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Journal of Organometallic Chemistry 686 (2003) 228-234



www.elsevier.com/locate/jorganchem

Synthesis and structural characterization of *trans*-tactic siloxylenevinylene-*p*-phenylene polymers via ADMET copolymerization and silylative coupling (SC) polycondensation

Bogdan Marciniec*, Mariusz Majchrzak

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

Received 7 April 2003; accepted 7 July 2003

Abstract

The first *trans*-tactic stereo-regular vinylene-siloxylene-*p*-phenylene copolymer **1** with perfect vinylsiloxane linkage was obtained via acyclic diene metathesis copolymerization of divinyltetraethoxydisiloxane with 1,4-divinylbenzene (DVB) in the presence of Grubbs catalyst. The similar *trans*-tactic copolymers **2** and **3** but with no consecutive vinylsiloxane linkage was also prepared by silylative coupling copolycondensation of DVB with divinyltetra(methyl,ethoxy)disiloxane catalyzed by $[Ru(H)(Cl)(CO)(PCy_3)_2]$. \bigcirc 2003 Elsevier B.V. All rights reserved.

Keywords: ADMET copolymerization; Silylative coupling; Grubbs catalyst; Ruthenium complex; Divinyldisiloxane

1. Introduction

Acyclic diene metathesis (ADMET) polymerization represents a unique synthetic route to a variety of welldefined polyalkenylenes [1]. ADMET polymerization of silicon-containing dienes such as dialkenylenes and siloxanes (except vinyl derivatives) occurs smoothly in the presence of highly active metallacarbenes (W, Mo, Ru) (for review see [2]). A wide variety of unsaturated homopolymers can be synthesized using this methodology, including carbosilane and carbosiloxane units [3] (Eq. (1)).

Vinyl derivatives of organosilicon compounds, which are of fundamental industrial importance, are completely inert to productive homometathesis due to stereoelectronic effects of silyl group stimulating non productive cleavage of disilylmetallacyclobutene [4].

On the other hand, in the presence of ruthenium complexes that initially contain (or generate) Ru–H and Ru–Si bonds, derivatives of silicon compounds (e.g.

where: $R = -SiMe_2$ -, $-Me_2$ -SiOSiMe_2-;n>o

divinyltetramethyldisiloxane [5], divinyldimethylsilane [6], divinyltetramethyldisilazane [7] and bis(vinyldimethyl)benzene [8]) undergo a silylative coupling (SC)

^{*} Corresponding author. Tel.: +48-61-8291-366; fax: +48-61-8291-508.

E-mail address: marcinb@main.amu.edu.pl (B. Marciniec).

⁰⁰²²⁻³²⁸X/03/\$ - see front matter \odot 2003 Elsevier B.V. All rights reserved. doi:10.1016/S0022-328X(03)00667-3

polycondensation to linear products according to the following Eq. (2):

On the other hand, our recent report on efficient cross-metathesis of 1,9-decadiene with trialkoxy- and



where: $R = -SiMe_2$ -, $-Me_2Si$ -O- $SiMe_2$ -, $-Me_2Si$ -NH- $SiMe_2$ -; $[Ru] = [RuCl_2(PPh_3)_3]$, $M_w = 1510$, PDI = 1.19; $[RuCl_2(PPh_3)_3]$, $M_w = 1815$, PDI = 1.16; $[Ru(H)(Cl)(CO)(PPh_3)_3]$, $M_w = 2385$, PDI = 1.21,

Under the optimum conditions (e.g. $[RuCl_2(CO)_3]_2$ catalyst), linear *trans*-tactic silylene-vinylene-alkylenesilylene [9] and silylene-phenylene-vinylene [8] polymers have been synthesized. The ruthenium complex catalyzed SC-copolymerization was also used for synthesis of well-defined silylene-vinylene-phenylene polymers [10]. The optimum conditions for stereo- and regioselective synthesis of *trans*-tactic polymers were established according to the following Eq. (3):

The mechanism of catalysis of the reactions of monovinylsilanes is well-established (for reviews see [11]) and involves a cleavage of =C-Si bond of vinylsilane and the =C-H of olefin (e.g. styrene) as shown in Scheme 1 for stereo- and regio-selective synthesis of *trans*-product.

trisiloxy-substituted vinylsilanes [12] and above all— ADMET copolymerization of 1,9-decadiene with divinyltetraalkoxysiloxane [13], both catalyzed by the first generation Grubbs catalyst have opened a convenient route for the synthesis of siloxylene-vinylene-alkenylene copolymers. However, although in the latter reaction vinylsiloxane content in the polymer was relatively high (the molar ratio of siloxane/diene building block 1/1.7) no consecutive vinylsiloxane units were detected by NMR [13]. Also an earlier attempt of ADMET copolymerization of divinyldimethylsilane with 1,9 decadiene in the presence of tungsten carbene failed to give much more than 6% mol of divinylsilane unit in the polymer [3a].

The viability of using ADMET for copolymerization of divinylsubstituted siloxane (containing no methyl





where: [M] = Ru, Rh, Co; R = alkyl, aryl, alkoxyl, siloxyl

Scheme 1.

groups) with 1-divinylbenzene to produce siloxylenevinylene-*p*-phenylene copolymers with consecutive vinylsiloxane linkage is reported in this communication. These types of copolymers have been attempted to be synthesized via SC polycondensation of the same substrates, but in the case of divinylsiloxane, containing also methyl groups.

2. Experimental

2.1. Instrumentation

All catalytic tests and syntheses of polymeric product were carried out under argon. ¹H-NMR (300 MHz), ¹³C-NMR (75 MHz) and ²⁹Si-NMR (60 MHz) spectra were recorded on Varian XL 300 MHz spectrometer in CDCl₃. Mass spectra of the products were obtained by GC-MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m)) and an ion trap detector. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD. Highresolution mass spectroscopiec (HRMS) analyses were done on a AMD-402 instrument. Gel permeation chromatography (GPC) analysis was performed using a Gilson HPLC system equipped with UV absorbance detector and RI detector. The GPC was equipped with a phenogel column 300×7.80 mm, 50, 500, 10^4 Å (analysis condition: mobile phase-THF; flow rate-0.7 ml min⁻¹; temperature—ambient; injection volume-20 µl). Average molecular weight and dispersity indices of the copolymers were determined by polystyrene standard calibration.

2.2. Materials

The chemicals were obtained from the following sources: Grubbs benzylidene catalyst-[$(PCy_3)_2Cl_2Ru(= CHPh)$] was purchased from Strem Chemicals, divinyl-

tetraethoxydisiloxane (I), divinyltetramethyldisiloxane (III) from Gelest, vinyltriethoxysilane, hexane, benzene, styrene, triethylamine, methylene chloride, methanol and silica gel (60 mesh) from Fluka, *n*-decane from Aldrich, CDCl₃ from Dr Glaser A.G. Basel. CH₂Cl₂ was additionally passed through a column with alumina and after that it was degassed by repeated freeze–pump– thaw cycles. [Ru(H)(Cl)(CO)(PCy₃)₂] was prepared according to the procedures described in Ref. [14]. Pure 1,4-divinylbenzene (DVB) (II) was synthesized by Ni-catalysed coupling reaction [15] between vinyl bromide and 1,4-bis(bromomagnesium)benzene under an inert argon atmosphere.

2.3. General procedure for catalytic tests

The glass reactor with a condenser and a magnetic stirring bar was charged under argon with CH_2Cl_2 (1.4 ml-0.25 M), *n*-decane (internal standard, 5% volume of mixture), the vinyltriethoxysilane 134 mg (0.71 mmol); 270 mg (1.42 mmol); 538 mg (2.38 mmol) and DVB 46 mg (0.35 mmol). Then ruthenium benzylidene complex 11.6 mg (0.014 mmol) was added. The reaction mixture was stirred and heated to maintain a gentle reflux. The progress of reactions was monitored by GC and GCMS. The conversion of DVB was calculated by the internal standard method. The details are presented below.

2.4. Ruthenium-catalyzed ADMET copolymerization of 1,3-divinyl-1,1,3,3,-tetraethoxydisiloxane with 1,4-divinylbenzene

2.4.1. Poly[(1,1,3,3-tetraethoxy-1,3-disila-2-oxy)-(E)-vinylene-p-phenylene-(E)-vinylene], (1)

A mixture of 25 mg $(3.0 \times 10^{-2} \text{ mmol})$ -[(PCy₃)₂Cl₂Ru(=CHPh)] in 1.5 ml (0.5 M) of methylene chloride, 0.23 g $(7.5 \times 10^{-1} \text{ mmol})$ 1,3-divinyl-1,1,3,3tetraethoxydisiloxane (I) and 0.098 g $(7.5 \times 10^{-1} \text{ mmol})$ (II) was placed in a 5 ml mini-reactor. The mixture was heated at 40 °C under an argon flow for 18 h. The progress of the reaction was monitored by GC and ¹H-NMR. After the reaction had been completed, the resulting polymeric product was isolated and purified by use of chromatography column with silica gel (mobile phase: hexane/CH₂Cl₂-2:1/Et₃N-1% volume). Then the excess of solvents was removed under vacuum and dissolved in hexane (a light yellow solution). The final reaction yield was 69%. The isomer structure was confirmed by DEPT analysis.

¹H-NMR (CDCl₃, δ (ppm)): 1.28 (t, $-\text{OCH}_2\text{C}H_3$); 3.90 (q, $-\text{OC}H_2\text{C}H_3$); 5.25 (d, 1H, $J_{HH} = 11$ Hz; > C-HC=CH₂, at terminal vinyl group—trace); 5.75 (d, 1H, $J_{HH} = 18$ Hz, > C-HC=CH₂, at terminal vinyl group—trace); 5.9–6.2 (m, 3H, Si-HC=CH₂, at terminal vinyl group—trace); 6.23 (d, 1H, $J_{HH} = 19$ Hz, > C-HC=CH-Si); 6.76 (dd, 1H $J_{HH} = 11$, 18 Hz, >C-*H*C=CH₂, at terminal vinyl group—trace); 7.24 (d, 1H, $J_{HH} = 19$ Hz, >C-HC=C*H*-Si); 7.43 (s, 4H, -C₆*H*₄-). ¹³C-NMR (CDCl₃, δ (ppm)): 18.34 (-OCH₂*C*H₃); 58.64 (-OCH₂CH₃); 118.84 (>C-HC=CH-Si); 126.91 (-C₆H₄-); 137.85 (>C-HC= CH-Si); 147.93 (>C-HC=CH-Si). ²⁹Si-NMR (CDCl₃, δ (ppm)): -64.44. UV $\lambda_{max} = 298$ nm. $\varepsilon =$ 24 300 [M cm⁻¹] per one mer. GPC: $M_w = 8100$, PDI = 3.6.

2.5. Ruthenium-catalyzed silylative coupling polycondensation of 1,3-divinyl-1,1,3,3,tetraethoxydisiloxane with 1,4-divinylbenzene

2.5.1. Poly[(1,1,3,3-tetraethoxy-1,3-disila-2-oxy)-(E)-vinylene-p-phenylene-(E)-vinylene](2)

A mixture of 5.46 mg $(7.52 \times 10^{-3} \text{ mmol})$ -[Ru(H)(Cl)(CO)(PCy₃)₂] in 1.5 ml (0.5 M) of toluene, $0.23 \text{ g} (7.5 \times 10^{-1} \text{ mmol})$ 1,3-divinyl-1,1,3,3-tetraethoxvdisiloxane (I) and 0.098 g (7.5×10^{-1} mmol) (II) was placed in a 5 ml mini-reactor. The mixture was heated in oil bath under stirring at 80 °C for 6 days. The progress of the reaction was monitored by GC and ¹H-NMR. The monomers were found to have disappeared after 36 h. After the reaction had been completed, the resulting polymeric product was isolated and purified by use of chromatography column with silica gel (mobile phase: hexane/CH₂Cl₂-1:1/Et₃N-1% volume). Then the excess of solvents was removed by vacuum system and dissolved in hexane (a light yellow solution). The final reaction yield was 72%. The isomer structure was confirmed by DEPT analysis.

¹H-NMR (CDCl₃, δ (ppm)): 1.28 (t, $-OCH_2CH_3$); 3.90 (q, $-OCH_2CH_3$); 6.23 (d, 1H, $J_{HH} = 19$ Hz, >C-HC = CH-Si); 7.04 (s, 2H, Si-HC = CH-Si, silylative homo-coupling); 7.24 (d, 1H, $J_{HH} = 19$ Hz, >C-HC = CH-Si); 7.43 (s, 4H, $-C_6H_4-$). ¹³C-NMR (CDCl₃, δ (ppm)): 18.34 ($-OCH_2CH_3$); 58.64 ($-OCH_2CH_3$); 118.84 (>C-HC = CH-Si); 126.91 ($-C_6H_4-$); 137.85 (>C-HC = CH-Si); 147.93 (>C-HC = CH-Si), 150.2 (Si-HC = CH-Si): ²⁹Si-NMR (CDCl₃, δ (ppm)): -64.44. Anal. Calc. for ($C_{18}H_{28}O_5Si_2$)_n: C, 56.81; H, 7.42. Found: C, 56.14; H, 7.23%. UV $\lambda_{max} = 298$ nm. $\varepsilon = 24300$ [M cm⁻¹] per one mer. GPC: $M_w = 12100$, PDI = 3.2.

2.6. Ruthenium-catalyzed silylative coupling polycondensation of 1,3-divinyl-1,1,3,3,tetramethyldisiloxane with 1,4-divinylbenzene

2.6.1. Poly[(1,1,3,3-tetramethyl-1,3-disila-2-oxy)-(E)-vinylene-p-phenylene-(E)-vinylene](3)

A mixture of 5.46 mg $(7.52 \times 10^{-3} \text{ mmol})$ – [Ru(H)(Cl)(CO)(PCy₃)₂] in 1.5 ml (0.5 M) of toluene, 0.139 g $(7.5 \times 10^{-1} \text{ mmol})$ 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (III) and 0.098 g $(7.5 \times 10^{-1} \text{ mmol})$ (II) was placed in a 5 ml mini-reactor. The mixture was heated in oil bath under stirring at 80 °C for 6 days. The progress of the reaction was monitored by GC and ¹H-NMR. The monomers were found to have disappeared after 30 h. After the reaction had been completed, the resulting polymeric product was isolated and purified by use of chromatography column with silica gel (mobile phase: hexane/CH₂Cl₂-1:1). Then the excess of solvents was removed by vacuum system. The final reaction yield was 77% of light yellow powder of polymeric material. The isomer structure was confirmed by DEPT analysis.

¹H-NMR (CDCl₃; δ (ppm)): 0.24 (s, $-CH_3$, at the terminal silicon atoms—trace); 0.27 (s, $-CH_3$, at the internal silicon atoms); 6.45 (d, 1H, $J_{HH} = 19$ Hz, > C - HC = CH - Si); 6.83 (s, 2H, -Si - HC = CH - Si, silylative homo-coupling); 6.87 (d, 1H, $J_{HH} = 19$ Hz, > C - HC = CH - Si); 7.40 (s, 4H, $-C_6H_4 -$). ¹³C-NMR (CDCl₃; δ (ppm)): 0.34 ($-CH_3$, at the terminal silicon atoms—trace); 1.03 ($-CH_3$, at the internal silicon atoms); 126.65 ($-C_6H_4 -$); 128.57 (> C - HC = CH - Si); 136.34 (Si $-HC = CH_2$); 137.86 (> C - HC = CH - Si); 140.90 (Si $- HC = CH_2$); 143.73 (> C - CH = CH - Si); 152.3 (SiHC = CH - Si). ²⁹Si-NMR (CDCl₃; δ (ppm)): - 21.65. Anal. Calc. for ($C_1_4H_{20}OSi_2$)_n: C, 64.55; H, 7.74. Found: C, 64.23; H, 7.68%. UV $\lambda_{max} = 295$ nm. $\varepsilon = 32.800$ [M cm⁻¹] per one mer. GPC: $M_w = 10.500$, PDI = 2.8.

2.7. Spectroscopiec data of 1,4-divinylbenzene silyl derivatives

2.7.1. 4-{(*E*)-2-(*Triethoxysilyl*)-ethenyl}styrene (monosubstituted)

¹H-NMR (CDCl₃; δ (ppm)): 1.20 (t, 9H, -CH₃); 3.86 (q, 6H, $-OCH_2$ -); 5.65 (d, 1H, $J_{HH} = 9$ Hz, -HC = CH_2); 5.68 (d, 1H, $J_{HH} = 17$ Hz, $-HC = CH_2$); 6.30 (d, 1H, $J_{HH} = 19$ Hz, Si-HC=CH-C₆H₄-); 6.57 (dd, 1H, $J_{HH} = 11$, 18 Hz, $-HC = CH_2$; 7.12 (s, 2H, $-C_6H_4 - C_6H_4$); HC=CH₂); 7.19 (s, 2H, $-C_6H_4$ -Si); 7.39 (d, 1H, ¹³C-NMR $Si-HC=CH-C_6H_4-$). $J_{HH} = 19$ Hz, $(CDCl_3; \delta (ppm)): 18.77 (-CH_3); 58.86 (-OCH_2CH_3);$ 114.12 $(-HC=CH_2)$; 119.44 $(-C_6H_4-HC=CH_2)$; 127.25 $(-C_6H_4-HC=CH_2)$; 127.36 $(-C_6H_4-Si)$; 137.36 $(-HC=CH_2)$; 137.96 (> $C-HC=CH_2$); 138.43 (> C-HC=CH-Si); 148.52 (Si-HC=CH-). ²⁹Si-NMR (CDCl₃; δ (ppm)): -56.75. Anal. HRMS for C₁₆H₂₄O₃Si—Calc. 292.1495; Found: 292.1497%.

2.7.2. 1,4-Bis {(E)-2-(triethoxysilyl)-ethenyl}benzene (disubstituted)

¹H-NMR (CDCl₃; δ (ppm)): 1.20 (t, 18H, -CH₃); 3.86 (q, 12H, -OCH₂-); 6.30 (d, 1H, J_{HH} = 19 Hz, Si-HC=CH-C₆H₄-); 7.12 (s, 4H, -C₆H₄-); 7.39 (d, 1H, J_{HH} = 19 Hz, Si-HC=CH-C₆H₄-). ¹³C-NMR (CDCl₃; δ (ppm)): 18.77 (-CH₃); 58.86 (-OCH₂CH₃); 119.44 (-C₆H₄-HC=CH-); 127.36 (-C₆H₄-); 138.43 (>C-HC=CH-Si); 148.52 (Si-HC=CH-). ²⁹Si-NMR

232

ViSi(OEt) ₃ / DVB	Conversion of ViSi(OEt) ₃ (%)	Conversion of DVB (%)	Yield of monodisubstituted (%)	Yield of disubstituted (%)	[mono-]/[di-] ≈
2:1	63	> 99	75	25	3:1
4:1	33	> 99	53	40	1.3:1
8:1	20	> 99	38	61	1:1.6

Table 1 Cross-metathesis of vinyltriethoxysilane with DVB

Reaction conditions: $[(PCy_3)_2Cl_2Ru(=CHPh)]$: $[DVB] = [4 \times 10^{-2}]$: 1; time = 6 h, open system, CH₂Cl₂, reflux.

(CDCl₃; δ (ppm)): -56.73. Anal. HRMS for C₂₂H₃₈O₆Si₂—Calc.: 454.2207. Found: 454.2205. Anal. Calc. for C₂₂H₃₈O₆Si₂: C, 58.11; H, 8.42. Found: C, 58.06; H, 8.39%.

3. Results and discussion

As we have already mentioned, divinyltetraethoxydisiloxane (I) undergoes efficient ADMET copolymerization with 1,9-decadiene in the presence of the Grubbs catalyst leading to the formation of siloxylene-vinylenealkenylene polymer but no consecutive vinyl-siloxane linkage was detected in the product [13]. In order to find the optimum conditions for effective copolycondensation of (I) with DVB (II), catalytic screenings, in particular to check the reactivity of the two vinylic group in (II) were performed using the model reaction of vinyltriethoxysilane with (II) which occurs as follows (Eq. (4)):



Fig. 1. The fragment of ¹H-NMR spectrum of copolymer 1.



A vinylsilane conversion and the yields of mono- and disubstituted silyl derivatives were measured under excess of vinylsilane. The latter does not undergo *homo*-metathesis which, was confirmed earlier [4]. The results are presented in Table 1.

Stereo-selective formation of both products in the presence of the Grubbs catalyst has stimulated a study aimed at synthesis and isolation of *trans*-tactic polymer. The tests allowed us to optimize the concentration of ruthenium–carbene to be used in the synthesis of the copolymer. Since the synthetic procedure requires the consecutive cross-metathesis, all of the attempts have been performed at the 1:1 ratio of the substrates. Results of the ¹H- and ¹³C-NMR and DEPT analysis of the

polymeric product excluded the presence of quaternary carbon atoms in the chain. The ¹H-NMR spectrum of one shows signals at 6.23 ppm (d, 1H, $J_{HH} = 19$ Hz) and 7.24 ppm (d, 1H, $J_{HH} = 19$ Hz) assigned to the 1silylene-2-phenylene Si- $HC=CH-C_6H_4-$ and unambiguously excludes the absence of the signal attributed to Si-HC=CH-Si fragment (see Fig. 1).

Only *trans* geometry around the siloxy and phenyl units was observed. The signals at 147.93 and 118.84 ppm can be assigned to the *trans* =CH-Si and =CH- C_6H_4 -, respectively.

The molecular mass of the copolymer, $M_w = 8100$ was determined by GPC. The polydispersity, PDI = 3.6 is rather high even for ADMET copolymerization.



Fig. 2. The fragment of ¹H-NMR spectrum of copolymer 2.

The above analytical data allowed us to propose a linear and *trans*(stereo)-regular structure of copolymer 1 prepared according to the Eq. (5). This is the first example of ADMET copolymerization of divinylsubstituted silicon compound with diene containing perfect consecutive vinylsiloxane linkage.

spectra of copolymer 2 assigned to the Si-HC=CH-Si fragment.

The ¹H-NMR spectra (see Fig. 2) show a signal at 7.04 ppm attributed to Si-HC=CH-Si and ¹³C-NMR spectrum shows additional signals in the olefin region, as compared to those in the spectrum of copolymer 1, i.e. at 150.2 assigned to Si-HC=CH-Si.

Quantitative analysis of the olefinic region of the ¹H-NMR spectrum and signals from the ethoxy group at silicon enabled us to calculate the molar ratio of both building blocks in the copolymer 2, so the following linear and stereo-regular structure of the copolymer can be proposed (see Fig. 3).



Fig. 4. Linear and stereo-regular copolymer 3.

As we have reported earlier for vinylsubstituted silicon compounds containing at least one methyl substituent at silicon, e.g. divinyltetramethyldisiloxane (III) no metathetical conversion can be observed, which is due to decomposition of Grubbs catalysts in the



 $[Ru(=CHPh)] = [(PCy_3)_2Cl_2Ru(=CHPh)]$



linear and trans-regular copolymer 1

Both substrates I and II have undergone the SC polycondensation catalyzed by Ru-H complex proceeding via non-metallacarbene mechanism to obtain the product 2.

- CH₂=CH₂

The synthetic procedure is described in Section 2, and the copolymer was isolated and also characterized by ¹H- and ¹³C-NMR spectroscopy and GPC analysis $(M_{\rm w} = 12\,100, \, \text{PDI} = 3.2)$. DEPT analysis also excluded the presence of quaternary carbon atoms in the chain.

The signal assignments in the ¹H-NMR spectra of copolymers 1 and 2 were the same confirming the *trans*geometry of the vinylene-siloxylene and vinylene-phenylene units, except for one additional signal in the

presence of vinylmethylsilicon compound via β-transfer of silyl group to ruthenium in the ruthenacyclobutane as an intermediate [16].

Therefore, an attempt was made to subject III (a commercially important compound) to SC polymerization with DVB. The synthetic procedure is the same as for 2 with a slightly different way of isolation of the final copolymer 3. The NMR spectroscopy (see Section 2) and GPC analysis $(M_w = 10500, PDI = 2.8)$ of the copolymer permitted structural characterization of the copolymer (Fig. 4) whose structure is similar to that of copolymer 2 also with no consecutive vinylsiloxane linkage.



Fig. 3. Linear and stereo-regular copolymer 2.

4. Conclusions

(1) *Trans*-tactic stereo-regular vinylene-siloxylene-p-phenylene copolymers 1–3 can be produced via AD-MET copolymerization and/or SC polycondensation of DVB with divinyltetraethoxydisiloxane (ADMET) and divinyl(tetramethyl- or tetraethoxy)-disiloxanes (SC).

(2) Copolymer 1 synthesized by ADMET copolymerization of divinyltetraethoxysiloxane with DVB catalyzed by the Grubbs complex is the first copolymer with perfect vinylsiloxane linkage obtained via ADMET polymerization procedure.

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