

ADMET copolymerization of divinyltetraethoxydisiloxane with 1,9-decadiene catalyzed by Grubbs' catalyst

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Abstract

The acyclic diene metathesis (ADMET) copolymerization of divinyltetraethoxydisiloxane with 1,9-decadiene, catalyzed by $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$, is the first example of a siloxylene–vinylene–alkenylene copolymer reported in the literature. This copolymer was isolated and characterized by ^1H , and ^{13}C NMR spectroscopy and GPC analysis ($M_n = 18\,000$, $\text{PDI} = 2.9$).

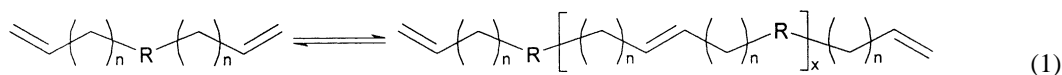
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1. Introduction

Acyclic diene metathesis (ADMET) polymerization represents a unique synthetic route to a variety

of well-defined polyalkenylenes, e.g. [1,2]. ADMET polymerization of silicon-containing dienes such as di-alkenylsilanes and siloxanes (except vinyl derivatives) proceeds smoothly in the presence of molybdenum and tungsten alkylidenes [3–5], e.g. $[(\text{CF}_3)_2\text{MeCO}]_2(\text{ArN})\text{M}=\text{CH}(t\text{-Bu})$, where $\text{M} = \text{Mo}$ and W , and



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where $\text{R} = -\text{SiMe}_2, -\text{Me}_2\text{Si}-\text{O}-\text{SiMe}_2-$, $n = 1-4$.

Finkel'shtein et al. [10,11] reported that the ADMET reaction of di(allyl, butenyl)silanes and silacyclobutanes and siloxanes as well as diallyltetra-ethylidisiloxanes proceeds effectively in the presence of a heterogeneous catalyst, $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3 + \text{SnR}_4$ (or PbR_4), giving predominantly a mixture of both cyclic and linear products.

However, vinyl derivatives of organosilicon compounds, which are of fundamental industrial

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importance, are completely inert to productive homometathesis presumably due to the steric hindrance of silyl groups stimulating nonproductive cleavage of disilylmetallacyclobutane [12]. Recent reports on the ADMET oligomerization of tetravinylsilane and divinyl-disubstituted silanes in the presence of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3 + \text{SnBu}_4$ indicate the formation of oligomers, which were identified by GPC methods in a very low yield (around 10–15%) [13,14]. Recent data on the metathetical transformation of vinylsilanes in the presence of the well-defined, functional group tolerant molybdenum and ruthenium carbenes has provided a new opportunity for the wide application of olefin metathesis in organosilicon chemistry. The reactivity of vinylsilanes has been confirmed in the following processes: ring opening metathesis/cross-metathesis (AROM/CM) of substituted norbornene with vinylsilanes in the presence of molybdenum carbene [15], RCM of acyclic silyl ether dienes [16] and the CM of vinyl-substituted silsesquioxanes with alkenes [17] in the presence of molybdenum and ruthenium carbenes, CM of vinyltrialkoxo- and vinyltrisiloxysilanes with styrene [18], *p*-substituted styrenes, 1-alkenes, allyl derivatives [19], allyl alkyl ethers [20], 5-hexen-1-yl acetate [21] and degradation of 1,4-polybutadiene by vinyltriethoxysilane [22] catalyzed by Ru-carbenes.

On the other hand, the stepwise substitution of OR or OSiMe_3 in $\text{ViSi}(\text{OR})_3$ (where R = alkyl, SiMe_3) by a methyl group considerably reduces the efficiency of CM, presumably due to $\beta\text{-SiR}_3$ elimination in $\beta\text{-SiR}_3$ -substituted ruthenacyclobutanes followed by reductive elimination. This terminating step in the ruthenium carbene catalyzed CM is observed when at least one methyl group is attached to vinyltrisubstituted silanes [18,23].

The viability of using ADMET for the copolymerization of divinyl-substituted siloxanes (containing no methyl groups) with dienes, in order to produce siloxylene–vinylene–alkenylene copolymers, is reported in this work. These types of copolymers can be also synthesized via a coupling polycondensation of divinyl-substituted organosilicon compounds [24–26], followed by cross-coupling with dienes, e.g. divinylbenzene [27]. This reaction is catalyzed by ruthenium and rhodium complexes containing (or generating) M–H and/or M–Si bond.

2. Experimental

2.1. Materials

Grubbs' benzylidene ruthenium catalyst, $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$ [28], divinyltetraethoxydisiloxane [29], the second generation of Grubbs' catalyst— $(\text{IMesH}_2)\text{Cl}_2\text{Ru}(\text{=CHPh})(\text{PCy}_3)$ [30] were synthesized using the literature procedure. Divinyltetramethyldisiloxane was purchased from Gelest and 1,9-decadiene from Aldrich. Divinyltetraethoxydisiloxane, divinyltetramethyldisiloxane and 1,9-decadiene were dried overnight with CaH_2 , distilled under reduced pressure and degassed prior to use.

2.2. Instrumentation

All ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on either a General Electric QE-Series NMR superconducting spectrometer system or Varian Associates VXR, Mercury, or Gemini series 300 spectrometer. Chemical shifts for ^1H and ^{13}C NMRs were referenced to residual signals from CDCl_3 with 0.03% v/v TMS or without TMS as an internal reference. Gel permeation chromatography (GPC) was performed using a Waters Associates liquid chromatography U6K equipped with a tandem ABI Spectroflow 757UV absorbance detector and a Perkin-Elmer LC-25 RI detector. All molecular weights are relative to polystyrene standards. Polymer samples were dissolved in HPLC grade CHCl_3 (approximately 0.1% w/v) and filtered before injection (a volume of 20–40 μl). The GPC was equipped with a Ultrastayragel linear mixed-bed column. HPLC grade chloroform was used as the eluent at a constant flow of 1.0 ml/min. Retention times were calibrated against narrow molecular weight polystyrene standards (Scientific Polymer Products).

2.3. ADMET copolymerization of divinyltetraethoxydisiloxane with 1,9-decadiene

A 25 ml flame-dried, round-bottomed flask equipped with a magnetic Teflon stirring bar was charged in a glove box with divinyltetraethoxydisiloxane (0.6 g, 1.96×10^{-3} mol) and 1,9-decadiene (0.14 g, 9.8×10^{-4} mol) in a glove box under an Ar atmosphere. Then the ruthenium carbene complex

(Grubbs' catalyst) (0.0806 g , $9.8 \times 10^{-5}\text{ mol}$) was added. The flask was removed from the glove box and placed on a high-vacuum line. The reaction mixture was stirred at 50°C with intermittent applications of vacuum. After 72 h, the reaction was terminated by exposure of the mixture to the air. Polymeric product was dissolved in dry methylene chloride, precipitated by adding methanol, and dried in vacuo until constant weight was reached.

^1H NMR (300 MHz, CDCl_3), δ (ppm): 1.17–1.22, m ($-\text{CH}_3$), 1.89–2.22, m ($-\text{CH}_2-$), 3.76–3.83, m ($-\text{OCH}_2-$), 5.34–5.42, m ($=\text{CH}$ internal); ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 18.19 ($-\text{CH}_3$), 28.24, 29.04, 29.61, 32.58, 36.51 ($-\text{CH}_2-$), 58.32 ($-\text{OCH}_2-$), 119.68, ($\text{Si}-\text{CH}=\text{CH}$), 129.86 ($=\text{CH}$, *cis*), 130.31 ($=\text{CH}$, *trans*), 153.26 ($\text{Si}-\text{CH}=\text{CH}$). GPC: $M_n = 18000$ and polydispersity index (PDI) (M_w/M_n) = 2.90.

3. Results and discussion

When the mixture containing divinyltetraethoxydisiloxane and 1,9-decadiene was heated in the presence of Grubbs' catalyst (as described in experimental), the formation of polymeric product was observed. The ^1H NMR spectrum of the isolated product reveals no terminal vinylidene signals (indicating relatively high molecular mass of polymer) and the presence of both siloxane and octenylene units. Quantitative analysis of olefinic region of the spectrum and signals from the ethoxy group at silicon enabled a calculation of the molar ratio of both building blocks in the copolymer (siloxane:diene = 1:1.7). On the basis of the NMR data, the following scheme can be proposed to illustrate the formation of the copolymer (Scheme 1)

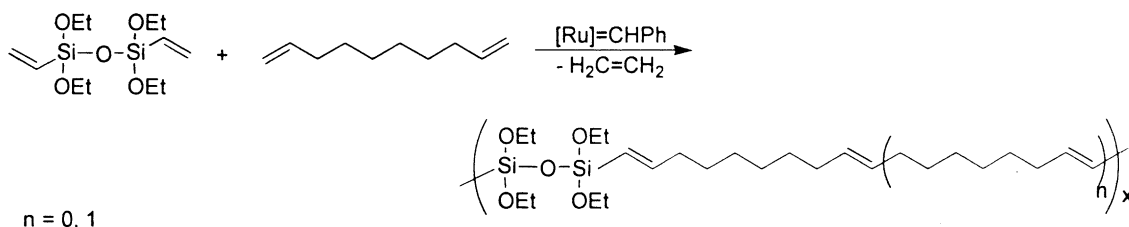
The ^{13}C NMR spectrum (Fig. 1) also confirmed the proposed structure. Only three major signals and

one minor appear in the olefinic region. A comprehensive NMR investigation of polyalkenamers reported earlier [31] has enabled the assignment of the signals of olefinic and methyldene carbons (see Fig. 1).

Signals at 129.98 and 130.31 ppm can be assigned to *cis* $=\text{CH}-$ and *trans* $=\text{CH}-$ (major), respectively, between two octenylene linkages in the copolymer. The assignment of the other signals (see Fig. 1) was made on the basis of the NMR data of similar monomeric material (e.g. [19]). Only *trans* geometry around the siloxy units was observed. No evidence of consecutive vinylsiloxane linkages was found in the NMR spectra. This observation is in good agreement with the mechanistic considerations reported earlier [18]. The molecular mass of the copolymer, $M_n = 18000$, was determined by GPC, and the chromatogram is presented in Fig. 2. The calculated polydispersity index (PDI) = 2.9 is rather high even for ADMET polymerizations.

In an analogous experiment, a mixture of divinyltetramethyldisiloxane and 1,9-decadiene was heated in the presence of (a) Grubbs' catalyst or (b) Grubbs' catalyst with *N*-heterocyclic carbene ligand (second generation Grubbs' catalyst) [32]. In the presence of the Grubbs' catalyst, a low conversion of diene and a very fast decomposition of carbene complex was observed. No polymeric product was detected. When the second generation Grubbs' catalyst was used, the reaction led to the formation of low molecular weight products. No polymeric or oligomeric products were detected in this case.

The formation of a copolymer from the reaction of divinyltrimethylsilane with 1,9-decadiene in the presence of tungsten alkylidene (Schrock's catalyst) was reported previously [3] ($M_n = 7800$, $M_w/M_n = 2.1$, 75% *trans*). Also in this case no consecutive vinylsiloxane linkages were detected.



Scheme 1.

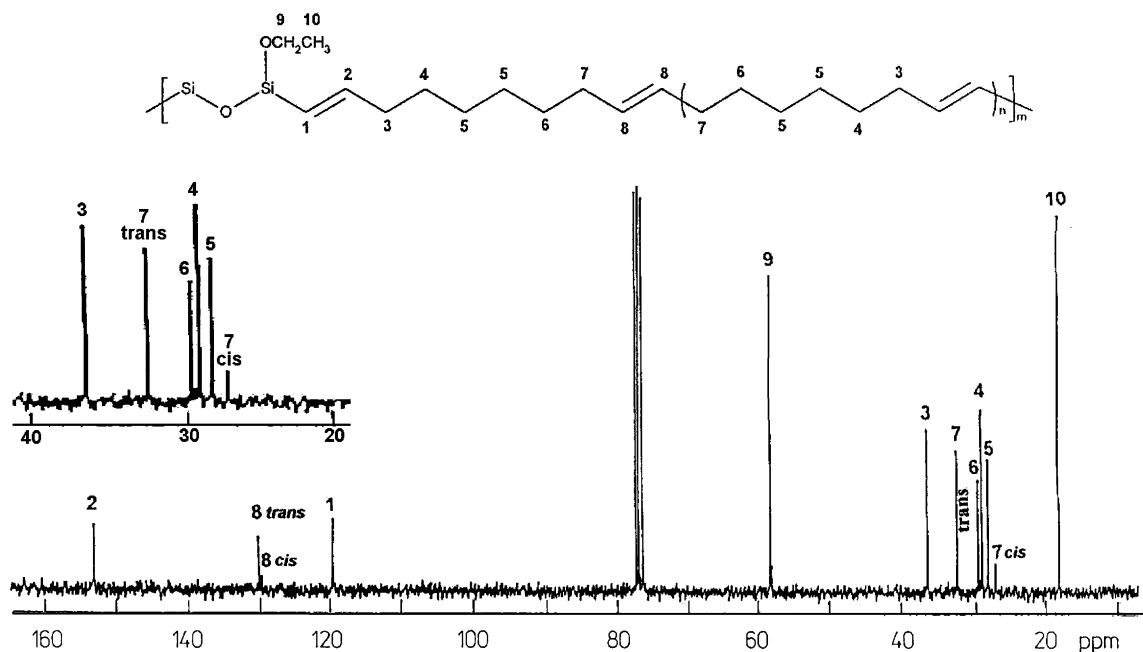


Fig. 1. ^{13}C NMR spectrum of siloxylene–vinylene–alkenylene copolymer.

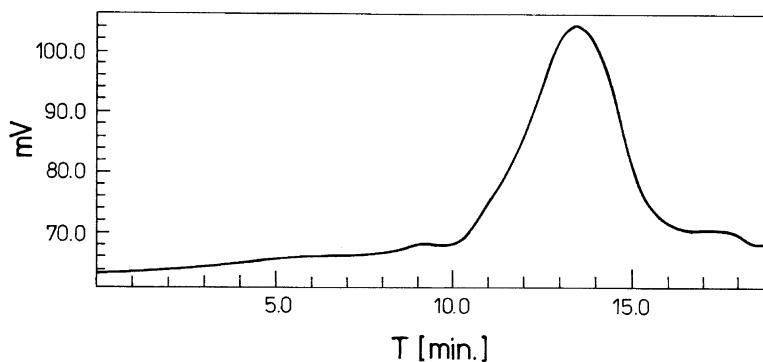


Fig. 2. GPC chromatogram of siloxylene–vinylene–alkenylene copolymer.

4. Conclusions

The first example of the effective copolymerization of a vinylsubstituted siloxane containing tetraalkoxy-substituents with a diene, catalyzed by ruthenium carbene, has been reported. ADMET copolymerization has been shown as a convenient method for the preparation of siloxylene–vinylene–alkenylene polymers. The dramatic effect of the substituents at the silicon atom on the efficiency of the meta-

thetic transformations of vinylsilanes was confirmed.

Acknowledgements

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