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13. ABSTRACT *(Maximum 200 words)*

Unsaturated carbosilane polymers have been prepared by anionic as well as metathesis polymerization of silacyclopent-3-enes.

Of particular interest, is unsaturated carbosilane polymers with Si-H substitution have been prepared. These complementary functionalities permit crosslinking by hydrosilation reactions to yield new coating materials which have low dielectric constants and moisture absorption. These polymers can be chemically modified by addition reaction, to the carbon-carbon double bonds.

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Personnel Working on Grant

Senior Investigator:

Professor W.P. Weber, principal investigator, worked 10% of his time from November 1, 1988 to May 31, 1989; September 1, 1989 to May 31, 1990; September 1, 1990 to May 31, 1991; and September 1, 1991 to January 31, 1992 on this contract. In addition, he worked 100% of his time during July 1 to 31, 1989; June 1 to 30, 1990; and 78% of his time during June 1 to 30, 1991.

Postdoctoral Research Associates:

Dr. J. Farahi worked on this project 100% of his time from 6-1-91 to 8-31-91 as a postdoctoral research associate.

Dr. S.S. Hu worked on this project 100% of his time from 11-1-88 to 3-31-89. Dr. Hu received his Ph.D. at the Institute for Organic Chemistry at the Chinese Academy of Science, Shanghai, China. Dr. Hu has gone on to a postdoctoral research position with Professor A. Brook of the University of Toronto, Canada.

Dr. W. Jiang worked on this project 100% of her time from 11-1-88 to 3-31-89. Dr. Jiang received her Ph.D. at Iowa State University working with Professor Glen Russell. She has gone on to a postdoctoral research position with Professor T. Tidwell at the University of Toronto, Canada.

Dr. H. Lee worked on this project 100% of his time from 12-1-90 to 6-30-91 and 10-1-91 to 10-31-91 as a postdoctoral research associate.

Dr. X. Liao worked on this project 100% of his time from 5-1-88 to 11-30-91 as a postdoctoral research associate. He was then promoted to Senior postdoctoral research associate from 12-1-91 to 12-31-91. Dr. Liao received his Ph.D. from the Institute for Organic Chemistry of the Chinese Academy of Sciences, Shanghai, China.

Dr. G. Manuel, Professor of Chemistry at the Université of Paul Sabatier, Toulouse, France, worked on this project 100% of his time from 8-1-89 to 8-31-89.

Dr. Q. Zhou worked on this project 100% of his time from 7-1-91 to 10-31-91 as a postdoctoral research associate.

Graduate Assistants:

Mr. G. Gregg, a second year graduate student, joined our group in March 1990. He was supported as a graduate assistant 50% of the time from 5-1-90 to 7-31-90. He passed his Ph.D. qualifying examination during the Spring semester 1990.

Mr. H. Hong, a third year graduate student, worked 50% of his time from 6-1-89 to 8-31-89, 6-1-90 to 8-31-90, and 1-16-91 to 5-31-91 on this project. Mr. Hong successfully completed his Ph.D. in February 1992 and is currently employed with Shin-Etsu Chemical Company.

Mr. H. Lee, worked 50% of his time from 5-1-89 to 8-31-90 and 11-1-90 to 12-31-90 on this project. Mr. Lee successfully completed his Ph.D. in December 1990. He was then employed as a postdoctoral research associate in our group.

Mr. Y.T. Park, worked 50% of his time from 11-1-88 to 11-30-90 on this project. Mr. Park successfully completed his Ph.D. in November 1990. He is currently employed as a postdoctoral research associate with Prof. J. Economy in the Materials Research Department at the University of Illinois.

Mr. D. Stonich, worked 50% of his time from 11-1-88 to 5-31-89 on this project. Mr. Stonich successfully completed his Ph.D. in July 1991. He is currently employed by ICI Americas in Richmond, CA.

Mr. M. Theurig is completing his Diplomarbeit from the University of Braunschweig, Germany. He was supported as a fellowship holder from 10-1-91 to 12-31-91.

Ms. L.M. Wang, joined our research group in February 1990 and has passed her Ph.D. qualifying examination in March 1991. She was supported as a graduate assistant 50% of her time from 6-1-90 to 8-31-90 and 25% of her time from 10-1-91 to 12-31-91.

Ms. Z.J. Xu joined our research group in January 1991 and has passed her Ph.D. qualifying examination in December 1991. She was supported as a graduate assistant 25% time from 10-1-91 to 12-31-91.

Mr. Q. Zhou, a fourth year graduate student, worked 50% of his time from 11-1-88 to 5-31-89 on this project. Mr. Zhou completed his dissertation in May 1989. He is now employed by Kabi Pharmacia in Monrovia, CA as a research chemist.

Equipment Purchased:

No equipment was purchased on this grant.

Publications:

1. Addition of Dichlorocarbene to Poly(1,1-dimethyl-1-sila-cis-pent-3-ene) and Poly(1,1-dimethyl-1-sila-cis- and -trans-pent-3-ene). Characterization of microstructures of ^{13}C and ^{29}Si NMR, Q. Zhou and W.P. Weber, Macromolecules, 22, 1300 (1989).
2. Addition of Difluorocarbene to Poly(1,1-dimethyl-1-sila-cis-pent-3-ene) and Poly(1,1-dimethyl-1-sila-cis- and -trans-pent-3-ene). Characterization of Microstructures by ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR, Q. Zhou and W.P. Weber, Macromolecules, 22, 2987 (1989).
3. Birch Reduction of the Dichlorocarbene Adduct of poly(1,1-Dimethyl-1-sila-cis-pent-3-ene) (Cl_2C-I). Synthesis and Characterization of poly(1,1-Dimethyl-3,4-methylene-1-sila-cis- pent-3-ene) (CH_2-I), Q. Zhou and W.P. Weber, Polymer Bulletin, 21, 173 (1989).
4. Photolysis of 1,1,2,2-Tetramethyl-1,2-bis(2'-thiophenyl)disilane, S.S. Hu and W.P. Weber, J. Organometallic Chem., 369, 155 (1989).
5. Synthesis and Photodegradation of poly[2,5-bis(dimethylsilyl)thiophene], S.S. Hu and W.P. Weber, Polymer Bulletin, 21, 133 (1989).
6. Reductive Silylation of Chloroprene, W. Jiang and W.P. Weber, Polymer Bulletin, 21, 335 (1989).
7. Reaction of E-1,4-poly(2-triethylsilyl-1,3-butadiene) with Iodine Monochloride, W. Jiang and W.P. Weber, Polymer Bulletin, 21, 427 (1989).
8. Addition of Dichlorocarbene to cis-1,4-poly(1-trimethylsilylmethyl-1,3-butadiene). Fluoride catalyzed elimination of trimethylchlorosilane from cis-1,4-poly(2,3-dichloromethylene-2-trimethylsilylmethyl-1,3-butadiene, W. Jiang, Y-X. Ding and W.P. Weber, Polymer Bulletin, 21, 541 (1989).
9. Stereospecific Anionic Ring Opening Polymerization of Silacyclopent-3-enes, X.

Zhang, Q. Zhou and W.P. Weber, "Advances in Chemistry," Proceedings of the International Topic Workshop "Advances in Silicon-Based Polymer Science," eds. J.M. Zeigler and F.W. Gordon Fearon, ACS, Washington, D.C., Vol. 224, p. 679 (1990).

10. Stereoregular 1,4-Polymerization of 2-Triethylsilyl-1,3-butadiene, Y.X. Ding and W.P. Weber, "Advances in Chemistry," Proceedings of the International Topic Workshop "Advances in Silicon-Based Polymer Science," eds. J.M. Zeigler and F.W. Gordon Fearon, ACS, Washington, D.C., Vol. 224, p. 687 (1990).
11. Copolymerization of 1,1-Dimethyl-1-silacyclopent-3-ene and 1,1-Diphenyl-1-silacyclopent-3-ene. Characterization of Copolymer Microstructures by ^{1}H, ^{13}C and ^{29}Si NMR Spectroscopy, Q. Zhou and W.P. Weber, Macromolecules, 23, 1583 (1990).
12. Synthesis and Photodegradation of poly[1,4- bis(dimethylsilyl)naphthalene, S.J.H. Lee and W.P. Weber, Polymer Bulletin, 22, 355 (1989).
13. Anionic Ring Opening Polymerization of 1,1,3-Trimethyl-1-silacyclopent-3-ene. Effect of Temperature on poly(1,1,3-Trimethyl-1-sila-cis-pent-3-ene) Microstructures, Y.T. Park, G. Manuel and W.P. Weber, Macromolecules, 23, 1911 (1990).
14. Anionic Ring Opening Polymerization of 3,4-Benzo-1,1-dimethyl-1-silacyclopentane. Properties of poly(3,4-benzo-1,1-dimethyl-1-silapentene), Y.T. Park, Q. Zhou and W.P. Weber, Polymer Bulletin, 22, 349 (1989).
15. Synthesis and Photodegradation of poly[2,5-bis-(Dimethylsilyl)furan], H.H. Hong and W.P. Weber, Polymer Bulletin, 22, 363 (1989).
16. Anionic Ring Opening Polymerization of 2-methyl-2-silaindan. Characterization of the Polymer and Mechanism of Polymerization, S.Q. Zhou and W.P. Weber, Makromol. Chem. Rapid Commun., 11, 19 (1990).
17. Mechanism of Anionic Ring Opening Polymerization of Silacyclopent-3-enes, W.P. Weber, Y.T. Park, and S.Q. Zhou, Polymer Preprints, 31, 44 (1990).
18. Cyclopropanation of poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene). Synthesis and Characterization of poly(1-methyl-3,4-methylene-1-phenyl-1-sila-cis-pent-3-ene), X.

Liao, H.S.J. Lee and W.P. Weber, Makromol. Chem., 191, 2173 (1990).

19. Anionic Ring Opening Polymerization of 1-Silacyclopent-3-ene. Characterization of poly(1-sila-cis-pent-3-ene) by ^{1}H, ^{13}C and ^{29}Si NMR Spectroscopy, S.Q. Zhou, Y.T. Park, G. Manuel and W.P. Weber, Polymer Bulletin, 23, 491 (1990).
20. Synthesis of 3-Methylene-1,1-Dichloro-1- Silacyclobutane and 1,1-Dichloro-1-Silacyclopent-3-ene, R. Damrauer, A. Laporterie, G. Manuel, Y.T. Park, R. Simon and W.P. Weber, J. Organometal. Chem., 391, 7 (1990).
21. Addition of Difluorocarbene to Poly(1-Methyl-1-Phenyl-1-sila-cis-pent-3-ene) Characterization of Microstructure by ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR Spectroscopy, H.S.J. Lee and W.P. Weber, Polymer Preprints, 31, 424 (1990).
22. Synthesis and Anionic Ring Opening Polymerization of 1- Germa-1,1-dimethyl-[3,4]-c-thienocyclopentene, S.Q. Zhou, P. Mazerolles, C. Laurent and W.P. Weber, Polymer Bulletin, 23, 583 (1990).
23. Synthesis and Dimerization 2,3-Dimethyl-5- Silaspiro[4,4]nona-2,7-diene, Y.T. Park, S.Q. Zhou, D. Zhao, G. Manuel, R. Bau, and W.P. Weber, Organometallics, 9, 2811 (1990).
24. Mechanism of Anionic Ring Opening Polymerization of Silacyclopent-3-enes, W.P. Weber, Y.T. Park, and S.Q. Zhou, Makromol. Chem. Macromol. Symp. 42/43, 259 (1991).
25. Preparation and Properties of High Molecular Weight poly(1-germa- or 1-sila-cis-pent-3-enes), S.Q. Zhou, L. Wang, X. Liao, G. Manuel and W.P. Weber, J. Inorg. and Organometal. Polymers, 1, 199 (1991).
26. Synthesis and Polymerization of 5-Silaspiro[4,4]-nona-2,7-dienes, Y.T. Park, S.Q. Zhou, G. Manuel and W.P. Weber, Macromolecules, 24, 3221 (1991).
27. Synthesis and Microstructure of Poly(1-phenyl-1-sila-cis-pent-3-ene), X. Liao, Y.Ho. Ko, G. Manuel and W.P. Weber, Polymer Bulletin, 25, 63 (1991).
28. Chemical Modification of Poly(1-methyl-1-phenyl-1- sila-cis-pent-3-ene) by Addition of Dichloroketene, H.S.J. Lee and W.P. Weber, Polymer Preprints, 32, 621 (1991).

29. Partial and Complete Chemical Modifications of Poly(1,1-dimethyl-1-sila-cis-pent-3-ene) by Addition of Dichloroketene, H.J.S. Lee and W.P. Weber, Polymer, in press (1991).
30. Partial and Complete Chemical Modifications of Poly(1-methyl-1-phenyl-1-sila-cis-pent- 3-ene) by Addition of Dichloroketene, H.S.J. Lee and W.P. Weber, Macromolecules, 24, 4749 (1991).
31. Bromide Ion Catalyzed Dimerization of 6-Oxa-3,3-diphenyl-3-silabicyclo-[3.1.0]-hexane. Structure Determination and Ring Substitution of 1,5-Dioxa-2,2,6,6-tetraphenyl-1,6-disila-4,8-divinylcyclooctane. Synthesis of 1,3-dioxa-2,2,4,4-tetraphenyl-2,4-disila-6-vinylcyclohexane, Y.T. Park, G. Manuel, R. Bau, D. Zhao and W.P. Weber, Organometallics, 10, 1586 (1991).
32. Ring Opening Metathesis Polymerization of 1,1-Diphenyl-1-silacyclopent-3-ene. Synthesis of Poly(1,1-diphenyl-1-sila-cis-pent-3-ene), D.A. Stonich and W.P. Weber, Polymer Bulletin, 25, 629 (1991).
33. Synthesis of Poly(1-methyl-1-phenyl-1-silapentane) by Chemical Reduction of Poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene) with Diimide, X. Liao and W.P. Weber, Polymer Bulletin, 25, 621 (1991).
34. Synthesis and Characterization of Poly[(2-trimethylsilyl-2-cyclopentene-1,4-diyl)-vinylene], D.A. Stonich and W.P. Weber, Polymer Bulletin, 26, 493 (1991).
35. Synthesis and Characterization of Poly([3,4,c]furano-1-germa-1,1-dimethyl-pentane), X. Liao, W.P. Weber, P. Mazerolles, C. Laurent and A. Faucher, Polymer Bulletin, 26, 499 (1991).
36. Synthesis and Characterization of Poly(3,4-benzo-1-phenyl-1-silapentane) and Poly(3,4-benzo-1-silapentene), Y-H. Ko and W.P. Weber, Polymer Bulletin, 26, 487 (1991).
37. Anionic Ring Opening Polymerization of 1-Phenyl-1-vinyl-1-silacyclopent-3-ene. Synthesis and Characterization of Poly(1-phenyl-1-vinyl-1-sila-cis-pent-3-ene), X. Liao, R.T. Liebfried and W.P. Weber, Polymer Bulletin, 26, 625 (1991).

Meetings Attended:

Attended "Silicon Symposium XXII," Philadelphia, PA, April 7-8, 1989.

Attended the Pacifichem Conference '89 sponsored by the American Chemical Society, Honolulu, HI, December 17-21, 1989.

Attended the "Recent Advances in Polyimides and Other High Performance Polymers" meeting sponsored by the Division of Polymer Chemistry of the American Chemical Society, San Diego, CA, January 22-25, 1990.

Attended "Silicon Symposium XXIII," Midland, MI, April 20-21, 1990.

Attended the 199th National American Chemical Society Meeting, Boston, MA, April 22-27, 1990.

Attended the 200th National American Chemical Society Meeting, Washington, D.C., August 26-30, 1990.

Attended the 2nd International Silicon Workshop sponsored by the Polymer Division of the American Chemical Society, Honolulu, HI, December 15-20, 1990.

Attended the XXIV Silicon Symposium at the University of Texas at El Paso, April 11-13, 1991.

Scientific Visits:

The Non-Metallic Materials Laboratory (Dr. Charles Lee) at Wright Patterson AFB, October 26, 1990.

The Army Electronic Laboratory (Dr. Ed Poindexter) at Fort Mammoth, NJ, January 9, 1991.

The Naval Research Laboratory (Dr. James Griffith), January 11, 1991.

The Non-Metallic Materials Composite Laboratories (Dr. Terry St. Claire) at NASA Langley , July 1, 1991.

Papers Presented at Meetings:

"Synthesis and Polymerization of 5-silaspiro[4.4]nona-2,7-dienes," Poster presented at Silicon Symposium XXIII, Midland, MI, April 20-21, 1990.

"Polymerization of 1-Silacyclopent-3-ene Polymer. Characterization of Microstructure by End Group Analysis by ^{1}H, ^{13}C and ^{29}Si NMR. Pyrolysis of poly(1-silapent-3-ene)," Lecture presented at Silicon Symposium XXIII, Midland, MI, April 20-21, 1990.

"Mechanism of Anionic Ring Opening Polymerization of Silacyclopent-3-enes," Invited Symposium Lecture at the 199th National American Chemical Society Meeting, Boston, MA, April 22-27, 1990.

"Addition of Difluorocarbene to Poly(1-Methyl-1-Phenyl-1- sila-cis-pent-3-ene). Characterization of Microstructures by ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR Spectroscopy," Invited Lecture at the Chemical Modification of Polymers Symposium at the 200th National American Chemical Society, Meeting, Washington, D.C., August 26-30, 1990.

Presented paper, XXIV Organosilicon Symposium, University of Texas at El Paso, April 11-13, 1991.

"Addition of Dichloroketene to Poly(1-methyl-1-phenyl-1- sila-cis-pent-3-ene)," Paper presented at the 201st National American Chemical Society Meeting, April 17-19, 1991.

Seminars Presented:

"Synthesis and Reactivity of Unsaturated Silyl Substituted Polymers," presented at:

Pierce College, November 7, 1988

Rhone Poulenc, Lyon, France, May 18-19, 1989

Universite Paul Sabatier, France, May 23, 1989

Universite of Bourdeaux, France, May 26, 1989

California State University, San Diego, February 26, 1990.

Ato Chem, Elf Aquataine, Sommerville, NJ, March 15, 1990.

Non-Metallic Materials Laboratory, Wright Patterson Air Force Base, October 25, 1990

Hercules Research Center, Wilmington, Delaware, October 26, 1990

"Ring Opening Polymerization of Silacyclopentenes," presented at:

Universite Paul Sabatier, May 14, 1991

Universite Montepellier, May 16, 1991

Institute for Organic Chemistry, Chinese Academy of Sciences, Shanghai, PRC, July 16, 1991

Fudan University, Shanghai, PRC, July 18, 1991

Peking University, July 22, 1991

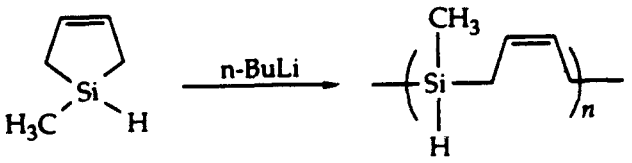
Institute for Chemistry, Chinese Academy of Sciences, Beijing, July 23, 1991

Tsing Hua University, Beijing, July 25, 1991

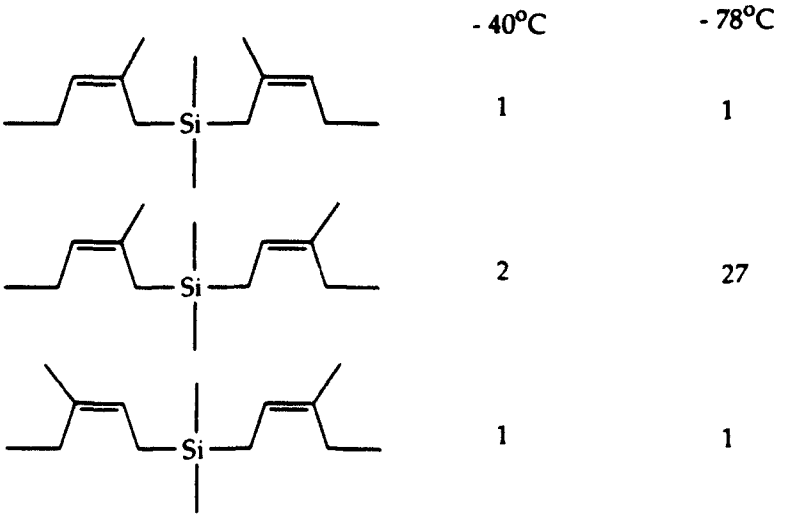
Naval Weapons Laboratory, China Lake, August 8, 1991

Significant Scientific Results:

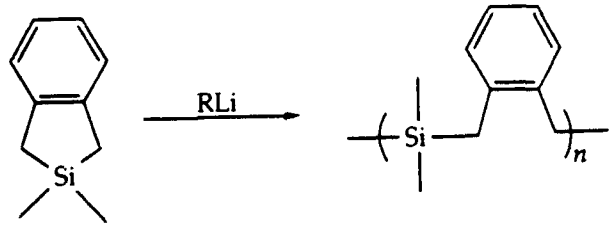
Anionic ring opening polymerization of silacyclopent-3-enes which have Si-H bonds has been accomplished. This leads to polymers which possess both reactive Si-H and carbon-carbon double bonds. The presence of these mutually reactive functional groups permits platinum catalyzed crosslinking reactions. In this way, these polymers can be converted to novel matrix materials for composite materials as well as corrosion resistant coatings under mild conditions. (See publications 16, 17, 19, 20, 24, 36.)



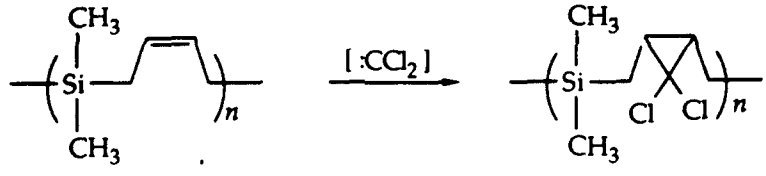
The mechanism of the anionic ring opening polymerization of 1,1-dimethyl-1-sila-cyclopent-3-ene and related systems has been studied. This information permits preparation of higher molecular weight polymers which have increased thermal stability. Control of polymer microstructure in poly(1,1,3-trimethyl-1-sila-cis-pent-3-ene) can be achieved. (See publications 9, 11, 13, 23, 24, 25, 26.)



Anionic ring opening polymerization of 3,4-benzo-1,1-dimethyl-1- silacyclopentene and related systems has been achieved. These are remarkably thermally stable polymers. (See publications 14, 16, 22, 36.)



Addition of dichlorocarbene, difluorocarbene, methylene, hydrogen, and dichloroketene to the reactive carbon-carbon double bonds of poly(1,1-dimethyl-1-sila-cis-pent-3-ene), and related polymers has been achieved. (See publications 1, 2, 3, 8, 18, 21, 28, 29, 30, 33, 37.) The microstructure and thermal stability of these adduct polymers has been determined.



Alternate copolymers made up of aromatic systems and disilyl units have been prepared (see publications 4, 5, 12, 15). Extended interaction of the aromatic pi system with the adjacent disilyl units has been detected. Ultraviolet absorption bands shift to longer wavelength with increasing copolymer molecular weight. Photodegradation of these copolymer systems have been studied.