms of a non-metallacarbene mechanism.

If the metathesis of divinylsilanes proceeds in a similar way to that of 1,4-alkadiene [6], the following metathesis reaction will occur.



In the equation, when the substituent Y is a vinyl group, the spiro compounds together with oligo(silylenevinylene) may be obtained. The poly(silylenevinylene) and spiro compounds with σ - π conjugation are of growing interest and importance as a partly conjugated optical material with high transparency and relatively high second hyperpolarizability predicted by ab-initio molecular orbital calculation [27]. The products display also a variety of properties (potential electric conductivity, nonlinear optical response, electro- and photoluminescence) and thus are interesting materials for many applications.

Here, we report a novel synthesis of oligo(silylenevinylene)s by an ADMET of tetravinylsilane and acyclic divinyl-disubstituted silanes over a $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst promoted with SnBu_4 as a cocatalyst. The oligomers were structurally characterized.

2. Experimental

A $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst (80–100 mesh) was prepared by using the impregnation technique described in previous papers [1,3]. The Re_2O_7 content was 18.1 wt.%, as determined by inductively coupled plasma on a Shimadzu ICPS-500 spectrometer.

Tetravinylsilane, dimethyldivinylsilane, diphenyldivinylsilane and diethoxydivinylsilane used as the starting materials and *n*-dodecane as an internal standard were dried over molecular sieves 5 Å. *n*-Decane used as a solvent was dried over P_2O_5 and distilled. SnBu_4 was used as purchased without further purification (> 99% purity).

The reactions were carried out in the liquid phase at atmospheric pressure of nitrogen gas in a Schlenk type glass reactor with stirring. The catalyst (0.5 g) was oxidized at 480°C for 1 h in dry oxygen gas flow and activated in situ at 500°C for 2 h in dry nitrogen gas flow, followed by cooling to reaction temperature. The catalyst was pretreated with SnBu_4 (30 mmol) before dosing the reactant. The reactant of 2.9 mmol (0.40 g), Sn/Re molar ratio 0.37, *n*-decane (4 ml) as a solvent and *n*-dodecane as an internal standard were used as a standard procedure.

Reaction products were analyzed by gas chromatography on a Shimadzu GC-12A equipped with an FID and a chemically bonded capillary column HP-5 (25 m \times 0.32 mm). Mass spectroscopy data were obtained with a Shimadzu GCMS-QP5000, gas chromatograph/mass spectrometer, equipped

with Shimadzu GC-17A gas chromatograph with a chemically bonded capillary column DB-1 (60 m × 0.25 mm).

^1H - and ^{13}C -NMR spectra were measured on JEOL JNM-EX270 (270 MHz). Chloroform- d was used as solvent and tetramethylsilane as the internal standard. Each oligomer separated by using gel permeation chromatography (GPC) on a Shodex SD-4 were used for the identification and characterization of reaction products.

3. Results and discussion

The effects of reaction temperature on catalytic activity are shown in Fig. 1 as a function of reaction time. The catalytic activity increased with increasing reaction temperatures.

Since $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts have usually high activity for the metathesis of various kinds of olefin even at room temperature, the reaction rate of tetravinylsilane seems very slow. One of reasons could be the steric hindrance caused by the two substituents, two vinyl groups in this case, on the Si atom in the stage of interaction between metal–carbene and reactant, and/or following formation of metallacyclobutane intermediate. Another reason could be the stabilization of metal–carbene complex caused by the interaction between the vacant 3d orbitals of the Si atom and the carbene center [14].

The GC chart for the metathesis of tetravinylsilane as an example, shown in Fig. 2, illustrates the very clean nature of the ADMET reaction. By-products were virtually not formed and thus the selectivities of metathesis products remained constant (ca. 100%) within the reaction temperature investigated.

The product distribution is shown in Fig. 3. The ratio of higher oligomers increased with increasing in reaction time (conversion), suggesting that the intermolecular metathesis proceeds as a series of successive reactions.

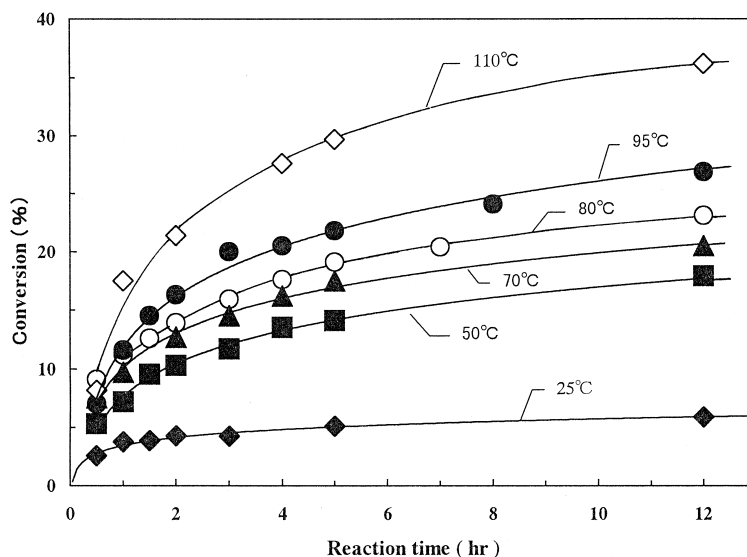


Fig. 1. Effects of reaction temperature on catalytic activity. Catalyst: $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$, 0.5 g; Sn/Re (mol/mol): 0.37; reactant: tetravinylsilane, 0.4 g (2.9 mmol); solvent: 4 ml.

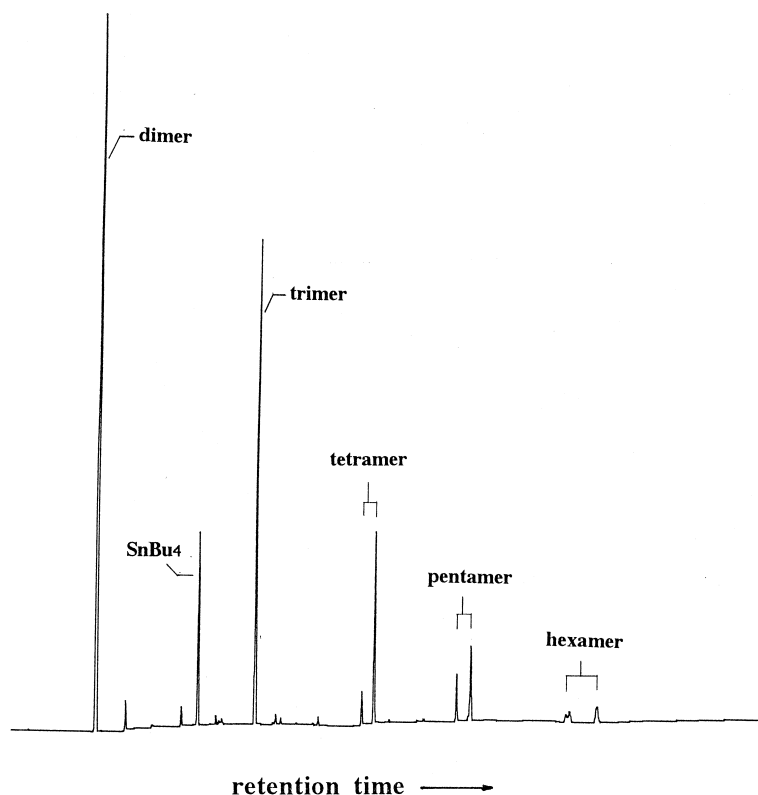


Fig. 2. GC chart of reaction products of tetravinylsilane. Catalyst: $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$.

Oligomers were isolated by GPC and characterized by ^1H - and ^{13}C -NMR spectra [28]. The structures of oligomers and the isomer ratio of tetramer to hexamer were determined from GC and NMR data. 1,1-Disilyethenes formed by a non-metallacarbene mechanism over the Ru catalysts

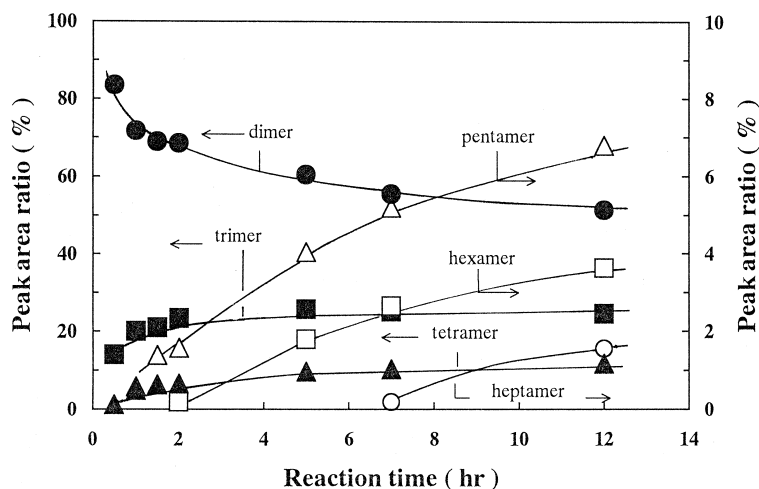


Fig. 3. Product distribution as a function of reaction time. Reaction temperature: 50°C ; catalyst: $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$, 2.0 g; Sn/Re (mol/mol): 0.37; reactant: tetravinylsilane, 0.4 g (2.9 mmol); solvent: 4 ml.

[25,26] were not detected. All oligomers were acyclic type as shown in Table 1 and this shows that they were produced through olefin metathesis mechanism, carbene mechanism. Cyclic spiro compounds were not detected by GC-MS. The absorption band assigned to the σ - π conjugation was observed at 220 nm for the all oligomers [28].

Table 1
Structures and isomer ratio. Catalyst: $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$.

dimer			
trimer			
tetramer	 85%	 15%	
pentamer	 63%	 35%	 2%
hexamer	 38%	 36%	 26%

It was found that ADMET of diphenyldivinylsilane, diethoxydivinylsilane and dimethyldivinylsilane proceeded over $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst and also $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst promoted with SnBu_4 [28]. The following order of increasing reactivity was determined: diphenyldivinylsilane < diethoxydivinylsilane < dimethyldivinylsilane < tetravinylsilane [28].

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] K.J. Ivin, J.C. Mol. Olefin Metathesis and Metathesis Polymerization, Academic Press, 1997.
- [12] R.A. Fridman, S.M. Nosakova, J.B. Krukov, A.N. Bashkirov, N.S. Naetkin, V.M. Vdovin, *Izv. Akad. Nauk, SSSR, Ser. Khim.* 20 (1971) 2100.
- [13] R.A. Fridman, S.M. Nosakova, L.G. Liberov, N. Bashkirov, *Izv. Akad. Nauk, SSSR, Ser. Khim.* 26 (1971) 678.
- [14] E.Sh. Finkel'shtein, N.V. Ushakov, E.B. Portnykh, *J. Mol. Catal.* 76 (1992) 133.
- [15] K.B. Wagener, D.W. Smith Jr., *Macromolecules* 24 (1991) 6073.
- [16] B. Marciniak, C. Pietraszuk, *J. Chem. Soc., Chem. Commun.* (1995) 2003.
- [17] B. Marciniak, C. Pietraszuk, *J. Organomet. Chem.* 412 (1991) C1.
- [18] B. Marciniak, C. Pietraszuk, Z. Foltynowicz, *J. Organomet. Chem.* 474 (1994) 83.
- [19] B. Marciniak, J. Galinski, *J. Organomet. Chem.* 266 (1984) C19.
- [20] B. Marciniak, H. Maciejewski, J. Gulinski, L. Rzejak, *J. Organomet. Chem.* 362 (1989) 273.
- [21] B. Marciniak, L. Rzejak, J. Gulinski, Z. Foltynowicz, W. Urbaniak, *J. Mol. Catal.* 46 (1988) 329.
- [22] Y. Seki, K. Takeshita, K. Kawamoto, *J. Organomet. Chem.* 369 (1989) 117.
- [23] B. Marciniak, Z. Foltynowicz, C. Pietraszuk, J. Gulinski, H. Maciejewski, *J. Mol. Catal.* 90 (1994) 213.
- [24] B. Marciniak, Z. Foltynowicz, M. Lewandowski, *J. Mol. Catal.* 90 (1994) 125.
- [25] B. Marciniak, M. Lewandowski, *J. Polym. Sci., Part A: Polym. Chem.* 34 (1996) 1443.
- [26] B. Marciniak, M. Lewandowski, *Tetrahedron Lett.* 38 (1997) 3777.
- [27] J. Abe, Y. Shirai, N. Nemoto, Y. Nagase, T. Iyoda, *J. Phys. Chem. B* 101 (1997) 145.
- [28] T. Kawai et al., unpublished data.