Pergamon

Tetrahedron Letters 41 (2000) 10303–10307

TETRAHE
LETTE

# Highly stereo- and regioselective synthesis of a phenylene–silylene–vinylene polymer via ruthenium-cataly polycondensation

Mariusz Majchrzak, Yujiro Itami, Bogdan Marciniec* and Piotr Pawluc

*Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzk*
*60-780 Poznan, Poland*

Received 12 July 2000; revised 9 October 2000; accepted 19 October 2000

## Abstract

$[RuCl_2(CO)_3]_2$ catalyzed cross-coupling polycondensation of 1,4-bis(vinyldimethylsilyl)benze appears to be a new, very efficient, method for highly stereo- and regioselective synthesis of phen silylene–vinylene polymers (**B**). © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* cross-coupling polycondensation; phenylene–silylene–vinylene polymers; ruthenium(II) complex.

Several series of poly(*p*-phenylene-vinylene)s (PPVs) have been extensively invest recently because of their efficient photoluminescence and potentially useful electrolumine properties.[1] There is also a growing interest in silicon-containing phenylene–vinylene pol since they are expected to have application as blue light emitting polymer materials. introduction of silicon atoms into π-conjugated systems seems to stimulate the LUMO π-conjugated system, and improves solubility and processibility due to increased chain flex Moreover, the presence of Si-atoms reduces the barrier of carrier injection and transpor processes, compared with those of other polymers containing saturated spacer groups.[3]

Polymers containing phenylene–silylene–vinylene units are usually synthesized by P Rh-catalyzed hydrosilylation.[3] In these cases the molecular weight of the polymers seems rather low[3a] and their polydispersity ranges between 1.7 and 3.1[3a] or 2.6 and 5.5.[3c] Additi the polymer-chain structures were presented as mixtures of *gem*-, *cis*-1,2-, and *trans*-1,2-iso fragments due to the regio- and stereoselection of the hydrosilylation process.[3]

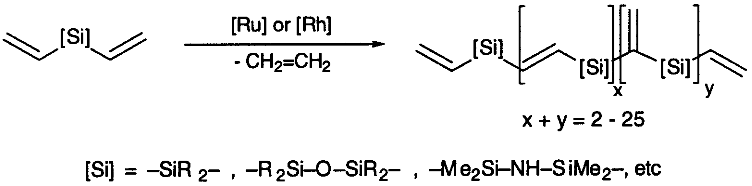
Well-defined unsaturated organosilicon polymers can also be prepared by ADMET po ization of dialkenylsilicon compounds.[4] However, vinyl-substituted silicon compounds, could be effective precursors for silylene–vinylene polymers, are completely inert to prod ADMET polymerization.

---

* Corresponding author.

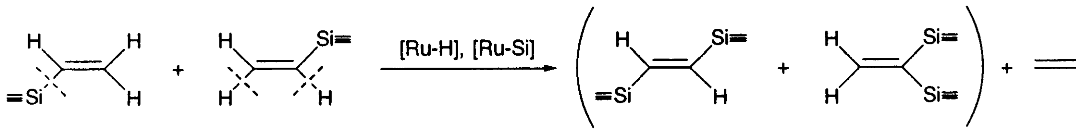
PII: S0040-4039(00)01849-9

On the other hand, breaking through this synthetic disadvantage, we recently reported f first time that ruthenium and rhodium complexes effectively catalyze cross-coupling polyco sation of divinyl-substituted silicon compounds, i.e. silanes,[5a] siloxanes,[5b] and silazanes. reaction occurs to give linear oligomers ($M_w = 1500–2400$) containing a chain with *trans*-1 meric fragments, as well as 1,1-isomeric fragments (Scheme 1).



Scheme 1.

The mechanism of this polycondensation is based on the same pathway as deethyl silylative cross-coupling reactions of monovinyl-[6] and divinyl-substituted silanes[7] as we re previously. This coupling reaction occurs via activation of $C_{vinyl}$–H and $C_{vinyl}$–Si bonds vinylsilanes[6,7] (Scheme 2). Instead of cleavage of the C=C bond characteristic of the metathesis.



Scheme 2.

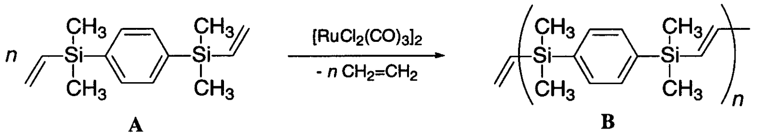
In this communication, we present synthetic data on ruthenium-catalyzed polycondensat 1,4-bis(vinyldimethylsilyl)benzene (**A**) to afford the well-defined phenylene–silylene–vi polymer (**B**) effectively. Several preliminary catalytic tests were performed (Table 1) in or find out the conditions for selective synthesis of a well-defined *trans*-tactic polymer.

Table 1
Catalytic tests for polycondensation of 1,4-bis(vinyldimethylsilyl)benzene (**A**)[a]

| Catalyst | Conversion (%) | Ratio of products (%)[b] | | | Selectivity |
|---|---|---|---|---|---|
| | | Dimers | Trimers | Rest | [1,2-]:[1,1- |
| $RuHCl(CO)(PPh_3)_3$ (**I**) | 89 | 19 | 17 | 64 | 3:1 |
| $RuCl(SiMe_3)(CO)(PPh_3)_2$ (**II**) | 88 | 19 | 18 | 63 | 11:1 |
| $RuCl_2(PPh_3)_3$ (**III**) | 97 | 6 | 8 | 86 | 5:1 |
| $[RuCl_2(CO)_3]_2$ (**IV**) | 82 | 23 | 22 | 55 | >99:1 |

[a] Reaction conditions: [cat.]:[monomer] = 1:100, 24 h, 110°C, in toluene, in glass ampoules, under Ar.
[b] Identified by GPC and GC–MS.
[c] Calculated from $^1H$ NMR and no *cis*-fragment was observed.

While Ru–phosphine catalysts (**I–III**) gave mixtures of *trans*-1,2-isomeric frag (Si–CH=CH–Si) and 1,1-isomeric fragments ($Si_2C{=}CH_2$), $[RuCl_2(CO)_3]_2$ (**IV**) gave only 1,2-isomeric fragments. Similarly high selectivity has also been reported from our grc condensation of vinylsilanes[8] and divinylsilanes,[9] as well as in polycondensation of divi ramethyldisilazane, although the molecular weight remained low ($M_w = 813$).[5c] Therefo used $[RuCl_2(CO)_3]_2$ (**IV**) as a catalyst for a long-time (one week) reaction occurring acc to the following equation (Scheme 3) to obtain polymer (**B**) (90% yield, $M_w = 7100$, $M_w$ 1.50, $n = 23$) (Fig. 1).



Scheme 3.

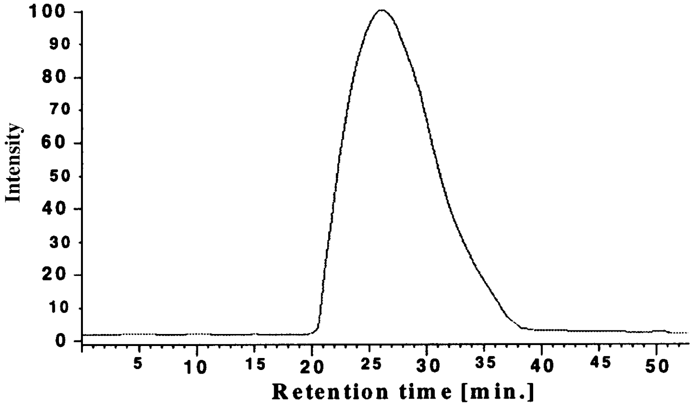


Figure 1.

Compared with other phenylene–silylene–vinylene polymers synthesized by hydrosily this polymer has exclusively high selectivity for *trans*-1,2-isomeric fragments (>99%).

The structure of polymer (**B**) was characterized and determined by $^1H$, $^{13}C$, and $^{29}Si$ as well as IR and Raman spectroscopy, and clear evidence of a highly selective transf tion from monomer (**A**) to the resulting polymer (**B**) is presented on the basis of $^1H$ spectroscopy (Fig. 2).[10] The absence of quaternary $Si_2C{=}CH_2$ fragments was also revea DEPT spectroscopic analysis.

It is therefore quite obvious that polymer (**B**) is an extraordinarily well-defined *trans* polymer and the procedure constitutes a novel and efficient method for selective synth phenylene–silylene–vinylene polymers. Further investigations of their properties are way.

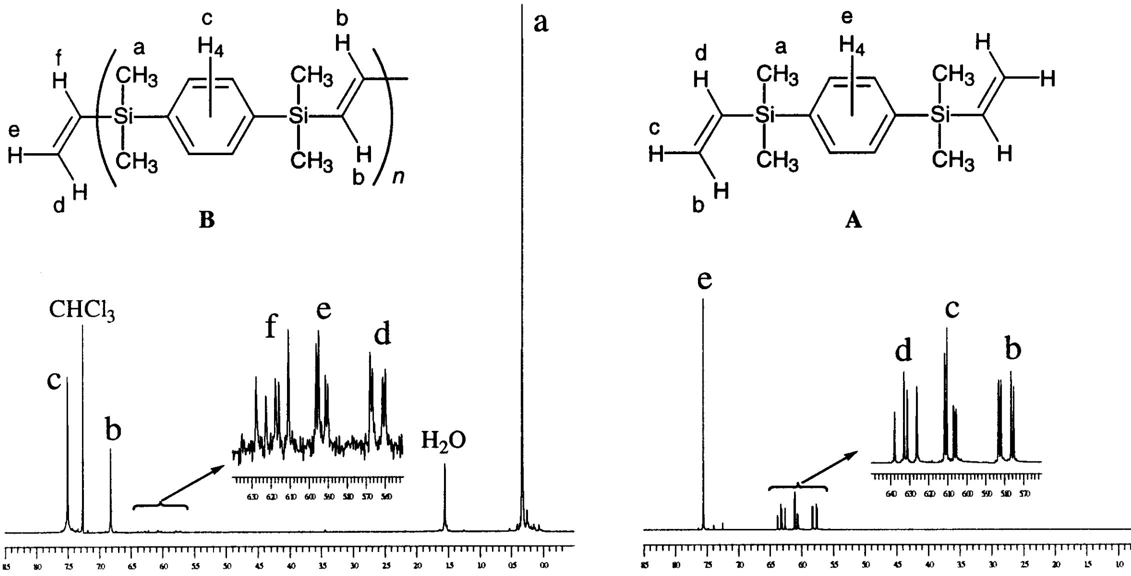


Figure 2.

## Acknowledgements

Financial support by the State Committee for Scientific Research (Project PBZ-KBN 1
99/01g) is kindly acknowledged.

## References

1. (a) Travis, J. *Science* **1994**, *263*, 1700 and references cited therein. (b) Sandman, D. J. *Trends Polym. Sc* *2*, 44; **1997**, *5*, 71 and references cited therein. (c) Benfaremo, N.; Sandman, D. J.; Tripathy, S.; Kumar, J. K.; Rubner, M. F.; Lyons, C. *Macromolecules* **1998**, *31*, 3595.
2. (a) Kim, H. K.; Ryu, M. K.; Kim, K. D.; Lee, S. M.; Cho, S. W.; Park, J. W. *Macromolecules* **1998**, *3* (b) Ryu, M. K.; Lee, S. M.; Zyung, T.; Kim, H. K. *Polym. Mater. Sci. Eng.* **1996**, *75*, 408. (c) Kim, H. K M. K.; Lee, S. M. *Macromolecules* **1997**, *30*, 1236.
3. (a) Kim, D. S.; Shim, S. C. *J. Polym. Sci. Part A*, *Polym. Chem.* **1999**, *37*, 2933. (b) Son, D. Y.; Bucce, D.; T. M. *Tetrahedron Lett.* **1996**, *37*, 1576; (c) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiy *Macromolecules* **2000**, *33*, 15.
4. (a) Wagener, K. B.; Smith Jr., D. W. *Macromolecule*s **1991**, *26*, 6073. (b) Smith Jr., D. W.; Wagener *Macromolecules* **1991**, *26*, 3533.
5. (a) Marciniec, B.; Lewandowski, M. *J. Polym. Sci.*, *Part A*, *Polym. Chem.* **1996**, *34*, 1443. (b) Marcin Lewandowski, M. *J. Inorg. Organomet. Polym.* **1995**, *34*, 115. (c) Marciniec, B.; Malecka, E. *Macromol* *Commun.* **1999**, *20*, 475.
6. (a) Wakatsuki, Y.; Yamazaki, H.; Nakano, N.; Yamamoto, Y. *J. Chem. Soc.*, *Chem. Commun.* **1991**, Marciniec, B.; Pietraszuk, C. *J. Soc. Chem.*, *Chem. Commun.* **1995**, 2003. (c) Marciniec, B.; Pietras *Organometallics* **1997**, *16*, 4320.
7. Marciniec, B. *Molecular Crystals and Liquid Crystals*, accepted for publication.
8. Marciniec, B.; Pietraszuk, C.; Foltynowicz, Z. *J. Organomet. Chem.* **1994**, *474*, 83.
9. Marciniec, B.; Lewandowski, M. *Tetrahedron Lett.* **1997**, *38*, 3777.
10. Typical experimental procedure to the synthesis of polymer (**B**) is described below. 0.5 ml (1.85 m 1,4-bis(vinyldimethylsilyl)benzene (**A**) and 4.74 mg ($1.85{\times}10^{-2}$ mmol) of $[RuCl_2(CO)_3]_2$ (**IV**) was taken u ml (0.5 M) of toluene. The reaction mixture was heated at 100°C under an argon flow for seven da

monomer was found to have been disappeared after 30 hours. After completion of the reaction, the re
polymer was isolated and purified by repeated reprecipitation from methanol to afford a white pow
polymer (**B**) (0.45 g, 90% yield). $^1$H NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 0.33 (s, $-CH_3$, at internal and t
silicon atoms); 5.75 (dd, $J=4$, 24 Hz, $=CH_2$, at terminal vinyl group); 6.04 (dd, $J=4$, 14 Hz, $=CH_2$, at t
vinyl group); 6.30 (dd, $J=14$, 24 Hz, $=CH-$, at terminal vinyl group); 6.82 (s, $=CH-$, at internal vinylene
7.50 (s, $-C_6H_4-$). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$ (ppm): −2.9 ($-CH_3$, at internal silicon atoms); −1.77 (–
terminal silicon atoms); 132.0 ($=CH_2$, at terminal vinyl group); 132.8 ($=CH-$, at terminal vinyl group)
($-CH-$, at benzene ring); 139.2 ($=C-$, at benzene ring); 152.2 ($=CH-$, at internal vinylene group). $^{29}$Si N
MHz, $CDCl_3$), $\delta$ (ppm): −11.78 ($-Si(CH_3)_2-$). IR $\nu$ (cm$^{-1}$): 3047, 2955, 1407, 1379, 1250, 1171, 1134, 105
(*trans*-CH=CH–), 836, 814, 796, 772. UV: $\lambda_{max}=264.5$ nm. Anal. calcd for $C_{13}H_{19}Si_2$: C, 67.46; H, 8.27.
C, 65.66; H, 8.41.