Aqueous Ring-Opening Metathesis Polymerization of Carboximide-Functionalized 7-Oxanorbornenes[†]

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ABSTRACT: The ring-opening metathesis polymerization (ROMP) of *exo*-*N*-methyl-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide (1) was accomplished in aqueous solution under mild conditions using the simple ruthenium(II) coordination complex $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) (2). The polymerization yield was nearly quantitative. The resultant high molecular weight polymer (poly-1) exhibited a glass transition temperature (T_g) of 225 °C and was thermally stable up to 402 °C. The thermal and radiative stabilities of poly-1 were further investigated. Poly-1 was hydrogenated to yield its saturated analogue, which had a lower T_g (170 °C) but a higher temperature of decomposition (430 °C). Complex 2 was deactivated by coordination of free maleimides formed during the polymerization of carboximide-functionalized monomers capable of undergoing retro Diels–Alder chemistry. The scope of this polymerization was therefore limited to carboximide-functionalized monomers that are stable toward retro Diels–Alder reactions at the polymerization temperature. Both ruthenium (II)–1 and ruthenium(II)–*N*-methylmaleimide olefin complexes were identified.

Introduction

The design and synthesis of functional polymers, polymers whose properties depend to a significant extent on the functional group substituents along the backbone of the macromolecule, is an active area of research.[1,2] The synthesis of these polymers through the polymerization of functionalized monomers is ideal, as it enables the direct incorporation of functionality into the polymer backbone and thus circumvents the potential difficulty of chemical transformations on a polymeric substrate. An increase in the variety and availability of functionalized polymers requires the further development of polymerizations that are compatible with functionality in the monomer. In the case of the ring-opening metathesis polymerization (ROMP),[3-6] initial efforts in the search for a catalyst system effective for the polymerization of functionalized substrates were met with limited success.[4,7,8] One overwhelming problem with most of the early transition metal ROMP catalysts is the high reactivity of the catalysts with polar functionality present in the monomer. As a result, poisoning of the catalyst and polymerization become competitive processes. At the present time, the industrially useful polymers prepared via ROMP contain only olefinic functionality (Figure 1).[9]

Recent advances in the preparation of functionalized polymers via ROMP include the polymerization of functionalized norbornenes and 7-oxanorbornenes employing well-defined molybdenum-based catalysts.[10-13] Late transition metal metathesis catalysts have been shown to be more tolerant of polar substrates than their early transition metal counterparts.[4] For example, the emulsion polymerization of norbornene and its derivatives by ruthenium, iridium, and osmium complexes in *aqueous ethanol* was reported over 20 years ago.[14,15] The polymerization of functionalized monomers with these catalysts was possible, but not very efficient.[16] Recently, we reported that simple ruthenium(II) complexes effected the polymerization of functionalized 7-oxanorbornenes under air in an *entirely aqueous* environment.[17] Water was shown to have the beneficial effect of decreasing the initiation time of the polymerization as compared to the polymerization in organic solvents. The simple ruthenium coordination complex $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) (2) was found to be the most active catalyst employed, giving high molecular weight, low-dispersity materials in almost quantitative yields. In addition, 2 was recyclable for a minimum of 14 consecutive polymerizations and was active for the polymerization of a variety of 7-oxanorbornene derivatives including hydroxyl-, carboxyl-, and alkoxy-substituted monomers.[17,18] Feast and Harrison have also successfully polymerized 7-oxanorbornenes in water using ruthenium, iridium, and osmium chlorides as catalysts.[19,20] The enhanced tolerance of the late transition metal coordination catalysts toward polar solvents, polar functional groups, and air enabled the following investigation of the polymerization of carboximide-functionalized 7-oxanorbornenes.

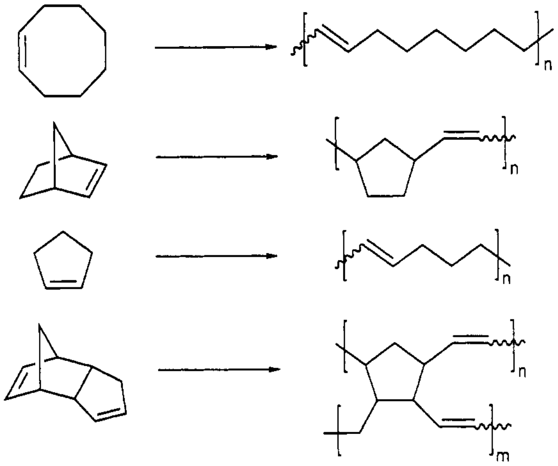

Figure 1. Industrially useful polymers prepared via ROMP.

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Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4A molecular sieves (Linde). NMR spectra were recorded on a JEOL GX-400 spectrometer (399.65-MHz ^{1}H, 100.40-MHz ^{13}C). All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne Model 7125 injector with a 100-μL injection loop, through either three Shodex Styragel columns (KF 803, KF 804, and KF 805) or an American Polymer Standards 10-μm mixed-bed column, and a Knauer differential refractometer; methylene chloride was used as the eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7, and thermogravimetric analysis was accomplished on a Perkin-Elmer TGA-2. Photolysis was conducted with a 450-W high-pressure mercury Hanovia lamp.

Materials. Distilled deionized water was used for most of the polymerizations. All other solvents were reagent grade and used without purification. For the polymerizations using degassed solvent, the solvent was degassed by sparging with argon or repeated freeze–pump–thaw cycles. Furan, *N*-methylmaleimide, *N*-phenylmaleimide, and maleimide were purchased from Aldrich Chemical Co. and used without further purification. *endo*-1 and 4 were synthesized according to literature procedures.[21] $Ru^{II}(H_2O)_6(tos)_2$ (2) was prepared according to literature procedures.[22,23] $[Ir(COD)(PCy_3)(py)]^+PF_6^-$ (Crabtree's catalyst) was kindly supplied by Crabtree's group.

Preparation of *exo*-*N*-Methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (1). A mixture of 13.1 mL of furan (12.3 g, 0.18 mol) and 10 g (0.09 mol) of *N*-methylmaleimide in 50 mL of Et_2O was degassed in a large heavy-walled flask equipped with a Teflon seal. The flask was sealed under vacuum and then heated to 90 °C in a oil bath for 4 h. White crystals formed in the reaction flask upon cooling. The crystals were collected, washed with Et_2O, and dried under dynamic vacuum (95% yield). The product was determined to be pure exo isomer by ^{1}H NMR spectroscopy. Further purification of this product can be accomplished by recrystallization from water or ethyl acetate. Mp 142–143 °C. ^{1}H NMR ($CDCl_3$): δ 2.81 (s, 2 H), 2.95 (s, 3 H), 5.23 (s, 2 H), 6.48 (s, 2 H). ^{13}C NMR (D_2O): δ 179.63, 137.11, 81.67, 48.21, 25.58.

General Polymerization Procedure. In a typical polymerization the monomer (1, 1.09 g, 6.07 mmol), catalyst (2, 22 mg, 0.04 mmol), and a magnetic stirbar were degassed as solids in a Schlenk flask for 1 h. Degassed water or a water/ethanol solution (15 mL) was added with syringe to the Schlenk flask through a septum under argon. The reaction mixture was allowed to stir for 1 h under argon. The flask was then placed in a oil bath at 55–60 °C under argon. A white precipitate formed after 3–5 min. After 3 h, the flask was removed from the oil bath, and the polymer was filtered through a glass frit and washed with water and then acetone. The polymer was then dried under dynamic vacuum overnight at room temperature. Poly-1 can be purified by dissolution in methylene chloride and precipitation from methanol. Yields ranged from 85 to 98%. ^{1}H NMR ($CDCl_3$): δ 6.03 (bs), 5.78 (bs), 4.97 (bs), 4.47 (bs), 3.33 (bs), 2.96 (bs). ^{13}C NMR (CD_2Cl_2): δ 176.09, 132.81, 131.48, 81.14, 77.49, 52.85, 25.22.

Hydrogenation of Poly-1 Employing Crabtree's Catalyst.[24] In a typical hydrogenation experiment, poly-1 was dissolved in methylene chloride in a flask equipped with a Teflon seal and degassed via freeze–pump–thaw cycles. Crabtree's catalyst, $[Ir(COD)(PCy_3)(py)]^+PF_6^-$, was introduced under argon in an amount such that the molar ratio of carbon–carbon double bonds to [Ir] was between 40 and 100. The solution was then stirred under an atmosphere of hydrogen at room temperature for 1 h. The polymer was precipitated from methanol and dried under dynamic vacuum overnight. The yield was greater than 90% in all cases. ^{1}H NMR ($CDCl_3$): δ 3.84 (bs), 3.11 (bs), 2.93 (bs), 1.92 (bs). ^{13}C NMR ($CDCl_3$): δ 176.27, 81.13, 80.91, 52.25, 31.69, 31.16, 30.86, 25.44, 24.87.

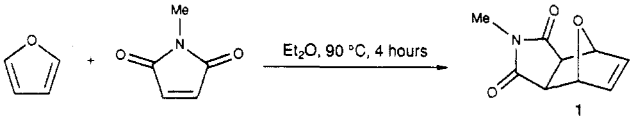

Figure 2. Preparation of 1.

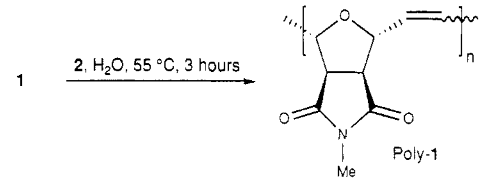

Figure 3. Polymerization of 1.

Exchange of Bound 1 for *N*-Methylmaleimide. In a small flask, 54 mg of 1 (0.30 mmol) was heated to 55 °C in 0.7 mL of D_2O in the presence of 6.7 mg of $Ru^{II}(H_2O)_6(tos)_2$ (0.01 mmol) under argon for 2.5 h. The polymer that formed was pushed down to the bottom of the flask, and the yellow polymerization solution was transferred with a pipet into an NMR tube. The ^{1}H NMR spectrum was acquired. *N*-Methylmaleimide (13 mg, 0.01 mmol, 1 equiv) was then introduced into the NMR tube, and the tube was placed in an oil bath at 55 °C for 30 min. The tube was removed and another ^{1}H NMR spectrum was acquired. This procedure was repeated after an additional 6.5 h in the oil bath. The initial olefin complex, 3, was completely converted into the *N*-methylmaleimide complex. The chemical shifts of 3 and Ru–*N*-methylmaleimide are as follows: 3, ^{1}H NMR (D_2O) δ 2.78 (s, 2 H), 3.59 (s, 3 H), 5.08 (s, 2 H), 5.19 (s, 2 H); Ru–*N*-methylmaleimide, ^{1}H NMR (D_2O) δ 2.55 (s, 2 H), 5.97 (s, 2 H).

Results and Discussion

The ROMP of carboximide-functionalized norbornenes has been independently investigated, and the polymers obtained possessed high T_g's, high thermal resistances, and good mechanical properties.[25,26] In one case, however, only a 7% yield was reported for the polymer obtained from the polymerization of the Diels–Alder adduct of cyclopentadiene and *N*-propylmaleimide employing a classical tungsten-based metathesis catalyst.[25] The desirable properties of these carboximide-functionalized ROMP polymers in combination with the efficiency, mildness, and robust characteristics of the aqueous system mentioned above prompted this investigation of the polymerization of carboximide-functionalized 7-oxanorbornenes.[27]

Monomer Preparation. The Diels–Alder adduct of furan and *N*-methylmaleimide, *exo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (1), was easily prepared by combining furan and *N*-methylmaleimide in diethyl ether, degassing the reaction mixture, and heating to 90 °C for 4 h in a glass tube (Figure 2). The product (1) crystallized from the reation upon cooling and was isolated in 95% yield. The reaction was conducted on a multigram scale, and the white crystalline material was stored at room temperature, under air, for several months with no detectable decomposition. Monomer 1 can be recrystallized from water or ethyl acetate. However, the as-synthesized material was of high purity as determined by ^{1}H NMR spectroscopy and was polymerized without further manipulation. The adduct formed is entirely the exo isomer, as determined by ^{1}H and ^{13}C NMR spectroscopy.[28,29] The endo isomer can be synthesized at lower temperatures and subsequently isomerized to the exo isomer by heating to 90 °C in the presence of excess furan.

Polymerization Procedure. The polymerization of 1 was conducted in pure water or water/ethanol solutions at 55–60 °C employing $Ru^{II}(H_2O)_6(tos)_2$[22,23] (2) as the catalyst (Figure 3). Complex 2 was the most active catalyst for this polymerization and was used throughout the study

($RuCl_3$ and K_2RuCl_5 were also effective catalysts for the polymerization of 1 but had longer initiation times). The general polymerization procedure consisted of adding either degassed ethanol/water (1:1 (v/v)) or pure water to a mixture of 1 and 2 under argon (typically, [monomer] $\approx$ 0.4 M and [Ru] $\approx$ 0.003 M). The reaction was heated to 55–60 °C in an oil bath for 3 h. As the monomer dissolved, the polymerization solution turned yellow, consistent with the formation of a ruthenium–olefin complex.[17,30] Within 3–5 min polymer (poly-1) particles began to precipitate from the solution, and immediately thereafter the reaction flask became filled with polymer. After 3 h the polymer was filtered, washed with water and acetone, and dried. The crude yield of the off-white polymer was between 85 and 98% in all cases.

The polymerization can be achieved under air without any degassing of the solvents;[31] however, there was a marked effect of oxygen on the molecular weight of the resultant polymer. When the polymerization was run under rigorously oxygen-free conditions, the polymer formed had a molecular weight average triple that of the polymer obtained from a nondegassed solution. When water that had been sparged with oxygen was used in the polymerization, no poly-1 was formed, and the resulting polymerization solution became dark green. This color is presumably due to oxidation of the ruthenium to an inactive oxidation state for polymerization. This supports the claim that ruthenium(II) is the necessary oxidation state for catalyst initiation.[17,18] The exact role that oxygen plays in the polymerization mechanism is not fully understood.[32]

Polymer Characterization. Poly-1 is a white, flocculent solid that is soluble in methylene chloride, chloroform, DMF, and DMSO and can be cast into tough films from these solutions. Poly-1 was purified by dissolution in methylene chloride and precipitation from methanol. It was stable for months under air at room temperature as evidenced by no change in its molecular weight, solubility, polydispersity index (PDI), and ^1H NMR spectrum. In contrast, polynorbornenes and other poly(alkenylene)s undergo radical-induced cross-linking reactions under air in the absence of a stabilizer.[33] The ^1H and ^{13}C NMR spectra of poly-1 are consistent with the unsaturated polymer backbone of ROMP polymers. The ^1H NMR spectrum is shown in Figure 4. Both cis and trans resonances are observed for the the olefinic protons and the allylic protons. The backbone double bonds are predominantly trans (80%), as determined by integration of the olefinic region of the ^1H NMR spectrum of poly-1, and initial investigations show that the polymer is essentially atactic (see below). The IR spectrum of poly-1 shows characteristic absorptions for the imide carbonyl stretch (1779 cm^{-1}) as well as the olefinic C–H bend (970 cm^{-1}). All of the polymer samples synthesized were of high molecular weight. The M_w, as determined by gel permeation chromatography (GPC) using polystyrene standards, of the polymer samples prepared ranged from 200 000 to 1 000 000, and the PDI ranged from 1.7 to 4.5.[34]

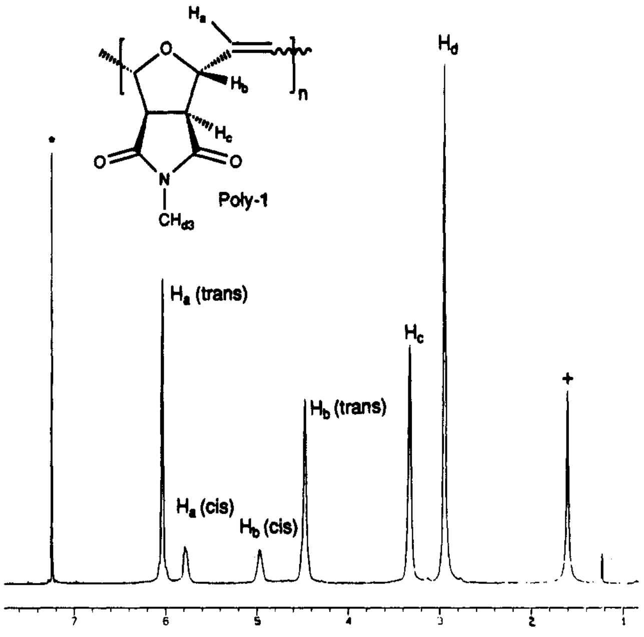

Figure 4. ^1H NMR spectrum of poly-1 ((*) solvent; (+) H_2O impurity).

The thermal properties of poly-1 are of interest since it has been reported that the norbornene analogue of poly-1 exhibits a high glass transition temperature (T_g).[25,26] Initial differential scanning calorimetry (DSC) results showed that poly-1 undergoes an irreversible exothermic reaction between 230 and 260 °C under argon, and no T_g or melting point was observed before the onset of the exotherm or during repeated scans. In a melting point apparatus, an abrupt change in the color of poly-1 from white to yellow was observed between 245 and 255 °C, and the yellow polymer was no longer soluble in the solvents previously mentioned. The exothermic transition between 230 and 260 °C, the insolubility of the resultant polymer, and the change in color were presumably due to a thermally induced cross-linking reaction. However, when poly-1 was rigorously purified by dissolution in methylene chloride and precipitation in methanol three times, dried under dynamic vacuum overnight, and then heated to 230 °C at a scanning rate of 20 °C/min, a T_g was observed at 225 °C. The T_g was seen upon cooling the sample and reheating, but the heat capacity per gram of polymer decreased with every cycle, the characteristic "step" became broader, and the inflection point moved to higher temperatures. Thermal mechanical analysis of a thin film of poly-1 shows a softening temperature around 210 °C and corroborated the value of the T_g as determined by DSC. These results indicated that poly-1 has a high T_g (225 °C), but at temperatures close to the T_g the polymer undergoes a degradative process believed to be cross-linking of the polymer backbone. The temperature at which this cross-linking reaction occurred was dependent on the purity of the sample tested. Trace amounts of ruthenium may have catalyzed decomposition of the polymer sample prior to or around the glass transition temperature.

As mentioned previously, poly-1 was stable under air for months at room temperature. The temperature at the onset of substantial mass loss (T_d) for poly-1 under an argon atmosphere was determined by thermogravimetric analysis (TGA) to be 402 °C (Figure 5). The T_d dropped to 373 °C under an atmosphere of air. Isothermal aging of the poly-1 was also performed, and the percent weight loss over a 4-h period, at three temperatures, under both argon and air was determined. These results are summarized in Table I. Poly-1 underwent substantial weight loss under air at both 300 and 350 °C, but at 250 and 300 °C under argon the polymer lost less than 1% of its mass. This observation is in accordance with the supposition that the polymer undergoes cross-linking at 250 and 300 °C under argon, but decomposition with concomitant loss of small molecules is not occurring at these temperatures.

The susceptibility of poly-1 to cross-linking reactions upon exposure to ultraviolet (UV) radiation was investigated. Since poly-1 could easily be cast into a film, examination of the change in the infrared (IR) spectrum

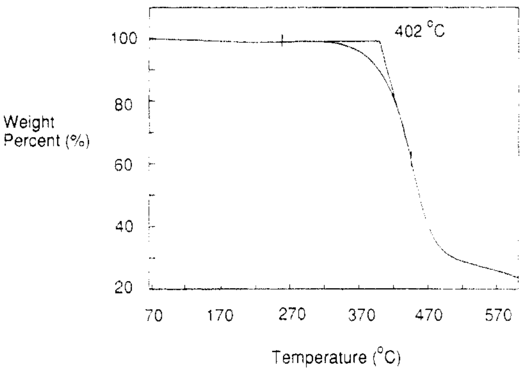

Figure 5. Thermogravimetric analysis of poly-1 under argon.

Table I
Isothermal Aging of Poly-1 under Argon and Air at 250, 300, and 350 °C

sample	temp (°C)	atmosphere	% wt remaining after 4 h
1	250	argon	99
2	300	argon	99
3	350	argon	92
4	250	air	97
5	300	air	90
6	350	air	78

of the polymer over time upon exposure to UV radiation was an effective means of investigating cross-linking in the polymer sample. The polymer was cast into a thin film and mounted in a homemade IR cell. The IR spectrum of the polymer film was taken, and the film was then mounted in a photolysis box and subjected to a UV lamp. The IR spectrum showed a general broadening of absorptions over time. The transoid carbon–carbon double-bond stretch at 965 cm^{-1} diminished, and the aliphatic C–H bending region became broader and more intense. This region is shown in Figure 6. After 18.5 h the polymer film changed from colorless to dull yellow and became extremely brittle and insoluble. These results suggest that cross-linking occurred upon exposure to UV light, and the polymer lost it structural integrity. A thin film of poly-1 exposed to sunlight for a few weeks also became slightly yellow and tore much more easily than a film stored in the dark.

Polymer Hydrogenation. Hydrogenation of poly(alkenylene)s is a useful method for generating new products and for increasing the oxidative and thermal stability of polymers.[35-37] The hydrogenation of poly-1 was explored using both catalytic and stoichiometric hydrogenation methods. Limited success was obtained using diimide (generated from the decomposition of *p*-toluenesulfonhydrazide at 110 °C in DMF) as a stoichiometric hydrogenation method. The resultant products were sparingly soluble or insoluble and therefore difficult to characterize. Catalytic hydrogenation of poly-1 was more successful. Partial hydrogenation was accomplished at room temperature using Wilkinson's catalyst, $[RhCl(PPh_3)_3]$,[38] under a flow of hydrogen, and complete hydrogenation, as determined by lack of olefinic resonances in the ^{1}H NMR spectrum, of poly-1 was achieved using Crabtree's catalyst, $[Ir(\eta\text{-}1,5\text{-cyclooctadiene})(PCy_3)(py)]^+PF_6^-$,[24] at room temperature under a hydrogen atmosphere (Figure 7). A ratio of double-bond concentration to catalyst concentration of 100 was necessary for complete hydrogenation (ratios greater than this result in only partial hydrogenation).

Hydrogenated poly-1 was a white solid that could be cast into tough films that were more flexible than their unsaturated counterparts. The totally hydrogenated samples had GPC chromatographs similar to those obtained for the unsaturated analogues. Hydrogenated poly-1 had a T_g of 170 °C and a T_d of 430 °C. In fact, all of the partially hydrogenated samples had lower T_g's and higher T_d's than poly-1. The decrease in the T_g was interpreted as an increase in the flexibility of the polymer backbone upon hydrogenation. The increase in the T_d of hydrogenated poly-1 suggests that the initial decomposition process in poly-1 involved chemistry at the carbon–carbon double bond. Unlike the DSC trace of poly-1, the DSC trace of hydrogenated poly-1 showed no thermal transition other than a T_g below 350 °C, and the polymer did not change color upon heating to 300 °C. Analysis of the ^{13}C NMR spectrum of hydrogenated poly-1 indicated that the polymer is essentially atactic. This observation was not surprising since the lability of water ligated to the ruthenium(II) metal center offers more than one site for the incoming olefin to react with the propagating carbene. Thus, the polymerization becomes random with respect to stereoregularity along the polymer backbone. Similar results have been obtained for the polymerization of other 7-oxanorbornenes employing 2 as the catalyst.[39]

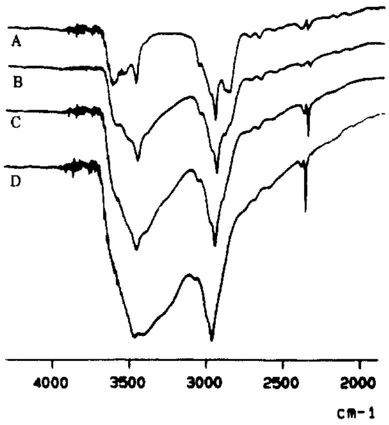

Figure 6. IR spectrum over time of a poly-1 film exposed to UV radiation: (A) initial: (B) 1 h; (C) 4 h; (D) 18.5 h.

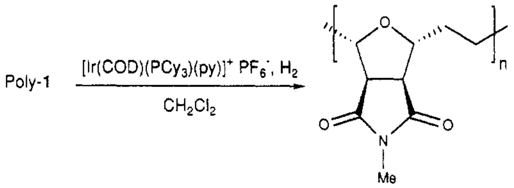

Figure 7. Hydrogenation of poly-1 using $[Ir(\eta\text{-}1,5\text{-cyclooctadiene})(PCy_3)(py)]^+PF_6^-$.

Polymerization Catalysis. In the aqueous polymerizations we reported earlier,[17] a ruthenium–monomer olefin complex was observed by NMR spectroscopy in the polymerization solution. These monomer complexes were reported to be highly active catalysts for subsequent polymerizations and were shown to be recyclable. In the present case of the aqueous polymerization of 1, a ruthenium-1 complex (3) was also characterized in the polymerization solution (Figure 8). Approximately 70% of the initial $Ru^{II}(H_2O)_6(tos)_2$ was converted to 3 as determined by ^{1}H NMR spectroscopy. Polymerization solutions containing 3 proved to be active polymerization catalysts and can be recycled for the catalysis of subsequent polymerizations. Olefin complexes of this type were prepared for other derivatives of 1, including *exo*-*N*-phenyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (4) and the endo isomer of 1. However, neither the endo isomer of 1 nor 4 polymerized under the conditions described above. It was discovered that both of these compounds

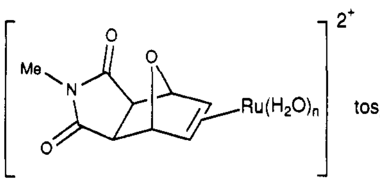

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Figure 8. Olefin complex (**3**) observed in the polymerization solution.

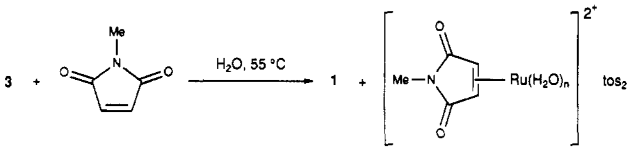

Figure 9. Exchange of **3** with *N*-methylmaleimide.

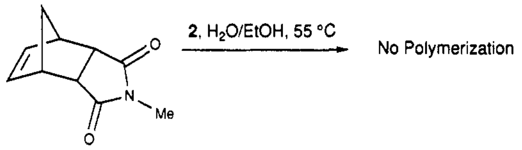

Figure 10. Attempted polymerization of **5**.

undergo an endo–exo isomerization at the polymerization temperature. The formation of free maleimides in solution is a result of this isomerization. Maleimides are excellent π acceptors[40] capable of forming strong olefin complexes with the ruthenium(II) metal center, and, consequently, in the attempted polymerization of the endo isomer of **1** a 1:1 ruthenium(II)–*N*-methylmaleimide complex formed and no polymer was isolated. The analogous *N*-phenylmaleimide complex was also observed during the unsuccessful polymerization of **4**. The lack of reactivity of *endo*-**1** and **4** was attributed to the facile retro Diels–Alder chemistry at the polymerization temperature. The role of maleimides as catalyst poisons was further substantiated by the failure of **1** to polymerize in the presence of *N*-methylmaleimide. The polymerization solution did become yellow, suggestive of an olefin complex formation. This species was identified as a 1:1 ruthenium(II)–*N*-methylmaleimide complex by ^{1}H NMR spectroscopy and cyclic voltammetry. Also, in an NMR experiment it was observed that *N*-methylmaleimide quantitatively displaced **1** from the olefin complex **3** at 55 °C (Figure 9). If a ruthenium–**1** olefin complex is on the pathway to an initiating species for the polymerization, the presence of maleimides effectively eliminates catalyst activation.

The endo isomer of **1** was the kinetic product of the Diels–Alder reaction of furan and *N*-methylmaleimide, and the isomerization to the thermodynamic exo isomer occurred at the polymerization temperature. The kinetic isomer in the Diels–Alder addition of cyclopentadiene and *N*-methylmaleimide (**5**) was also the endo isomer. Although **5** was stable toward retro Diels–Alder chemistry at the polymerization temperature of 55–60 °C, it did not polymerize under the typical polymerization conditions (Figure 10). The inertness of endo isomers toward ROMP employing late transition metal catalysts has previously been reported.[4,5] Two explanations for this lack of reactivity have been suggested: (1) chelation of the catalyst by the olefin and the endo functionality and (2) the steric restrictions due to transannular crowding of the four cis substituents on the five-membered ring in the repeat unit. In the case of the endo isomer of **1**, however, the lack of reactivity may also be attributed to the poisoning of the catalyst by *N*-methylmaleimide.

Conclusions

The scope of the aqueous ruthenium polymerization system was expanded to include the polymerization of carboximide-functionalized 7-oxanorbornenes. In the case of **1**, the polymerization was accomplished under mild conditions using a simple ruthenium(II) catalyst to yield high molecular weight polymer in near-quantitative yields. The resultant polymer possessed a high degree of thermal and oxidative stability as well as a high glass transition temperature. Catalytic hydrogenation of poly-**1** yielded its saturated analogue, which had a higher decomposition temperature and a lower glass transition temperature than the parent polymer. Furthermore, it was determined that a requirement for the successful polymerization of carboximide-functionalized substrates is that they be stable toward retro Diels–Alder chemistry, since the presence of maleimides in the polymerization solution poisons the catalyst by forming a stable maleimide complex. Further studies of the chemistry of this type of ruthenium–olefin complex[30] and the extension of this polymerization system to the preparation of other functionalized polymers are currently being investigated in our group.

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