



Pergamon

Tetrahedron Letters 41 (2000) 1127–1130

TETRAHEDRON
LETTERS

Dehydrogenative condensation of SiH and SH bonds. A metal-catalyzed protocol to stable thiopolysiloxanes

Bhanu P. S. Chauhan and Philip Boudjouk *

Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, ND-58105, USA

Received 26 October 1999; accepted 1 December 1999

Abstract

Dehydrocoupling of polyhydrosiloxanes with thiols proceeded smoothly in the presence of Wilkinson's catalyst to furnish polythioethers in high yields under mild conditions. The process is free of rearrangement and cross-linking reactions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: dehydrocoupling; poly(methylhydro)siloxane; polythiosilylethers; sol-gel; transition metal.

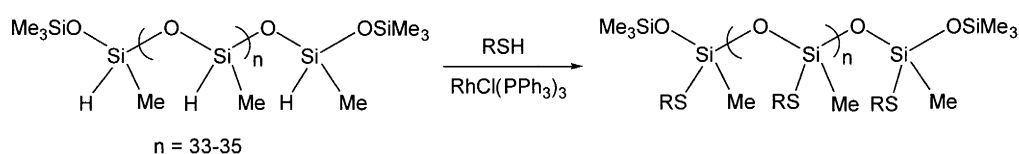
The chemistry of efficient construction of Si–heteroatom bonds via transition metal (TM) catalysis is emerging rapidly.^{1,2} Particularly interesting and challenging in this category are the transformations which can be employed to construct heteroatom-substituted polymers.³ Transition metal catalyzed dehydrocoupling of hydrosilanes with amines (SiH/NH) has been shown to give linear and/or cross-linked polysilazanes.^{1–3} Dehydrocoupling of SiH/OH moieties in the presence of transition metals has been studied in detail and applied to the preparation of polymers of industrial importance.⁴ In contrast, transition metal catalyzed condensation of SiH/SH groups has attracted much less attention largely because catalyst poisoning by sulfur is a major deterrent.^{5–7}

Our interest in thio linkers arises from the recent discovery that thioether spacers in polysiloxanes inhibit crystallization and that the introduction of sulfur permits the systematic modification of mesophasic properties such as transition temperature, mesophase nature, and stability.^{8,9} Prompted by these findings, we sought to develop convenient methods of converting silanes and siloxanes to polymers or polymer precursors containing Si–S linkages.

Recently we reported that Wilkinson's catalyst efficiently promotes the coupling of Si–H bonds of polymeric siloxanes with alcohols to give well-defined designer silicones.^{10,11} The reaction is free of drawbacks such as rearrangement and cross-linking reactions commonly encountered in metal catalyzed substitution reactions of Si–H bonds.¹² In this communication, we report that this approach is applicable for dehydrocoupling of thiols with cyclic and linear polysiloxanes containing Si–H bonds.

* Corresponding author. Tel: +1 (701)-231-8601; fax: +1 (701)-231-7947; e-mail: boudjouk@plains.nodak.edu (P. Boudjouk)

In a typical experiment, a mixture of benzylthiol (0.124 mL, 1 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (0.010 g, 0.01 mmol) in benzene (0.40 mL) was degassed by three freeze–pump–thaw cycles prior to the addition of PMHS (0.60 mL, 1 mmol). Essentially quantitative conversion of Si–H bonds to Si–S CH_2Ph bonds was achieved after 2 h at 78 °C. Gas evolution (presumably H_2) and a gradual color change from yellow to orange was observed during the course of the reaction. Secondary and tertiary thiols could also be used (Scheme 1). Scale-up (6.00 g of PMHS) posed no problems. The reaction progress and loading ratios were conveniently monitored by ^1H NMR. The integration of the remaining Si–H/S–H and Si– CH_3 /S– CH_2 resonances provided incorporation ratios of the thiol moiety into the polymer backbone. In all cases, reaction was continued until complete consumption of the Si–H and S–H signals was observed. Yields were calculated after catalyst separation as described in Ref. 13.

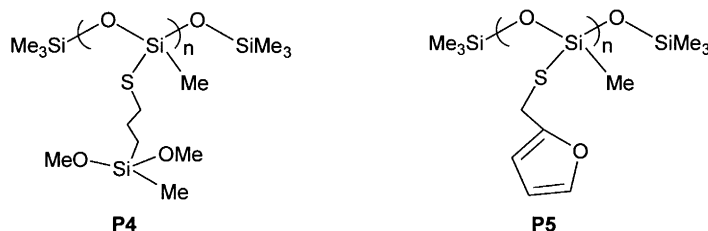


Polymer	R	Conditions ^a	Yield(%) ^b
P1	PhCH_2	C_6H_6 , 78 °C, 2.5 h	96
P2	$(\text{CH}_3)_2\text{CH}$	C_6H_6 , 78 °C, 2.5 h	94
P3	$(\text{CH}_3)_3\text{C}$	C_6H_6 , 78 °C, 4 h	92

^aAll reactions were performed under argon. ^b Isolated yields (see ref 13)

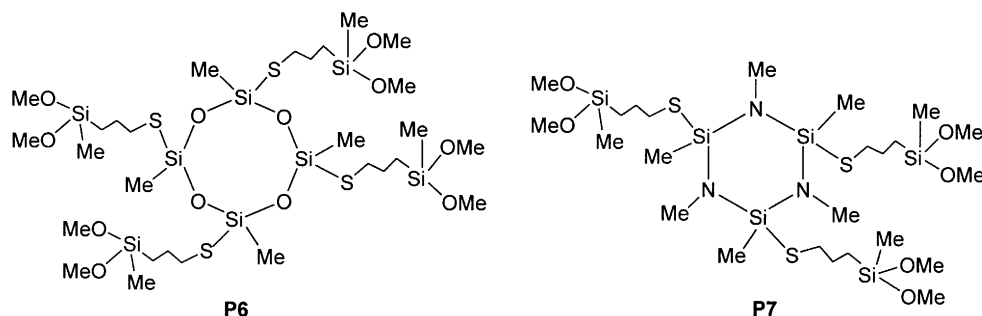
Scheme 1. Dehydrocoupling of polymethylhydrosiloxane and thiols

Similarly, treatment of PMHS with 3-(dimethoxymethylsilyl)-1-propanethiol and furfuryl mercaptan led to the corresponding sulfur-substituted polymers **P4** and **P5** in high yields. The structure of these polymers was established by NMR (^{29}Si , ^{13}C , ^1H), IR and elemental analysis.¹⁴ Polymers containing alkoxy silane pendant functional groups are important precursors to sol-gels.^{15,16}



All polymers are stable as solids or in solution for more than three months. In an NMR tube, **P5** was dissolved in benzene and a 2.5-fold excess of D_2O was added. Polymer degradation was monitored by NMR.¹⁷ After 2 h at rt, <10% conversion of Si–S bonds to Si–O(H) bonds was observed. Even after 2 h of heating at 78 °C only 25% of the Si–S bonds were cleaved. The hydrolysis products were not identified.

In the view of the applications of cyclic building blocks,^{18,19} dehydrocoupling of 1,3,5,7-octamethylcyclosiloxane (D_4H) and 1,2,3,4,5,6-hexamethyltricyclosilazane with thiols were also examined. Reaction of dimethoxymethylpropylthiosilane with D_4H and tricyclosilazane led to the corresponding substituted cyclic precursors **P6** and **P7** in quantitative yields.¹² Ring opening or rearrangement reactions were not observed. **P6** and **P7** are stable towards oxidation in solution and in the solid state for 2 months at room temperature.



In conclusion, we have shown that dehydrogenative coupling of SiH and RSH groups can be achieved via a simple one-step Rh-catalyzed protocol. Since the major byproduct is hydrogen gas, isolation of the target polymers is easy. The methodology is applicable to linear and cyclic polysiloxanes. We are currently exploring the practical applications of these polymers as materials for mesophasic control and sol-gel applications.

Acknowledgements

Financial support of the National Science Foundation (Grant No. 9874802) and the Air Force Office of Scientific Research through Grants F49620-96-1-0360 and F49620-99-1-0283 is gratefully acknowledged.

References

- Seyferth, D. In *Silicon-Based Polymer Science. A Comprehensive Resource*; Adv. Chem. Ser. 224; Ziegler, J. M.; Fearon, F. W., Eds.; American Chemical Society: Washington, DC, 1990; p. 565.
- Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. in Organomet. Chem.* **1998**, *42*, 363.
- Laine, R. M.; Blum, Y. D.; Tse, D.; Glaser, R. *Inorganic and Organometallic Polymers*; ACS Symp. Ser. 360; Zeldin, M.; Wynne, K. I.; Allcock, H. R., Eds.; American Chemical Society: Washington, DC, 1988; p. 124.
- For a review see: Lukevics, E.; Dzintara, M. J. *J. Organomet. Chem.* **1985**, *295*, 265.
- Baruah, J. B.; Osakada, K.; Yamamoto, T. *Organometallics* **1996**, *15*, 456 and references cited therein.
- Corriu, R. J. P.; Fernandez, J. M.; Guerin, C.; Kpton, A. *Bull. Soc. Chem. Belg.* **1980**, *39*, 783.
- Sommer, L. H.; Citron, J. P. *J. Org. Chem.* **1967**, *32*, 2470.
- Milano, J. C.; Robert, J. M.; Vernet, J. L.; Gallot, B. *Macromol. Chem. Phys.* **1999**, *200*, 1580.
- Milano, J. C.; Robert, J. M.; Vernet, J. L.; Gallot, B. *Macromol. Chem. Phys.* **1999**, *200*, 180.
- Chauhan, B. P. S.; Boudjouk, P. *Tetrahedron Lett.* **1999**, *40*, 4123.
- Arruda, A. F.; Campiglia, A. D.; Chauhan, B. P. S.; Boudjouk, P. *Anal. Chim. Acta* **1999**, *396*, 263.
- Rahn, J. A. 214th National Meeting of the American Chemical Society, Las Vegas, NV, September 7–11, 1997. Abstract No. INOR 230.
- Catalyst separation was accomplished by column chromatography. Filtration of the reaction mixture through a short dry Florisil column (eluent: hexane) and subsequent removal of the solvent at room temperature under vacuum (0.2 torr) furnished pure polymers in high yields. In some cases this process was repeated 2–3 times in order to remove the remaining traces of the catalyst.
- Selected analytical and spectral data of representative polymers: **P1**: ^1H NMR (C_6D_6), 0.48 (s, OSiMe_3); 0.83 (s, broad, SiMe); 4.24 (s, broad, PhCH_2S); 7.32, 7.68 (broad, Ph). ^{13}C NMR (C_6D_6), 1.35 (OSiMe_3); 2.10 (broad, SiMe); 30.64 (broad, PhCH_2S); 127.05, 128.60, 128.79, 139.86 (Ph). ^{29}Si NMR (C_6D_6), -27.75 , -27.97 , -28.03 (SiMe); 11.90 (OSiMe_3). **P4**: ^1H NMR (C_6D_6), 0.18 (s, OSiMe_3); 0.33 (s, broad, SiMe); 0.59 (s, broad, SiMeOMe), 0.84 (broad, SiCH_2); 1.96 (broad, CCH_2C); 2.92 (broad m, SCH_2C); 3.46 (s, broad, SiOMe). ^{29}Si NMR (C_6D_6), -28.51 , -28.93 , -29.09 (broad, OSiSMeO); -3.029 (broad, CH_2SiOMe). **P5**: ^1H NMR (C_6D_6), 0.13 (s, OSiMe_3); 0.49 (s, broad, SiMe); 3.91 (s, broad, CH_2SSi); 6.02,

- 6.13, 7.05 (broad, $CH=CH$). ^{13}C NMR (C_6D_6), 1.10 ($OSiMe_3$); 1.74 (broad, $SiMe$); 22.59 (CH_2S); 107.31, 110.59, 141.97, 152.88 ($CH=CH$). ^{29}Si NMR (C_6D_6), -28.00, -28.11, -28.24 ($SSiMe$); 11.78 ($OSiMe_3$). **P6**: 1H NMR (C_6D_6), 0.03 (t, broad, $SiMeOMe_2$); 0.59, 0.56, 0.47, 0.40 (s, $OSiSMeO$), 0.74 (m, broad, $SiCH_2$); 1.78 (m, CCH_2C); 2.68 (m, SCH_2C); 3.34, 3.33, 3.32, 3.31 (s, $SiOMe$). ^{29}Si NMR (C_6D_6), -25.93, -25.97, -26.03, -26.11, -26.51, -26.79 ($OSiSMeO$, mixture of isomers); -2.66, -2.68, -2.76, -2.79 ($CSiOMe$). **P7**: 1H NMR (C_6D_6), 0.21 (t, broad, $SiMeOMe_2$); -0.06, -0.05, -0.04 (s, $NSiSMeN$), 0.59 (m, broad, $SiCH_2$); 1.59 (m, CCH_2C); 2.42 (m, SCH_2C); 2.55 (broad, NCH_3); 3.27, 3.28, 3.30 (s, $SiOMe$). ^{29}Si NMR (C_6D_6), -2.67, -2.80, -2.86 ($NSiSMeN$, mixture of isomers); 1.26, 1.17, 1.09 ($CSiOMe$).
15. Lev, O.; Wu, Z.; Bharathi, S.; Glezer, V.; Modestov, A.; Gun, J.; Rabinovich, L.; Sampath, S. *Chem. Mater.* **1997**, *9*, 2354.
16. Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420.
17. The $^{29}Si(H)$ NMR spectrum of PMHS shows two types of resonance. The main signal is centered at -34.20 (-34.16, -34.20, -34.26) ppm and is due to the skeletal $-O-Si(Me)(H)-O-$ groups. That at lower field (10.58 ppm) is assigned to the terminal Me_3Si-O groups. The spectrum of the product **P5** displays a lowfield resonance (Me_3Si-O ; 11.78) and a new set of resonances at -28.00, -28.11, -28.24 ppm. These peaks were assigned to central silicon atoms that have undergone *S*-silylation. Degradation of polymer **P5** via oxidation leads to new peaks at ca. -50 and/or -65 ppm. We assign these to $-O-Si(Me)(OH)-O-$ and $-O-Si(Me)(OSi)-O-$ linkages. For detailed studies on hydrolysis reactions of polysiloxanes and their characterization by ^{29}Si NMR see: Lestel, L.; Cheradame, H.; Boileau, S. *Polymer* **1990**, *31*, 1154.
18. For example see: Harrison, P. G. *J. Organomet. Chem.* **1997**, *542*, 141 and references cited therein.
19. Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262.