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Communications to the Editor

Living Ring-Opening Metathesis Polymerization of Bicyclo[3.2.0]heptene Catalyzed by a Ruthenium Alkylidene Complex†

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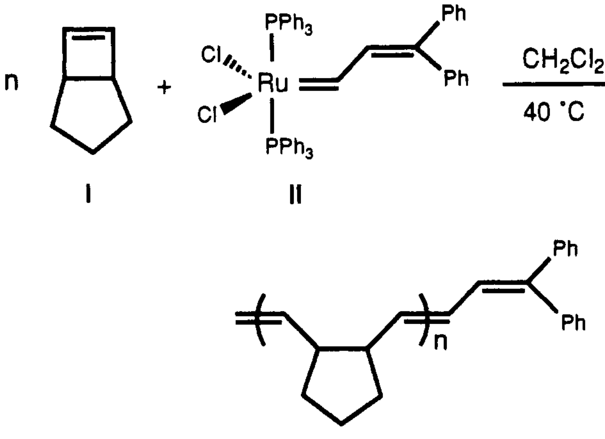
Living polymerizations using ring-opening metathesis catalysts (ROMP) have allowed the synthesis of polymers with controlled structure and properties.[1,2] In the past few years, efforts have been focused on developing novel transition-metal alkylidene complexes that catalyze this reaction and provide either access to new product or easier synthesis.[2] All of the catalysts developed to date are high oxidation state organometallic complexes, which exhibit limited tolerance to polar functional groups, and only catalyze the living polymerization of norbornene and its derivatives.[3] Recently, we have synthesized a ruthenium alkylidene complex that exhibits exceptional tolerance to a variety of polar functional groups and also catalyzes the living ROMP of norbornene.[4] Because we were interested in elucidating the details of this living polymerization,[5] we investigated the ROMP of highly reactive monomer bicyclo[3.2.0]heptene (**I**),[6] catalyzed by the late-transition-metal complex $(PPh_3)_2(Cl)_2Ru({=}CHCH{=}CPh_2)$ (**II**; eq 1). We hope that an investigation of this system will provide us with a better understanding of the mechanism of polymerization catalyzed by late-transition-metal alkylidene complexes[7] and eventually allow us to control molecular weight in the preparation of functionalized polymers with potential uses in biological applications.[8]



(1)

Initial investigations of the polymerization of **I** by several well-defined tungsten and molybdenum alkylidene complexes showed that the rate of polymerization is much greater than that of initiation,[9] which is probably due to the fact that the propagating alkylidene is less hindered than the bulky starting alkylidene. The highly strained monomer[10] thus reacts more rapidly with the propagating alkylidene than with the starting alkylidene. Given these considerations, we thought that monomer **I** might react more rapidly with the starting alkylidene based on **II** and thus catalyze the polymerization of **I** in a living fashion. Indeed, **II** catalyzes the polymerization of **I** in a controlled manner. The addition of 20 equiv of monomer **I** to a solution of **II** in methylene chloride at 40 °C results in complete initiation of the starting alkylidene. Throughout the polymerization, three new propagating species are observed by ^1H NMR spectroscopy at δ = 18.06 (multiplet), 17.38 (doublet), and 16.90 ppm (doublet) in a ratio of 2.0:1.9:1.0 with coupling constants J_{H-P} = 14.60, 14.25, and 6.83 Hz, respectively.[11] The intensities of these propagating species remain constant during the polymerization (as measured by integration relative to a dichloroethane internal standard). Examination of the reaction mixture by ^{31}P NMR spectroscopy reveals resonances at 41.7 and 29.17 ppm, as well as the presence of free triphenylphosphine at −4.9 ppm.[12] In contrast, the polymerization of norbornene exhibits only one resonance at 17.6 ppm by ^1H NMR spectroscopy and 30.06 ppm by ^{31}P NMR spectroscopy for the propagating species.

In the polymerization of **I** by **II**, dissociation of the phosphine is probably aided by the chelation of the double bond on the growing polymer chain adjacent to the metal carbene bond. Chelation of this type is favored because it leads to the formation of a stable five-membered ring.[13] Consistent with this hypothesis is the observation by ^1H NMR spectroscopy that the propagating alkylidene is stable at room temperature for several hours without decomposition. We believe that possible bimetallic decomposition pathways are inhibited by the bulky cyclopentyl substituent on the metal carbene.[14]

The kinetics of the polymerization of **I** was followed by ^1H NMR spectroscopy at 40 °C. The rate of polymerization is first order with respect to both monomer and catalyst concentrations with $k_p = 0.183\ \text{min/M}^{-1}$ and $k_p/k_i = 6.5$ (where k_p and k_i are the rate constants for propagation and initiation, respectively).[15] The polymerization of **I** in the presence of 10 equiv of deuterium-labeled PPh_3 was also followed by ^1H NMR spectroscopy, and the observed rate constant for the polymerization ($k_p' = 0.011\ \text{min/M}^{-1}$) was determined.[16]

In a typical bulk polymerization, 170 equiv of **I** was allowed to react with 0.007 M **II** in methylene chloride for approximately 1 h at 40 °C and then with 30 equiv of ethyl vinyl ether,[17] followed by stirring for another 20 min. The resulting mixture was then diluted with benzene and passed through a short column of silica gel to give polymer in essentially quantitative yield having a molecular weight of 16 500 and a polydispersity (M_w/M_n) of 1.2.[18] Analysis by ^{13}C NMR spectroscopy indicated that this polymer had a 58% *cis* configuration of double bonds in the backbone, while the polynorbornene obtained using **II** has a 13% *cis* configuration of double bonds in the backbone. The high *cis* content in the former polymer can be interpreted using Ivin's model,[19a,b] but the polymer exhibits only a small degree of blockiness ($\gamma_c\gamma_t = 1.2$).[19c] The polymer is atactic, which was confirmed by hydro-

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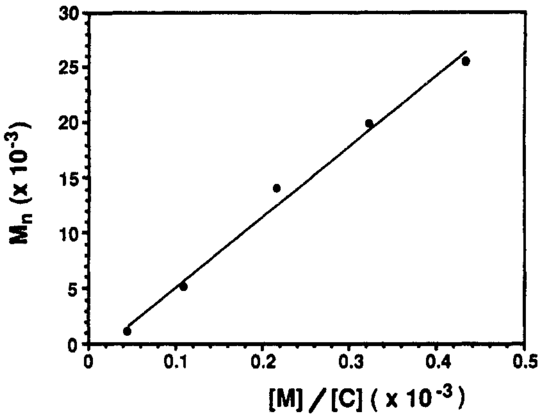

Figure 1. Plot of molecular weights versus the ratios of monomer/catalyst in the polymerization of I by II. The line through the points was determined by linear least squares with ρ = 0.995.

genation with *p*-tosylhydrazide in xylene at 120 °C.[20] Although no melting point was observed, a glass transition temperature T_g of 34 °C was observed by differential scanning calorimetry (DSC). These observations are consistent with the polymer having an amorphous structure.

We have found that the molecular weights obtained from these polymerizations are proportional to the ratio of monomer to catalysts as shown in Figure 1. This observation is consistent with a living polymerization. Further evidence for the living polymerization of I is the facile preparation of block copolymers. Diblock or triblock copolymers of norbornene and I can be synthesized by sequential addition of either I or norbornene to catalyst II. For example, 27.8 equiv of I was added to a solution of methylene chloride containing 0.007 M II at 40 °C, and the polymerization followed by ^{1}H NMR spectroscopy. When the polymerization of I was complete, 41.7 equiv of norbornene was added to the reaction mixture. The propagating alkylidene resonances of poly-I (vide supra) completely disappeared, and the resonance corresponding to the propagating species of polynorbornene (δ = 17.6 ppm) grew in. After the norbornene polymerization was complete, another 27.8 equiv of I was added to the reaction mixture. As expected, the NMR signal corresponding to the ruthenium alkylidene end group based on ring-opened norbornene vanished, and the resonances corresponding to the propagating species derived from I reappeared (integration relative to the resonance of triphenylphosphine showed that this process was quantitative). The triblock copolymer thus obtained had a molecular weight of 41 500 and a polydispersity of 1.2.

We have also found that when a 50/50 mixture of I and norbornene is added to a solution containing catalyst II in methylene chloride, polymerization of norbornene does not initiate until the polymerization of I is complete. This observation suggests that the reactivity ratios[21] of chain propagation have the following constraints: $\gamma_{cc} = k_{cc}/k_{cn} \gg 1$ or $\gamma_{nn} = k_{nn}/k_{nc} \ll 1$ (where k_{cn} is the rate constant of poly-I reacting with norbornene; k_{cc} is the rate constant for the polymerization of I; k_{nc} is the rate constant for the propagating ruthenium–carbene based on norbornene reacting with I; k_{nn} is the rate constant for the polymerization of norbornene). This can be explained by the fact that the double bond in I is less hindered than the double bond in norbornene; thus I approaches the propagating alkylidene at a faster rate than norbornene. We have found by homopolymerization studies that the rate constants k_{cc} and k_{nn} are comparable. On the basis of these observations, it can be concluded that the rate constant k_{nc} is substantially larger than k_{cn} ($k_{nc} \gg k_{cn}$).

This paper reports that bicyclo[3.2.0]heptene can be polymerized in a living fashion by a ruthenium alkylidene complex[22] and demonstrates that this functional group-tolerant carbene complex shows all the desirable features of the early-transition-metal complexes studied earlier.[2,3,5] The polymerization of I fits the criteria for a living polymerization.[23] We are currently investigating the use of this system and other related systems for the preparation of functionalized polymers and new block copolymers.

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References and Notes

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(9) Wu, Z.; Grubbs, R. H., unpublished results. For example, the polymerization of 100 equiv of I using (t-BuO)$_2$(N-2,6-diisopropylphenyl)Mo(CH-t-Bu) as an initiator results in a polymer having a molecular weight of 42 000 and a polydispersity of 2.3.

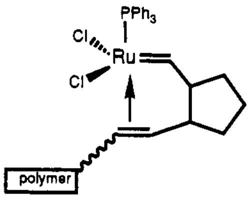
(10) Strain energy of I is estimated to be 37 kcal/mol using AM1 calculations (semiempirical calculations). See: Dewar, M. J. S.; Zoebish, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(11) Variable-temperature analysis by ^{1}H NMR spectroscopy at low temperatures indicates that the three propagating species are in equilibrium. For example, as the temperature was lowered to −40 °C, the ratio of the three propagating species changed to 8.0:1.6:1.0. When 8 equiv of triphenylphosphine was added to the reaction mixture at room temperature, the intensities of two upfield resonances (δ = 16.9 and 17.38 ppm) decreased and the intensity of a downfield resonance (δ = 18.06 ppm) increased. Furthermore, when the polymerization is carried out in the presence of 10 equiv of deuterium-labeled PPh$_3$, only one propagating resonance (δ = 18.06 ppm) was observed. Due to the above observations and observed coupling patterns, we believe that the downfield resonance corresponds to a diphosphine adduct and two upfield resonances correspond to monophosphine adducts.

(12) Chemical shifts were measured relative to phosphoric acid. The resonance at 41.7 ppm (broad) and the resonance corresponding to free PPh$_3$ have similar intensities. This observation, together with the observation that the ratio of monophosphine adducts to diphosphine adduct is approximately 3:2 at room temperature by ^{1}H NMR spectroscopy, which is consistent with the ratio observed by ^{31}P NMR spectroscopy, suggests that the resonance at 41.7 ppm corre-

sponds to monophosphine adducts and the one at 29.17 ppm corresponds to a diphosphine adduct.

(13) (a) McGrath, D. V.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3611. (b) The proposed sturcture of the monophosphine adduct:



(c) When the model compound 1,5-hexadiene is reacted with catalyst **II**, similar resonances corresponding to a monophosphine adduct and free PPh_3 are observed by ^{31}P NMR spectroscopy. There are, however, no new metal carbenes observed by ^{1}H NMR spectroscopy.

(14) (a) Thirty percent of the propagating alkylidene remains after the reaction mixture is left at room temperature for 2 days. (b) For example, see: Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857. Casey, C. P.; Anderson, R. L. *Chem. Commun.* **1975**, 895.

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(16) The observation that PPh_3 inhibits the rate of polymerization, coupled with the observation of free PPh_3 in the absence of added PPh_3, suggests to us that dissociation of PPh_3 from **II** facilitates the polymerization (although an associative inhibition mechanism has not been ruled out).

(17) Ethyl vinyl ether reacts rapidly with the propagating alkylidenes to generate an ethoxy-substituted Fischer-type alkylidene, which does not exhibit metathesis activity: Wu, Z.; Nguyen, S. T.; Grubbs, R. H., unpublished results.

(18) Molecular weights were determined by gel permeation chromatography (GPC, AMGel, linear 10-μm column) using polystyrene standards purchased from Polysciences.

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