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Application of electrochemically generated molybdenum-based catalyst system to the ring-opening metathesis polymerization of norbornene and a comparison with the tungsten analogue

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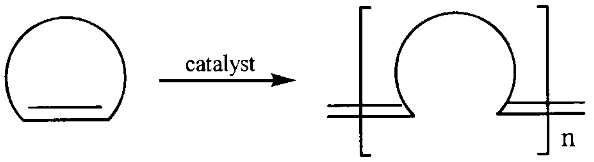
This study describes the application of the electrochemically generated molybdenum-based catalyst system $MoCl_5-e^--Al-CH_2Cl_2$ to ring-opening metathesis polymerization of bicyclo[2.2.1]hept-2-ene (norbornene). The results are compared with those previously obtained by the $WCl_6-e^--Al-CH_2Cl_2$ system. The polymer product has been characterized by ^1H and ^{13}C NMR, IR and gel-permeation chromatography techniques. This molybdenum-based catalyst system has led to a mainly trans stereoconfiguration (ca 60%) of the double bonds, in contrast to the polymer obtained with the tungsten-based analogue, where the cis content is 60%. Analysis of the poly(1,3-cyclopentylenevinylene) microstructure by ^{13}C NMR spectroscopy revealed that the polymer having $\sigma_c = 0.41$ (fraction of double bonds with cis configuration) contains a slightly blocky distribution ($r_tr_c > 1$) of the double-bond dyads ($r_tr_c = 1.44$). In addition, the influence of reaction parameters, e.g. reaction time, electrolysis time and catalyst aging time, on conversion has been analysed in detail.

KEYWORDS: ring opening; metathesis; catalyst; $MoCl_5$; WCl_6; norbornene; cyclic olefins; polymerization; electrochemistry

INTRODUCTION

Ring-opening metathesis polymerization (ROMP) of cyclic olefins by transition-metal catalysts (usually tungsten, molybdenum or rhenium) is a unique process of olefin metathesis, which leads to unsaturated linear homopolymers and copolymers (Eqn (1)). This type of polymerization reaction has been the subject of many investigations since bicyclo[2.2.1]hept-2-ene (norbornene) was polymerized with titanium-based catalysts by Anderson and Merckling[1] to an unsaturated polymer and later cyclopentene by Eleuterio[2] with a heterogeneous molybdena/alumina catalyst.



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The polymerization of norbornene is an important area of research because the microstructure of polynorbornene can provide useful insight into the mechanism of ROMP reactions. There are numerous studies involving the applications of a wide range of different catalyst systems in the ROMP of norbornene and its derivatives. Initial studies in this area were based on 'classical catalyst systems' consisting of transition-metal compounds, cocatalysts such as $EtAlCl_2$, R_3Al or R_4Sn (R = Ph, Me, Et, Bu) and sometimes promoters, including O_2, EtOH or PhOH.[3–14] Recent efforts have been directed toward the preparing of well-defined catalysts (or initiators) developed by Grubbs and co-workers[15–18] and Schrock and co-workers.[19–23] Therefore, it has become possible to control their activity closely, study the details of the reaction mechanism, ultimately control polymer structure and synthesize polymers with novel topologies.

Current interest in our group has been focused on the application of electrochemically generated tungsten-based active species in the catalysis of metathesis-related reactions. Electrochemistry seems to be a useful tool for the synthesis of catalytic moieties, because the number of electrons transferred can be easily checked and, consequently, by controlling the

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electrode potential one can often obtain specifically different oxidation states. Furthermore, the absence of cocatalyst avoids the side reactions occurring when chemical reducing agents such as organoaluminium or organotin compounds are used. Moreover, the organoaluminic or organotin cocatalysts are, in practice, very dangerous to handle and very often give by-products arising from isomerization or alkylation of the substrates. It was first reported by Gilet *et al.* that the electrochemical reduction of transition-metal salts, such as WCl_6 and $MoCl_5$, under controlled potential at a platinum cathode with an aluminium anode in chlorinated solvents, results in the formation of stable and active olefin metathesis catalysts.[24] The subsequent report demonstrated the crucial roles of the aluminium anode and the chlorinated solvent, CH_2Cl_2, in this electrochemical system.[25] Although the exact structure is not presently available, the active catalyst involves the metal at high oxidation state as confirmed by electron spectroscopy chemical analysis and electron spin resonance studies.[25,26] The $WCl_6-e^--Al-CH_2Cl_2$ system catalyses olefin metathesis-related reactions with good activity.[27–31]

In a previous paper, we reported the application of the $WCl_6-e^--Al-CH_2Cl_2$ catalyst system to the ROMP of norbornene.[29] This electrochemical tungsten-based catalyst produced a mainly *cis*-polynorbornene ($\sigma_c = 0.61$) with high conversions and at short periods. In this study we describe the application of the $MoCl_5-e^--Al-CH_2Cl_2$ system to the ROMP of norbornene and compare the results, in terms of the reaction conditions and polymer microstructure with those previously observed with the tungsten analogue.

EXPERIMENTAL

Materials

$MoCl_5$ was supplied from Aldrich (>99.9%) and used as received. 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 colourless, 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 aluminium 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 because of its deleterious effect on the catalyst system. For this reason, the distance between the platinum working and aluminium 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. $MoCl_5$ (0.15 g, 0.55 mmol) was introduced into the electrochemical cell containing CH_2Cl_2 (20 ml), and a red solution was observed. Reductive electrolysis at +0.7 V (at first reduction potential) was applied[25] to the red solution. The colour 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 was performed by varying the olefin/catalyst ratio (40 : 1 to 400 : 1), reaction time (0.5 to 16 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 (TMS) as the reference. IR spectra of polymers were obtained from KBr pellets. IR analyses were performed using a Mattson 1000 Model FT-IR spectrophotometer. 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

A series of polymerizations was conducted at ambient temperature in order to estimate the polymer yield quantitatively. At first, a set of experiments was performed by varying the olefin/catalyst ratio from 40 : 1 to 400 : 1. Conversion to polymer was obtained in maximum yield when the olefin/catalyst ratio was 160. This ratio has been previously found as 125 for the tungsten-based catalyst system.[29]

Figures 1 and 2 show the influences of different reaction times and electrolysis times on the amount of polynorbornene for electrochemical molybdenum- and tungsten-based systems. Polymerization conversion first increased with reaction time and reached a plateau value at around 4 min. Both molybdenum- and tungsten-based systems conducted the polymerization of norbornene with high conversions and at short periods, as also shown in Fig. 1. A comparison with some catalyst systems applied in the ROMP of norbornene in terms of polymerization conditions, polymer yield and molecular weight is given in Table 1. With prolonged electrolysis time, the concentration of the active catalyst formed during the electrolysis and conversion to the polymer increased, and the maximum conversion was obtained approximately in 2.5–3 h of electrolysis time for both catalyst systems (Fig. 2). The effect of catalyst aging on norbornene conversion is given in Fig. 3. In a previous study, we found that the catalytically active species formed from WCl_6 during electrolysis retain their activity for nearly 2 days when kept under nitrogen atmosphere. With the $MoCl_5–e^-–Al–CH_2Cl_2$ system, this period was shorter than for the tungsten-based system (Fig. 3). The activity towards ROMP of norbornene slowly diminished and was completely lost after 2 days. The average rate of decrease in the polymerization yield is 2.3% for every 1 h passing for catalyst aging, which also indirectly indicates the rate of the catalyst decay. More detailed kinetic studies about the stability of the catalyst are under consideration.

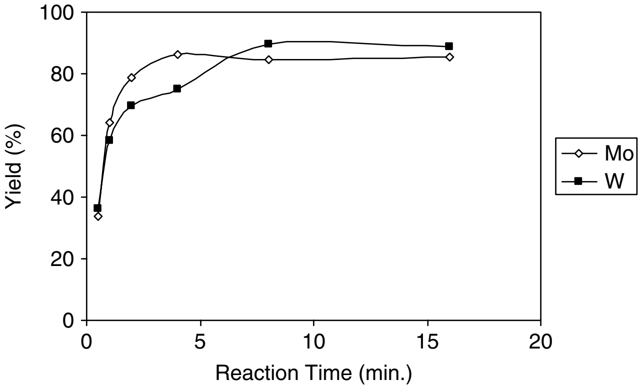


Figure 1. The influence of reaction time on the conversion of ROMP of norbornene in CH_2Cl_2 at room temperature (olefin/Mo = 160; olefin/W = 125; catalyst = 0.025 mmol).

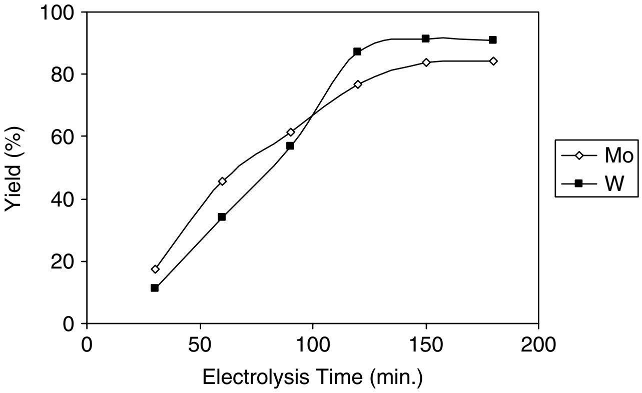


Figure 2. The influence of electrolysis time on the conversion of ROMP of norbornene in CH_2Cl_2 at room temperature (olefin/Mo = 160; olefin/W = 125; current range: 200–400 μA; $E_{cathodic}$ = +700 mV and +900 mV vs Ag/AgCl for $MoCl_5$ and WCl_6 respectively).

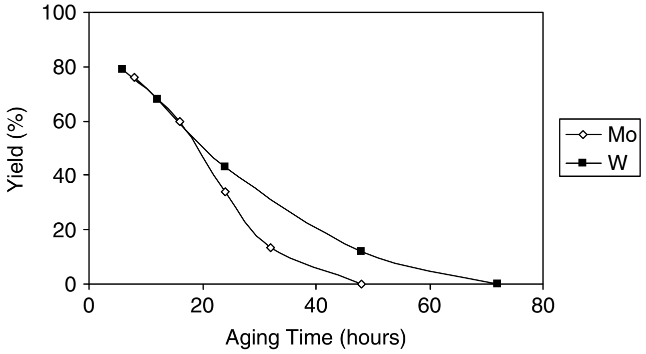
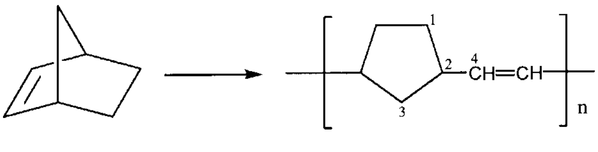


Figure 3. The influence of catalyst aging on the conversion of ROMP of norbornene in CH_2Cl_2 at room temperature (olefin/Mo = 160; olefin/W = 125).

The ring-opening polymerization of norbornene by olefin metathesis catalysts leads to a polymer, with chains containing 1,3-disubstituted cyclopentane rings (Eqn (2)). The polymers obtained were characterized by ^1H and ^{13}C NMR and GPC techniques. GPC performed in THF allowed determination of $\overline{M}_w = 130\,000$ and polydispersity index PDI = 2.15 (Table 2). The resulting polynorbornenes are completely soluble in common organic solvents. As shown in Table 2, the electrochemical molybdenum-based system leads to polymers of higher molecular weight and lower polydispersity in comparison with the electrochemical tungsten-based system.



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^1H and ^{13}C NMR spectroscopic data for the resulting polymer obtained in the presence of the $MoCl_5–e^-–Al–CH_2Cl_2$ system are consistent with the data previously reported for

Table 1. A comparison of results of metathesis polymerization of norbornene using various catalyst systems

Catalyst	Olefin/catalyst	Reaction time	Temperature[k] (°C)	Yield (%)	$\overline{M}_w$	Ref.
$MoCl_5$–e^-–Al–CH_2Cl_2[a]	160	4 min	25	87	130 000[l]	This study
Molybdenum(VI) salt[b]	—	—	rt	52	57 100[l]	10
Molybdenum complex[c]	300	16 h	40	68	2 253 000[l]	11
Molybdenum alkylidene[d]	400	1 h	rt	>98	119 000[l]	32
Molybdenum(II) complex[e]	100	24 h	25	45	16 000[l]	33
Molybdenum–nitrosyl complex[f]	100	10 min	rt	75	236 000[l]	34
Ruthenium alkylidene[g]	100	1 h	rt	99	46 530[m]	18
Tungsten alkylidene[h]	25	10 min	rt	90	68 000[m]	35
Titanium initiator[i]	100	8 h	70	—	23 875[m]	36
Osmium complex[j]	50	2 h	rt	95	433 600[l]	37

[a] Generated after 3 h of electrolysis time.
[b] $(cin\text{-}H_4)[Mo_8O_{26}(cin)_2]$.
[c] $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$.
[d] $Mo(CHMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$.
[e] $[(CO)_4Mo(\mu\text{-}Cl_3)]Mo(SnCl_3)(CO)_3]$.
[f] $[Mo(NO)_2Cl_2(MeCN)_2]Cl$.
[g] $RuCl_2(=CHPh)(PPh_3)_2$.
[h] $W(NPh)(CHCMe_3)(PMe_3)[(NSiMe_3)_2C_6H_4]$.
[i] Dimethyltitanocene.
[j] $(\mu\text{-}H)_2Os_3(CO)_{10}$.
[k] rt: room temperature.
[l] Determined by GPC (calibration with polystyrene standards).
[m] Calculated from the original $\overline{M}_n$ values determined by GPC.

Table 2. A comparison of ROMP of norbornene by the $MoCl_5$–e^-–Al–CH_2Cl_2 and WCl_6–e^-–Al–CH_2Cl_2 catalyst systems

Catalyst	$\overline{M}_n$	$\overline{M}_w$	PDI	σ_c	r_t	r_c	r_tr_c	Type of distribution	Ref.
$MoCl_5$–e^-–Al–CH_2Cl_2	60 480	130 000	2.15	0.41	2.32	0.62	1.44	Slightly blocky	This study
WCl_6–e^-–Al–CH_2Cl_2	15 160	47 600	3.14	0.61	1.33	2.53	3.37	Blocky	29

the polymers of norbornene prepared via ROMP by other catalyst systems.[38–40]

Table 3. ^{13}C NMR peak assignments (ppm from TMS) of polynorbornene produced by the electrochemical molybdenum-based catalyst system

Chemical shift δ (ppm)	Assignment	Chemical shift δ (ppm)	Assignment
33.22	1 tt	43.15	2 tt
32.36	1 tc	43.44	2 tc
32.92	1 ct	132.88	4 ctt
33.09	1 cc	133.04	4ctc ≡ 4 ttt
38.42	2 ct	133.15	4 ttc
38.66	2 cc	133.76	4 cct
41.38	3 tt	133.83	4 ccc
42.10	3 tc ≡ 3 ct	133.92	4 tct
42.76	3 cc	133.99	4 tcc

The geometric structure of polynorbornene was determined from ^1H and ^{13}C NMR spectra according to Ivin and co-workers.[41–44] The ^{13}C NMR spectrum (Fig. 4) 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 cis- and trans-ethylenic carbon atoms give two multiplets, related to C^4 carbon, centered respectively at 133.88 ppm and 133.02 ppm. A comparison of these two peaks corresponding to C^4 carbon allows estimation of the trans 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.[41–44] Table 3 gives the peak assignments of polymer obtained in the presence of the $MoCl_5$–e^-–Al–CH_2Cl_2 system. 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 43.44 (tc), 43.15 (tt), 38.66 (cc) and 38.42 (ct). Here, the chain carbon atoms that are located between two double bonds are labelled 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,

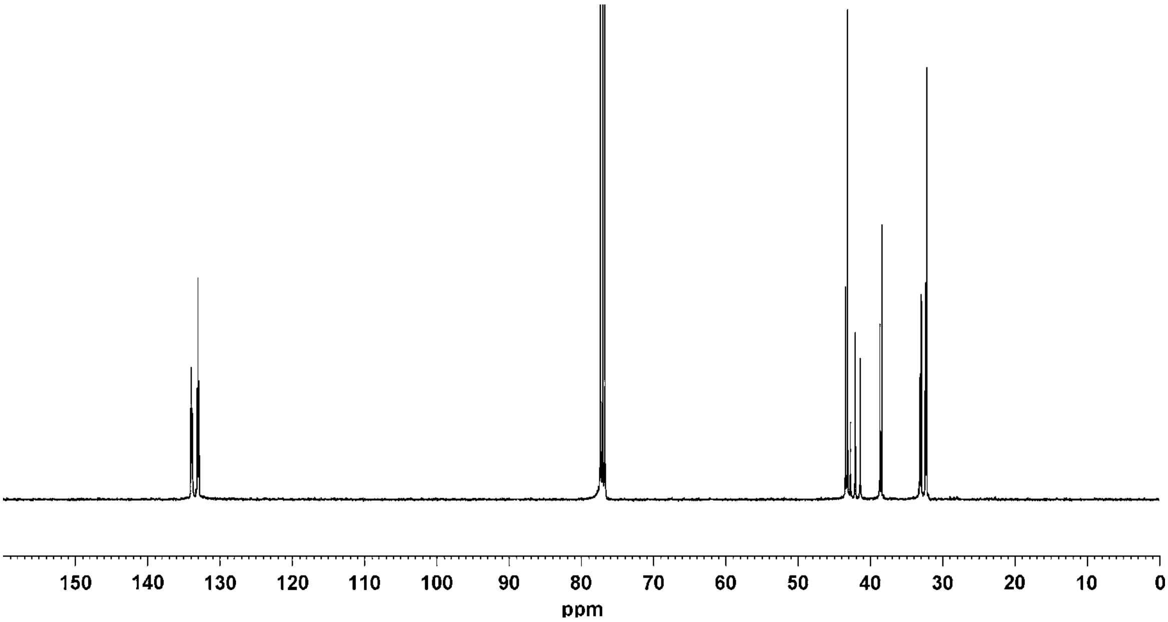

Figure 4. ^{13}C NMR spectrum of polynorbornene made using the $MoCl_5$–e^-–Al–CH_2Cl_2 catalyst system (in $CDCl_3$).

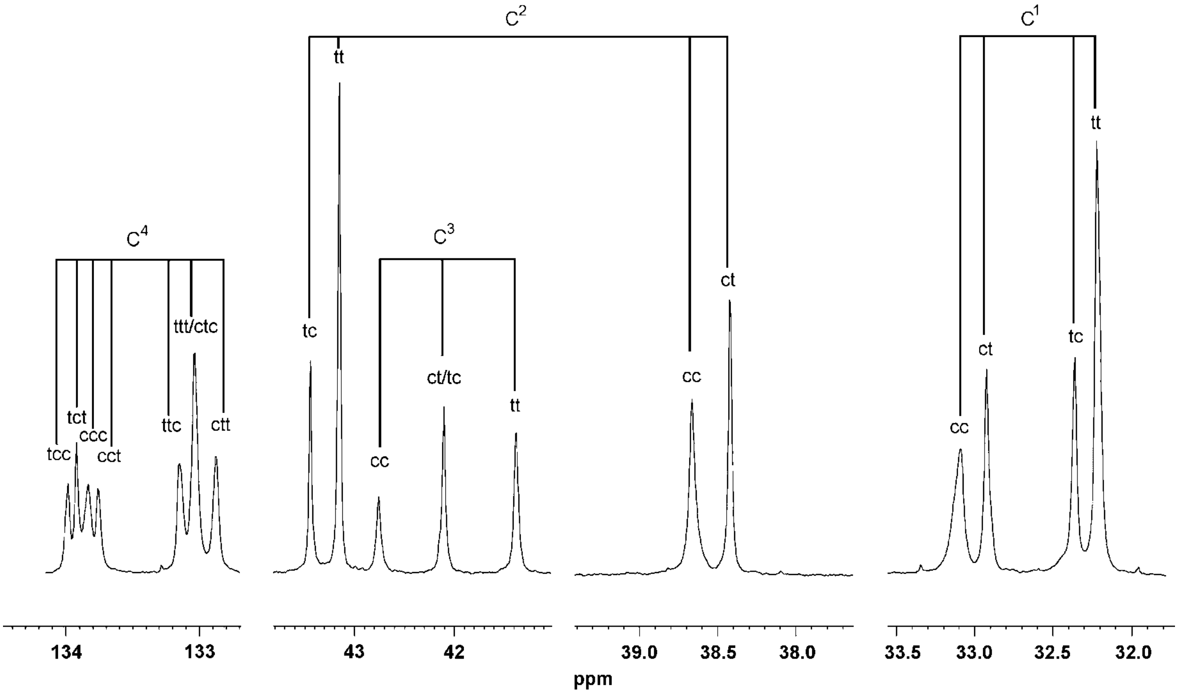

Figure 5. Expanded ^{13}C NMR spectrum of polynorbornene made using the $MoCl_5$–e^-–Al–CH_2Cl_2 catalyst system (in $CDCl_3$).

the reactivity ratios, $r_t = \mathrm{tt/tc}$ and $r_c = \mathrm{cc/ct}$, were calculated as $r_t = 2.32$ and $r_c = 0.62$, giving an $r_t r_c$ value of 1.44. The fraction of cis double bonds σ_c was estimated as 0.41 (average of four values derived from C^4, C^2, C^1 and C^3 signals) (Fig. 5). The σ_c and $r_t r_c$ values thus obtained characterize a highly trans polymer with a slightly blocky distribution of cis and trans structures. Ivin *et al.*[43] reported that polynorbornenes with a fraction of cis-double bond σ_c up to 0.35 showed a 'random' distribution of cis and trans structures ($r_t r_c = 1$), whereas polymers having $\sigma_c = 0.35$–0.85 showed a 'blocky' distribution ($r_t r_c > 1$) with $r_t r_c > 5$ in some cases. Also, an increase of σ_c increases and reduces the r_c and r_t values respectively.[43,45] A comparison of the fraction of cis double bonds σ_c, the reactivity ratios r_c and r_t, and $r_t r_c$ values ($r_t r_c > 1$ related to blocky

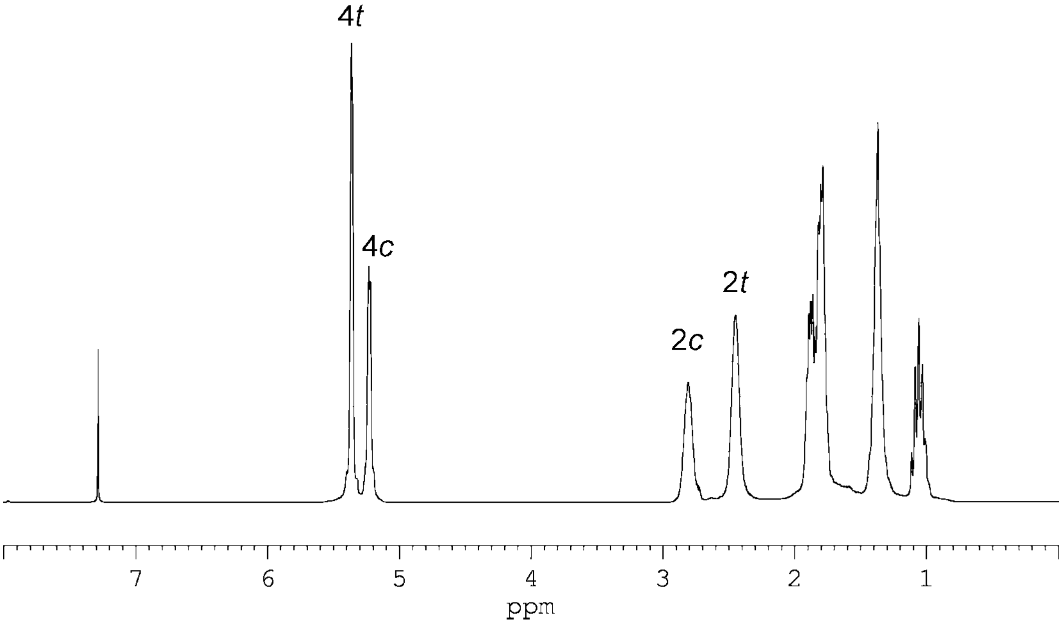

Figure 6. ^{1}H NMR spectrum of polynorbornene made using the $MoCl_5$–e^-–Al–CH_2Cl_2 catalyst system (in $CDCl_3$).

distributions of cis and trans double bonds) in the polymerization of norbornene with the electrochemical molybdenum- and tungsten-based catalyst systems are shown in Table 2. It is remarkable that the $MoCl_5$–e^-–Al–CH_2Cl_2 catalyst system gave a polynorbornene of a high trans content (ca 60% trans), whereas the WCl_6–e^-–Al–CH_2Cl_2 catalyst system produced a polymer with a high cis content (ca 60% cis), exhibiting similar stereochemical characteristics seen in the previous ROMP systems based on $MoCl_5$ and WCl_6. The results correlate well with the literature, that the polymers produced from WCl_6-based systems are of intermediate cis content.[43,45–47] According to Ivin *et al.*,[43] steric interactions around the active centre and the higher oxidation state of the metal favour 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.[26] The observed higher cis fraction of the polymer obtained with WCl_6–e^-–Al–CH_2Cl_2 catalyst system conforms with the suggested mechanism that the olefin entering the cage around tungsten(VI) prefers the cis orientation, leading to cis double bonds in the polymer.

The trans stereoselectivity determined by ^{13}C NMR is in good agreement with that obtained from the ^{1}H NMR spectrum as shown in Fig. 6. 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 trans may also be seen from its ^{1}H NMR spectrum, when the two signals at 5.23 ppm and 5.36 ppm, respectively demonstrating the cis and trans olefinic protons attached to the C^4 carbon atom, were considered. The cis percentage of polymer (ca. 40%) estimated from the ^{1}H NMR spectrum agrees well with that obtained from ^{13}C NMR. Furthermore, the fraction of cis double bonds ($\sigma_c = 0.41$) calculated from the integrals of the signals at $\delta_H = 2.81$ (HC^2, *cis*-polynorbornene) and at $\delta_H = 2.45$ (HC^2, *trans*-polynorbornene) confirms the same cis content of the polymer.

So, the NMR spectra confirm that there is no loss of C=C double bond during polymerization and indicate the formation of a mainly trans compound with one acyclic C=C double bond and one cyclopentane unit.

Here, it is particularly important to note that no evidence of the addition chemistry is apparent in the NMR spectra except for the retention of the C=C double bonds during polymerization. IR spectroscopy was also used to support the retention of unsaturation in the polymer and high trans stereochemistry was assigned. Figure 7 illustrates the

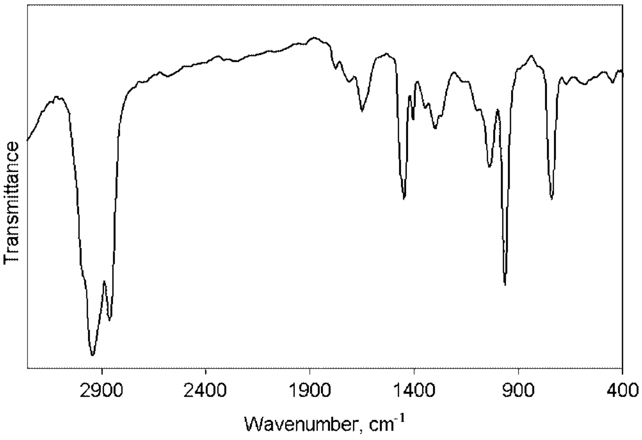

Figure 7. FTIR spectrum of polynorbornene made using the $MoCl_5$–e^-–Al–CH_2Cl_2 catalyst system.

FTIR spectrum of the polymer. The trans content of the polymer is confirmed by the stronger absorption of the trans C=CH out-of-plane bending at 966 $\mathrm{cm^{-1}}$ with respect to the absorption at 742 $\mathrm{cm^{-1}}$ arising from the cis C=CH out-of-plane bending. The absorption at 1649 $\mathrm{cm^{-1}}$, belonging to the C=C stretching, indicates the retention of the double bonds in the polymer obtained via the ROMP mechanism.

CONCLUSIONS

The $\mathrm{MoCl_5{-}e^-{-}Al{-}CH_2Cl_2}$ system catalyses the ROMP of norbornene. The electrochemical molybdenum-based system leads to a mainly trans product ($\sigma_c = 0.41$), in contrast to the mainly cis polymer ($\sigma_c = 0.61$) previously obtained with the tungsten-based analogue in the production of polynorbornene, which exhibits similar stereochemical characteristics to those seen in the other ROMP systems based on $\mathrm{MoCl_5}$ and $\mathrm{WCl_6}$. The polynorbornene produced is slightly blocky, with a higher cis composition ($\sigma_c = 0.41$) when compared with the random commercial polymer 'Norsorex' ($\sigma_c = 0.21$). The catalytic activity is retained for about 32 h under nitrogen atmosphere. The electrochemically generated molybdenum- and tungsten-based catalysts both seem to be more active than the other catalyst systems in the ROMP of norbornene due to higher polymerization yields and shorter reaction periods.

Acknowledgements

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