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Electrochemically generated tungsten-based active species as catalysts for metathesis-related reactions: 2. Ring-opening metathesis polymerization of norbornene

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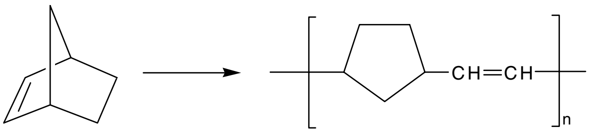
The present work reports the application of the WCl_6–e^-–Al–CH_2Cl_2 catalyst system to the ring-opening metathesis polymerization of norbornene. Analysis of the polynorbornene microstructure by means of ^1H and ^{13}C NMR spectroscopy indicates that the polymer contains a mainly cis stereoconfiguration of the double bonds ($\sigma_c = 0.61$) and a blocky distribution ($r_t r_c > 1$) of cis and trans double bonds ($r_t r_c = 3.37$). This catalytic system is reluctant to facilitate the competing addition reactions of cycloalkenes while proceeding with the polymerization reactions with good conversions and at short periods. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ring opening; metathesis; catalyst; WCl_6; norbornene; cyclic olefins; polymerization; electrochemistry

INTRODUCTION

The polymerization of norbornene is an active area of research because the microstructure of polynorbornene can provide useful insight into the mechanism of ring-opening metathesis polymerization (ROMP) reactions (Eqn 1). There are numerous studies involving the application of a wide range of different catalyst systems in the ROMP of norbornene. The variability of catalysts extending from the classical catalyst systems[1–11] to the well-defined initiators developed by Grubbs and co-workers[12–15] and Schrock and co-workers[16–20] allows the use of ROMP in the synthesis of polymers with novel topologies.



Current work in our group has been focused on the application of electrochemically generated tungsten-based active species in the catalysis of metathesis-related reactions. It was first reported by Gilet *et al.*[21] that the electroreduction of WCl_6 and $MoCl_5$ produces metathetically active species. The mechanism is thought to arise from *in situ* generated M=CH_2 initiators.[22] A recent study reveals the crucial role of WCl_5^+ as the only possible active species in the WCl_6–e^-–Al–CH_2Cl_2 system to produce the initial carbene by a 1,2-hydride shift following complexation with the olefin.[23]

We have previously reported the acyclic diene metathesis (ADMET) polymerization of 1,9-decadiene[24] and cross-metathesis of non-functionalized olefins[25] using this catalytic system. The present work demonstrates that the WCl_6–e^-–Al–CH_2Cl_2 system is also a convenient catalyst for the ROMP of norbornene.

EXPERIMENTAL

Materials

WCl_6 (Aldrich) was purified by sublimation at 220 °C under nitrogen to remove the more volatile WO_2Cl_2 and $WOCl_4$ impurities. Norbornene was supplied from Aldrich and used as received. Dichloromethane (Merck, $\epsilon = 9.1$) was first washed with concentrated H_2SO_4 until the acid was colorless,

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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. Tetrahydrofuran (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 an aluminum foil ($2\ cm^2$) counter electrode. The reference electrode consisted of AgCl coated on a silver wire in CH_2Cl_2–0.1 M 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[22] to the red solution. The color of the solution darkened progressively. Aliquots from this catalytic solution were used in polymerization reactions.

Polymerization reactions

All reactions were initiated in the solution, at room temperature and under dry nitrogen atmosphere. To optimize the reaction conditions, a series of experiments were performed by varying the olefin/catalyst ratio (30 : 1 to 300 : 1), reaction time (1 to 30 min) and electrolysis time (30 min to 3 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 norbornene (0.30 g, in 1 ml of dichloromethane) 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 30 min. The polymers formed were washed with methanol, dissolved in THF and reprecipitated with methanol to remove the catalytic residues, dried and weighed. Polymerization yield (%) was defined by comparing the weight of the polymer with the weight of the monomer used.

Characterization

^1H 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. 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 (0.5% w/v) 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

From the early stages of ROMP chemistry, it is generally accepted that ultimate conversions are not fully dependent on the activity of the catalyst. For a quantitative estimation of polymer yield, a series of polymerizations was performed at ambient temperature by varying the olefin/catalyst ratio. Conversion to polymer was obtained in maximum yield when the olefin/catalyst ratio was 125. After the addition of the catalyst to the monomer, maximum conversion was obtained in about 8 min.

Figures 1 and 2 show the influence of electrolysis time and catalyst aging on norbornene conversion. With prolonged electrolysis time, the concentration of the active catalyst formed during the electrolysis and conversion to the polymer increased and maximum conversion was obtained in 3 h of electrolysis time (Fig. 1). The catalyst formed during electrolysis was found to retain its activity when kept under nitrogen atmosphere. The activity towards ROMP of norbornene slowly diminished and was completely lost after 3 days (Fig. 2). The average rate of decrease in the polymerization yield is 1.5% for every 1 h passing for catalyst aging, which indirectly indicates the rate of the catalyst decay as well. More detailed kinetic studies about the stability of the catalyst are under consideration.

The polymers obtained with the WCl_6–e^-–Al–CH_2Cl_2 system were characterized by ^1H and ^{13}C NMR and GPC techniques. GPC performed in THF allowed determination of $\overline{M}_w = 47\,600$ and PDI = 3.14. A comparison with some catalyst systems applied in the ROMP of norbornene in terms

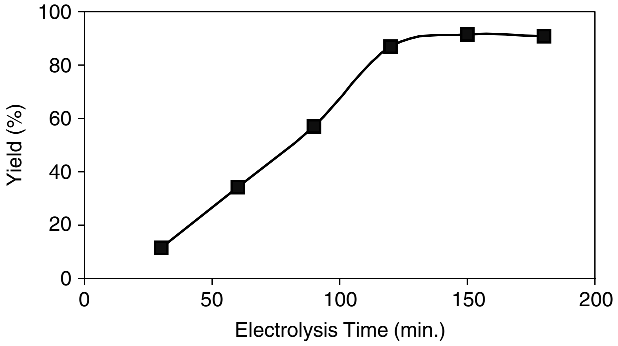

Figure 1. Effect of electrolysis time on norbornene conversion in CH_2Cl_2 at room temperature (olefin:catalyst = 125, catalyst = 0.025 mmol).

Table 1. ROMP of norbornene

Catalyst	Monomer/ catalyst	Reaction time	Temp. (°C)	Yield (%)	$\overline{M}_w$	Ref.
WCl_6–e^-–Al–CH_2Cl_2[a]	125	8 min	25	91	47 600[b]	This work
W-alkylidene	500	15 min	25	—	147 840[c]	26
W-alkylidene	25	10 min	~25	90	68 000[c]	27
Ru-alkylidene	100	1 h	~25	99	46 530[c]	15
Ti-initiator	100	8 h	70	—	23 875[c]	28
W-alkylidene	250	30 min	70	~100	—	29
W(II) complex	100	5 h	75	76	920 000[b]	30

[a] Generated after 3 h of electrolysis time.
[b] Determined by GPC (calibration with polystyrene standards).
[c] Calculated from the original $\overline{M}_n$ values determined by GPC.

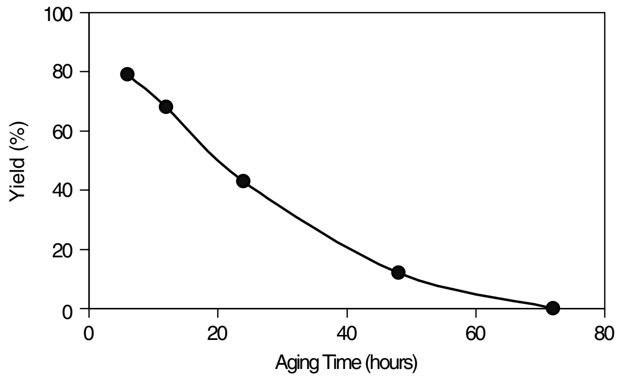

Figure 2. Effect of catalyst aging on norbornene conversion in CH_2Cl_2 at room temperature (olefin:catalyst = 125).

of polymerization conditions, polymer yield and molecular weight is given in Table 1.

The microstructure of the resulting polymer has been analyzed by its ^1H and ^{13}C NMR spectra and is consistent with analogs produced by other catalyst systems.[31–33]

The ^{13}C NMR spectrum (Fig. 3) consists of a group of olefinic carbon peaks ($\delta = 130$–135 ppm), and a group of upfield peaks ($\delta = 30$–50 ppm) due to the ring carbon atoms. The two multiplets corresponding to C^4 carbon centered at 134.26 ppm and 133.41 ppm refer to cis- and trans-olefinic carbon atoms respectively. A comparison of these two peaks related to C^4 carbon allows estimation of the cis stereoselectivity of this catalyst system. Since the C^2, C^1 and C^3 chemical shifts in the polymer are sensitive to the cis or trans configuration of the two nearest double bonds, a detailed analysis of the ^{13}C NMR spectrum provides a rich source of information concerning the microstructure of the polymer chain.[34–37] The relative proportions of double bond sequences, represented as trans–cis (tc), trans–trans (tt), cis–cis (cc) and cis–trans (ct) units were determined from the four methine carbon (C^2) signals at δ_c 43.71 (tc), 43.42 (tt), 38.95 (cc) and 38.74 (ct). Here, the chain carbon atoms that are located between two double bonds are labeled as cc, ct, tc or tt. The first letter denotes the cis or trans structure at the nearest double bond; the second letter, at the next nearest double bond. In this way, the reactivity ratios, r_t = tt/tc and

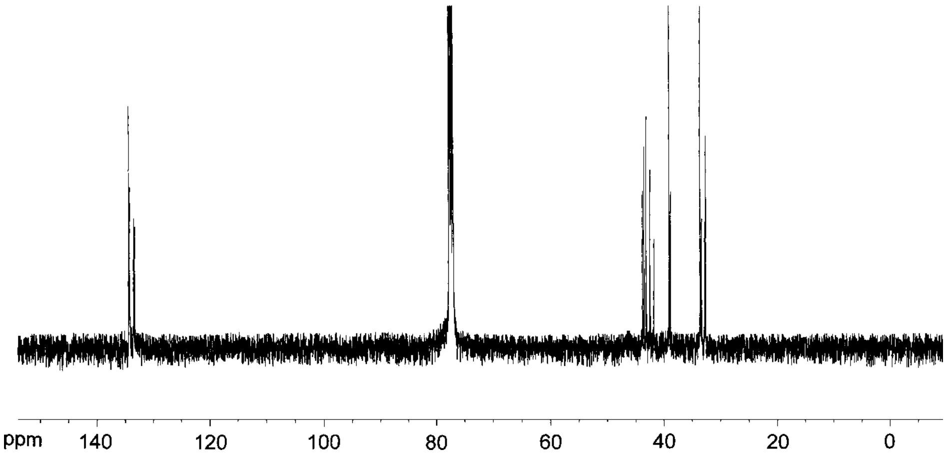

Figure 3. ^{13}C NMR spectrum of polynorbornene catalyzed by electrochemically generated active tungsten species (in $CDCl_3$).

r_c = cc/ct, were calculated as $r_t = 1.33$ and $r_c = 2.53$, giving an $r_t r_c$ value of 3.37. The fraction of cis-double bonds (σ_c) was estimated as 0.61 (average of four values derived from C^4, C^2, C^1 and C^3 signals; Fig. 4). The σ_c and $r_t r_c$ values thus obtained characterize a highly cis polymer with a blocky distribution of cis and trans structures since polymers having $\sigma_c = 0.35-0.85$ show a blocky distribution ($r_t r_c > 1$) while polymers with $\sigma_c < 0.35$ show a random distribution of cis and trans structures ($r_t r_c = 1$).[36,38]

The results obtained by ^{13}C NMR are consistent with the ^1H NMR spectrum shown in Fig. 5. The spectrum shows signals in both the olefinic region ($\delta = 5.0-6.0$ ppm) and in the alkyl region ($\delta = 1.0-3.0$ ppm). The fact that the polymer is mainly cis may also be visualized from its ^1H NMR spectrum, when the resonances at 5.23 ppm and 5.36 ppm, assigned respectively to the cis and trans ethylenic protons, were considered. The σ_c (ca 60%) calculated from the ^1H NMR spectrum agrees well with that obtained from the ^{13}C NMR. Additionally, the relative integrated peak areas of the two signals at 2.83 and 2.45 ppm, demonstrating the cis and trans protons attached to C^2 carbon in the cyclopentane ring, indicate a similar cis-content of the polymer.

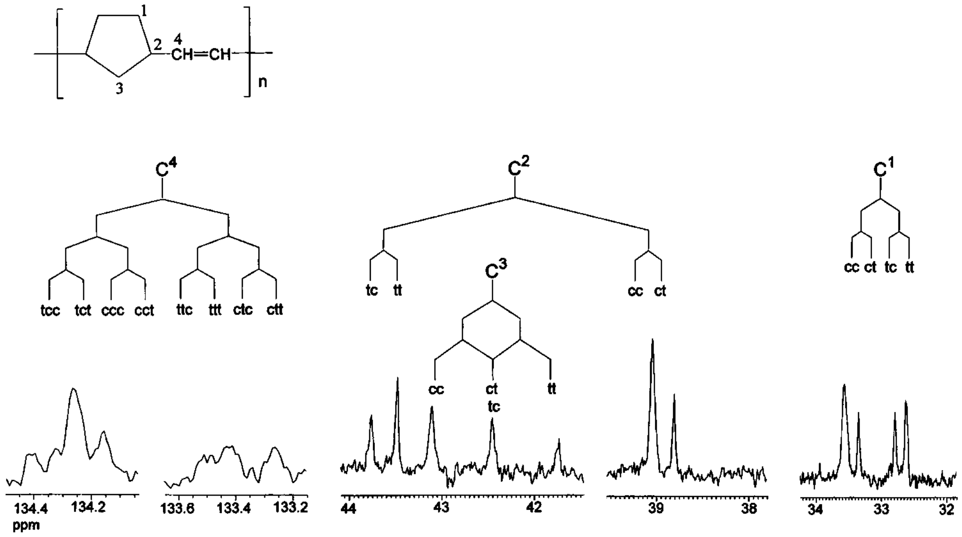

Figure 4. Expanded ^{13}C NMR spectrum of polynorbornene catalyzed by electrochemically generated active tungsten species (in $CDCl_3$).

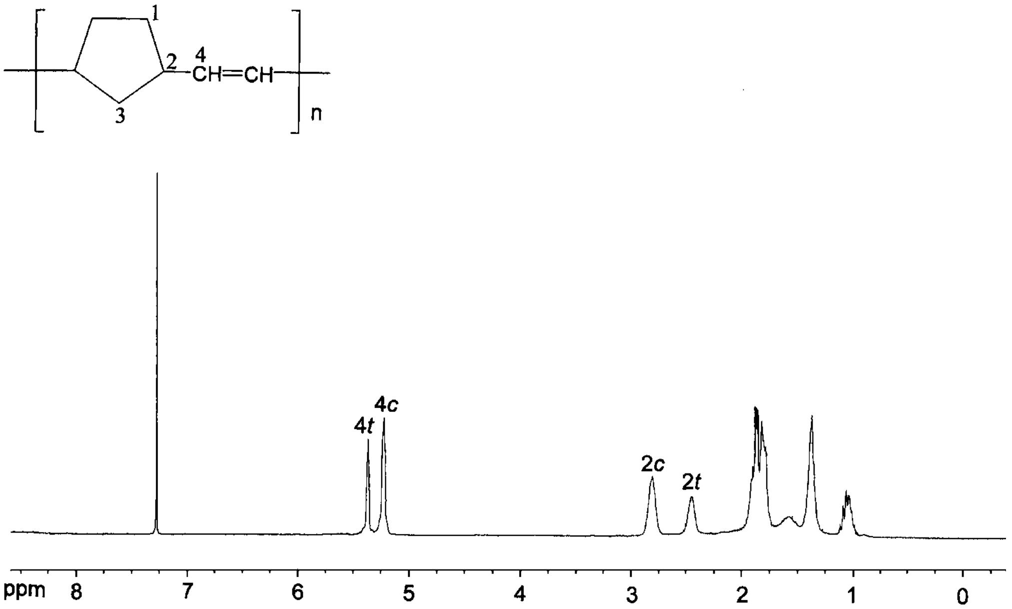

Figure 5. ^1H NMR spectrum of polynorbornene catalyzed by electrochemically generated active tungsten species (in $CDCl_3$).

The results correlate well with the literature, that polymers produced from WCl_6-based systems are of intermediate cis-content.[36,38–40] Steric interactions around the active center and the higher oxidation state of the metal favor the formation of cis-double bonds. The mechanism proposed in the WCl_6–e^-–Al–CH_2Cl_2 catalyst system involves the initial formation of the olefin adduct with the WCl_5^+ species.[23] The observed higher cis fraction of the polymer conforms with the suggested mechanism that the olefin entering the cage around W(VI) prefers the cis-orientation, leading to cis-double bonds in the polymer.

CONCLUSIONS

The WCl_6–e^-–Al–CH_2Cl_2 system catalyzes the ROMP of norbornene. As a class of catalyst, it functions accordingly in the production of polynorbornene while exhibiting similar stereochemical characteristics seen in the previous ROMP systems based on WCl_6. The polynorbornene produced is somewhat blocky, with a higher cis composition ($\sigma_c = 0.61$) compared with the random commercial polymer 'Norsorex' ($\sigma_c = 0.21$). The active species are not very sensitive to atmospheric oxygen and the catalytic activity is retained for about 10 h. The versatile properties of this system are expected to aid in future achievements in controlling the microstructure of the polymer for an improved cis stereoselectivity.

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