JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2003; **16:** 818–823

Synthesis and structural characterization of *trans*-tactic vinylene–silylene(siloxylene) polymers[†]

Bogdan Marciniec* and Ewa Małecka

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

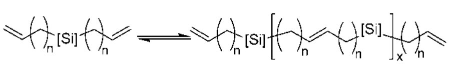
Received 17 March 2003; revised 14 May 2003; accepted 30 May 2003

ABSTRACT: Divinyldimethylsilane (**1**), divinyldiphenylsilane (**2**), divinyltetramethyldisiloxane (**3**) and divinyltetraethoxydisiloxane (**4**) in the presence of [{$RuCl_2(CO)_3$}$_2$] (**I**) as a catalyst undergo effective silylative coupling (SC) polycondensation giving stereoselectively *trans*-tactic polymers (**5**–**8**) ($M_w = 3800$–8500), yield 75–84%. The products isolated and characterized by ^1H and ^{13}C NMR and GPC methods cannot be synthesized via ADMET polymerization. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: *trans*-tactic vinylene–silylene(siloxylene) polymers; divinyldiorganosilanes; divinyltetraorganodisiloxanes; stereoselectivity; ruthenium carbonyl catalyst

INTRODUCTION

Acyclic diene metathesis (ADMET) polymerization catalyzed by highly active tungsten and molybdenum metathesis catalysts such as Schrock's alkylidene, e.g. [{$CF_3)_2MeCO)$}$_2ArN$—M═CH(^tBu)], where M = Mo and W,[1] and Grubbs' catalysts, [$RuCl_2$(═CHPh)($PCy_3)_2$] and [$RuCl_2$(═CHPh)($IMesH_2$)(PCy_3)],[2] is a universal route for the synthesis of linear well-defined unsaturated polymers.[3] ADMET polymerization of silicon-containing dienes such as dialkenylsilanes and siloxanes (except vinyl derivatives) furnishes a variety of unsaturated homopolymers including carbosilanes and carbosiloxane units:[4]

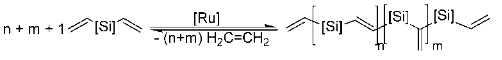


(1)

where [Si] = —$Si(CH_3)_2$—, —$(CH_3)_2SiOSi(CH_3)_2$—.

ADMET polymerization of di(allyl,butenyl)silanes and silacyclobutanes and siloxanes proceeds effectively in the presence of a heterogeneous catalyst [$Re_2O_7/Al_2O_3 + SnR_4(PbR_4)$], giving predominantly a mixture of both cyclic and linear products.[5] Unfortunately, vinyl derivatives of silicon compounds which are of most industrial importance are completely inert to productive homometathesis, presumably owing to steric hindrance of silyl groups stimulating non-productive cleavage of disilyl metallacyclobutane.[6] This supposition is based on the analogy with the inactivity of metallacarbenes in self-metathesis of vinyl-substituted silicon compounds.

In contrast to the inactivity of metallacarbenes in ADMET polymerization, in the presence of ruthenium and rhodium complexes containing or generating M—H and M—Si bonds (M = Ru, Rh), divinyldiorganosilicon compounds undergo intermolecular polycondensation under optimized conditions (ruthenium catalysts) yielding linear unsaturated polymers according to the following reaction:



(2)

where [Si] = —$Si(CH_3)_2$—,[7a] —$(CH_3)_2Si$—O—$Si(CH_3)_2$—[7b] or —$(CH_3)_2Si$—NH—$Si(CH_3)_2$—;[7c] catalysts: [$RuCl_2(PPh_3)_3$], 130 °C, 120 h, $M_w = 1510$, $M_w/M_n = 1.19$, DP = 17;[7a] [$RuCl_2(PPh_3)_3$], 130 °C, 72 h, $M_w = 1815$, $M_w/M_n = 1.16$, DP = 10;[7b] [RuHCl(CO)($PPh_3)_3$], 130 °C, 1 week, $M_w = 2385$, $M_w/M_n = 1.21$, DP = 15.[7c]

Previous reports have shown that less active ruthenium complexes, i.e. [{$RuCl_2(CO)_3$}$_2$] (**I**), catalyze the polycondensation of divinyl-substituted silazane[7c] as well as bis(silyl)benzene[7d] {while [RuH(OAc)(CO)($PPh_3)_2$] catalyzes the reaction of silylstyrene}[7e] to give stereoregular *trans*-tactic linear polymers.

The condensation (silylative coupling) of monovinyl-substituted silicon compounds proceeds through cleavage of the ═C—Si bond of the vinyl-substituted silicon compound and the activation of the ═C—H bond of

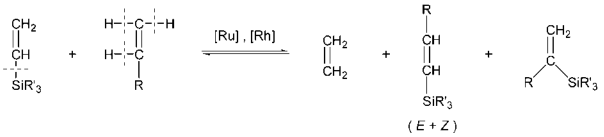
---

**Correspondence to:* B. Marciniec, Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland.
E-mail: marcinb@amu.edu.pl

[†] Dedicated to Professor Marek Krygowski on the occasion of his 65th birthday in recognition of his significant contributions to physical organic chemistry.

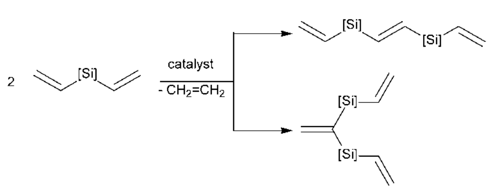
Contract/grant sponsor: State Committee for Scientific Research; *Contract/grant number:* K026/T09/2001.

the second vinylsilane molecule according to the following equation (for recent reviews on the silylative coupling of alkenes with vinylsilanes, see Ref. 8):



(3)

The evidence for the non-metallacarbene mechanism of monovinylsilane transformation has been reported previously,[9a–c] but can be generalized for dimerization of divinyl-substituted silicon compounds [see Eqn. (4)] leading subsequently to competitive linear oligomerization and ring-closing silylative coupling.[10,11]



(4)

In the presence of [{$RuCl_2(CO)_3$}$_2$], the 1,2-*trans*-dimer is exclusively obtained,[12] whereas [{RhX(cod)}$_2$], X = μ-Cl or μ-$OSiMe_3$, preferably catalyze the formation of the 1,1-product, and ruthenium–phosphine complexes [$RuCl_2(PPh_3)_3$] and [$RuHCl(CO)(PPh_3)_3$] furnish both dimeric products.[12]

The aim of this work was to apply this new synthetic route to prepare stereoselectively *trans*-tactic poly[vinylene–silylene(siloxylene)]s via polycondensation of divinyldiorganosilanes and divinyltetraorganodisiloxanes in the presence of [{$RuCl_2(CO)_3$}$_2$] as a catalyst.

EXPERIMENTAL

General considerations. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Gemini series NMR superconducting spectrometer system or a Varian 300 XL instrument in C_6D_6 as a solvent. ^{1}H NMR and ^{13}C NMR spectra are reported as δ (ppm) with reference to the residual signals from C_6D_6. Infrared spectra (KBr plates) were recorded using a Brucker IFS-113v FT-IR spectrometer. The mass spectra of all products were determined by gas chromatographic–mass spectrometric (GC–MS) analysis on a Varian 3300 gas chromatograph equipped with a 30 m DB-1 capillary column and a Finnigan Mat 800 ion trap detector. GC analyses were carried out on a Varian 3300 gas chromatograph.

Gel permeation chromatographic (GPC) data were collected using a Gilson HPLC system with a 2 × 250 × 10 mm Jordi-Gel divinylbenzene (DVB) column, 500 and 100 Å, and polysiloxane standards (mobile phase, tetrahydrofuran (THF); flow-rate, 1.2 ml min^{-1}; temperature, ambient; injection volume, 20 μl). Average molecular weights and polymer dispersity indices (PDI) of the polymers were determined by polysiloxane calibration.

Elemental analyses were carried out by Atlantic Microlab, Polish Academy of Sciences.

Materials. Chemicals were obtained from the following sources: divinyldimethylsilane (**1**), divinyltetramethyldisiloxane (**3**), divinyltetraethoxydisiloxane (**4**) and dichlorodiphenylsilane from ABCR, THF and magnesium from POCh, vinyl bromide from Aldrich, hexane from Merck, benzene-d_6 from Dr Glasser (Basel), [{$RuCl_2(CO)_3$}$_2$] (**I**) from Strem and [$RuHCl(CO)(PPh_3)_3$] from Aldrich. [$RuCl(SiMe_3)(CO)(PPh_3)_2$] was prepared according to the method described earlier[9a,c] and [$RuCl_2(PPh_3)_3$] according to the standard procedure. All these complexes were used without further purification. THF prior to use was dried over sodium and benzophenone and stored under argon and freshly distilled prior to use. Vinylmagnesium bromide was synthesized via a well-known procedure.

Synthesis and characterization of divinyldiphenylsilane (2). A 0.1 mol amount of vinylmagnesium bromide in dry THF was introduced into a flame-dried, Ar-purged, three-necked, 500 ml round-bottomed flask equipped with a stirrer bar, a condenser and a dropping funnel. Dichlorodiphenylsilane in 100 ml of dry pentane was subsequently added dropwise over 5 h. The mixture was allowed to warm to room temperature and stirred under reflux for 12 h, then extracted three times with aqueous NH_4Cl and the organic layers were dried over $MgSO_4$. The combined organic extracts were filtered off and evaporated under reduced pressure. The product was then placed over CaH_2, stirred overnight and distilled off under reduced pressure after filtration of CaH_2. Crude monomer **2** with b.p. 130–131 °C at 0.05 mmHg was distilled off. The yield of the monomer was 80%. The spectral properties observed were as follows: ^{1}H NMR [C_6D_6, δ (ppm)]: 5.79–6.16 (m, 4H, —SiCH=C*H*$_2$), 6.41–6.53 (m, 2H, —SiC*H*=CH$_2$), 7.12–7.23 and 7.58–7.64 (m,=CH in phenyl). Elemental analysis: calculated for $C_{16}H_{16}Si$, C 72.72, H 6.06; found, C 72.70, H, 6.03%.

General procedure for silylative coupling (SC) polycondensation to get *trans*-tactic polymers. The following procedure was used to prepare polymers **5**–**8**. The monomer was degassed and distilled from CaH_2 prior to polycondensation, which was carried out in the bulk placed in a 10 ml flasks equipped with a magnetic stirrer bar and reflux. In a typical reaction, 1.5 ml of monomer **1** (9.8 mmol), **2** (6.4 mmol), **3** (6.3 mmol) or **4** (4.8 mmol) was combined with [{$RuCl_2(CO)_3$}$_2$] (**I**). The monomer to catalyst ratio typically used was 100 : 1. The reaction mixture was stirred in an oil-bath at 90 °C until its viscosity increased. After 10 days, the reactions were terminated. The polymer was filtered off on SiO_2 using hexane as eluent. The polymer was dissolved in methylene chloride, precipitated in dry CH_3OH, and dried in an evaporator to constant weight.

Characterization of 5–8

5. ^{1}H NMR (300 MHz, C_6D_6), δ (ppm): 0.22 (s,—SiCH_3), 6.91 (s, —CH=CH—). ^{13}C NMR (75 MHz, C_6D_6), δ (ppm): 1.18 (—Si—CH_3, at internal silicon atoms), 150.98 (—CH=CH—). GPC: $M_w = 8200$; PDI = 1.32, $n = 97$. Elemental analysis: calculated for (C_4H_8Si), C 57.14, H 9.52; found, C 57.16, H 9.56%.

6. ^{1}H NMR (300 MHz, C_6D_6), δ (ppm): 5.60–5.95 (m, —SiCH=CH_2,), 6.28 (s, —SiCH=CH_2), 6.68 (s, —CH=CH—), 7.18–7.76 (m, =CH in phenyl). ^{13}C NMR (75 MHz, C_6D_6), δ (ppm): 128.89 (—SiCH=CH_2), 129.29 (—SiCH=CH_2), 152.86 (—CH=CH—), 133.08–136.29 (m, —CH, in phenyl); GPC: $M_w = 3800$; PDI = 1.50, $n = 17$. Elemental analysis: calculated for ($C_{14}H_{12}Si$), C 80.77, H 5.80; found, C 80.01, H 5.55%.

7. ^{1}H NMR (300 MHz, C_6D_6), δ (ppm): 0.18–0.98 (m, —SiCH_3), 6.80 (s, —CH=CH—). ^{13}C NMR (75 MHz, C_6D_6), δ (ppm): 0.48, 1.07, 1.91 (—SiCH_3), 151.35 (—CH=CH—). GPC: $M_w = 8500$; PDI = 1.51, $n = 53$. Elemental analysis: calculated for ($C_6H_{14}Si_2O$), C 45.57, H 8.86; found, C 45.26, H 8.86%.

8. ^{1}H NMR (300 MHz, C_6D_6), δ (ppm): 0.93–0.98 (m, —SiOCH_2CH_3, in terminal group), 1.15–1.21 (m, —SiOCH_2CH_3, in chain), 3.32–3.40 (m, —SiOC$H_2$$CH_3$, in terminal group), 3.82–3.99 (m, —SiOC$H_2$$CH_3$, in chain), 5.79–6.00 (m, —SiCH=CH_2), 6.02–6.13 (m, —SiCH=CH_2), 6.23–6.27 (m, —CH=CH—). ^{13}C NMR (75 MHz, C_6D_6), δ (ppm): 18.51 (—SiO$CH_2$$CH_3$, in terminal group), 18.91 (—SiOCH$_2$ CH_3, in chain), 59.34 (—SiOCH$_2$$CH_3$, in terminal group), 58.78 (—SiO$CH_2$$CH_3$, in chain), 130.98 (—SiCH=CH$_2$), 136.28 (—SiCH=CH_2), 146.53 (—CH=CH—). GPC: $M_w = 4900$; PDI = 1.58, $n = 17$. Elemental analysis: calculated for ($C_{10}H_{22}Si_2O_5$), C 43.16, H 7.91; found, C 43.54, H 7.78%.

RESULTS AND DISCUSSION

As we reported earlier, divinyldimethylsilane (**1**)[7a] and divinylteramethyldisiloxane (**3**)[7b] in the presence of ruthenium–phosphine complexes, e.g. $[RuCl_2(PPh_3)_3]$, undergo polycondensation leading to predominantly linear silylene(siloxylene) oligomers. In order to find the optimum conditions for effective polycondensation, in this work catalytic screenings were perfomed using the model processes of divinyldiphenylsilane (**2**) and divinyltetraethoxydisiloxane (**4**) to measure silane (siloxane) conversion and the yield of dimers, trimers and higher oligomers using GC–MS and GPC methods. The results are presented in Table 1.

Stereoselective synthesis of linear dimers performed in the presence of $[\{RuCl_2(CO)_3\}_2]$[12] stimulated a study aimed at the optimization of the synthesis of *trans*-tactic polymers.

Results of the spectroscopic analyses of the products (5–8) obtained in the presence of this catalyst excluded the occurrence of quaternary carbon atoms, i.e. 1,1-bis(silyl)ethene fragments, in the polymer chains.

An exemplary ^{13}C NMR spectrum of the product **5** is presented in Fig. 1.

The signal observed at 150.98 ppm corresponded to the ternary carbon atoms =CH of the 1,2-bis(silyl)ethene group. No quaternary carbon atom is observed in the ^{13}C NMR spectrum.

Concerning the polycondensation of divinyldiphenylsilane, the ^{1}H NMR, ^{13}C NMR and DEPT analyses of the polymeric products also excluded the presence of quaternary carbon atoms in the chains of the polymer obtained. The signal at 152.86 ppm in the ^{13}C NMR spectrum was assigned to the carbon atoms of the 1,2-bis(silyl)ethene fragments.

GC–MS analysis of the post-reaction mixture of (**1**) and/or (**2**) in the initial stage revealed a signal in the region corresponding to dimers, which was assigned to linear products of molecular weight 224 for **1** and 443 for **2**, in the case of (**1**) also with a cyclic dimeric product of molecular weight 196.

Table 1. Effect of catalyst on the conversion of divinyldiphenylsilane (**2**) and divinyltetraethoxydisiloxane (**4**) and the yields of dimers, trimers and oligomers

Compound	Catalyst	Conversion (%)	Yield (%)			
			Dimers			Higher oligomers
			Linear	Cyclic	Trimers	
2 (80 °C, 24 h)	$[RuCl(SiMe_3)(CO)(PPh_3)_2]$	70	18	2	28	52
	$[RuHCl(CO)(PPh_3)_3]$	75	19	2	23	56
	$[RuCl_2(PPh_3)_3]$	92	19	3	13	65
	$[\{RuCl_2(CO)_3\}_2]$	79	28	0	20	52
4 (130 °C, 24 h)	$[RuCl(SiMe_3)(CO)(PPh_3)_2]$	85	16	14	20	50
	$[RuHCl(CO)(PPh_3)_3]$	82	15	18	19	48
	$[RuCl_2(PPh_3)_3]$	94	6	9	15	70
	$[\{RuCl_2(CO)_3\}_2]$	97	8	3	11	74

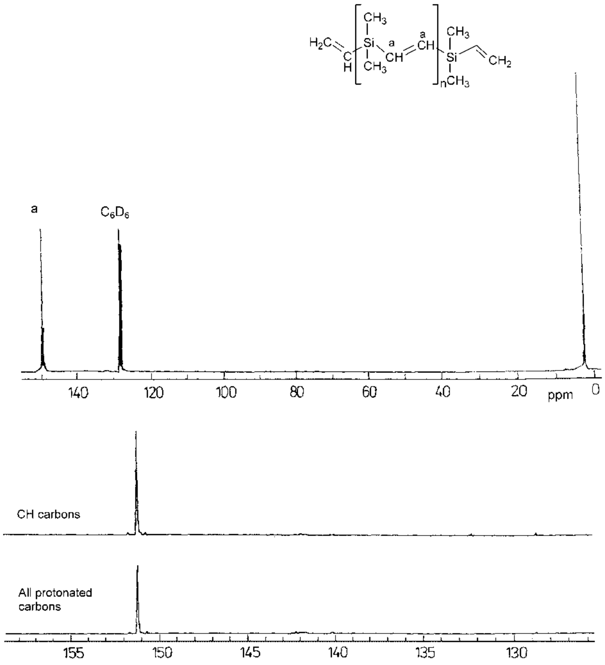
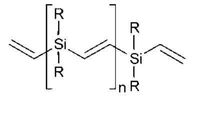


Figure 1. ^{13}C NMR and DEPT spectra of polymer **5**

On the basis of the above data, the proposed structural formula of polymers **5** and **6** obtained is



where for **5** R = —CH_3, $n \approx 97$ and for **6** R = —C_6H_5, $n \approx 17$.

As has been reported earlier, the silylative coupling polycondensation of divinyltetramethyldisiloxane catalyzed by [$RuCl_2(PPh_3)_3$] yielded a polymer containing 1,2-bis(silyl)ethene and 1,1-bis(silyl)ethene fragments.[7b] Results of the spectroscopic analyses of the products of the polycondensation of divinyltetramethyldisiloxane (**3**) and divinyltetraethoxydisiloxane (**4**) catalyzed by [{$RuCl_2(CO)_3$}$_2$] also excluded the presence of quaternary carbon atoms in the chains of the polymer obtained, which confirmed the absence of 1,1-bis(silyl)ethene fragments in the polymer chains. The ^{13}C NMR spectrum of the products **7** and **8** revealed signals at 151.35 ppm (**7**) and 146.53 (**8**), assigned to the ternary carbon atoms included in the 1,2-*trans* isomer in the polymer chain.

The GC–MS results in the initiating period of the reaction confirmed the structure of a linear dimer revealing only two signals in the region corresponding to dimers. One of the signals corresponded to a linear dimer and the other to a cyclic dimer.

The ^{1}H and ^{13}C NMR spectra revealed signals assigned to the polymer terminal groups in the region corresponding to alkenes.

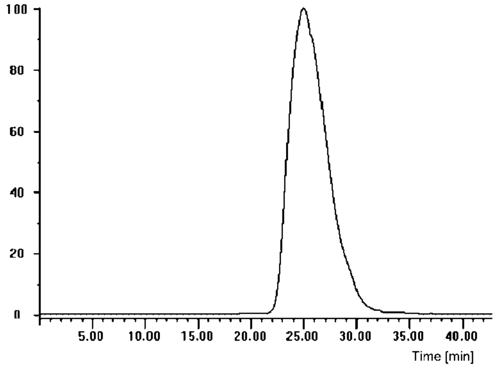
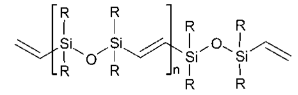


Figure 2. GPC of polymer **5**

On the basis of the above-discussed results, the structural formula of polymers **7** and **8** is



where for **7** R = —CH_3, $n \approx 53$ and for **8** R = —OC_2H_5, $n \approx 17$.

The polymer chemistry is clean, with no evident side-products except pure ethylene and trace amounts of cyclic products. A typical GPC trace of exemplary product **5** is presented in Fig. 2. The low PDI values of the polymers (see Fig. 2 and Table 2) are due to the loss of some low molecular weight fractions on purification.

The effect of the solvent on the mass of the polymer products formed was tested using **3** as a substrate. All the reactions were carried out according to the general procedure described in the Experimental section, using 1 M solutions of **3**. The results of NMR analysis confirmed the structure of poly(1,1,3,3-tetramethyldisiloxa-1-ethene)s formed in all reactions examined. The results given in Table 3 show that polymerization in solvents leads to products of much lower M_w and slightly greater PDI.

Table 2. Yields, molecular weights and polydispersity of *trans*-tactic vinylene–silylene(siloxylene) polymers **5**–**8** prepared via silylative coupling polycondensation of **1**–**4**

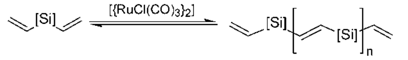
Polymer	Yield (%)	M_w	M_n	PDI
5	79	8200	6210	1.32
6	75	3800	2530	1.50
7	82	8500	5600	1.51
8	84	4900	3100	1.58

Table 3. Effect of solvent on the M_w and the PDI of the product of silylative coupling polycondensation of divinyltetramethyldisiloxane (**3**) in the presence of **I**[a]

Solvent	M_w	PDI
None	8500	1.51
Benzene	4800	1.65
Toluene	4500	1.68
Chlorobenzene	3300	1.85

[a] Reaction conditions: [siloxane]: [Ru] = 100: 1; reflux, 90 °C, 10 days; 100% conversion of **3**.

All the spectroscopic characterization results confirm that polycondensation of **1**–**4** catalyzed by **I** occurs stereoselectively to give *trans*-tactic vinylene–silylene(siloxylene) polymers **5**–**8** according to the following equation:



(5)

where $[Si] = —Si(CH_3)_2—$, $—Si(C_6H_5)—$, $—(CH_3)_2Si—O—Si(CH_3)_2—$, $—(C_2H_5O)_2Si—O—Si(OC_2H_5)_2—$.

The mechanistic pathways for silylative coupling of monovinylsilanes are well established[8] and exemplary schemes for the condensation of divinyl-substituted silicon compounds have been given earlier for divinyldimethylsilane,[7a] divinyltetramethyldisiloxane[7b] and divinyltetramethyldisilazane[7c] and also for 1,4-bis(vinyldimethylsilyl)benzene[7d] and 4-(dimethylvinylsilyl)styrene.[7e]

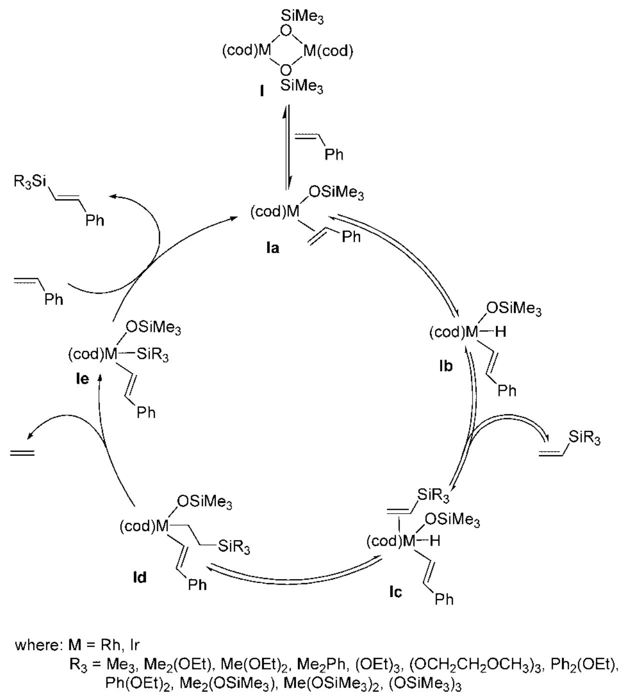
The mechanism of catalysis involves the insertion of vinylsilicon dienes into the Ru—H and M—Si bonds, followed by β-Si and β-H elimination to yield ethene and two isomeric *trans*- and *gem*-bis(vinylsilyl)ethenes, respectively. If the process is catalyzed by $[\{RuCl_2(CO)_3\}_2]$ (**I**) as a precursor, *trans*-$CH_2{=}CH[Si]CH{=}CH[Si]CH{=}CH_2$ is exclusively formed, so under the optimum conditions the well-defined *trans*-tactic vinylene–silylene(siloxylene) polymers **5**–8 can be effectively formed.

There is no evidence for the real ruthenium catalyst structure in this reaction. Our preliminary mechanistic study on the transformation of monovinylsilicon compounds has shown that in the presence of non-phosphine ruthenium complexes such as $[\{RuCl_2(CO)_3\}_2]$ and $[Ru_3(CO)_{12}]$ the *trans* products of the general structure$\equiv SiCH{=}CHSi\equiv$ are stereoselectively formed.[13] A previously reported scheme of the catalysis by $[Ru_3(CO)_{12}]$ involves hydrovinylation (activation of $=$C—H bond) of the ruthenium complex in which the generation of an Ru—H and an Ru—Si bond is followed by elimination of the product. Spectroscopic analysis of the catalyst $[Ru_3(CO)_{12}]$ treated with vinyltrimethylsilane indicated the presence of the Ru—Si bond.[13]

A comprehensive mechanistic study of the silylative coupling of styrene with vinylsilanes catalyzed by non-phosphine dimeric rhodium and iridium siloxide complexes of the general formula $[(cod)M\mu\text{-}(OSiMe)_3]_2$ (where M = Rh, Ir) provided the evidence for the activation of $=$C—H in styrene by these complexes which occurs as follows.[14]

A mechanistic study confirmed that catalysis occurs via generation of M—H and M—Si intermediates according to a dissociative pathway, i.e. there is no migratory insertion of the alkene into the M—Si bond involved. Instead, a lower activated step of reductive elimination of the product takes place (Scheme 1).

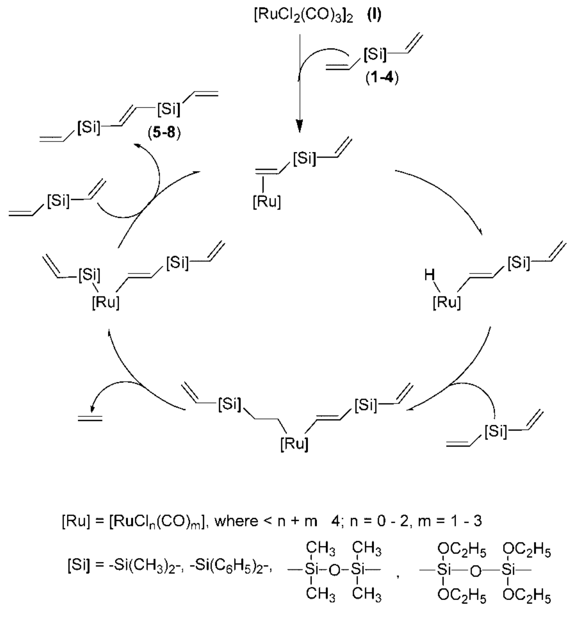
By analogy with the well-documented $[Ru_3(CO_{12}]$[13] and $[(cod)M(OSiMe_3)_2]_2$ (where M = Rh, Ir)[14] catalyzed reactions of monovinylsilanes, the silylative coupling dimerization of divinylsilane and divinylsiloxane by the dimeric complex $[\{RuCl_2(CO)_3\}_2]$ is proposed to occur also via hydrovinylation as the key step initiating polycondensation via the formation of monomeric active ruthenium–carbonyl complexes (Scheme 2).



where: M = Rh, Ir
$R_3 = Me_3, Me_2(OEt), Me(OEt)_2, Me_2Ph, (OEt)_3, (OCH_2CH_2OCH_3)_3, Ph_2(OEt), Ph(OEt)_2, Me_2(OSiMe_3), Me(OSiMe_3)_2, (OSiMe_3)_3$

Scheme 1. Catalysis by transition metal siloxides of the silylative coupling of styrene with vinylsilanes

A detailed mechanistic examination of the silylative coupling condensation of styrene with vinylsilanes catalyzed by $[\{RuCl_2(CO)_3\}_2]$ (**I**) is in progress.



$[Ru] = [RuCl_n(CO)_m]$, where < n + m 4; n = 0 - 2, m = 1 - 3

[Si] = $-Si(CH_3)_2-$, $-Si(C_6H_5)_2-$, $—\underset{CH_3}{\overset{CH_3}{Si}}—O—\underset{CH_3}{\overset{CH_3}{Si}}—$, $—\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}—O—\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}—$

Scheme 2. Silylative coupling condensation of divinyl-substituted silanes and siloxanes

CONCLUSIONS

In the presence of [{$RuCl_2(CO)_3$}$_2$], divinyldiorganosilanes of the general formula $R_2Si(CH{=}CH_2)_2$, where R = CH_3, C_6H_5, and divinyltetraorganodisiloxanes of the formula $CH_2{=}CHR'_2SiOSiR'_2CH{=}CH_2$ where R′ = —CH_3, —OC_2H_5, undergo silylative coupling polycondensation giving stereoselectively *trans*-tactic polymers (**5**–**8**).

Owing to the steric hindrance of the silyl group in vinylsilanes, the products **5**–**8** cannot be synthesized via ADMET polymerization.

This catalytic process opens up a new synthetic route to vinylene–silylene(siloxylene) *trans*-tactic polymers of prospective importance as new precursors for materials of special application.

Acknowledgment

This work was supported by Grant No. K026/T09/2001 from the State Committee for Scientific Research (Poland).

REFERENCES

1. Schrock RR, Murdzanek JS, Bazan GC, Robbins J, Dimone M, O'Regan M. *J. Am. Chem. Soc*. 1990; **112**: 3875–3886.
2. Schwab P, France MB, Ziller JW, Grubbs RH. *Angew. Chem., Int. Ed. Engl.* 1995; **34**: 2039–2041.
3. (a) Ivin KJ, Mol JC. *Olefin Metathesis and Metathesis Polymerization*. Academic Press: New York, 1997; Chapt. 8; (b) Wagener KB, Boncella JM, Nel JG. *Macromolecules* 1999; **24**: 2649–2657.
4. (a) Wagener KB, Smith DW Jr. *Macromolecules* 1991; **24**: 6073–6078; (b) Smith DW Jr, Wagener KB. *Macromolecules* 1993; **26**: 3533–3537; (c) Smith DW Jr, Wagener KB. *Macromolecules* 1993; **26**: 1633–1642; (d) Brzezinska KR, Wagener KB, Burns GT. *J. Polym. Sci., Part A: Polym. Chem.* 1999; **37**: 849–856; (e) Brzezinska KR, Schitter R, Wagener KB. *J. Polym. Sci., Part A: Polym. Chem.* 2000; **38**: 1544–1550; (f) Church AC, Pawlow JH, Wagener KB. *J. Organomet. Chem.* 2001; **620**: 287–295.
5. (a) Finkel'shtein ES, Portnykh EB, Ushakov NV, Vdovin BM. *Izv. Akad. Nauk SSSR, Ser. Khim*. 1981; 641–645; (b) Finkel'shtein ES, Portnykh EB, Ushakov NV. *J. Mol. Catal*. 1992; **76**: 133–144; (c) Finkel'shtein ES, Portnykh EB, Ushakov NV, Marciniec B. In *Silicon-containing Polymers*, Jones RG (ed). Royal Society of Chemistry: Cambridge, 1995; 29; (d) Finkel'shtein ES. *Vysokomol. Soedin*. 1995; **37**: 718.
6. Schrock RR, De Pue RT, Feldman J, Schverin CJ, Dewan SC, Liu AH. *J. Am. Chem. Soc*. 1988; **110**: 1423–1435.
7. (a) Marciniec B, Lewandowski M. *J. Polym. Sci., Part A: Polym. Chem.* 1996; **34**: 1443–1445; (b) Marciniec B, Lewandowski M. *J. Inorg. Organomet. Polym*. 1995; **5**: 115–122; (c) Marciniec B, Malecka E. *Macromol. Rapid Commun.* 1999; **20**: 475–479; (d) Majchrzak M, Itami Y, Marciniec B, Pawluc P. *Tetrahedron Lett.* 2000; **41**: 10303–10307; (e) Majchrzak M, Itami Y, Marciniec B, Pawluc P. *Macromol. Rapid Commun*. 2001; **22**: 202–205.
8. (a) Marciniec B. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Cornils B, Herrmann WA (eds). VCH: Weinheim, 2002; Chapt. 2.6; (b) Reichl JA, Berry DH. *Adv. Organomet. Chem.* 1998; **43**: 203; (c) Marciniec B. *Appl. Organomet. Chem.* 2000; **14**: 527–538; (d) Marciniec B, Pietraszuk C. *Curr. Org. Chem.* 2003; 7691–7735; (e) Marciniec B. In *Ring Opening Metathesis Polymerization and Related Chemistry*, Kosravi E, Szymanska-Buzar T (eds). Kluwer: Dordrecht, 2002; 331–224.
9. (a) Wakatsuki Y, Yamazaki H, Nakano N, Yamamoto Y. *J. Chem. Soc., Chem. Commun.* 1991; 703–704; (b) Marciniec B, Pietraszuk C. *J. Chem. Soc., Chem. Commun.* 1995; 2003–2004; (c) Marciniec B, Pietraszuk C. *Organometallics* 1997; **16**: 4320–4326.
10. Marciniec B. *Mol. Cryst. Liq. Cryst.* 2000; **353**: 173–182.
11. Marciniec B, Malecka E, Majchrzak M, Itami Y. *Macromol. Symp.* 2001; **174**: 137–144.
12. Marciniec B, Lewandowski M. *Tetrahedron Lett.* 1997; **36**: 3777–3780.
13. Marciniec B, Foltynowicz Z, Pietraszuk C, Gulinski J, Maciejewski H. *J. Mol. Catal*. 1994; **90**: 213–224.
14. (a) Marciniec B, Walczuk-Gusciora E, Blazejewska-Chadyniak P. *J. Mol. Catal*. 2000; **160**: 165–171; (b) Marciniec B, Walczuk-Gusciora E, Pietraszuk C. *Organometallics* 2001; **20**: 3423–3428; Marciniec B, Kownacki I, Kubicki M. *Organometallics* 2002; **21**: 3263–3270.