

The acyclic diene metathesis (ADMET) polymerization approach to silicon containing materials

Piotr P. Matloka, Kenneth B. Wagener*

*The George and Josephine Butler Polymer Research Laboratory,
Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA*

Available online 2 August 2006

Abstract

The utility of acyclic diene metathesis (ADMET) polymerization in the synthesis of silicon–carbon hybrid materials is reviewed. Silicon containing macromolecules are synthesized from organosilicon α,ω -dienes (except those which are divinyl substituted). As an extension of olefin metathesis, ADMET is catalyzed by many transition metal complexes which either initiate the formation of carbene complexes (“ill-defined” catalysts) or by metallocarbene complexes (“well-defined” catalysts). Constant developments of catalytic systems have made this methodology more viable by allowing incorporation of numerous silicon containing functionalities into the polymer’s backbone or pendant to it. Divinyl substituted organosilicon derivatives are inert to ADMET conditions; they undergo silylative coupling (SC) polycondensation catalyzed by ruthenium and rhodium complexes yielding metathesis-like products, although this transformation proceeds via a non-metallocarbene mechanism.

© 2006 Elsevier B.V. All rights reserved.

Keywords: ADMET; Metathesis; Catalysis; Silylative coupling; Polycondensation

1. Introduction

As an inherent part of organometallic chemistry, organosilicon chemistry is one of the rapidly developing fields of science. Throughout nature, there are many well known inorganic and polymeric compounds containing silicon; however, there are no naturally occurring organosilanes. Organosilicon chemistry has blossomed since Kipping’s [1] pioneering work at the beginning of the 20th century. Numerous applications [2–5] have been reported in the manufacture of synthetic reagents and intermediates, bioactive molecules, biomedical materials, electronic devices, specialty plastics, elastomers, coatings, and fibers. Throughout the years researchers have focused on silicon–carbon hybrid compounds rather than purely inorganic structures.

Silicon/carbon hybrid polymeric materials have garnered considerable attention due to their enhanced properties, some of which cannot be attained by using polymers based on carbon alone. The uniqueness of the silicon–carbon copolymers comes

from their high thermal stability, good electrical resistance, low surface tension, release and lubrication properties, high hydrophobicity, low glass transition temperature, and low toxicity for the natural environment [5]. Incorporation of the siloxane unit or the silicon atom into a carbon-based polymer backbone can be used to tailor the desired properties of the resultant material [3,6]. Several synthetic methods involving anionic ring-opening polymerization, thermal cyclopolymerization, condensation and coupling reactions have been applied to synthesize such hybrids [2,5].

Olefin metathesis has been investigated for over 50 years as one of the most motivating discoveries in organometallic chemistry, widely used in both academic and industrial settings [7–9]. In 2005 professors Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock were awarded the Nobel Prize in Chemistry “for the development of the metathesis method in organic synthesis.” [10] The name, proposed by Calderon, Chen, and Scott [11] in 1967, originates from the Greek word “metathesis” meaning changing or exchanging positions. The metathesis process involves reaction of two carbon–carbon double bonds that yields two new olefins (Fig. 1) and is described as an intramolecular and intermolecular exchange of substituents on 1,2 di-, tri-, or tetrafunctional double bonds and “can be compared to a dance in which the couples change partners” [10]. This process can be divided into three categories:

Abbreviations: ADMET, acyclic diene metathesis; CM, cross-metathesis; DP, degree of polymerization; RCM, ring-closing metathesis; ROMP, ring-opening metathesis polymerization; SC, silylative coupling

* Corresponding author. Fax: +1 352 392 9741.

E-mail address: wagener@chem.ufl.edu (K.B. Wagener).

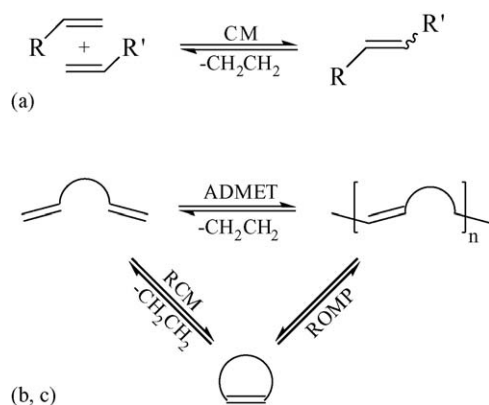


Fig. 1. Types of olefin metathesis.

- (a) Simple exchange reactions
- metathesis reaction involving two equal olefins and
 - cross-metathesis (CM) reaction involving two different olefins.
- (b) Metathesis polymerizations
- ring-opening metathesis polymerization (ROMP) and
 - acyclic diene metathesis polymerization (ADMET).
- (c) Ring-closing metathesis (RCM).

This review focuses on the ADMET approach to silicon containing polymers and copolymers catalyzed by “well-defined” catalyst systems (Fig. 2). The silylative coupling (SC) polycondensation of divinyl organosilicon derivatives, which exhibit low metathesis activity, is described briefly as a complementary method to ADMET polymerization.

2. Introduction to ADMET polymerization

The discoveries and developments in the field of olefin metathesis and organometallic chemistry have made olefin metathesis a convenient synthetic tool for the synthesis of functionalized and non-functionalized polyolefins [8]. As previously mentioned there are two modes of olefin metathesis polymerization: ring-opening metathesis polymerization (ROMP) [8] and acyclic diene metathesis polymerization (ADMET) [8]. ROMP falls into chain-addition type polymerization category. It is an exothermic reaction, thermodynamically driven by the release of ring strain in a cyclic olefin monomer. ADMET is step-growth condensation type polymerization and thermally neutral. It is important to understand the requirements and consequences for these classifications.

Acyclic diene metathesis is a step-growth condensation type polymerization that normally employs an α,ω -diene in conjunction with a metathesis catalyst to produce high molecular unsaturated polymer. The reaction is driven by removal of a small condensate, usually ethylene. ADMET follows the same rules as any other polycondensation reaction, meaning that high conversions (>99%) with no side reactions are necessary to produce high molecular weight polymers [12]. This reaction, as in the case of any condensation polymerization, is an equilibrium process, which proceeds in a stepwise fashion to form dimer, trimer, tetramer, and so on to obtain high molecular polymer. The size of the polymer increases continuously with time (conversion) at relatively slow rate.

High molecular weight polymer is obtained at the end of polymerization when the conversion of monomer is larger than that of 99%. Thus, a highly active catalytic system is required throughout the polymerization; most catalysts however, show higher activity towards terminal olefins for steric hindrance reasons, and so α,ω -diene monomers are often used in acyclic diene metathesis polymerization.

Early investigations of polymerization of 1,5-hexadiene and 1,9-decadiene, by Wagener and co-workers in the mid-1980s, demonstrated that “classical” catalysts such as $WCl_6/EtAlCl_2$ can lead to both cationic vinyl addition chemistry and in addition to polycondensation chemistry [7,13], thereby defining the need for active and well-defined catalysts for metathesis. Fortunately, in 1986, Schrock and co-workers [14] successfully prepared the first well-defined, single site catalyst, a breakthrough in this field. This breakthrough led to more stable ruthenium based catalytic systems discovered by Grubbs.

Like many other polycondensation reactions, ADMET polymerization is best performed in the bulk (neat) to maximize the molar concentration of monomer (terminal olefins) and to promote a shift in the equilibrium of the reaction from monomer towards unsaturated polymer formation. Bulk polymerization also minimizes undesired cyclization, a well known concurrent reaction in polycondensation chemistry [12]. Moreover, high vacuum is applied to remove the condensate ethylene, which further shifts the reaction towards polymer formation.

The mechanism of the ADMET polymerization cycle has been well documented [13,15]. Each step in this mechanism is in true chemical equilibrium, and the ultimate driving force for the reaction is removal of ethylene. The catalytic cycle starts with coordination of an olefin, followed by formation of a metallacyclobutane intermediate and productive cleavage that leads to the formation of the metathesis active alkylidene complex. These subsequent reactions produce a methylidene complex followed

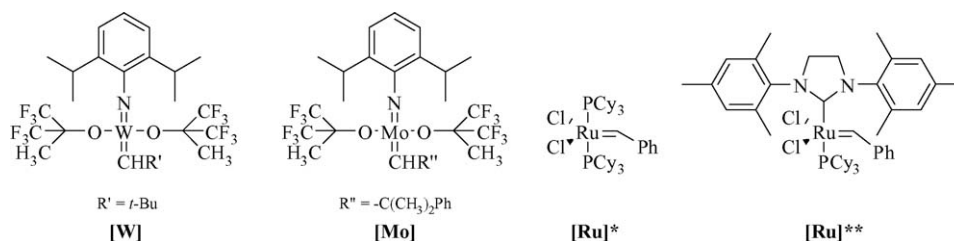


Fig. 2. Well-defined catalysts for metathesis.

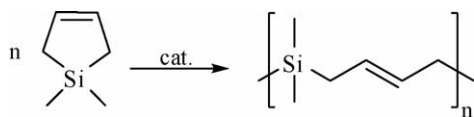


Fig. 3. ROMP of 1,1-dimethyl-1-silacyclopent-3-ene.

by the coordination of another monomer. Productive cleavage of another metallacyclobutane results in release of ethylene - one molecule for each “coupling” reaction.

The developments in the field of well-defined catalysts along with the clean mechanism of ADMET have become instrumental in the synthesis of novel polymers with controlled architectures. The design starts with the preparation of a α,ω -diene bearing the desired type of functionality or specific type of branching. The resultant polymer retains this functionality and a specific backbone sequence. ADMET has produced unsaturated polymers where the functionalities have been ethers [16], esters [17], carbonates [18], sulfides [19] and many more functionalities [20,21]. Consequently, ADMET bypasses typical synthetic obstacles in the synthesis of polymers and copolymers, and allows creating polymer structures that cannot be prepared via other routes.

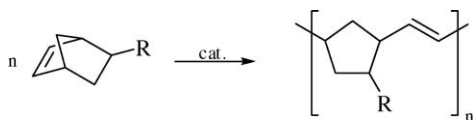
3. Olefin metathesis chemistry of compounds containing silicon

In the early seventies, research on metathesis was predominantly focused on producing materials from simple silicon functionalized olefins. In 1971, Friedman described the first example of these materials by the metathesis of monoalkenylsilanes in the presence of $\text{MoO}_3/\text{Al}_2\text{O}_3$ [22]. In addition to these simple materials, a variety of organosilicon compounds can be produced using metathesis and can be divided into three categories based on choice of polymerization method and structure of monomer:

- (1) ROMP of unsaturated silacycloalkenes,
- (2) ROMP of silylsubstituted cycloalkenes, and
- (3) ADMET of α,ω -dienes containing silicon.

First, the ROMP of the unsaturated silacycloalkenes leads to polymers containing silicon atoms incorporated in the carbon backbone, as exemplified in Fig. 3. The metathesis of 1,1-dimethyl-1-silacyclopent-3-ene proceeds in the presence of tungsten [23] or alumina-rhenium [24] and offers a broad scope for all silacycloalkenes, except for the thermodynamically stable silacyclohexene derivatives.

Second, the ROMP of silylsubstituted olefins leads to unsaturated polymers (Fig. 4) containing pendant silyl groups used



R = SiMe_3 ; $\text{SiMe}_2\text{CH}_2\text{SiMe}_3$; SiCl_3 ; $\text{Si}(\text{OEt})_3$

Fig. 4. ROMP of silylsubstituted norbornenes.

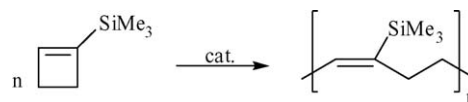


Fig. 5. ROMP using Casey's carbene complex.

to modify the properties of the polymer's backbone. One such example is the ROMP of silylsubstituted norbornenes in the presence of either a homogeneous tungsten catalyst or a heterogeneous alumina-rhenium catalyst [25].

An interesting example of ROMP is the reaction of 1-(trimethylsilyl)cyclobut-1-ene in the presence of Casey's carbene complex (Fig. 5) [26]. The resultant polymer shows a repeating head-to-tail structure containing only the *cis* double bond configuration. Moreover, these trimethylsilyl groups can be easily converted into different functionality making them a surrogate for the functional group before metathesis.

Third, the ADMET polymerization of α,ω -dienes containing silicon leads to the formation of unsaturated polymers which, depending on the structure of monomer, can either include silicon functionality incorporated into polymer backbone or as a pendant groups along the polymer chain. Contrary to ROMP which can be limited to the use of strained cyclic monomers, ADMET offers wide spectrum of polymer structures. Thus, utility of ADMET polymerization will be discussed in the next section.

4. Acyclic diene oligomerization and polymerization of dienes containing silicon

Acyclic diene metathesis polymerization of silicon containing compounds is the most universal method amenable for the synthesis of unsaturated organosilicon oligomers and polymers. The clean and efficient chemistry of ADMET combine desired material properties of both carbon and silicon based polymers in the random linear copolymer. Moreover, the high selectivity of olefin metathesis facilitates an introduction of a wider range of possible “functional handles” to manipulate the overall material properties.

Metathesis of dialkenylsilicon derivatives can be achieved either by an intramolecular or an intermolecular approach. The intermolecular ADMET reaction between α,ω -dienes (with exceptions of divinyl derivatives) produces linear, unsaturated polycarbosilane or polycarbosiloxane oligomers or polymers. Unsaturated heterocyclic organosilicon can also be produced by an intramolecular reaction if preferred. The mechanism of reaction is strictly dependent on the structure of the initial α,ω -diene and substituents on silicon; note that in some cases a six membered ring compound will be preferentially formed as the most thermodynamically stable product. Since all possible pathways are in equilibrium, both the seven and five membered rings are rarely observed. Product formation can be influenced to some extent by the presence or absence of solvent in the reaction environment.

As mentioned, the divinyl derivatives of silicon compounds do not undergo homometathesis, mainly due to the steric and electronic effects of two silyl groups present on the adjacent

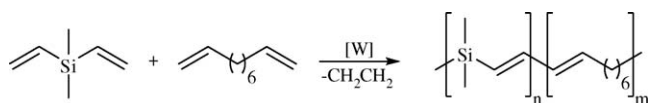


Fig. 6. Copolymerization of divinyl dimethylsilane with 1,9-decadiene.

carbon atoms in the intermediate metallacyclobutane [27]. However, while studying the hydrosilative activity of simple Ru(II) and Ru(III) complexes, Marciniec and co-workers [28–31] have shown that catalytic metathesis of alkoxyvinylsilanes is a competing reaction. However, soon after was found that this process does not operate through metallacyclobutane mechanism. Thus, application of this silylative coupling (SC) polycondensation in the formation of macromolecular structures containing silicon will be described in the later in separate section.

4.1. ADMET catalyzed by “well-defined” catalytic systems

In the early 90’s Wagener and co-workers [32–35] opened a new chapter in the synthesis of unsaturated polymers and copolymers containing silicon by preparing polycarbosilanes and polycarbosiloxanes with acyclic diene metathesis polymerization using well-defined catalysts (Fig. 2).

4.2. Polycarbosilanes

Polycarbosilanes are an interesting class of polymers due to the presence of a covalent bond between silicon and carbon atoms in the backbone. Potential applications of these materials in the broad range of fields have triggered considerable interest in their preparation [3]. The first silane diene, dimethyldivinylsilane [32], subjected to ADMET polymerization did not polymerize in the presence of the tungsten based Schrock’s catalyst [W], where the lack of productive metathesis was attributed to the steric influence of the trisubstituted silicon atom adjacent to the double bond. Similar results were obtained by Schrock et al. [36] in the attempted metathesis of vinyltrimethylsilane. The steric influence was further demonstrated via copolymerization of divinylsilane with 1,9-decadiene [32], where the divinyl repeat unit was found to insert in a singular manner along the backbone, Fig. 6.

Finkelshtein [37] provides a different explanation for the lack of reactivity of divinyl dimethylsubstituted silanes in the ADMET polymerization. His rationalization is based on the formation of the highly stable silylated carbene complex and its reactivity under copolymerization conditions. During the homopolymerization of divinylsilanes, formation of the metathesis active methylidene complex competes with an inactive silylated carbene. The reaction goes through the thermo-

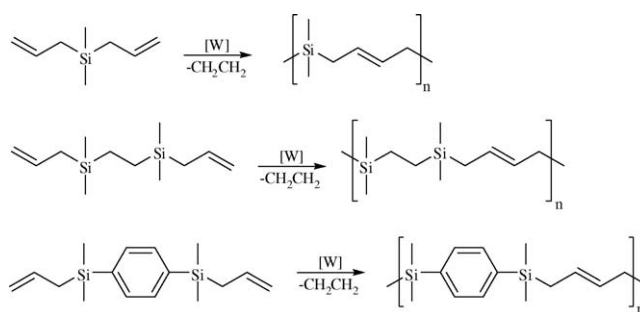


Fig. 7. Polycarbosilanes via ADMET.

dynamically more favorable process that leads to formation of the stronger stabilized silylated carbene, and thus the metathesis product is not observed. In the case of copolymerization, the stability of both carbene complexes does not differ significantly and two pathways are possible. The productive copolymer formation is realized along with the unproductive formation of the starting divinylsilanes.

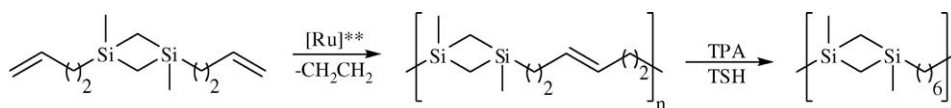
Further investigations have shown that monomers with the methylene spacers incorporated between the silicon atom and the olefin are able to undergo productive metathesis polymerization (Fig. 7) [32]. Successful ADMET polymerization produces unsaturated polymers containing predominately (80%) *trans* double bonds. Exceptions are observed while polymerizing stiffer carbon segments; for example, the polymerization of 1,4-bis-(dimethylallylsilyl)benzene results in a 47% *cis* configuration along the unsaturated backbone [32].

Similar study to Finkelshtein [38,39] that involves polymerization of α,ω -diene bearing highly reactive silacyclobutane using ADMET methodology and “well-defined” catalytic system was conducted by Interrante and co-workers [40]. The carbosilane polymers and copolymers were synthesized with the disilacyclobutane rings imbedded into the copolymer’s backbone (Fig. 8).

Unsaturated materials were hydrogenated using methodology developed by Hahn [41], which does not require the use of high-pressure H₂, and the disilacyclobutane rings were thermally induced to open resulting in a transparent, crosslinked solid material.

4.3. Polycarbosiloxanes

A similar to carbosilanes, investigation of ADMET has shown that siloxanes are also polymerizable with the Schrock’s molybdenum catalyst (Fig. 9). Polymerization leads to formation of unsaturated polycarbosiloxanes [33,34]. As in the case of divinyl dimethylsilane, sterics has a predominant effect



TPA: tripropylamine
TSH: *p*-toluenesulfonhydrazide

Fig. 8. Polycarbosilanes with the disilacyclobutane rings.

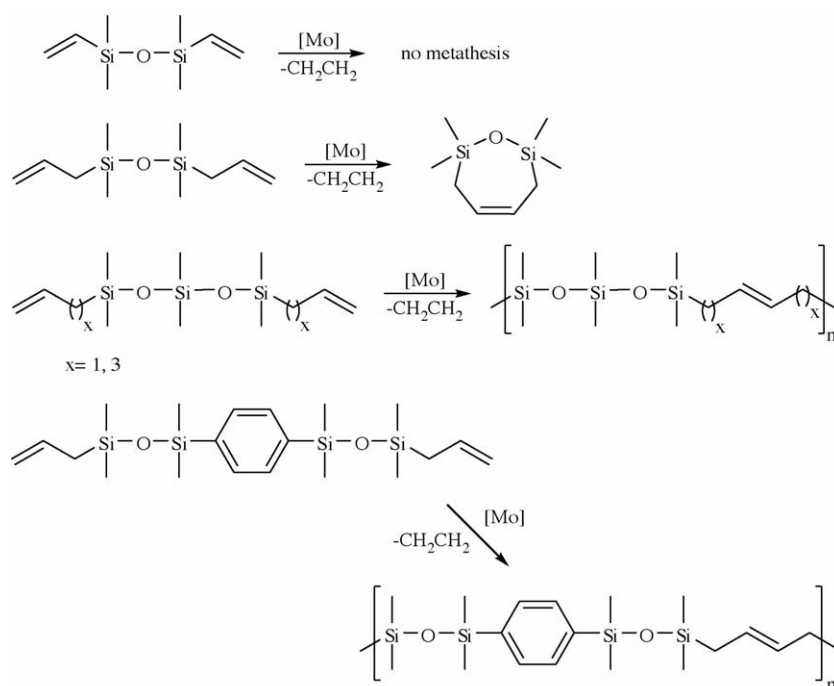


Fig. 9. ADMET polymerization of siloxane containing dienes.

on both the productive and non-productive metathesis rates of vinylcarbosiloxane. On the other hand, the reaction of 1,3-diallyl-1,1,3,3-tetraethoxydisiloxane where the siloxane group is “spaced out” by one methylene unit, leads to the ring formation [42] and essentially quantitative conversion for cyclization of diallyl disiloxane was observed. This exclusive and fast cyclization with no oligomerization indicates great thermodynamic stability of this seven membered ring. Thus, an increased flexibility of siloxanes requires longer distances between the olefin and silicon to produce ADMET linear polymers, as shown in Fig. 9.

Another noteworthy example of ADMET copolymerization is an insertion of an aromatic diene repeat unit into an unsaturated polycarbosiloxane [34]. Smith et al. have shown that slow addition of small diene monomer to unsaturated oligomer offers more than statistical control of copolymer by kinetically inhibiting homometathesis of the added diene (Fig. 10).

As previously shown in Fig. 9, divinyl siloxane derivatives are reluctant to homometathesis; however, like divinyl silane they undergo copolymerization. The first successful copolymerization of divinyltetraethoxydisiloxane with 1,9-decadiene in the presence of the Grubbs’ catalyst **[Ru]**** was reported by Malecka et al. Fig. 11 [43]. No consecutive linkage of divinyltetraethoxydisiloxane was observed. Surprisingly, in the similar experiment where divinyltetraethoxydisiloxane was substituted with divinyltetramethyldisiloxane, copolymerization failed and no polymeric or oligomeric products were detected. The lack of metathetical activity of divinyltetramethyldisiloxane in copolymerization was attributed to the decomposition of the Grubbs’ catalyst due to the β -transfer of silyl group to ruthenium in the metallacyclobutane, previously observed by Pietraszuk and Fischer [44].

Marciniec and Majchrzak [45] have subjected divinyltetradisiloxane to ADMET copolymerization con-

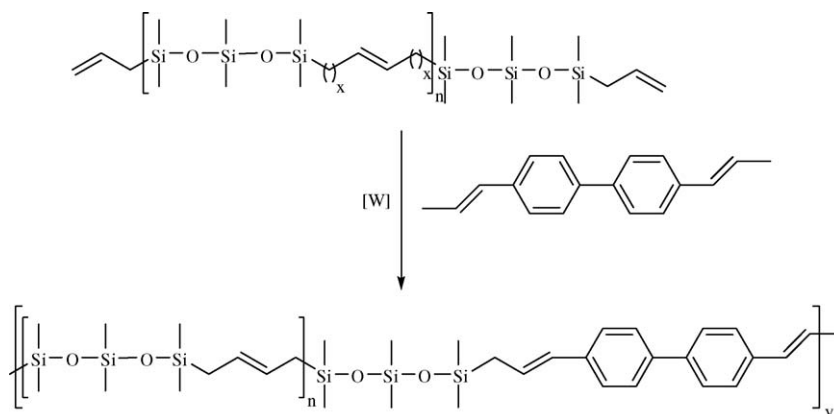


Fig. 10. Controlled diene insertion via ADMET.

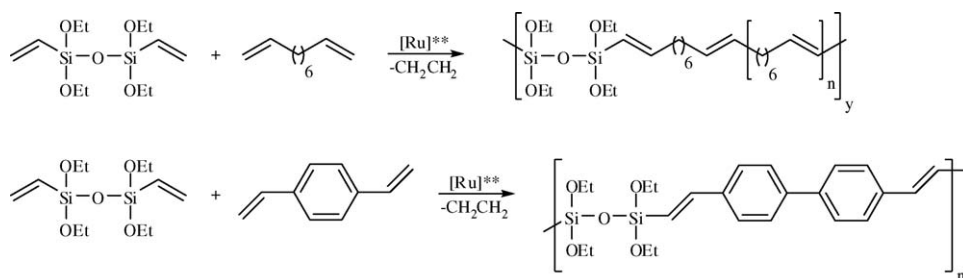


Fig. 11. ADMET copolymerization of divinyltetraethoxydisiloxane.

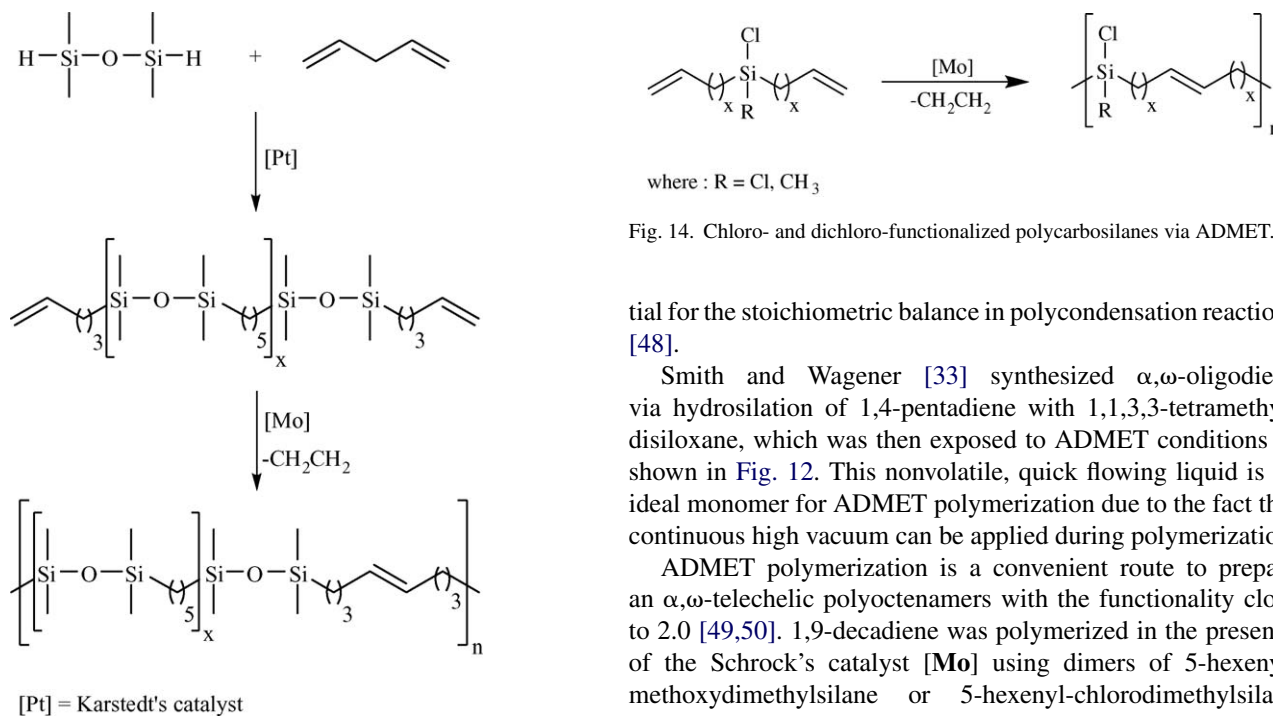
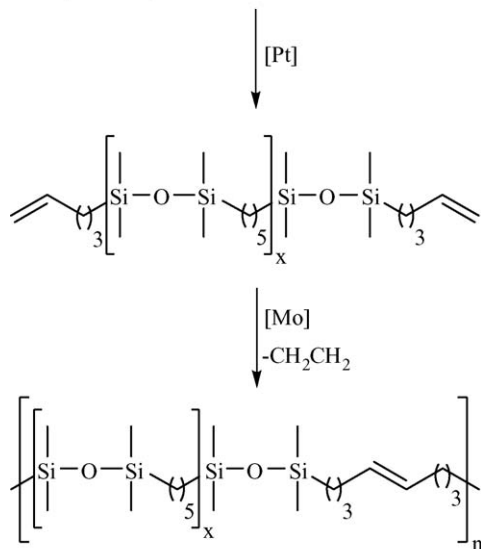


Fig. 14. Chloro- and dichloro-functionalized polycarbosilanes via ADMET.



[Pt] = Karstedt's catalyst

Fig. 12. ADMET polymerization of α,ω -telechelic diene macromonomer.

ditions in the presence of 1,4-divinylbenzene (Fig. 11). Analysis of this copolymer showed the structure to be perfectly linear and *trans*(stereo)-regular.

4.4. Telechelic oligomers

Telechelic polymers are macromolecules which contain one or more functional end groups that can form bonds with another molecule. They offer potential use, e.g. in the formulation of model networks [46] or in the preparation of thermoplastic elastomers [47]. Preparation of this type of macromolecule is not trivial, especially those possessing a functionality of 2.0 essen-

tial for the stoichiometric balance in polycondensation reactions [48].

Smith and Wagener [33] synthesized α,ω -oligodiene via hydrosilation of 1,4-pentadiene with 1,1,3,3-tetramethyldisiloxane, which was then exposed to ADMET conditions as shown in Fig. 12. This nonvolatile, quick flowing liquid is an ideal monomer for ADMET polymerization due to the fact that continuous high vacuum can be applied during polymerization.

ADMET polymerization is a convenient route to prepare an α,ω -telechelic polyoctenamers with the functionality close to 2.0 [49,50]. 1,9-decadiene was polymerized in the presence of the Schrock's catalyst [Mo] using dimers of 5-hexenylmethoxydimethylsilane or 5-hexenyl-chlorodimethylsilane as chain limiters Fig. 13. As expected, the number average molecular weights for these telechelic oligomers were proportional to the ratio of the monomer to the chain limiter. Further, these highly reactive macromonomers were exploited to synthesize ABA block copolymer of polydimethylsiloxane–polyoctenamer–polydimethylsiloxane.

4.5. Functionalized polycarbosilanes

The polycarbosilanes presented earlier possess a simple silicon–carbon backbone. In order to introduce functionality along the polymer's backbone, Cummings et al. [51,52] synthesized chloro- and dichlorosilane α,ω -dienes, that undergo successful ADMET polymerization (Fig. 14) in the presence of the Schrock's catalyst [Mo].

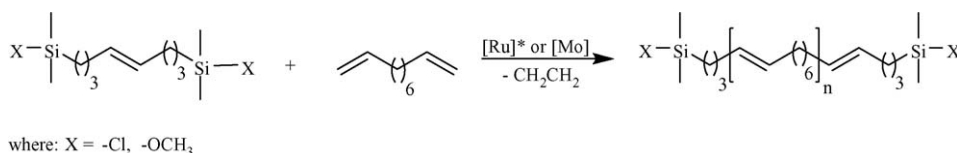


Fig. 13. Telechelic polymers via ADMET.

These chlorofunctionalized thermoplastic materials were exposed to different nucleophilic organolithium salts yielding polymers with various physical properties depending on the bulkiness of the nucleophiles. This concept was previously used by Allcock and co-workers [5] to tailor desired properties of polyphosphazanes. Allcock has also showed that cycloliner phosphazane containing polymers that can be obtained via ADMET polymerization [53,54]. Subsequently, Church et al. [55,56] demonstrated the utility and flexibility of ADMET in the one-pot synthesis of alkoxy-functionalized carbosilanes. They demonstrated that functionalization can be facilitated either via macromolecular substitution or by substitution on the α,ω -diene monomer (Fig. 15). As noted above both pendant groups on the carbosilane polymer backbone have a significant effect on the physical properties of resultant polymer. These alkoxy-functionalized polymers can be further crosslinked using sol-gel chemistry to yield a polymer network.

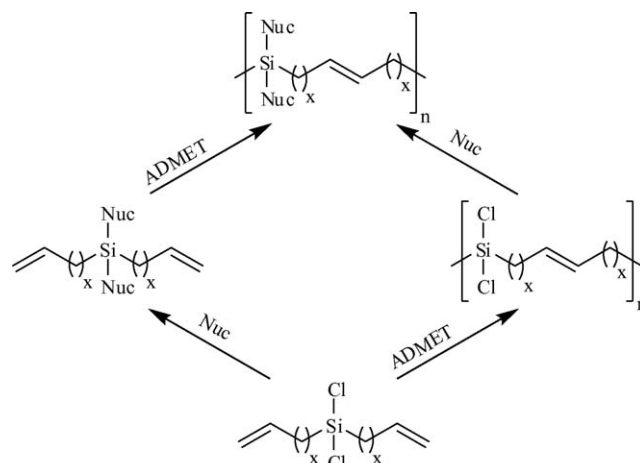


Fig. 15. Two routes to polymer modification.

4.6. Latent reactive elastomers

The functionalized polycarbosilanes via ADMET described above offer a new approach to the synthesis of materials exhibiting variable physical properties. This research has led to a new type of synthesis involving “latent reactive” carbosilane/carbosiloxane copolymers by Brzezinska [35] (Fig. 16), illustrating the random incorporation of “latent reactivity” throughout polycarbosiloxane backbone in the form of the alkoxy-substituted carbosilane.

It is well known that the methyl silyl ether bond, while inert during ADMET chemistry, easily hydrolyzes in the presence of moisture and condenses to form stable siloxane linkage [57]. Consequently, the physical properties of ADMET carbosilane/carbosiloxane copolymers can be tuned by selecting the appropriate molar concentrations of each monomer. Fig. 17 illustrates this modular approach and shows its extensive application in the generation of a large number of materials exhibiting physical properties from elastic materials to plastics.

Recent work has focused on elastomer structure/property relationships [58] in an effort to enhance mechanical perfor-

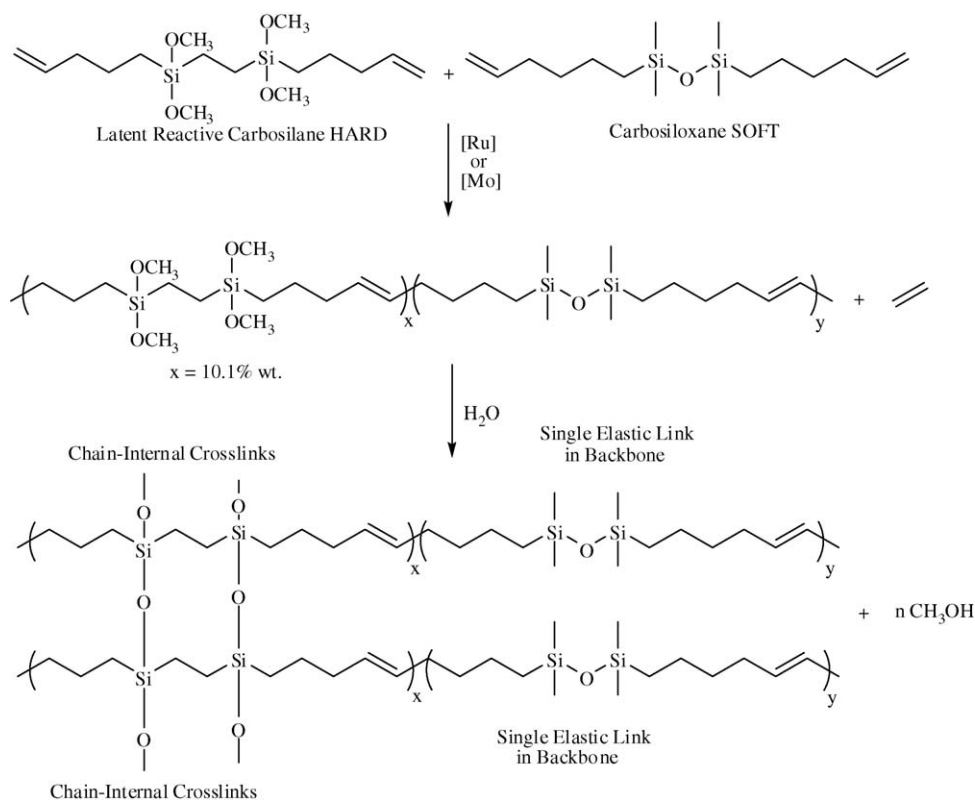


Fig. 16. Thermosets from latent reactive carbosiloxane/carbosilane copolymer.

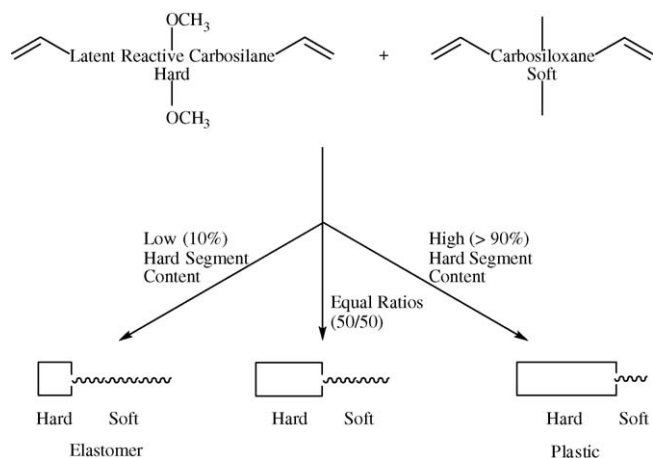


Fig. 17. The latent reactivity concept to attain diverse behavior of materials.

mance of these new materials [35]. The mechanical response of these hybrid silicone materials has been improved by the introduction of “chain-end” crosslinks; this innovation has resulted in a more ideal network structure by limiting the formation of dangling chains, and by introducing longer soft segments composed of polyoxyethylene. A 10× increase in the modulus of these materials has been observed as a result of introducing chain-end crosslinking, exceeding “typical” expectations for this structural modification. This crosslinking is achieved by simple exposure of the latent sites to moisture, taking advantage of a well-known reaction using to “cure” silicon containing materials. At this stage of the research no curing catalysts have been used to achieve this improvement in mechanical performance. The absence of a curing catalyst should allow for greater long-term durability of the elastomer or tough plastic that is formed. Recently, families of novel hybrid segmented networks from “fully latent” reactive copolymers have been prepared (Fig. 18) and remain under investigation.

These new thermosets exhibit materials behavior from elastic to flexible plastics depending on the structure of polyethylene oxide monomer. Prior to the introduction of chain-end crosslinking, initial modulus values were in the range of 0.16 MPa; these values can be increased to as high as 60 MPa, depending upon the composition of the materials. Elasticity can be controlled as well, again depending upon composition. Tough plastics show an elasticity of about 20% whereas compositions found on the elastomer side can exhibit 400% elasticity.

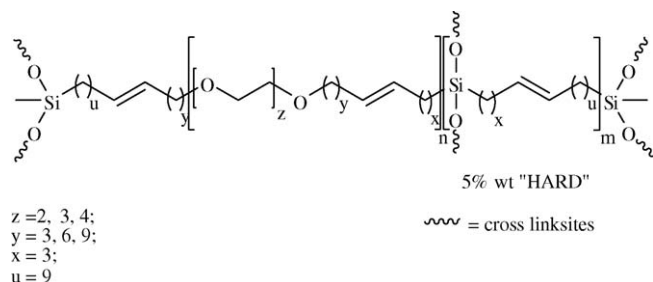
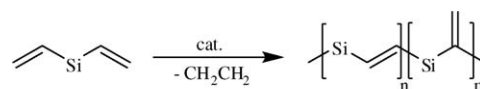


Fig. 18. Novel hybrid network via ADMET.



where:
Si = silane, siloxane
cat. = $\text{RuCl}_2(\text{PPh}_3)_3$ or $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$

Fig. 19. SC polycondensation of divinylsubstituted silicon monomers.

5. Silylative coupling (SC) polycondensation

Previously mentioned, ADMET polymerization is an universal method to obtain unsaturated organosilicon polymers. A vast number of α,ω -dienes containing silicon functionality tend to be active in this process, when catalyzed by well-defined carbene complexes. On the other hand divinyl organosilicon compounds are an exception, since they remain inert under conditions of acyclic diene metathesis polymerization. It happens that the sterics of silyl groups stimulate a nonproductive cleavage of disilylmetallacyclobutane [27].

The Marciniak research group has found an important way to solve this problem. Divergent to well-defined olefin metathesis catalysts, numerous ruthenium and rhodium complexes that contain or generate *in situ* metal-hydrogen or metal-silicon bonds catalyze intermolecular polycondensation of divinyl diorganosilicon derivatives.

At first, Marciniak et al. [29] proposed a mechanism in which carbene is formed by rearrangement of a metal hydride complex. Soon after it was found that catalysis operates via a non-metallacarbene mechanism [59,60]; instead, series of σ -complexes are involved via insertion–elimination reactions. These transformations were termed silylative coupling polycondensation (SC) (or as referred by Finkelshtein [37] may as well be called Marciniak’s metathesis). Complexation of the olefin to electrophilic metal center is followed by metal insertion into the C–H bond. Elimination of ethylene yields a metal-silyl complex that coordinates another vinylsilane, which inserts into M–Si bond followed by reductive elimination of homometathesis product while regenerating hydride complex. Formation of the 1,1-bis(silyl)ethene as product along with *cis/trans* 1,2-bis(silyl)ethenes distinguish this reaction from olefin metathesis where only former two are formed.

Early attempts at polymer synthesis via SC polycondensation of divinylsilanes and bisvinylsiloxanes (Fig. 19) catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ yielded polymers in moderate conversions [61,62], too low for step-growth polymer chemistry.

While rhodium-based catalysts were used, two monomers of divinyltetramethyldisiloxane have undergone ring closure which subjected to X-ray spectroscopy revealed a boat conformation [63].

Further studies in the synthesis of polycarbosilanes and polycarbosiloxanes from divinyl organosilicon derivatives were conducted by Malecka et al. [64–66], who demonstrated the dependence of catalyst identity on polymer’s morphology. SC polycondensation of divinyl organosilicon compounds catalyzed by ruthenium–phosphine complexes, such as shown in Fig. 19,

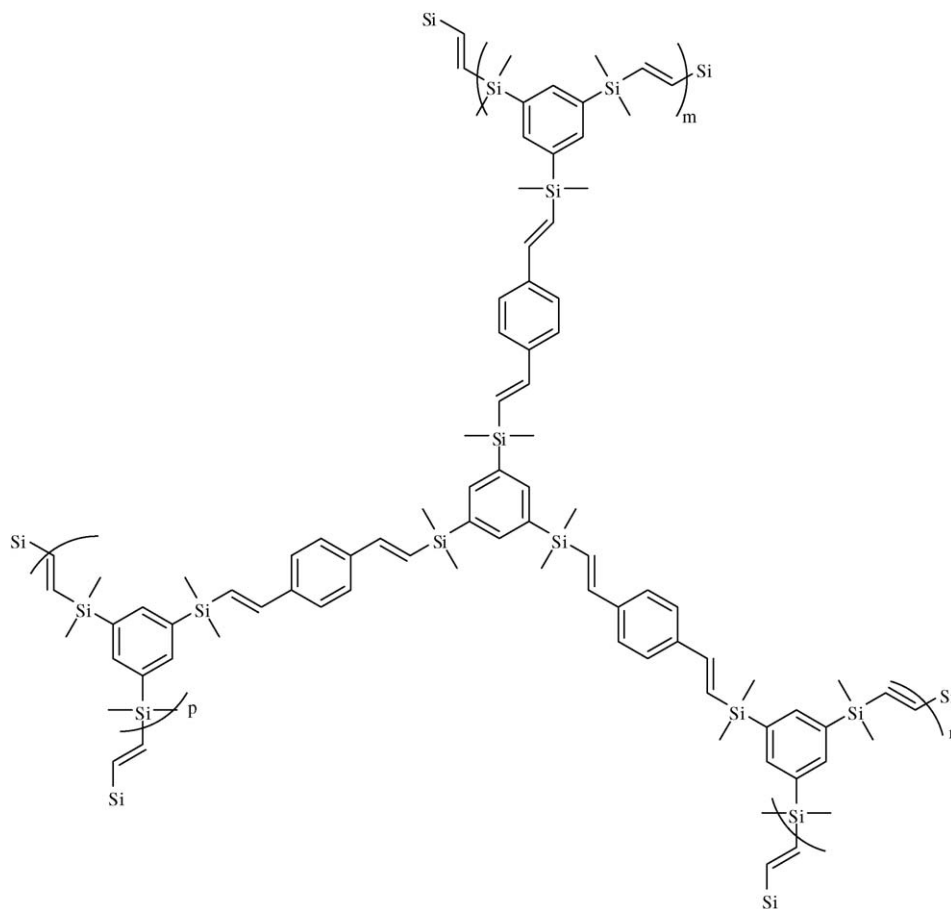


Fig. 20. Starburst oligomer via SC.

yielded linear polycarbosilanes or polycarbosiloxanes. Both *trans*-1,2- and *gem*-1,1- fragments were present in the polymer's backbone, while highly stereoselective *trans*-tactic structures were formed when $[\text{RuCl}_2(\text{CO})_3]_2$ was used. Moderate molecular weights of polymers were obtained as well.

Majchrzak et al. [45,67–69] have successfully synthesized numerous phenylene-silylene-vinylene and siloxylene-vinylene-phenylene polymers and copolymers via SC polycondensation, producing highly stereo- and regioselective structures with values of M_w from 13,100 to 34,800 g/mol [69]. Alternate ruthenium complexes were screened in order to find a catalyst that promotes these regular structures. Furthermore, they have extended the utility of SC polycondensation to the synthesis of organosilicon starburst materials that contains the silicon-bridged π -conjugated structure [70,71], as shown in Fig. 20.

6. Conclusions

The utility of ADMET polymerization in the synthesis of silicon/carbon hybrid materials has been presented. Discoveries and developments in the synthesis of novel catalytic systems made this methodology more feasible. ADMET chemistry has been proven to be a useful tool in the synthesis of novel polycarbosilanes, polycarbosiloxanes, functionalized polycarbosilanes, telechelic polymers and “latent reactive”

carbosilane/carbosiloxanes, many of which would be difficult or unattainable to synthesize by other methods. Recent developments in silylative coupling polymerization in preparation of such hybrids from divinyl organosilicon compounds, which are inert under ADMET conditions, serve as complementary synthetic method. Both methods lead to formation of unsaturated polymeric systems that might be valuable materials as gas separation membranes, precursors to ceramics, low-temperature coatings, thermosetting products and more. It remains clear that the utilization of these two polymerization reactions in the synthesis of organosilicon materials is still not fully explored.

Acknowledgments

We would like to acknowledge Army Research Office and National Science Foundation for financial support. We would like to thank Dr. Travis Baughman, Dr. Kornelia Matloka and Mr. James Leonard for help with the preparation of this article.

References

- [1] F.S. Kipping, Proc. Chem. Soc. 20 (1904) 15.
- [2] M.A. Brook, Silicon in Organic, Organometallic and Polymer Chemistry, J. Wiley, New York, 2000.
- [3] M. Zeldin, K.J. Wynne, H.R. Allcock, Inorganic and Organometallic Polymers: macromolecules Containing Silicon, Phosphorus and

- Other Inorganic Elements, American Chemical Society, Washington, 1988.
- [4] B. Arkles, *Chemtech* 13 (1983) 542–555.
- [5] J.E. Mark, H.R. Allcock, R. West, *Inorganic Polymers*, Oxford University Press Inc., New York, NY, 2005.
- [6] P.J. McDermott, T.E. Krafft, J.D. Rich, *J. Polym. Sci. Pol. Chem.* 29 (1991) 1681–1689.
- [7] K.J. Ivin, I.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, 2nd ed., Academic Press Inc., San Diego, 1997.
- [8] R.H. Grubbs, *Handbook of Metathesis*, Wiley-VCH, Weinheim, Germany, 2003.
- [9] M.R. Buchmeiser, *Chem. Rev. (Washington, DC, U. S.)* 100 (2000) 1565–1604.
- [10] <http://nobelprize.org/chemistry/laureates/2005/press.html>.
- [11] N. Calderon, *Chem. Eng. News* 45 (1967) 51.
- [12] G.G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, 1991.
- [13] M. Lindmarkhamberg, K.B. Wagener, *Macromolecules* 20 (1987) 2949–2951.
- [14] C.J. Schaverien, J.C. Dewan, R.R. Schrock, *J. Am. Chem. Soc.* 108 (1986) 2771–2773.
- [15] K.B. Wagener, J.M. Boncella, J.G. Nel, *Macromolecules* 24 (1991) 2649–2657.
- [16] K. Brzezinska, K.B. Wagener, *Macromolecules* 25 (1992) 2049–2052.
- [17] J.T. Patton, J.M. Boncella, K.B. Wagener, *Macromolecules* 25 (1992) 3862–3867.
- [18] K.B. Wagener, J.T. Patton, M.D.E. Forbes, T.L. Myers, H.D. Maynard, *Polym. Int.* 32 (1993) 411–415.
- [19] J.E. O'Gara, J.D. Portmess, K.B. Wagener, *Macromolecules* 26 (1993) 2837–2841.
- [20] T.W. Baughman, K.B. Wagener, *Adv. Polym. Sci.* 176 (2005) 1–42.
- [21] S.E. Lehman, K.B. Wagener, in: R.H. Grubbs (Ed.), *Handbook of Metathesis*, Wiley-VCH, Weinheim, Germany, 2003, p. 3 v.
- [22] R.A. Fridman, S.M. Nosakova, Y.B. Kryukov, Bashkiro, N.S. An, V.M. Nametkin, Vdovin, B. Acad. Sci. USSR Ch+ (1971) 2100.
- [23] H. Lammens, G. Sartori, J. Siffert, N. Sprecher, *J. Polym. Sci. Pol. Lett.* 9 (1971) 341.
- [24] E.S. Finkelshtein, E.B. Portnykh, N.V. Ushakov, V.M. Vdovin, B. Acad. Sci. USSR Ch+ 30 (1981) 483–487.
- [25] K.L. Makovetsky, E.S. Finkelshtein, I.Y. Ostrovskaya, E.B. Portnykh, L.I. Gorbacheva, A.L. Goldberg, N.V. Ushakov, Y.P. Yampolsky, *J. Mol. Catal.* 76 (1992) 107–121.
- [26] T.J. Katz, S.J. Lee, M.A. Shippey, *J. Mol. Catal.* 8 (1980) 219–226.
- [27] R.R. Schrock, R.T. Depue, J. Feldman, C.J. Schaverien, J.C. Dewan, A.H. Liu, *J. Am. Chem. Soc.* 110 (1988) 1423–1435.
- [28] B. Marciniak, J. Gulinski, *J. Organomet. Chem.* 266 (1984) C19–C21.
- [29] B. Marciniak, L. Rzejak, J. Gulinski, Z. Foltynowicz, W. Urbaniak, *J. Mol. Catal.* 46 (1988) 329–340.
- [30] Z. Foltynowicz, B. Marciniak, *J. Organomet. Chem.* 376 (1989) 15–20.
- [31] Z. Foltynowicz, B. Marciniak, C. Pietraszuk, *J. Mol. Catal.* 65 (1991) 113–125.
- [32] K.B. Wagener, D.W. Smith, *Macromolecules* 24 (1991) 6073–6078.
- [33] D.W. Smith, K.B. Wagener, *Macromolecules* 26 (1993) 1633–1642.
- [34] D.W. Smith, K.B. Wagener, *Macromolecules* 26 (1993) 3533–3537.
- [35] K.R. Brzezinska, R. Schitter, K.B. Wagener, *J. Polym. Sci. Pol. Chem.* 38 (2000) 1544–1550.
- [36] R.R. Schrock, R.T. Depue, J. Feldman, K.B. Yap, D.C. Yang, W.M. Davis, L. Park, M. Dimare, M. Schofield, J. Anhaus, E. Walborsky, E. Evitt, C. Kruger, P. Betz, *Organometallics* 9 (1990) 2262–2275.
- [37] E.S. Finkelshtein, *Vysokomol. Soedin.* 37 (1995) 718–736.
- [38] E.S. Finkelshtein, N.V. Ushakov, E.B. Portnykh, *J. Mol. Catal.* 76 (1992) 133–144.
- [39] N.V. Ushakov, E.B. Portnykh, N.A. Pritula, E.S. Finkelshtein, B. Acad. Sci. USSR Ch+ 38 (1989) 2561–2567.
- [40] Z. Wu, J.P. Papandrea, T. Apple, L.V. Interrante, *Macromolecules* 37 (2004) 5257–5264.
- [41] S.F. Hahn, *J. Polym. Sci. Pol. Chem.* 30 (1992) 397–408.
- [42] M.D.E. Forbes, J.T. Patton, T.L. Myers, H.D. Maynard, D.W. Smith, G.R. Schulz, K.B. Wagener, *J. Am. Chem. Soc.* 114 (1992) 10978–10980.
- [43] E. Malecka, B. Marciniak, C. Pietraszuk, A.C. Church, K.B. Wagener, *J. Mol. Catal.* 190 (2002) 27–31.
- [44] C. Pietraszuk, H. Fischer, *Organometallics* 20 (2001) 4641–4646.
- [45] B. Marciniak, M. Majchrzak, *J. Organomet. Chem.* 686 (2003) 228–234.
- [46] H. Schnecko, G. Degler, H. Dongowski, R. Caspary, G. Angerer, T.S. Ng, *Angew Makromol. Chem.* 70 (1978) 9–30.
- [47] E.J. Goethals, *Telechelic polymers: synthesis and applications*, CRC Press, Boca Raton, Fla, 1989.
- [48] G.G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, 1991, p. 146.
- [49] K.R. Brzezinska, K.B. Wagener, G.T. Burns, *J. Polym. Sci. Pol. Chem.* 37 (1999) 849–856.
- [50] K.R. Brzezinska, J.D. Anderson, K.B. Wagener, *Abstr. Pap. Am. Chem. S* 215 (1998) U418–U418.
- [51] S.K. Cummings, J.D. Anderson, K.B. Wagener, *Abstr. Pap. Am. Chem. S.* 212 (1996), 21-Poly.
- [52] S.K. Cummings, D.W. Smith, K.B. Wagener, *Macromol. Rapid Comm.* 16 (1995) 347–355.
- [53] H.R. Allcock, E.C. Kellam, M.A. Hofmann, *Macromolecules* 34 (2001) 5140–5146.
- [54] H.R. Allcock, E.C. Kellam, *Macromolecules* 35 (2002) 40–47.
- [55] A.C. Church, J.H. Pawlow, K.B. Wagener, *Macromol. Chem. Phys.* 204 (2003) 32–39.
- [56] A.C. Church, J.H. Pawlow, K.B. Wagener, *Macromolecules* 35 (2002) 5746–5751.
- [57] E.G. Rochow, *Silicon and Silicones*, Springer-Verlag, New York, 1987.
- [58] P.P. Matloka, J.C. Sworen, F. Zuluaga, K.B. Wagener, *Macromol. Chem. Phys.* 206 (2005) 218–226.
- [59] Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, *J. Chem. Soc. Chem. Comm.* (1991) 703–704.
- [60] B. Marciniak, C. Pietraszuk, Z. Foltynowicz, *J. Mol. Catal.* 76 (1992) 307–317.
- [61] B. Marciniak, M. Lewandowski, *J. Polym. Sci. Pol. Chem.* 34 (1996) 1443–1445.
- [62] B. Marciniak, M. Lewandowski, *J. Inorg. Organomet. P.* 5 (1995) 115–122.
- [63] B. Marciniak, M. Lewandowski, E. Bijpost, E. Malecka, M. Kubicki, E. Walczuk-Gusciora, *Organometallics* 18 (1999) 3968–3975.
- [64] B. Marciniak, E. Malecka, M. Scibiorek, *Macromolecules* 36 (2003) 5545–5550.
- [65] B. Marciniak, E. Malecka, M. Majchrzak, Y. Itami, *Macromol. Symp.* 174 (2001) 137–144.
- [66] B. Marciniak, E. Malecka, *J. Phys. Org. Chem.* 16 (2003) 818–823.
- [67] M. Majchrzak, Y. Itami, B. Marciniak, P. Pawluc, *Tetrahedron Lett.* 41 (2000) 10303–10307.
- [68] M. Majchrzak, Y. Itami, B. Marciniak, P. Pawluc, *Macromol. Rapid. Comm.* 22 (2001) 202–205.
- [69] M. Majchrzak, B. Marciniak, Y. Itami, *Adv. Synth. Catal.* 347 (2005) 1285–1294.
- [70] Y. Itami, B. Marciniak, M. Majchrzak, M. Kubicki, *Organometallics* 22 (2003) 1835–1842.
- [71] B. Marciniak, Y. Itami, M. Majchrzak, *Mol. Cryst. Liq. Cryst.* 417 (2004) 599–609.