

- (a) extend the metathesis reaction in polar and protic solvents including alcohols and even water or much more acidic environments (for example, phenols or strong acids such as trichloroacetic acid)
- (b) tolerate well many heteroatom-containing (for example, O, N, P, Cl, Br) functional groups, hence a wide profile of substrates
- (c) allow working under normal temperature and pressure, in common solvents, without special purification and
- (d) can be conveniently stored in air without substantial decomposition – even for weeks.

Recently a new generation of catalysts, derived mainly from Grubbs' ruthenium carbenes, has been designed and applied successfully in the metathesis of functionalised olefins and cycloolefins, in ring-closing and ring-opening metathesis and in living metathesis polymerisation of functionalised cycloolefins and heterocycloolefins. Particular attention is presently being devoted to creating attractive methods for the synthesis of new heterocycles, natural compounds with biological activity and sub-units of biologically-interesting organic compounds having complex architecture.

References

- 62 (a) S. Cummings, D. W. Smith, K. B. Wagener, R. Miller and E. Ginsburg, *Polymer Prep. (ACS, Div. Polymer Chem.)*, 1995, 36, 697; (b) D. W. Smith and K. B. Wegener, *Macromolecules*, 1993, 26, 1633; (c) D. W. Smith and K. B. Wegener, *ibid.*, 1993, 26, 13533
- 63 E. Sh. Finkel'stein, *Polymer Sci., Ser. B*, 1995, 37, 185
- 64 B. R. Maughon and R. H. Grubbs, *Macromolecules*, 1997, 30, 3459
- 65 M. Hillmyer, W. R. Laredo and R. H. Grubbs, *Macromolecules*, 1995, 28, 6311
- 66 C. Fraser and R. H. Grubbs, *Macromolecules*, 1995, 28, 7248
- 67 V. Heroguez, M. Fontanille and Y. Gnanou, 13th Int. Symp. on Olefin Metathesis and Related Processes, Rolduc, Kerkrade, The Netherlands, July 11–15, 1999, Abstracts, p. 23
- 68 R. H. Grubbs, *Polymer Prep. (ACS, Div. Polymer Chem.)*, 1992, 33, 163
- 69 M. A. Hillmyer, C. Lepetit, D. V. McGrath, B. M. Novak and R. H. Grubbs, *Macromolecules*, 1992, 25, 3345
- 70 (a) K. H. Mortell, M. Gingras and L. L. Kiessling, *J. Am. Chem. Soc.*, 1994, 116, 12053; (b) K. H. Mortell, R. V. Weatherman and L. L. Kiessling, *J. Am. Chem. Soc.*, 1996, 118, 2297
- 71 B. M. Novak, W. Risse and R. H. Grubbs, *Adv. Polymer Sci.*, 1992, 102, 47
- 72 M. B. France, R. H. Grubbs, D. V. McGrath and R. Paciello, *Macromolecules*, 1993, 26, 4742
- 73 T. Viswanathan, J. Jethmalani and A. Toland, *J. Appl. Polym. Sci.*, 1993, 47, 1477
- 74 D. M. Lynn, S. Kanaoka and R. H. Grubbs, *J. Am. Chem. Soc.*, 1996, 118, 784
- 75 V. Dragutan, I. Dragutan and A. T. Balaban, *Platinum Metals Rev.*, 2000, 44, (2), 58; *ibid.*, 2000, 44, (3), 112
- 76 C. W. Bielawski and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2000, 39, 2903

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Silphenylenesiloxane Polymers

Polysiloxanes are polymers with an alternating chain of silicon and oxygen atoms. Polysiloxanes have a range of very valuable properties which are utilised commercially: inertness, resistances to water and oxidation, and high thermal stabilities. However, little work has been done to develop dehydrocoupling polymerisation to give polysiloxanes. A team of scientists at the University of Cincinnati have now developed a general method of dehydrocoupling polymerisation to give alternating copolymers of silphenylenesiloxanes from bis-silanes and disilanol, under mild conditions, using Wilkinson's catalyst, $\text{RhCl}(\text{Ph}_3\text{P})_3$, (R. Zhang, J. E. Mark and A. R. Pinhas, *Macromolecules*, 2000, 33, (10), 3508–3510).

Silphenylenesilane polymers with controllable microstructures and average molecular weight of $10,100 \text{ g mol}^{-1}$ were produced. The best polymerisation occurred between *p*-bis(dimethylsilyl)benzene and *p*-bis(dimethylhydroxysilyl)benzene. Among other alternating copolymers produced were poly-(tetramethyl-*p*-silphenylenesiloxane) (poly-TMPS) and a combination of tetramethyl-*m*-silphenylenesiloxane and TMPS. The rhodium catalyst was very efficient and robust under the reaction conditions.