Chapter 1

An Introduction to Functional Polymers and ROMP

1.1 Synthetic Polymer Basics

Put simply, polymers are large molecules that consist of a number of repeat units linked together in a repetitive fashion. The small molecules that make up polymers are called monomers. While each monomer has a singular molecular weight, synthetic materials do not. A polymeric material generally consists of many polymer chains of varying number of monomeric units and hence, different size and shape.

1.1.1 Synthesis

The synthesis of polymers can generally be described by two types of classifications: *condensation* and *addition* or *step growth* and *chain growth*.[1] The first, *condensation* and *addition*, describes the composition and/or structure of the polymer, while the second classification, *step growth* and *chain growth* relates to the polymerization mechanism.[1] The term "condensation" arises from the synthesis of polyesters and polyamides where small molecules such as water, alcohols, or acids are released upon forming covalent bonds between monomers. Removal of these condensation products serves to drive the reaction towards completion. These types of polymerizations occur in a *step*-wise fashion, first combining monomers and making *dimers*, and then *trimers* and *tetramers*, etc. The molecular weight of condensation polymers grows large only at the very end of the reaction ($> 99\%$ conversion). The number of repeat units in a condensation polymerization is defined as $X_{\mathrm{n}} = 1/(1\text{-}\rho)$, where ρ is the percent conversion.[1] Conversely, *addition* polymers are usually made by a *chain growth* mechanism. There are many ways to prepare *addition* polymers and these include anionic, cationic, free radical, and metal-catalyzed polymerizations of vinyl monomers to name a few.[1] These polymers can reach very high molecular weights at low conversions, and make up the bulk of industrial commodity polymers such as polyethylene (PE), polypropylene (PP), and polystyrene (PS).

Many commercially produced polymers are pure hydrocarbons like PE, PP, and PS. Much effort has been devoted to make versions of these polymers with slight differences in polymer architecture and stereochemistry. For example, PE that contains a high amount of branching has very different properties than linear PE. The relative orientation (*tacticity*) of the pendent methyl groups in PP can determine whether the polymer is suitable to resist the high impact forces of a traffic accident or is better used as a plastic bag for groceries. There are also many polymers that contain polar functional groups. Functionalities that are pendent from the polymer main chain dramatically affect the properties of the resulting materials.[1] The regularity and relative spatial orientation (*tacticity*) of these functional groups can also produce large differences in polymer properties. Not all polymerization methods or catalysts, however, are amenable to polar monomers. Thus, the development of new methods to synthesize polar-functionalized polymers is an area of intense research.

1.1.2 Characterization

As mentioned earlier, since polymerizations produce materials with a broad distribution of molecular weights (MWs), it can be very misleading to report a single quantity for MW. Rather, it is much more useful to know something about the average and overall distribution of chain lengths in a polymer sample. Thus, MWs are reported as several values: the number average molecular weight, M_n, the weight average molecular weight M_w, as well as several others.[1, 2] The M_n value reported for a polymer states the average number of repeat units (monomers) times the monomer's MW for all of the polymer chains in the sample, while the M_w represents a weighted average whereby the longer chains bias the value. A measure of the distribution of a polymer's MW is termed *polydispersity index* (PDI) and is a ratio of two MW averages. The most common value of PDI is the ratio of $M_\mathrm{w}/M_\mathrm{n}$. As M_w is always $> M_\mathrm{n}$, the PDI of a polymer is always > 1. The PDIs of polymers made by step growth polymerizations are between 1 and 2 and are a function of conversion. On the other hand, the PDI of polymers made by chain growth polymerizations can vary greatly; controlled, "living" polymers can be made with PDIs of 1.01 while some metal-catalyzed or un-controlled free radical polymers have PDIs > 10.[2] Material properties can vary greatly depending on MW and PDI; therefore, the ability to control these values through synthetic methodology is highly valued. Furthermore, much information about the polymerization mechanism can be obtained by evaluating trends observed in MW and PDI data.

There are many ways to measure M_n, M_w, and PDI values for synthetic polymers. These include size exclusion chromatography (SEC, also known as gel permeation chromatography, GPC), endgroup analysis (integration of ^{1}H NMR spectrum), light scattering, and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), are just a few of the common methods and are all used in the chapters that follow.[2] Unfortunately, the structure and functionality in many polymers can make their detailed characterization extremely difficult and in certain instances, impossible. For example, most conducting polymers are intractable materials and cannot be characterized in the solution state. Thus, developing methods of solubilizing such materials to enable detailed characterization is an active area of research.[3–6]

1.2 Olefin Metathesis

Synthetic chemists take pride in the ability to make almost any molecule that can be drawn on a piece of paper. The construction of these molecules occurs by making and breaking chemical bonds in discrete chemical reactions. In synthetic organic chemistry, the carbon-carbon double bond (C=C) is the basis for a large number of chemical transformations. The aptly named olefin metathesis reaction[7–9] allows for the formation of C=C bonds and is a simple “transposition of two elements”; it involves breaking a C=C bond followed by the formation of a new one. This process is mediated by a metal carbene catalyst as shown in Figure 1.1. Upon binding of an olefin to the metal carbene catalyst, formation of a metallocyclobutane occurs.[10–14] This species can either form a new olefin and metal carbene or revert to the original olefin in a non-productive metathesis event.

Many useful transformations can be carried out via olefin metathesis as depicted in Figure 1.2. A diene can undergo a ring-closing metathesis (RCM) event to form

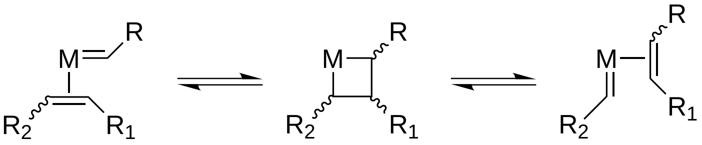


Figure 1.1: A simplified view of olefin metathesis.

a cyclic olefin, or, under conditions of very high concentration, may form a linear polymer through a process referred to as acyclic diene metathesis polymerization (ADMET).[14] The driving force behind both RCM and ADMET is the loss of a small molecule, ethlyene. In a process known as ring-opening metathesis polymerization (ROMP) cyclic olefins can be transformed into high molecular weight linear polymer. In contrast to RCM and ADMET, ROMP is driven by the release of ring strain inherent in cyclic olefin monomers. It is important to realize that all of these transformations are reversible and are controlled by a thermodynamic equilibrium.[9, 13]

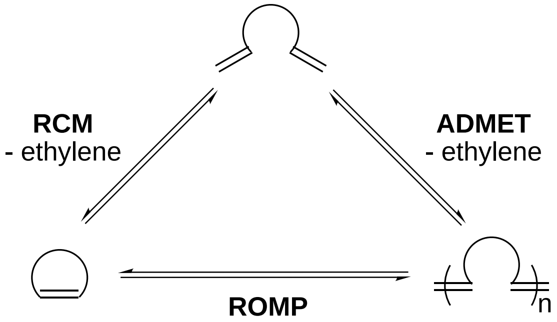
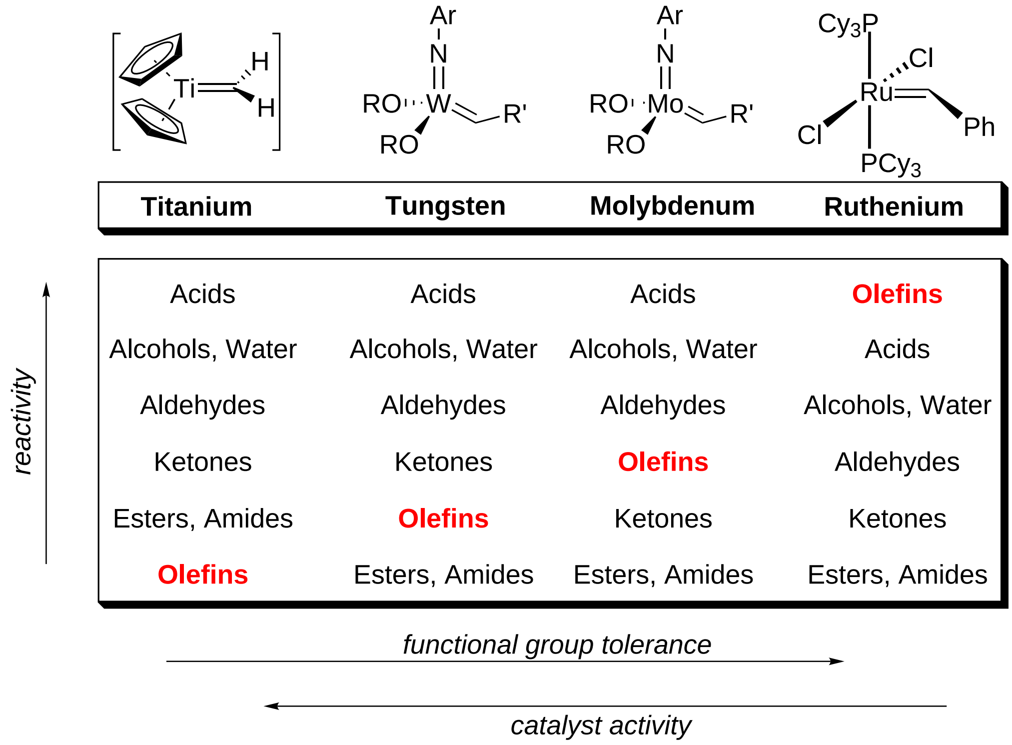


Figure 1.2: Chemical transformations by olefin metathesis.

1.2.1 Olefin Metathesis Catalysts

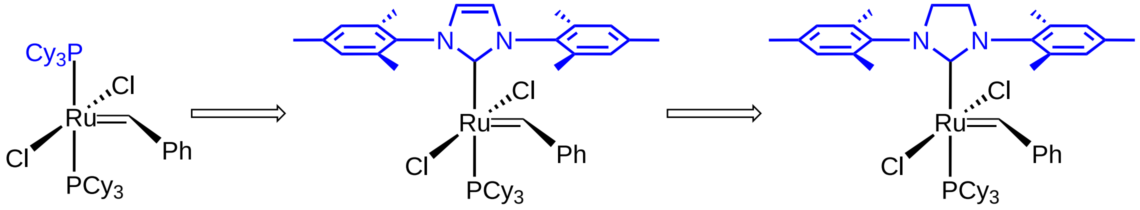
While a number of transition metals can catalyze olefin metathesis, early reports only focused on the ROMP of highly strained cyclic olefins with transition metal salts.[9, 14] Several decades of research produced well-defined early transition metal catalysts based on titanium, tungsten, and molybdenum as depicted in Figure 1.3.[9, 15] All of these catalysts, however, require very stringent handling conditions, are air sensitive, and do not tolerate many organic functional groups. While the reactivity of these catalysts is high, their selectivity for reaction with olefins is poor. In the mid-1990s, Grubbs *et al.* reported a family of late transition metal, ruthenium-based olefin metathesis catalysts which were capable of operating in the presence of many polar functional groups (Figure 1.3) such as ketones, esters, aldehydes, and even alcohols. The activity of the ruthenium catalysts, however, was much lower than that of early metal catalysts.[13, 14, 16–19]



Titanium	Tungsten	Molybdenum	Ruthenium
Acids	Acids	Acids	**Olefins**
Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
Ketones	Ketones	**Olefins**	Aldehydes
Esters, Amides	**Olefins**	Ketones	Ketones
Olefins	Esters, Amides	Esters, Amides	Esters, Amides

Figure 1.3: Reactivity of olefin metathesis catalysts.

Recently, further modifications of the ligand set addressed the lower activity of the ruthenium-based catalysts.[20] Figure 1.4 illustrates the replacement of a phosphine ligand with an N-heterocyclic carbene ligand. This ligand substitution greatly increased the catalyst activity while maintaining the functional group tolerance typical for the ruthenium systems.[12] In fact, the second-generation ruthenium catalyst is more active towards both RCM and ROMP than the first generation version by several orders of magnitude.[21] The development of well-defined, ruthenium-based catalysts has allowed for a wide variety of synthetically useful transformations and polymerizations to occur in the presence of many functional groups.



1 **2**

Figure 1.4: Recent advances in ruthenium olefin metathesis catalysts.

1.2.2 Ring-Opening Metathesis Polymerization

Both ADMET and ROMP are capable of producing linear polymers via olefin metathesis.[9] The driving forces for these reactions, however, are quite different, and the implications for the polymerizations are quite dramatic. For example, since the loss of ethylene drives ADMET polymerizations to high MW, the reaction follows a condensation, or step growth mechanism. Therefore high conversion is required for high MW polymer to form. Furthermore, high concentrations are necessary to ensure efficient coupling of terminal olefins and, unfortunately, slow diffusion due to high viscosity typically prevents the formation of high MW polymer.[9, 13]

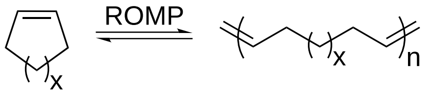


Figure 1.5: ROMP of a cyclic olefin.

Conversely, ROMP reactions use the release of ring strain inherent in the monomer to drive the reaction to completion (Scheme 1.5). Therefore, polymerizations can be carried out in dilute solutions which enable the formation of high MW material. Monomers which possess a high amount of ring strain such as cyclobutene and norbornene easily undergo ROMP at very low monomer concentrations.[9] However, monomers such as cyclopentene, cyclohexene, and cycloheptene are more difficult to polymerize as their strain energies are relatively low (Figure 1.6).[22] Since olefin metathesis is a reversible reaction governed by thermodynamic equilibrium, the strain energy of the monomer plays a large role in determining the polymerization yield in ROMP reactions. As ROMP is reversible, depolymerization reactions can occur over the course of a metathesis polymerization, through processes known as chain transfer or “backbiting.”[9, 23] This can have a great effect on the polymer MW and overall architecture.[24–26]

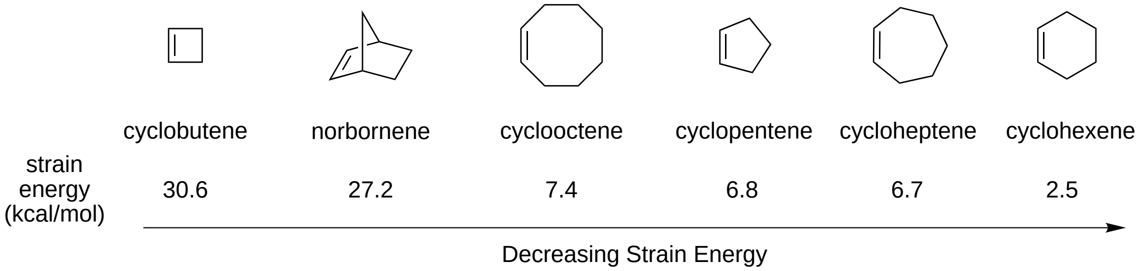
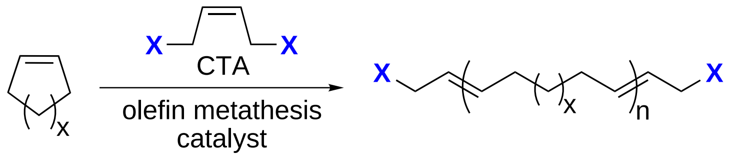


Figure 1.6: Representative cyclic olefin monomers and strain energies.[22]

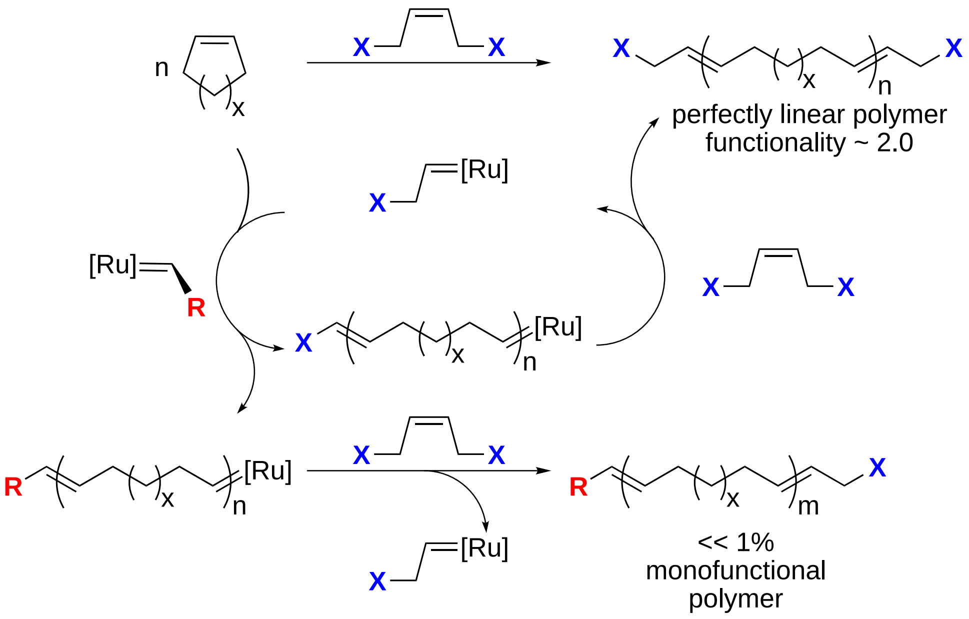
As ROMP can be carried out in solution, facile control of polymer MW can be achieved in several different ways. For highly strained monomers such as cyclobutene, norbornene, and oxanorbornene, living polymerization can be attained with fast initiating olefin metathesis catalysts leading to precisely controlled polymer architectures and MW.[15, 27] ROMP has been used to prepare block-copolymers through the sequential addition of monomers. Another method to control the MW and architecture of ROMP polymers is through the use of chain transfer agents (CTAs).[23, 24] When ROMP of a cyclic olefin is carried out in the presence of a symmetric CTA, such as an acyclic olefin, a linear, telechelic polymer will be formed as illustrated in Scheme 1.1. Telechelic polymers are end-functionalized polymers that have found application in cross-linking and polymer network formation, chain-extention processes, and in the solubilization of materials.[28]

Scheme 1.1: ROMP in the presence of a CTA to produce a linear, telechelic polymer.



A general reaction mechanism for ROMP with a CTA is outlined in Scheme 1.2. The propagating polymer chain can react with either a cyclic olefin monomer or with an acyclic CTA molecule. If a metathesis event occurs with the CTA, the functionality (**X**) of the CTA gets transferred to one *end* of the polymer chain. Later in the reaction, the other chain *end* will be formed by reacting with another CTA molecule. Therefore, at the end of the reaction, all of the chains will have functionality (**X**) transferred to *both* chain ends.* Moreover, with the advances in catalyst design over the last decade leading to late transition metal (ruthenium) catalysts, both cyclic and acyclic olefins bearing polar functional groups can now be employed in ROMP.[12] This has allowed for the synthesis of many new material architectures such as conducting polymers,[29–35] water-soluble polymers,[4] and surface-bound polymers,[36–38] all of which will be discussed in the following pages.

Scheme 1.2: Mechanism for the synthesis of telechelic polymers by ROMP.



---

[*] This requires that a high excess of CTA relative to catalyst is used.[23, 24]

1.3 Objectives of this Work

The research presented in this thesis describes my contributions in the areas of conducting polymers, surface-inititated polymers, and well-defined polar functional polymers that are prepared by ROMP. Chapter 2 introduces the synthesis of conducting polymers via ROMP and illustrates that catalyst activity plays an important role in the preparation of polymers such as polyacetylene. The use of late transition metal olefin metathesis catalysts such as ruthenium to form polyacetylene (Chapter 2) was extended to form telechelic, solubilized polyenes and polyacetylene block-copolymers through the use of chain transfer agents; this work is discussed in Chapter 3. The use of ROMP in surface-initiated polymerization is discussed in Chapters 4 and 5. In a collaboration with Dr. Agnes Juang and Prof. Nathan Lewis (Caltech), organic overlayers consisting of polynorbornene were grown from a Si (111) surface (Chapter 4). The ROMP polymer was covalently attached to the silicon surface with a direct Si-C linkage instead of through the traditional Si/SiO_2 linkers previously employed. This concept was further explored in a collaboration with Mr. Isaac Rutenberg (also a member of the Grubbs group at Caltech) and Dr. Zhenan Bao (Lucent Technologies) in order to prepare top-contact field-effect thin film transistors with a ROMP polymer as the dielectric layer (Chapter 5). Chapter 6 evaluates the ROMP of low-strain monomers such as cyclopentene and cycloheptene and discusses the thermodynamic considerations involved in ROMP. A model for predicting the ability of a cyclic olefin to undergo ROMP ("ROMP*ability*") is presented. Novel materials possessing a range of both polar and apolar functionalities can now be prepared in large scale. These materials include both telechelic polymers, block-copolymers, and polymers with main-chain functionality. Chapters 7 and 8 describe a synthetic strategy for achieving both *regioregular* and *stereoregular* polymers bearing alcohol functionalities. A set of rationally designed ethylene vinyl alcohol (EVOH) copolymers allowed for the detailed study of property–function relationships for functional polymers. Complementary to the EVOH synthesis by ROMP, Chapter 9 describes some results from a collaborative effort with Dr. Valeria Molinero (a postdoc in the Goddard group at Caltech) for the computational modeling of regioregular and stereoregular EVOH, and illustrates why the local polymer structure can effect material properties such as O_2 permeability.

References Cited

[1] Odian, G. *Principles of Polymerization;* Wiley & Sons: New York, 3rd ed.; 1991.

[2] Cowie, J. M. G. *Polymers: Chemistry and physics of modern materials;* Chapman and Hall: New York, 2nd ed.; 1991.

[3] Stelzer, F.; Grubbs, R. H.; Leising, G. *Polymer* **1991,** *32,* 1851–1856.

[4] Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1997,** *30,* 3978–3985.

[5] Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989,** *111,* 7989–8004.

[6] Krouse, S. A.; Schrock, R. R. *Macromolecules* **1988,** *21,* 1885–1888.

[7] Calderon, N.; Chen, H. Y.; Scott, K. W. *Tetrahedron Lett.* **1967,** *34,* 3327–3329.

[8] Calderon, N. *Acc. Chem. Res.* **1972,** *5,* 127–132.

[9] Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization;* Academic Press: London, 1997.

[10] Herisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1971,** *141,* 161.

[11] Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001,** *123,* 749–750.

[12] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001,** *123,* 6543–6554.

[13] Grubbs, R. H., Ed.; *Handbook of Metathesis;* Wiley-VCH: Weinheim, 2003.

[14] Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001,** *34,* 18–29.

[15] Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988,** *46,* 243–253.

[16] Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993,** *115,* 9858–9859.

[17] Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **1995,** *34,* 2039–2041.

[18] Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996,** *118,* 100–110.

[19] Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997,** *119,* 3887–3897.

[20] Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999,** *1,* 953–956.

[21] Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000,** *39,* 2903–2906.

[22] Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970,** *92,* 2377–2386.

[23] Hillmyer, M. A.; Grubbs, R. H. *Macromolecules* **1993,** *26,* 872–874.

[24] Hillmyer, M. A.; Grubbs, R. H. *Macromolecules* **1995,** *28,* 8662–8667.

[25] Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997,** *30,* 718–721.

[26] Bielawski, C. W.; Scherman, O. A.; Grubbs, R. H. *Polymer* **2001,** *42,* 4939–4945.

[27] Choi, T. L.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2003,** *42,* 1743–1746.

[28] Jerome, R.; Henrioullegranville, M.; Boutevin, B.; Robin, J. J. *Prog. Polym. Sci.* **1991,** *16,* 837–906.

[29] Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988,** *110,* 7807–7813.

[30] Klavetter, F. L.; Grubbs, R. H. *Synth. Met.* **1989,** *28,* D99–D104.

[31] Klavetter, F. L.; Grubbs, R. H. *Synth. Met.* **1989,** *28,* D105–D108.

[32] Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989,** *111,* 4413–4422.

[33] Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988,** *110,* 2973–2974.

[34] Edwards, J. H.; Feast, W. J. *Polymer* **1980,** *21,* 595–596.

[35] Scherman, O. A.; Grubbs, R. H. *Synth. Met.* **2001,** *124,* 431–434.

[36] Weck, M.; Jackiw, J.; Rossi, R.; Weiss, P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1999,** *121,* 4088–4089.

[37] Kim, N.; Jeon, N.; Choi, I.; Takami, S.; Harada, Y.; Finnie, K.; Girolami, G.; Nuzzo, R.; Whitesides, G. M.; Laibinis, P. *Macromolecules* **2000,** *33,* 2793–2795.

[38] Juang, A.; Scherman, O. A.; Grubbs, R. H.; Lewis, N. S. *Langmuir* **2001,** *17,* 1321–1323.