Polymer Synthesis and Organotransition Metal Chemistry

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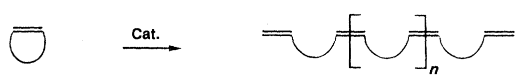
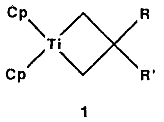
Mechanistic and synthetic studies in organometallic chemistry have provided considerable insight into olefin metathesis and Ziegler-Natta polymerization. New homogeneous olefin metathesis catalysts based on high oxidation state transition metals have opened new opportunities in polymer synthesis by providing unprecedented control in ring-opening polymerization of cyclic alkenes. The recent development of living coordinative polymerization systems has led to the preparation of a number of new, interesting materials, including block copolymers, conducting polymers or precursors, and ionophoric polymeric substrates.

THE DISCIPLINES OF ORGANOTRANSITION METAL CHEMISTRY and polymer synthesis have greatly benefited from a symbiotic relationship that has developed during the past few decades. Clear examples can be found in the coordinative polymerization and olefin metathesis of alkenes, both of which are catalyzed by high oxidation state transition metal complexes. Many of the roots of modern organometallic chemistry can be traced to the discoveries by Ziegler and Natta that transition metal complexes, in combination with strongly Lewis-acidic aluminum alkyl compounds, are efficient catalysts for the polymerization of ethylene and propylene (*1*). This early work, coupled with the subsequent discovery of the olefin metathesis reaction, has provided much of the driving force for the rapid development of whole new areas of organometallic chemistry. A large portion of the research effort involving carbene, alkene, and metallacycle complexes of transition metals has been oriented toward understanding these important catalytic sequences (*2*). The advances in organometallic chemistry spawned by the efforts to understand and build on these basic developments are now opening new opportunities in polymer synthesis.

We review the development of new homogeneous olefin metathesis catalysts that have provided unprecedented control in the ring-opening metathesis polymerization (*3*) (ROMP) of cyclic olefins (Eq. 1). Since a number of extensive review articles have been written on olefin metathesis (*4*) and Ziegler-Natta polymerization (*5*), both heterogeneous and homogeneous, our intent is to highlight the important recent mechanistic and synthetic aspects of carbene and metallacycle complexes of early transition metals in high oxidation states as well as their relation to polymer chemistry (*6*). The mechanistic details and the synthetic methods that have resulted from these studies are now being exploited in organic synthesis and polymer chemistry. We describe how one such system extensively studied in our laboratory (*7*), the bis(cyclopentadienyl) titanacyclobutanes (**1**), has resulted in the development of a well-controlled method of polymer synthesis for the production of a variety of new materials.



(1)



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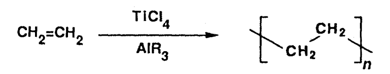
$(Cp = C_5H_5)$

Background

The early Ziegler-Natta catalysts for the addition polymerization of alkenes (Eq. 2) consisted of transition metal complexes combined with Lewis acid cocatalysts and were of undefined structure. Ziegler was examining the oligomerization of ethylene by aluminum alkyls when the reactor was contaminated with a nickel salt, which led to dimerization rather than high molecular weight oligomers. This unexpected result led to an investigation of other transition metal–based systems and eventually to the discovery that titanium halide–alkyl aluminum catalysts yielded high molecular weight polyethylene at unprecedented low temperatures and pressures. Natta's subsequent work on the synthesis and structure of polypropylene greatly advanced our understanding of stereoregular polymers. For their efforts, both were awarded the Nobel Prize in Chemistry in 1963. Although billions of pounds of polyolefins have been prepared by catalysts of the Ziegler-Natta type and the area has been extensively reviewed (*5*), the identity of the active catalytic species and the polymerization mechanism are still in debate today.



$$CH_2{=}CH_2 \xrightarrow[AlR_3]{TiCl_4} \left[CH_2 - CH_2 \right]_n \qquad (2)$$

These beginnings of coordinative polymerization led to intense studies on numerous olefinic monomers including cyclic olefins such as cyclopentene (Eq. 3), which subsequently led to the discovery of the olefin metathesis reaction. Eleuterio and Natta independently discovered that the use of Group 6 metals such as molybdenum resulted in the production of a new type of polymer from cyclic olefins (Eq. 4) rather than the products expected from normal addition polymerization (Eq. 3) (*8*). This new polymer no longer contained carbocyclic rings and was formed by an unprecedented process now termed ring-opening polymerization (Eq. 4). The products of ring-opening metathesis polymerization (ROMP) were eventually shown to arise from cleavage of the carbon-carbon double bonds in the cyclic olefin and reassembly of the opened

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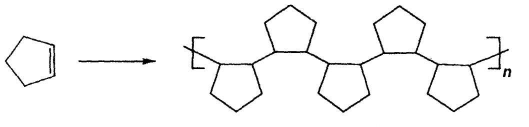
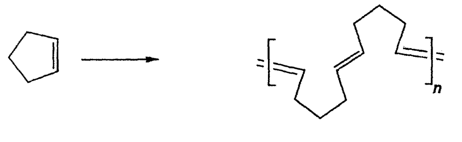
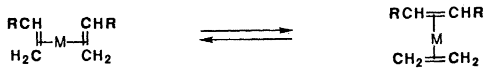
fragments (*3*). Calderon's group at Goodyear developed the first reliable homogeneous ROMP catalysts, provided much of the early mechanistic data, and suggested numerous commercial possibilities (*9*). An analogous reaction (alkylidene exchange) of acyclic olefins called the olefin metathesis reaction (*8*) was then discovered (Eq. 5). In part because of its origins, work on olefin metathesis has closely followed developments in olefin polymerization. In fact, there was considerable early confusion regarding the relation and mechanisms of olefin metathesis and Ziegler-Natta polymerization.


(3)


(4)

$$CH_3CH{=}CH_2 \rightleftharpoons CH_2{=}CH_2 + CH_3CH{=}CHCH_3 \qquad (5)$$

During the past two decades considerable effort has been expended in order to understand the olefin metathesis reaction and explore its potential. Most of the early work and the historical development of mechanistic proposals have been extensively reviewed (*4*). Early popular mechanisms proposed and supported by theoretical studies centered around a concerted pairwise process involving diolefin complexes and "pseudocyclobutane" metal complexes (Eq. 6). In order to account for observed product distributions in the metathesis reaction between cyclic and acyclic olefins, Herisson and Chauvin proposed a novel mechanism (*10*) that involved nonpairwise alkylidene exchange through the interconversion of metal-carbene and metallacyclobutane complexes (Eq. 7). This proposal was a bold one since only a few of these types of complexes were known at the time and the basic mechanistic step was totally unprecedented.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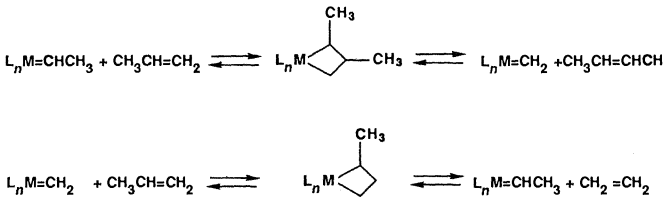
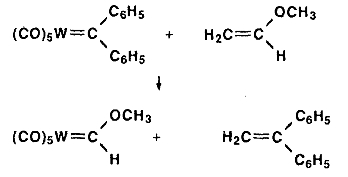

(7)

where M is metal and L is ligand.

Two general approaches were used to distinguish among possible olefin metathesis mechanisms that led to the eventual acceptance of the Chauvin mechanism: (i) classical mechanistic studies, for example, isotope labeling, kinetics, crossover experiments, and (ii) the preparation and study of proposed organometallic intermediates. Isotope labeling studies (*11*) on irreversible metathesis systems unequivocally demonstrated that the alkylidene units of the alkene are exchanged in a nonpairwise manner (totally scrambled) and effectively ruled out the concerted (pairwise) diolefin mechanism.

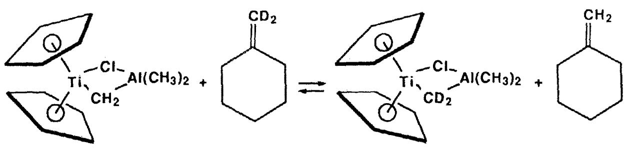
Metal-carbene complexes and metallacyclobutanes then became the target of intense investigation in order to determine the exact role of these intermediates in olefin metathesis. Studies in this area focused on synthesizing new complexes to model important catalytic steps as well as isolating such species from active catalytic reaction mixtures. Historically, this type of approach has proven valuable in the studies of catalytic systems. One interesting aspect of organometallic chemistry is that many catalytic intermediates are sometimes sufficiently stable to be detected and may even be isolated. Often, changes in the metal, ligands, solvent, or experimental conditions can perturb the energetics substantially so that a structure that was a transient intermediate in one system becomes a stable, isolable component in another system. Thus, mechanistic information can be gained through characterization of purported intermediates, and the feasibility of certain classes of intermediates can be shown. The most useful studies are those in which model complexes can be demonstrated to effect the catalytic sequence under investigation. Such studies have provided much of the excitement in organometallic chemistry during the past 20 years.

Numerous attempts to isolate the active components from olefin metathesis reaction mixtures and to model the metathesis reaction with the well-known low oxidation state Fischer carbenes or late-metal (for example, platinum) metallacyclobutanes met with little success (*2*). Several key observations that resulted from synthetic organometallic studies were, however, made in the mid- to late 1970s. Casey and co-workers discovered that the alkylidene carbons of an olefin and a tungsten Fischer carbene complex could be interchanged (*12*), albeit inefficiently, and thereby provided a model for the propagation step in catalytic olefin metathesis systems (Eq. 8).


(8)

$$(CO)_5W{=}C(C_6H_5)_2 + H_2C{=}C(OCH_3)H \rightarrow (CO)_5W{=}C(OCH_3)H + H_2C{=}C(C_6H_5)_2$$

Two major breakthroughs in our understanding and eventually the usefulness of homogeneous olefin metathesis can be traced to work initiated by Parshall's group at Du Pont Central Research on high oxidation state metal alkylidene complexes. This work eventually led to the present-day, efficient, homogeneous (ROMP) catalysts. Tebbe and co-workers investigated and structurally characterized the titanium methylidene complex **2** (*13, 14*). This work represented the first clean example of a catalytic olefin metathesis system that started with an isolated, well-characterized carbene complex that could be reisolated at the end of the reaction. The Tebbe reagent was formed by the reaction of titanocene dichloride and trimethylaluminum. This reagent, which can be considered an aluminum-protected titanocene methylidene, catalyzed the degenerate methylene exchange (metathesis) between isobutylene and methylene cyclohexane as shown by ^{13}C- and ^{2}H-labeling (Eq. 9). Schrock's group (*15*) also began extensive work on developing synthetic methods for early transition metal (Group 5, 6) alkylidenes. Early successes included the preparation of high oxidation state alkylidenes (Eq. 10). This work eventually led to the development of numerous highly efficient Ta, W, and Mo metathesis catalysts (*16*).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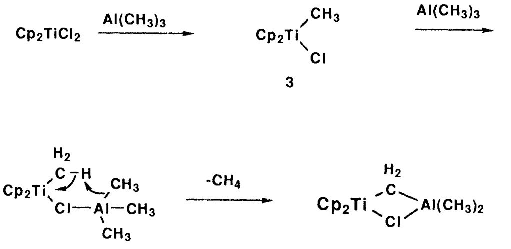
(9)

$$[(CH_3)_3CCH_2]_3TaCl_2 + (CH_3)_3CCH_2Li \rightarrow [(CH_3)_3CCH_2]_3Ta{=}CHC(CH_3)_3 \qquad (10)$$

Work by others, notably Osborn and co-workers (*17*) and Ivin, Rooney, and their co-workers (*18*) on metathesis systems that used metals in high oxidation states paralleled these developments. In addition to laying the groundwork that would provide efficient homogeneous metathesis catalysts and therefore much of the present-day excitement in coordinative polymerization, these studies led to the final acceptance of the Chauvin mechanism. Concurrent with this activity in homogeneous catalysis was a large effort in developing useful (and even commercially viable) heterogeneous catalytic systems for olefin metathesis and ROMP (*3, 4*).

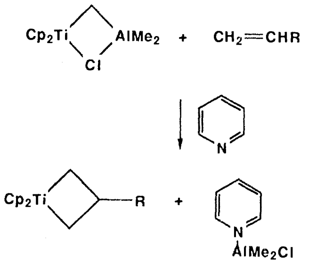
Titanacyclobutane Chemistry

The clean Ti-Al system reported by Tebbe *et al.* was ideal for mechanistic investigations. The formation of the Tebbe reagent (**2**) from Cp_2TiCl_2 and trimethylaluminum has been shown to proceed through α-hydrogen abstraction from an intermediate chlorotitanium methyl complex **3**, which is formed through initial transmetallation. The role of the aluminum in this sequence is believed to be twofold in that it both activates the methyl group and acts as a base to remove a hydrogen from the methyl group in the intermediate. A primary hydrogen isotope effect of 2.9 is consistent with those measured for similar α-elimination reactions (*19*).



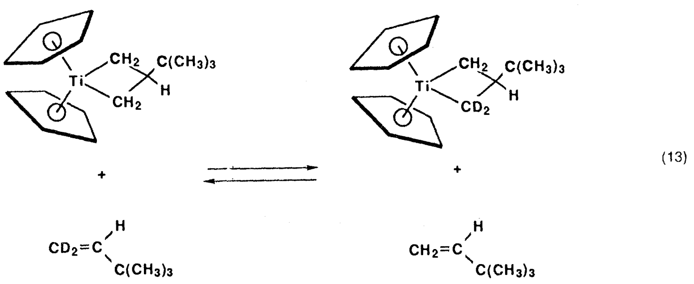
(11)

In further investigations of the Tebbe reagent and its metathesis activity, Howard *et al.* (*20*) discovered that it reacted with alkenes in the presence of a Lewis base such as pyridine or a vinylpyridine-styrene copolymer to produce isolable bis(cyclopentadienyl) titanacyclobutane complexes (Eq. 12). Although metallacyclobutane complexes of many transition metals had been prepared by a variety of methods, this report was the first example of their isolation from the cycloaddition reaction of a metal carbene and an olefin. This study constituted the first direct evidence for the involvement of metallacyclic intermediates in olefin metathesis, since these complexes were isolated from an active metathesis catalyst system. Moreover, the isolated complexes catalyzed the metathesis transformation at a rate that was consistent with their being intermediates in the overall catalytic sequence, thereby establishing their kinetic competence.



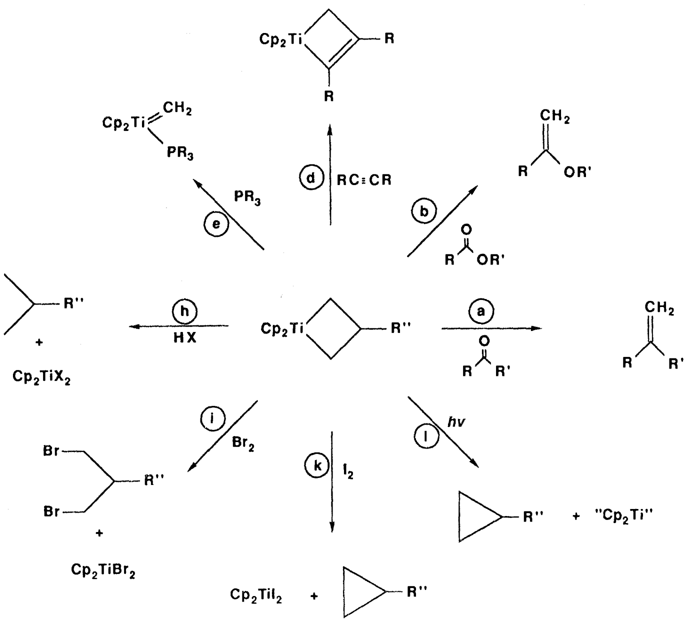
(12)

The synthesis of titanacyclobutanes from the Tebbe reagent, olefins, and a Lewis base has proven to be a general route; at least 30 complexes have been prepared and characterized. The structure, reactivity, and reaction mechanisms of these unsaturated (formally 16-electron) titanacycles have been extensively investigated by our research group. The solid-state and solution structures of these complexes have been determined by x-ray crystallography, nuclear magnetic resonance (NMR), and other spectroscopic techniques (*21*). In general, the four-membered ring is planar, fairly symmetrical, and lies in the equatorial plane between the two bent cyclopentadienyl rings where the valence orbitals of the titanium atom are located. NMR analysis, including M. Saunder's method of measuring isotopic perturbation of chemical shift (*21*), confirms a symmetric metallacyclic structure rather than equilibrating carbene-olefin complexes in solution. Theoretical studies have effectively corroborated these findings (*22*).



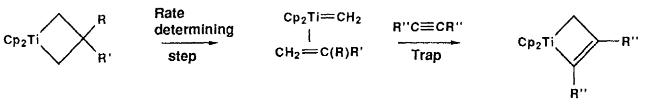
(13)

The titanacyclobutanes exhibit diverse reactivity. Among the numerous reactions, some of which are illustrated in Scheme 1, are: (a and b) methylene transfer to organic carbonyls such as ketones and esters (*7*), (c) formation of enolates from acid halides (*7*), (d) reaction with alkynes to produce titanacyclobutenes (*14, 23*), (e) generation of alkylidene-phosphine adducts (*23*), (f) complexation of transition metal halides (*24*), (g) electron-transfer chemistry with activated alkyl halides (*25*), (h and i) electrophilic cleavage of the Ti-C bonds by acids (H^+) or halogens (Br_2), (j and k) thermal (*26*) or photochemical (*27*) reductive elimination, and (l) insertion of carbon monoxide (*7*).



Scheme I

Most of the reaction chemistry of titanacyclobutanes, including olefin metathesis, can be understood within the context of the titanocene methylidene intermediate $Cp_2Ti{=}CH_2$ or a carbene-olefin complex, generated by retro [2 + 2] cycloaddition (Eq. 14), that is, formal trapping of $Cp_2Ti{=}CH_2$ (degenerate methylene exchange, metallacyclobutene formation, phosphine adduct formation) (*23*). Of particular relevance to polymer chemistry is the highly efficient and selective reaction with carbonyl compounds including ketones, esters, and amides that results in methylene transfer to produce alkenes. This alkylidene transfer, which can also be accomplished with the Tebbe reagent (*7, 13–15*) and tantalum (*28*) and tungsten (*16, 29*) alkylidene complexes is similar to the Wittig reaction of phosphorus ylides (*30*). By analogy, it most likely proceeds through a metallaoxetane intermediate formed by the cycloaddition of a carbonyl compound with $Cp_2Ti{=}CH_2$ (either free or bound) (Eq. 15). The driving force is the formation of extremely strong metal-oxygen bonds in the by-product oxide. The titanium reagents have opened new synthetic strategies and have become standard reagents in organic synthesis. Moreover, these reactions, particularly alkylidene transfer, are extremely useful in elaborating polymers as well, for example, end-capping.



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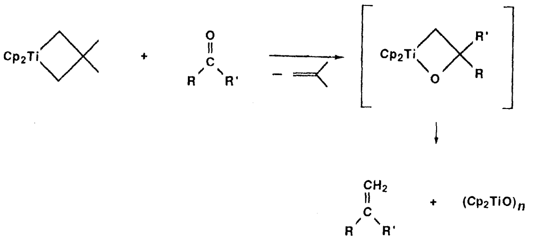
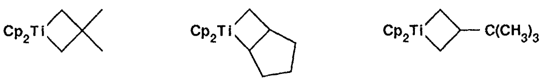


(15)

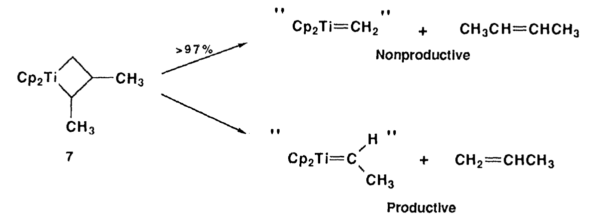
The kinetics and stereochemistry of the reaction of titanacyclobutanes with a number of trapping agents, including alkenes, alkynes, phosphines, dimethylaluminum chloride–etherates, and ketones, have been investigated (*23*). The reactions are first-order in metallacycle and exhibit saturation kinetics at high trap concentrations with rates that are essentially independent of the nature and concentration of the trap. All of the available data confirm a scheme involving rate-determining retro [2 + 2] cleavage to a carbene-olefin complex or free $Cp_2Ti{=}CH_2$ followed by reaction with added reagents (Eq. 14). The rate of cleavage is controlled by the stability and steric bulk of the olefin that is expelled from the metallacycle. For example, the metallacyclobutane **4** (Eq. 16) prepared from isobutylene cleaves with a half-life of ~5 min at 10°C, and that obtained from cyclopentene **5** cleaves at a comparable rate at 40° to 50°C, whereas the complex derived from neohexene (3,3-dimethyl-1-butene, **6**) reacts at a convenient rate at ~60°C [activation enthalpy $\Delta H^{\ddagger} = 27$ kcal/mol; activation entropy $\Delta S^{\ddagger} = 9$ entropy units (eu)]. By measuring the equilibria of a series of alkyl-substituted titanacyclobutanes with dimethylaluminum chloride–etherate complexes, Straus and Grubbs assessed a relative order of stabilities and reactivities (*31*). In general, β-substituted metallacycles are much more stable than α-substituted systems, and increased substitution is destabilizing.



4 5 6

(16)

This reactivity pattern has important implications for polymer synthesis. Although the titanacyclobutanes studied to date undergo clean [2 + 2] cycloreversion and can effect degenerate methylene exchange of terminal olefins, they are poor catalysts for the productive metathesis of acyclic olefins. This lack of activity is due to the propensity of α,β-disubstituted titanacyclobutanes to cleave to the unsubstituted methylidene (nonproductively liberating internal olefin) rather than to the substituted alkylidene required for productive metathesis. The bonding situation is such that substituents on the alkylidene carbon in the wedge formed by the bent cyclopentadienyl rings would have unfavorable steric interactions with the Cp rings. For example, metallacycles **7** and **5** cleave to produce "$Cp_2Ti{=}CH_2$" and the internal olefin almost exclusively (*31*) (Eqs. 17 and 18). As discussed more extensively below, one can force the cleavage toward a substituted alkylidene by using strained cyclic olefins in which the relief of the extra ring strain provides a driving force for productive cleavage, as illustrated by the metallacycle **8** (Eq. 19). In this case, the nearly 30 kcal/mol of additional ring strain in the cyclopropene that would be produced by nonproductive cleavage induces cleavage to the substituted alkylidene, as demonstrated by trapping studies (*32*). Recent studies have demonstrated that this retro [2 + 2] cleavage can also be induced photochemically, even at low temperatures (*27*).



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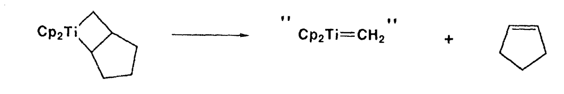
(17)



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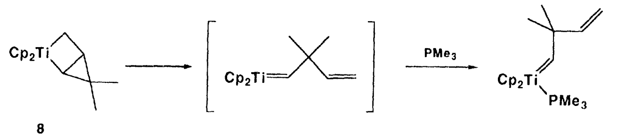
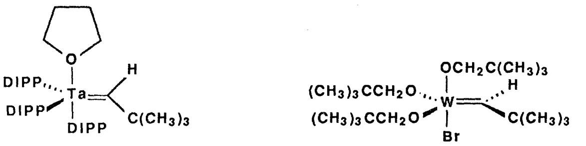


8

(19)

where PMe_3 is trimethylphosphine. Recently, numerous tantalum and tungsten carbene catalysts for olefin metathesis have also been prepared by Schrock and co-workers (*33*) and Osborn and co-workers (*34*). In these systems (Eq. 20), the resting state of the system is the carbene-olefin complex or the carbene and free olefin, in contrast to the titanium system in which the metallacyclobutane is the stable intermediate. Access to these two extreme cases has permitted a precise definition of the overall path of olefin metathesis. Moreover, all of these catalysts have proven very effective in the ring-opening polymerization of cyclic olefins as described below

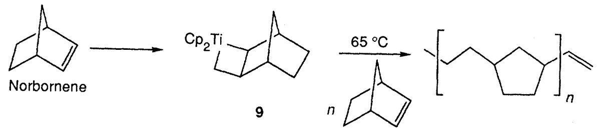


(20)

where DIPP is 2,6-diisopropylphenoxide.

Polymer Synthesis

Transition metal–catalyzed metathesis (alkylidene exchange) of cyclic olefins leads to polymerization affording ring-opened polymers (*5*). This important application of olefin metathesis has been extensively investigated; several polymers such as *trans*-polyoctenamer and polynorbornene are now produced commercially (*35*). Although a number of metal systems (both heterogeneous and homogeneous) catalyze ROMP, details concerning the initiation and propagation steps, as well as the techniques for the control of molecular weight distributions and polymer stereochemistry, were not available until recently. The last few years have seen significant advances in the understanding and control of ROMP due to the development of homogeneous catalysts that provide polymers of controllable molecular weight distribution and intermediates that can be well characterized. In 1984, Grubbs and Gilliom (*36*) reported the first living polymerization system (as defined below) for the ring-opening polymerization of cyclic olefins. Titanacyclobutanes catalyzed the polymerization of norbornene to give a polymer of narrow and controllable molecular weight distribution (Eq. 21). Moreover, the chain-propagating intermediates could be well characterized. As discussed below, this work has led to the controlled synthesis of new polymeric structures including end-capped polyalkenamers, copolymers containing monodispersed segments, conducting polymers and their polymeric precursors, and ion-chelating polyethers by our group and others.



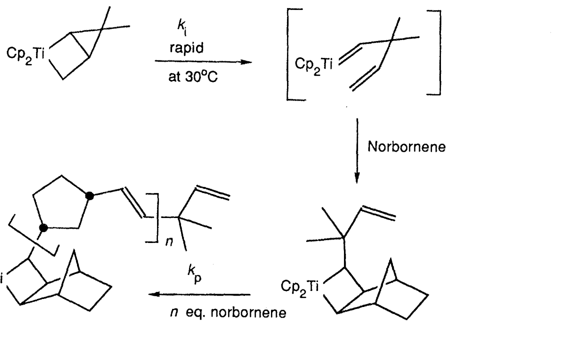
(21)

Before discussing the recent developments in ROMP, a brief classification of polymer reactions is appropriate. There are two basic modes of polymer synthesis (*37*): chain growth and step growth. In chain growth, the best example of which is radical polymerization, the polymer chain is initiated by a reactive species (for example, a free radical) added to the monomer and reaction can only occur at the reactive end of a growing polymer chain. Growth or chain propagation continues until termination or chain transfer occurs. Under these conditions, the equilibrium molecular weight of the polymer, M_n, is essentially independent of the extent of conversion (that is, a plot of M_n versus conversion is flat). In step-growth polymerization, such as polyester synthesis, the functional groups at the ends of the polymer and the functional groups on the monomer all have essentially the same reactivity. Consequently, M_n increases slowly until most of the monomer is consumed and then M_n increases rapidly.

Living polymerization is a special case of chain growth where chain transfer and chain termination are very slow relative to initiation and propagation. Since every monomer that is consumed results in the increase in length of a polymer in this case, a plot of M_n versus percent conversion would be linear with a zero intercept. If every chain starts to grow at the same time (that is, rate of initiation is greater than rate of propagation), then each event leading to chain growth is equally probable and the system is statistically well described by a Poisson distribution. The molecular weight distribution of a polymer is described by the polydispersity, which is the ratio of the weight average molecular weight, M_w, to the number average molecular weight, M_n. For a living system, M_w/M_n is equal to $(1 + 1/p)$, where p is the degree of polymerization. At very high molecular weights ($1/p \rightarrow 0$), a monodispersed polymer has M_w/M_n equal to unity.

Studies on ROMP catalysts initially focused on norbornene primarily due to the pioneering work by Ivin and Rooney and their co-workers on the microstructure of polynorbornenes and derivatives (*18*). The stereochemistry of these polymers can be analyzed by NMR spectroscopy and the molecular weight distributions can be measured with gel permeation chromatography. In the presence of excess norbornene, metallacycles **8** and **9** resulted in the production of polynorbornene upon heating (*36*). The molecular weight of the polymer increased linearly with time; a plot of molecular weight versus percent conversion extrapolated to a zero intercept. The ultimate molecular weight, M_n, is determined by the ratio of the number of equivalents of monomer consumed per titanium catalyst. This reactivity contrasts with the other metathesis catalysts that were known at the time. The "classic" catalysts exhibited standard chain-growth characteristics, such that the molecular weight and polydispersity changed very little after initial reaction. The M_n of the polymer produced by these standard catalysts is controlled by the inherent kinetics of the system and is not directly controllable by experimental variables. Polydispersities of polynorbornene produced with the titanacycles were well below 1.1, indicating that this process was a living polymerization. In this process a chain starts to grow on a catalyst and the active group remains at the end of the growing chain. Each polymer chain remains active ("alive") until the reaction is terminated by added reagents. The only well-documented examples of living polymerization are anionic (*38*), cationic (*39*), and group-transfer polymerization (*40*). These processes opened new control in polymer synthesis and, before the new ROMP catalysts, were the only methods to prepare block polymers and related structures of well-defined molecular weight. Living polymerization systems provide polymers of controllable molecular weight distribution as well as a means to change monomer as the polymer grows.

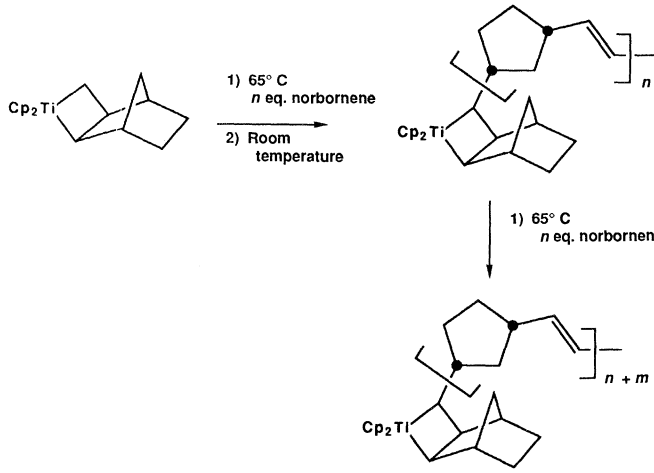
In addition to the aforementioned time dependence and narrow distribution of polymer molecular weight, considerable effort was expended to demonstrate that the titanium-catalyzed polymerization of norbornene was indeed living. Metallacycles **8** and **9** catalyzed norbornene polymerization by the same mechanism upon heating, except for differences in the initiation rate. Kinetic studies revealed that the initiation step was ring opening of the starting metallacycle to the substituted alkylidene. The more highly substituted **8** is more reactive than **9** and thus provided lower dispersities due to faster initiation rates (relative to propagation). The propagation step was shown to involve ring-opening of the stable, chain-carrying, trisubstituted titanacyclobutanes to the substituted alkylidene (growing polymer chain) which is then trapped by another equivalent of monomer to form the homologated metallacycle (Eqs. 22 and 23). Both the titanacycle and the growing polymer chain moieties could be detected in situ by NMR spectroscopy during the reaction. During the polymerization, addition of an aliquot of deuterated norbornene resulted in incorporation of the isotopic label in the metallacyclic positions and then into the polymer chain. A polymer containing a metallacycle could be isolated by cooling the reaction mixture and removing solvent and monomer. The polymerization then ensues upon heating in the presence of additional monomer. The resulting polymer was found to be identical to samples produced by the continuous reaction with the same amount of monomer. The isolated living polymer retains its activity for more than 3 months if protected from the atmosphere. Such systems with stable end groups can be considered hibernating polymers to distinguish them from the normal anionic systems in which the end groups are highly reactive and are difficult to stop and control with changes in temperature.



(22)

where k_i is the rate of initiation and k_p is the rate of polymerization and where eq. stands for "equivalents of."

Three key features for the design of living ROMP catalysts have emerged from the work on titanium metallacycles. The first feature, which is not usually found with the standard metathesis catalysts, is their low activity. A highly active catalyst would react with and degrade the polymer through chain transfer or termination and

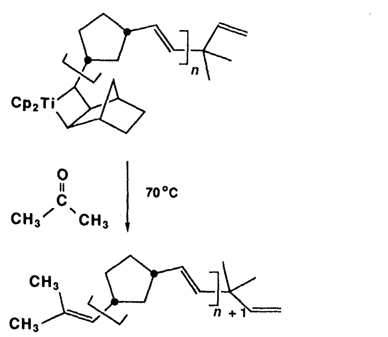


(23)

broaden the molecular weight distribution. A second special feature is the availability of propagation pathways that are much more favorable than termination steps. In contrast to Ziegler-Natta systems for addition polymerization, the mechanism for propagation in ROMP is very different from those available for chain termination (*2–5*). In Ziegler-Natta systems in which propagation involves insertion of olefins into metal-carbon single bonds and termination relies on the removal of an olefin with the formation of a metal-hydrogen bond, the transition states and therefore the controlling factors are similar for termination and propagation. In ring-opening polymerization, the low-energy pathway for the intermediate metallacycles is retro [2 + 2] cycloaddition, which contrasts with higher energy hydrogen elimination and other pathways. Olefin metathesis centers on the chemistry of metal-carbon double bonds, whereas Ziegler-Natta polymerization involves the chemistry of metal-carbon single bonds. The final key to the success of the titanacyclobutane systems is that chain growth is extremely sensitive to temperature. The reaction can be effectively terminated and reinitiated over a narrow temperature range. Apparently a number of stable, isolated carbene and metallacyclic metathesis catalysts can yield living systems. The living polymerization of norbornene has recently been reported for tantalum (*41*) and tungsten (*42*) catalysts as well. Of particular note is a tungsten system reported by Osborn and co-workers (*29*) in which both the propagating carbene and metallacyclobutane propagating species have been detected. This last system does not, however, yield monodispersed polymer because of problems associated with initiation rates and a number of propagating species.

Applications

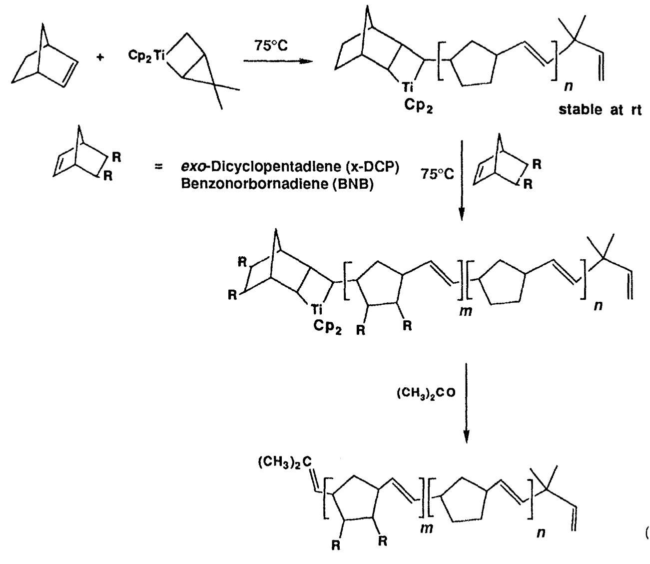
New living polymerization catalyst systems lead directly to the synthesis of new polymers of controlled structure. The ROMP systems are readily adapted to the preparation of end-capped polymers and block copolymers. The well-established organic chemistry of the high oxidation state carbene and metallacycle complexes can be used for end-capping ring-opened polymers. Thus far, alkylidene transfer reactions to ketones and aldehydes have been successfully used for end-capping either to provide for clean termination with a well-defined end group or to allow for further elaboration by functionalization of the polymer chain. To date, most of the work has involved simple carbonyl compounds as end groups (Eq. 24); however, this ability to manipulate living polymers makes the ROMP catalysts highly versatile (*43*).



(24)

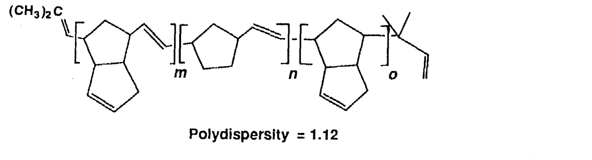
Perhaps the most immediate application of any new living polymerization system is the synthesis of block copolymers with monodispersed segments. Analogous to its living polymerization predecessors, especially anionic and group-transfer polymerization, ROMP can be used to make block copolymers with a wide range of properties not attainable with homopolymers or random copolymers. Block structures result in the introduction of stable nonhomogeneous segments within a polymer matrix and are essential for the assembly of macromolecular structures (*38, 40*). An example is the widely used SBS (styrene-butadiene-styrene) triblock thermoplastic elastomer formed via anionic polymerization (*39*). Of course, the ultimate functional, block copolymers are proteins and DNA.

A number of experimental techniques can be used to prepare block copolymers (*38*). The most straightforward synthesis that uses titanacyclobutane catalysts involves growing a homopolymer of the desired molecular weight of one monomer, cooling the reaction mixture to terminate the reaction, then heating in the presence of a second monomer and repeating this process until the desired polymer is prepared. Several triblocks with very low polydispersities have been prepared by this method (*44*) (Eqs. 25 and 26). Schrock *et al.* subsequently reported the synthesis of block polymers using Ta and W ROMP catalysts (*45*).



(25)

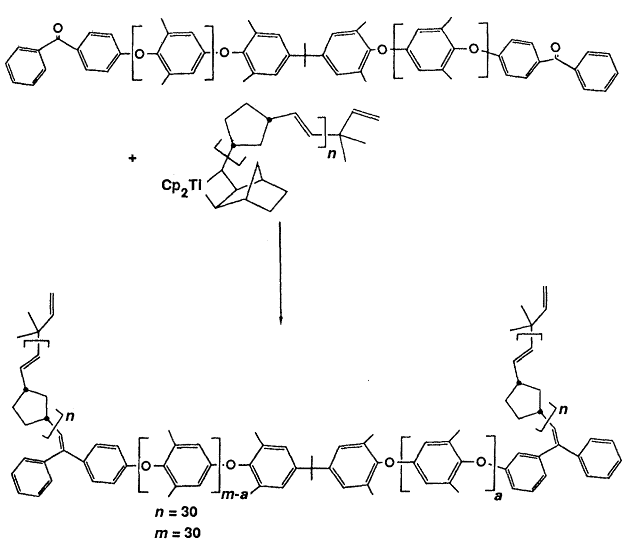
Polydispersity > 1.1



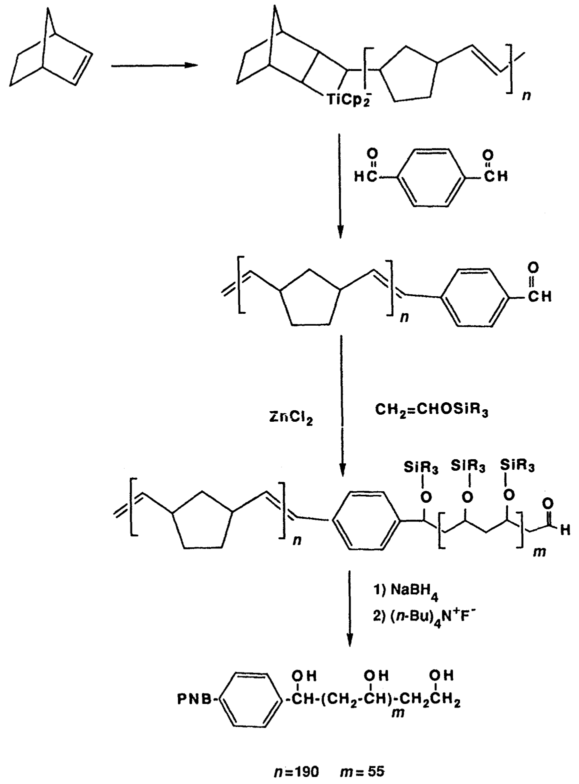
(26)

Polydispersity = 1.12

Block copolymers have also been prepared by grafting living ring-opened polymers onto polymers that contain carbonyl groups, a method that takes advantage of alkylidene transfer reactions (that is, end-capping a polymer with another polymer, Eq. 27) (*46*). Another method of block formation involves two monomers with very different reactivities in which the more reactive monomer essentially completely polymerizes before the other adds to the end of the chain. Preliminary studies reveal that the formation of these so-called tapered block polymers is a powerful synthetic technique (*47*). Blocks that are not prepared by ROMP can be added to ring-opened polymers, but methods must be used for efficiently changing the polymerization mechanism. A second block has been successfully grown on a ring-opened polymer with the use of group-transfer polymerization as illustrated by the example below (Eq. 28) (*48*). Since Ziegler-Natta polymerizations can be carried out on titanium centers, our research group is also attempting to develop methods to change the polymerization mechanism from ROMP to normal addition (Ziegler-Natta) polymerization.



(27)

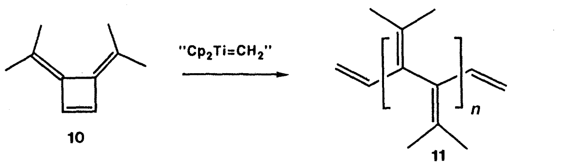


(28)

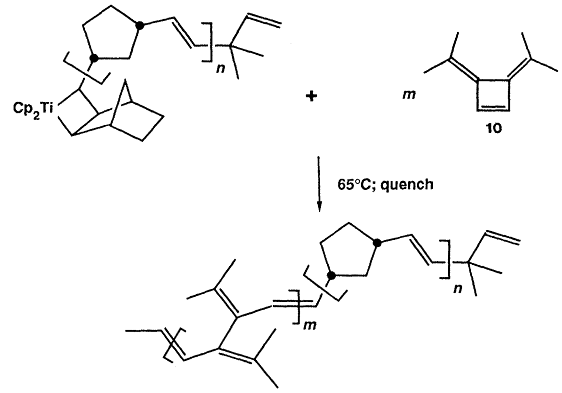
where PNB is polynorbornene.

Conducting Polymers

Organic polymers can exhibit a number of useful chemical or physical properties in addition to their obvious mechanical or structural functions. A number of polymers with unsaturated backbones (for example, containing carbon-carbon multiple bonds), the best example of which is polyacetylene, have been demonstrated to be rather good electrical conductors upon doping with reducing or oxidizing agents (*49*). Because ROMP produces polymers with carbon-carbon double bonds in the backbone, it is well suited for the preparation of materials with interesting electronic properties. For example, the new material poly(dimethylenecyclobutene), **11**, a cross-conjugated polymer prepared by ROMP of **10**, can be spin-cast, forms flexible films, and, upon doping, exhibits moderate conductivities (10^{-3} S cm^{-1}) (*50*) (Eq. 29). The doped material is brittle and insoluble, but these properties can be altered by forming block copolymers. Blocking this polymer with polynorbornene yields a rubbery material with more desirable mechanical properties but conductivities, after doping, that are similar to the homopolymer (Eq. 30).



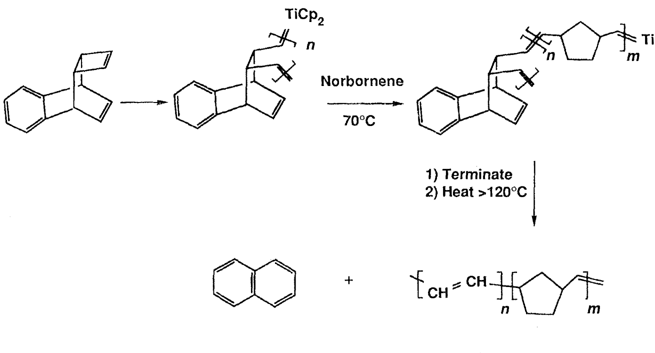
(29)



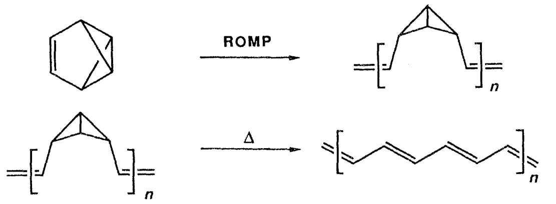
(30)

Many of the well-known conducting polymers, such as polyacetylene, are insoluble and difficult to process (*51*). The ROMP catalysts have been used to prepare polymeric, soluble polyacetylene precursors that can be processed. A block copolymer of polyacetylene and polynorbornene has been recently synthesized with the titanacycles. A living polymer prepared from the Feast monomer (a thermal precursor to polyacetylene) can be blocked with polynorbornene (*52*). Thermolysis of this material eliminates naphthalene to produce controllable block lengths of polyacetylene within a polymer matrix (Eq. 31). Schrock and co-workers have also reported the fabrication of polyacetylene precursor polymers through ROMP (*53*). A polymeric precursor route to polyacetylene that does not involve extrusion of molecular fragments was developed through the polymerization of the highly strained monomer, benzvalene (a valence isomer of benzene) (*54*). This material, which was produced with tungsten catalysts, forms soluble, castable films and can be isomerized to polyacetylene by treatment with mercury salts (Eq. 32).

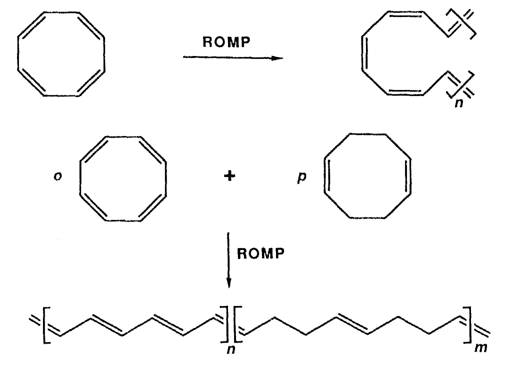
Ring-opening polymerization of cyclooctatetraene (COT) provides a powerful synthetic route to polyacetylenes (*47*). This high-boiling liquid can be bulk-polymerized to freestanding films of a variety of shapes and dimensions. Moreover, COT can also be copolymerized with other cyclic alkene monomers to yield polymers with conducting segments of controllable lengths (Eq. 33). For example, copolymerization of COT and cyclooctadiene leads to random copolymer films that range in color (and therefore conjugation length) from yellow to metallic black as the percentage of COT is changed from 20% to 100% of the copolymer feed. These materials with controllable variable conjugation lengths are being used to test theories of electrical conduction and may have applications in nonlinear optics as well. The same techniques are being applied to the synthesis of materials that, based on theoretical models, should exhibit interesting optical or magnetic properties.



(31)



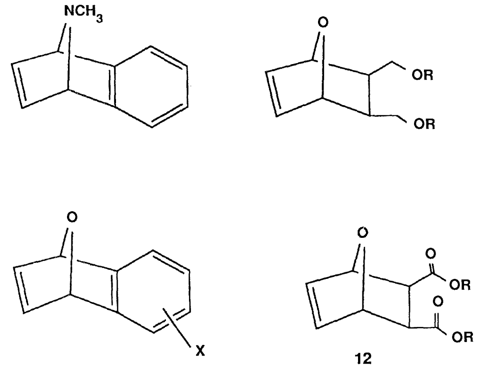
(32)



(33)

Functionalized Polymers

As illustrated above, a large majority of the new polymers prepared by ring-opening polymerization, to date, contain little functionality other than carbon-carbon multiple bonds. Although these systems can be highly useful for structural purposes or even electrical conduction, other applications or properties (for example, selective ion binding or water solubility) require the incorporation of other functionalities, particularly heteroatoms (such as oxygen and nitrogen). The classical metathesis catalysts contain highly Lewis-acidic additives and therefore cannot effectively polymerize monomers with pendant functionalities (*3, 4*). The newer generation of catalysts discussed above (Ti, Ta, Mo, and W) react under mild conditions and are not strong Lewis acids, so in certain cases, they can tolerate polar functional groups. Cannizzo, Gilliom, and Grubbs have found that the titanacyclobutanes catalyze the ring-opening polymerization of several cyclic amines and ethers illustrated below (*55*) (Eq. 34). Murdzek and Schrock (*56*) have developed a Mo-based catalyst that can also polymerize functionalized monomers such as **12**.

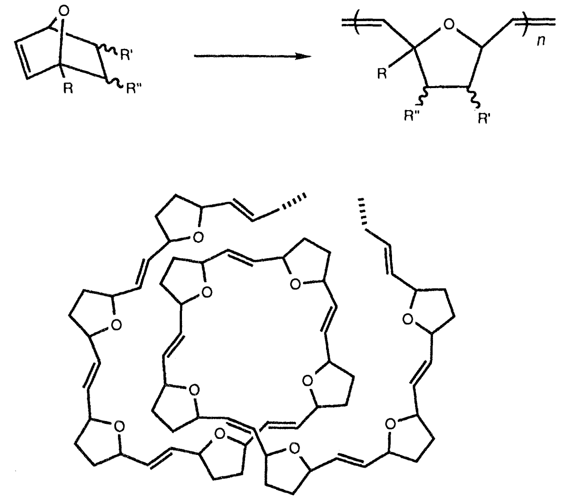


12

(34)

X = Alkyl, ether, halogen and so on

A new class of acyclic polymeric ionophores was recently reported by Novak and Grubbs (*57*). Ring-opening polymerization of 7-oxanorbornene derivatives affords the poly(ethenylidenetetrahydrofuran) materials (Eq. 35), which are capable of forming helical structures with ion-binding cavities analogous to the cyclic crown ethers and cryptands. Novel ionophoric materials such as these polymers that can be cast into thin films should find potential applications as ion-selective permeable membranes.



(35)

The obvious advantages and applications of polymers resulting from the ring-open polymerization of functionalized monomers that contain potentially reactive heteroatoms has led to investigations of catalysts based on metals in the middle of the transition series that should not be as Lewis-acidic as those resulting from early transition elements. Recent developments (*58*) have revealed that Ru and Os catalysts (*59*) can tolerate a wide range of functional groups and can even operate effectively in aqueous solution. For example, cyclic ethers can be ring-open polymerized in water without any protection from the atmosphere to afford latex polymers (*58*). These remarkable catalysts catalyze the ROMP of a number of monomers that are unreactive toward the early transition metal catalysts. Moreover, solutions of the catalyst can be used repeatedly. Unlike the catalysts discussed above, the polymerization mechanism has not been established for these aqueous systems. If they operate through similar pathways through metal carbenes and metallacycles, the reactivity of these intermediates must be reevaluated. Studies are presently under way to determine the structure of the active catalyst and whether controlled polymerization systems (even living ones) can be developed much along the same lines as the versatile early transition metal catalysts. Evidently, observations in polymer chemistry are again driving new efforts in organometallic chemistry and a reevaluation of organometallic chemical principles.

Conclusion

The research efforts in organometallic chemistry that were spawned by Ziegler's observations have now come full circle and are opening new horizons in polymer synthesis. The homogeneous ROMP catalysts that have recently been developed have opened new strategies for the controlled synthesis of polymers with well-defined structure. The living nature of many of these systems, coupled with their tolerance for a variety of functional groups and the clean synthetic chemistry of the metallacycle or carbene end groups, has provided a wide range of polymeric structures that are not accessible with other techniques. These developments along with significant advances in other areas of coordinative polymerization, notably the chiral, stereoselective Ziegler-Natta systems from the labs of Ewen, Brintzinger, Kaminsky, and others (*60*) have provided only a glimpse of the limitless possibilities in polymer synthesis.

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