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Electrochemically generated tungsten-based active species as catalysts for metathesis-related reactions: 1. Acyclic diene metathesis polymerization of 1,9-decadiene

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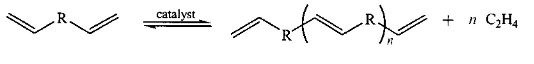
The application of the WCl_6–e^-–Al–CH_2Cl_2 system to acyclic diene metathesis polymerization of 1,9-decadiene is reported. The polyoctenamer formed is of a weight-average molecular weight of 9000 with a polydispersity of 1.92. IR and NMR spectral analyses indicate the retention of the double bonds in the polymer structure with high trans content as expected from a step condensation reaction. This relatively stable catalytic system, however, also activates the competing vinyl addition reactions while being inactive in ring-closure metathesis reactions. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: ADMET; metathesis; catalyst; WCl_6; 1,9-decadiene; polymerization; electrochemistry

INTRODUCTION

Intermolecular olefin metathesis reactions leading to high molecular weight step polymers and copolymers *via* olefin condensation are known as acyclic diene metathesis (ADMET) polymerizations (Eqn. (1)). This class of polymerization reactions has been well established and comprehensively studied by the Wagener group.[1–6] ADMET polymerization has also been a convenient route to linear polymers containing inorganic elements and functional groups for the preparation of new materials.[7]



(1)

ADMET chemistry requires the use of a Lewis-acid-free catalyst and eliminates competing side reactions like vinyl addition,[2] excluding trace amounts of cyclic products resulting from ring-closure metathesis (RCM) reactions. Most of the ADMET polymerization reactions have been accomplished using:

(i) the highly active Schrock's alkylidene catalysts of the type M(CHR′)(NAr)(OR)$_2$, where M = W[8] or M = Mo,[9] Ar = 2,6-C_6H_3-i-Pr_2, R′ = CMe_2Ph, R = CMe(CF)$_3$;
(ii) the less active, but more stable, Grubbs' ruthenium catalyst, $RuCl_2(=CHPh)(PCy_3)$;[10]
(iii) less commonly, the tungsten-based classical catalysts.[1,11] With carbene initiators, high polymers are obtained, whereas catalysts based on WCl_6 and Re_2O_7 give only low molecular weight products.

We now report the synthesis of unsaturated ADMET polymers catalyzed by active tungsten species generated electrochemically. It was first reported that the electrochemical reduction of transition metal salts, such as WCl_6 and $MoCl_5$, under controlled potential at a platinum cathode with an aluminum anode, results in the formation of stable and active olefin metathesis catalysts.[12] A subsequent report has demonstrated the crucial roles of the aluminum anode and the chlorinated solvent, CH_2Cl_2, in this electrochemical system.[13] Although the exact structure is not presently known, the active catalyst involves the metal in a high oxidation state, as confirmed by electron spectroscopy for chemical analysis and electron spin resonance studies[13] (and unpublished results). A careful analysis of the early products in olefin metathesis reactions within the WCl_6 ($MoCl_5$)–e^-–Al–CH_2Cl_2 system suggested the *in situ* formation of M=CH_2 initiators, and this assumption was further supported by injecting benzaldehyde as a carbene trap and by applying the ^{13}C NMR technique to detect the carbenic structure[13] (and unpublished results). However, questions remain as to the mechanism of the formation of the initial carbene.

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These stable and active catalysts have been reported to catalyze the normal metathesis of α- and β-olefins.[13] Continuing research within our group has verified the activity of this novel catalyst system not only in the metathesis of acyclic olefins, but also in other metathesis-related reactions (unpublished results). This study describes the application of the WCl_6–e^-–Al–CH_2Cl_2 system to the ADMET polymerization of 1,9-decadiene for the first time.

EXPERIMENTAL

Materials

Dienes were obtained from Aldrich and purified by refluxing over KOH followed by distillation over CaH_2 under nitrogen atmosphere. WCl_6 (Aldrich) was purified by sublimation at 220 °C under nitrogen to remove the more volatile WO_2Cl_2 and $WClO_4$ impurities. Dichloromethane (Merck, $\varepsilon = 9.1$) was first washed with concentrated H_2SO_4 until the acid was colorless, then in turn with water, an aqueous solution of NaOH (5% w/w) and water again. After drying over anhydrous $CaCl_2$ it was then distilled over P_2O_5 under nitrogen. THF and MeOH were supplied from Merck and used as received.

Electrochemical instrumentation

The electrochemical equipment consisted of a POS Model 88 potentiostat and EVI 80 Model voltage integrator (coulometer). The measurements were carried out under nitrogen atmosphere in a three-electrode cell having a jacket through which water from a constant-temperature bath was circulated. Exhaustive controlled-potential experiments were carried out in an undivided cell with a macro working platinum foil electrode ($2\ cm^2$) and a aluminum foil ($2\ cm^2$) counter electrode. The reference electrode consisted of AgCl coated on a silver wire in CH_2Cl_2/0.1 N tetra-*n*-butyl ammonium tetrafluoroborate ($TBABF_4$), which was separated from the electrolysis solution by a sintered glass disc. Electrolysis was carried out without the supporting electrolyte due to its deleterious effect on the catalyst system. For this reason, the distance between platinum working and aluminum counter electrode was kept constant and as small as possible (i.e. 2.0 mm) in order to keep the solution resistance to a minimum.

Preparation of catalyst

All operations were performed under pure and dry nitrogen. WCl_6 (0.2 g, 0.50 mmol) was introduced into the electrochemical cell containing CH_2Cl_2 (20 ml) and a red solution was observed. Reductive electrolysis at 0.9 V was applied[13] to the red solution. The color of the solution darkened progressively. Aliquots from this catalytic solution were used in polymerization reactions and optimum electrolysis time was determined as 3 h, where the highest percentage conversion to the polymer was obtained.

Polymerization reactions

All reactions were initiated in the bulk, at room temperature and under dry nitrogen atmosphere. Molecular weights were experimentally controlled by varying the monomer/catalyst ratio and reaction time. Reaction combinations ranged from 30:1 to 600:1 and 4 to 32 h . A typical reaction was as follows: 1 ml of the catalytic solution was taken with an automatic pipette from the cell and added to the monomer (0.20 g) in a Schlenk tube containing a magnetic stir bar. A rapid gelation was observed and stirring was continued until prevented by the viscosity increase. The reaction was quenched by methanol addition after 24 h to obtain 1,9-decadiene. The polymers formed were washed with methanol, dissolved in THF and reprecipitated with methanol to remove the catalytic residues, dried and weighed. Percentage conversion of the monomer to the polymer was defined on a weight basis.

Characterization

IR spectra were obtained from KBr pellets prepared by grinding the polymer; using a Mattson 1000 FTIR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker GmbH 400 MHz high-performance digital FT-NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane as the reference. Mass spectroscopic data were obtained using a Shimadzu GCMS-QP5050*A* instrument. Gel permeation chromatography (GPC) data were obtained using a Shimadzu LC-10AD*VP* liquid chromatograph equipped with a Shimadzu SPD-10A*VP* UV detector, relative to polystyrene standards. Samples were prepared in THF as eluent and passed through a μ-styragel column. A constant flow rate of $1\ ml\ min^{-1}$ was maintained at 25 °C.

RESULTS AND DISCUSSION

1,9-Decadiene was selected as a model monomer since its polymers (polyoctenamers) obtained *via* on ADMET process by other catalysts have been well-characterized.[1,2,4,6,14,15] To optimize the reaction conditions, several experiments were performed using different catalyst ratios to obtain high molecular weight polymer samples in the shortest possible electrolysis time and reaction time. The results shown in Table 1 summarize the optimum conditions for high conversion to polyoctenamer in comparison with those reported using other catalytic systems. The polymer obtained with the WCl_6–e^-–Al–CH_2Cl_2 system was characterized by IR, NMR and GPC techniques. The lower molecular weight fraction was soluble in THF, whereas the higher molecular weight fraction displayed very poor solubility in common organic solvents; GPC performed in THF allowed determination of $\overline{M}_n = 4700$ and $\overline{M}_w = 9000$ according to polystyrene calibration. Molecular weights of this order of magnitude are relatively lower than expected by ADMET-type polymerizations. It appears that inefficient stirring due to increased viscosity prevents the formation of

Table 1. ADMET polymerization of 1,9-decadiene (in bulk)

Catalyst	Monomer/ catalyst	Reaction time (h)	Temp (°C)	Conversion (%)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Ref.
WCl_6–e^-–Al–CH_2Cl_2[a]	58	24	25	86	9000[b]	4700[b]	1.92	This work
W-alkylidene	500	32	25	>95	–	2000[c]	–	2
W-alkylidene	11	32	25	–	108 000[d]	57 000[d]	1.89	4
Ru-alkylidene	1000	69	70	–	–	3300[b]	2.3	16
Ru-alkylidene	400	26	70	–	–	21 000[b]	3.8	16

[a] Generated after 3 h of electrolysis time.
[b] Determined by GPC (calibration with polystyrene standards).
[c] Determined by ^{13}C NMR (from the end-groups).
[d] Determined by size-exclusion chromatography (calibration with polybutadiene or polystyrene standards).

high molecular weight samples. A second factor might be the accompanying vinyl addition reactions leading to the formation of cross-linked, insoluble polymer as a side product. However, the polydispersity index (1.92) approaching 2.0 indicates that the soluble polymer was formed by an equilibrium step polymerization reaction.

Other important characteristics of ADMET polymerization are the evolution of ethylene and the presence of internal olefin signals in the IR and NMR spectra. Though we did not attempt to detect ethylene, the spectral correlations between the monomer and the polymer showed the loss of terminal olefin groups of the monomer with retention of the internal double bond character in the product. A comparison of the IR spectra of 1,9-decadiene and its polymer shows the virtual disappearance of the monomer's terminal absorption at 1640 cm^{-1} (C=C stretch) and appearance of the *trans*-CH wagging of the internal double bonds at 967 cm^{-1} (Fig. 1). The IR spectrum indicates that the polymer has a high trans content, since no significant peak at 1405 cm^{-1} due to in-plane bending of the *cis*-olefin units was observed. ^1H and ^{13}C NMR spectra also demonstrated the typical structure of a poly(octenamer) synthesized according to ADMET polymerization (Fig. 2). The spectral features are consistent with the data reported in the literature.[3,4] ^1H NMR spectra show

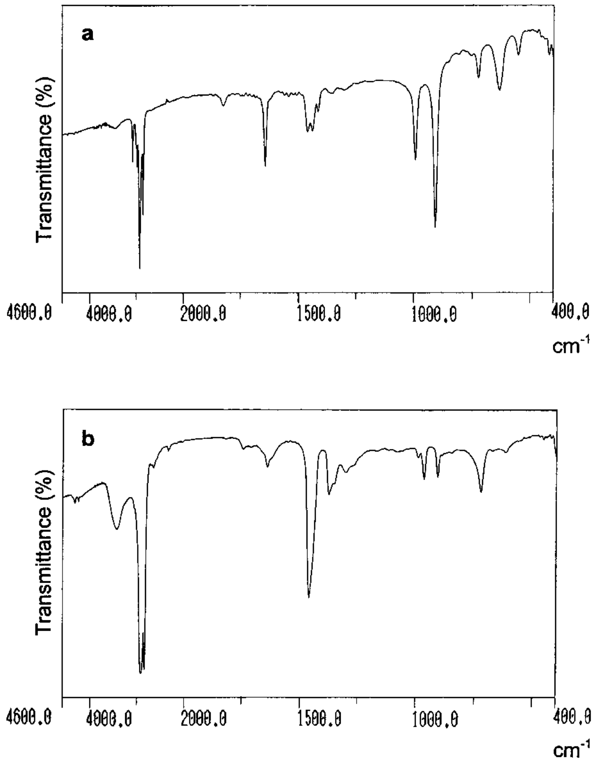


Figure 1. IR spectra of (a) before and (b) after polymerization of 1,9-decadiene.

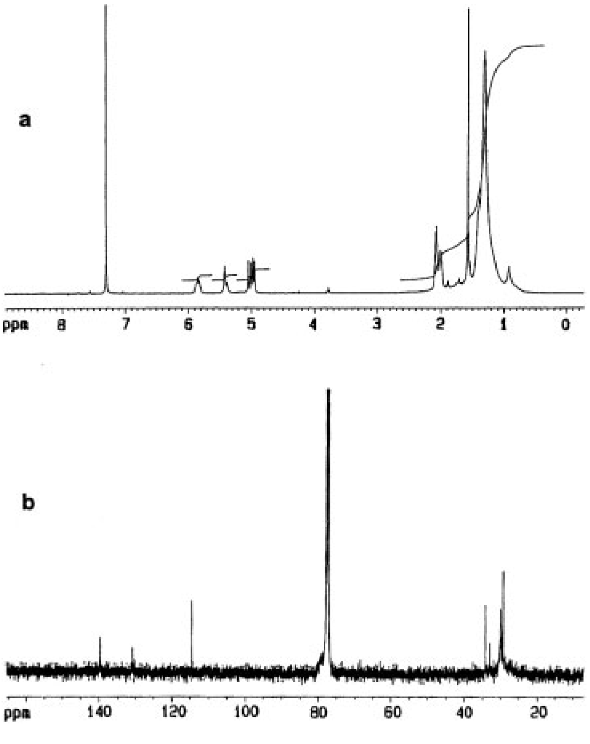
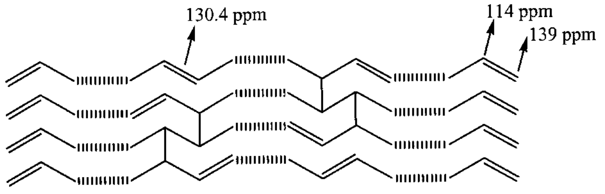


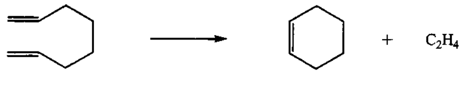
Figure 2. (a) ^1H NMR and (b) ^{13}C NMR spectra of poly(octenamer) obtained by the polymerization of 1,9-decadiene.



Scheme 1. The soluble fraction of the polyoctenamer.

signals in both the olefinic region ($\delta = 5.0$–6.0 ppm) and in the alkyl region ($\delta = 1.0$–3.0 ppm), where terminal vinyl methine proton (5.10 ppm), internal olefinic proton (5.35 ppm) , terminal vinyl methylene proton (5.85 ppm) and methylene proton signals (1.25 and 2.00 ppm) can be clearly visualized. The sp^2 region (129–131 ppm) in the ^{13}C NMR spectrum confirms the retention of the C=C bonds during polymerization. The two signals at 129.8 ppm and 130.4 ppm refer to *cis* and *trans* internal olefinic carbon atoms respectively. Based on the intensities of these peaks, the polymer is assigned to have a higher percentage of trans stereochemistry in accord with the IR observations. Although the ^{13}C NMR spectrum in the double bond region is as expected for a poly(octenamer), carbon resonances at 114 ppm (terminal methine) and 139 ppm (terminal methylene) also exist, indicating that some addition chemistry proceeds as well. Vinyl addition reactions through which the polymer chains are cross-linked to each other are known to be catalyzed by the Lewis acid cocatalysts of the classical systems. This difficulty has been offset a great deal by introducing a Lewis base, like propyl acetate, as the third component,[17] or by using aryloxy tungsten catalysts,[18] while eliminating the solvent. In this way, soluble, linear polymers can be synthesized. The $AlCl_3$ cocatalyst, produced by an electrode reduction during the reduction of WCl_6,[13] possibly promotes the vinyl addition reactions in this work. Considerable cross-linking results in the formation of an intractable fraction, whereas a smaller degree of cross-linking between shorter chains gives rise to a soluble polymer as described in Scheme 1 and as characterized by the ^{13}C NMR analysis.

A second type of side reaction in the ADMET polymerization of dienes is the ring closure reaction. In order to investigate the catalytic activity of the WCl_6–e^-–Al–CH_2Cl_2 system in RCM reactions we have repeated the polymerization experiments under the same conditions using 1,7-octadiene as the monomer, since its RCM produces a six-membered ring and is highly selective (Eqn. (2)).



(2)

The gas chromatography–mass spectrometry (GC–MS) analysis of the filtrate obtained after the polymerization of 1,7-octadiene showed minor quantities of cyclohexene and other cyclic products (chlorinated and alkylated cyclohexanes). When compared with the Re_2O_7–Al_2O_3–$CsNO_3$ system, which yields cyclohexene with 99% yield,[19] the electrochemically generated tungsten species are not very active towards RCM reactions. GC–MS analysis of the filtrate from the reaction mixture of 1,9-decadiene displayed almost no traces of cyclic compounds. The reasons for the RCM inactivity of the catalyst are unknown at this stage.

CONCLUSIONS

In this study, electrochemically generated tungsten-based active species have been demonstrated as novel catalysts for ADMET polymerization reactions. The system also catalyzes competing vinyl addition cross-linking reactions, possibly by *in situ* formed $AlCl_3$, as well as the desired metathesis reactions with low activity towards RCM reactions. Ongoing studies are aimed at the optimization of the reaction and application of the catalyst to other substrates or types of reaction. The ill-defined WCl_6–e^-–Al–CH_2Cl_2 system is distinguished from the well-known molybdenum and tungsten alkylidenes by being less sensitive to atmospheric oxygen and by retaining its activity for about 10 h, while the actual catalytically active species remain unknown.

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