APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 375–379 **Materials, Nanoscience and Catalysis** **AOC**

Ring-opening metathesis polymerization of cyclododecene using an electrochemically reduced tungsten-based catalyst

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Received 2 February 2004; Accepted 7 April 2004

The ring-opening metathesis polymerization of cyclododecene using an electrochemically reduced tungsten-based catalyst (WCl_6–e^-–Al–CH_2Cl_2) is described. In addition, the influence of reaction conditions on the polymerization yield was determined. The resulting polymer has been characterized by NMR, IR, gel permeation chromatography and differential scanning calorimetry. The glass transition temperature and melting point of the polydodecenamer are 19.6 °C and 70.0 °C respectively. Furthermore, cyclododecene has been polymerized into a low-molecular-weight polymer (12.0×10^3) with a polydispersity of 2.06 in high yields (94%). IR and NMR analysis indicate that the polydodecenamer has a high trans content (60%). Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ROMP; metathesis; catalyst; WCl_6; polymerization; electrochemistry; cyclododecene

INTRODUCTION

During recent years, olefin metathesis reactions have gained a position of increasing significance owing to their versatile applications in organic and polymer syntheses.[1] Cyclic olefins can be polymerized using transition-metal-based catalysts by ring-opening metathesis polymerization (ROMP), for which a great number of studies have been carried out.[2–10] This reaction is a special process in which the number of double bonds in a polymer is preserved. This paper reports the ROMP of cyclododecene carried out using active tungsten species generated electrochemically. The influence of reaction conditions, such as monomer/catalyst ratio and reaction time, on polymerization yield were analysed in detail. Electrochemical reduction of WCl_6 and $MoCl_5$ results in the formation of species exhibiting high catalytic activity and stability.[11,12] 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).[13] This system catalyses various olefin metathesis reactions with good activity.[14–16] ROMP of norbornene was previously reported by our group using this catalytic system.[17] The present study demonstrates that the WCl_6–e^-–Al–CH_2Cl_2 system has also been found to be active for ROMP of cyclododecene, which is a monocyclic olefin. Monocyclic olefins are less easily polymerized than polycyclic monomers, such as norbornene (because the ring strain in monocyclic monomers with five or more carbon atoms in the ring is less than that found in bicyclic monomers, where bond angles are significantly more strained).[18] In addition, the polymer chains derived from monocyclic monomers are more flexible than those derived from bicyclic monomers. This makes access of the active chain end to double bonds in the chain easier and intramolecular secondary metathesis more probable.

EXPERIMENTAL

Chemicals

WCl_6 was purified by sublimation from the more volatile impurities (WO_2Cl_2 and WCl_4O) under nitrogen at about 200 °C and kept under nitrogen atmosphere. CH_2Cl_2 was washed with concentrated sulfuric acid, then with aqueous carbonate solution and with water, followed by drying over $CaCl_2$. Thereafter, the CH_2Cl_2 was distilled over P_2O_5 and kept under nitrogen atmosphere. Cyclododecene was purchased from Aldrich, purified by distillation over CaH_2 and kept under nitrogen. Tetrahydrofuran (THF) and MeOH were supplied by Merck and used as received.

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Electrochemical instrumentation

The electrochemical instrumentation consisted of an EGG-PAR Model 273 coupled with a PAR Model Universal Programmer. The measurements were carried out under nitrogen atmosphere in a thermostatic three-electrode cell. Exhaustive controlled-potential experiments were carried out in an undivided cell with a macro working platinum foil electrode (2.0 cm^2) and an aluminium foil (2.0 cm^2) counter electrode. The reference electrode consisted of AgCl coated on a silver wire in CH_2Cl_2–0.1 M tetrabutylammonium fluoroborate that was also separated from the electrolysis solution by a sintered glass disc. Electrolysis was carried out without supporting electrolyte, owing to its deleterious effect on the catalyst system. For this reason, the distance between the platinum working and aluminium counter electrodes was kept constant and as small as possible (i.e. 2.0 mm) in order to keep the solution resistance at a minimum.

Preparation of catalyst

All manipulations involving polymerization reactions were carried out 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. The electrodes were introduced into the deep-red solution (10^{-2} M WCl_6 in CH_2Cl_2) and reductive electrolysis was done at +0.9 V and electrolysis conducted for 3 h in reductive mode. The colour of the solution darkened progressively. Aliquots from this catalytic solution were used in polymerization reactions.

Polymerization reactions

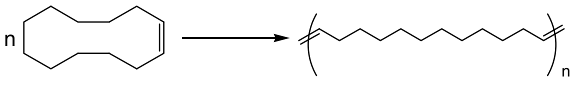
All polymerization reactions were initiated in the bulk, at room temperature and under nitrogen atmosphere. In this part of the study, in order to determine the optimum experimental conditions for the polymerization of cyclododecene, the effect of monomer/catalyst ratio and reaction time were studied using ranges from 20 : 1 to 90 : 1 and 5 to 60 min respectively. A typical reaction was as follows: 1 ml of 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 MeOH addition after 30 min to precipitate the polymers. The polymers formed were filtered, washed with MeOH, dissolved in THF and reprecipitated with MeOH to remove the catalytic residues. The yields of the polymerizations were determined gravimetrically.

Characterization

^1H and ^{13}C NMR spectra were recorded using a Bruker GmbH 400 MHz high-performance digital FT-NMR spectrometer. $CDCl_3$ was used as solvent with tetramethylsilane (TMS) as internal standard. IR spectra were obtained from KBr pellets using a Mattson 1000 FTIR spectrophotometer. Gel permeation chromatography (GPC) analyses were performed using a Shimadzu SPD-10AD*VP* UV detector, relative to polystyrene standards. The sample solutions (concentrations 1%) were prepared in THF as eluent and passed through a μ-styrogel column. A constant flow rate of 1 ml min^{-1} was maintained at 25 °C. Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC 60 over the temperature range of −50 to 500 °C at a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

The scope of ROMP has been expanded to the synthesis of polydodecenamer with WCl_6–e^-–Al–CH_2Cl_2 as catalyst system. The polymerization process is illustrated in Eqn (1):



(1)

At first, the polymerization time and monomer/catalyst ratio were varied in order to determine the optimum experimental conditions to achieve the desired molecular weight and polydispersity. Thus, a set of experiments was carried out. Figure 1 shows the effect of monomer concentration on the yields of polydodecenamer. As the monomer/catalyst ratio was increased from 20 : 1 to 60 : 1, the yield of the polymer also increased, reaching a maximum yield of 94% at 70 : 1 monomer/catalyst ratio. Figure 2 shows the influences of different reaction times on the amount of

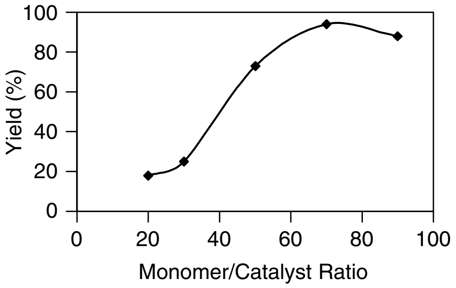


Figure 1. The effect of monomer concentration on the yield of ROMP of cyclododecene.

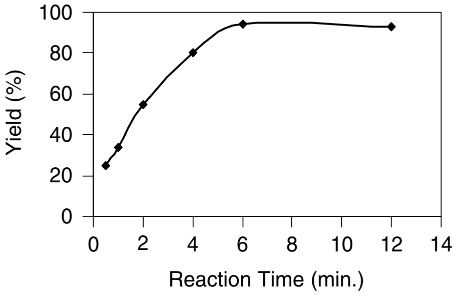


Figure 2. The effect of reaction time on the yield of ROMP of cyclododecene.

polydodecenamer. Polymerization yield first increased with time and reached a plateau value at around 6 min. A comparison of the polymerization results of cyclododecene is reported in Table 1 using various catalyst systems with WCl_6–e^-–Al–CH_2Cl_2. The polymers obtained with the WCl_6–e^-–Al–CH_2Cl_2 system were characterized by IR, NMR, GPC and DSC techniques. The resulting polymers are slightly soluble in organic solvents and their molecular weights are low. The average molecular weight M_W and molecular weight distribution M_w/M_n were 12.0×10^3 and 2.06 respectively. Polydodecenamer exhibits two transitions between −50 and 500 °C. The first transition is the glass transition temperature ($T_g = 19.6$ °C; Fig. 3), and the second is the melting temperature ($T_m = 70.0$ °C) of the polymer (Fig. 4). Polydodecenamer decomposed at about 425 °C. ^1H NMR and IR analysis indicate that the unsaturation in the polymers is retained, which is an indication of the ring-opening metathesis mechanism. In the IR spectra of the polymers, the high amount of trans double bonds is confirmed by the stronger absorption of the trans C=CH out-of-plane bending at 962 cm^{-1} compared with the absorption at 723 cm^{-1} for the cis C=CH out-of-plane bending. The absorption at 1650 cm^{-1} belongs to the C=C stretching. The stereochemistry of the double bonds in the resulting polymers has also been determined by ^1H NMR.

In the NMR analysis presented below, the subscript 'v' indicates a vinylic moiety, and other letters indicate the methylene units relative to the vinylic unit (see Scheme 1). In the ^1H NMR spectrum of polymer there are two groups of peaks: one group corresponds to non-olefinic proton signals between 1.0 and 2.2 ppm, and the second group of peaks is related to the olefinic proton signals at 5.3–5.5 ppm (Fig. 5). The signals due to the olefinic protons for both cis and trans geometries of the double bonds appear as slightly broadened triplets with the cis vinylic proton at 0.035 ppm upfield from the trans (5.41–5.39 ppm). In the ^{13}C NMR

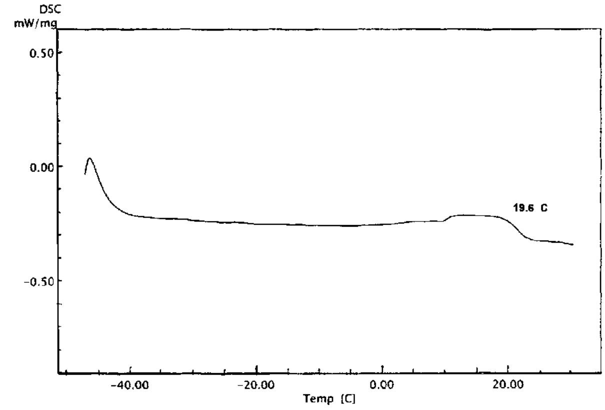


Figure 3. DSC curves of the polymers of polydodecenamer between −50.0 and 35.0 °C.

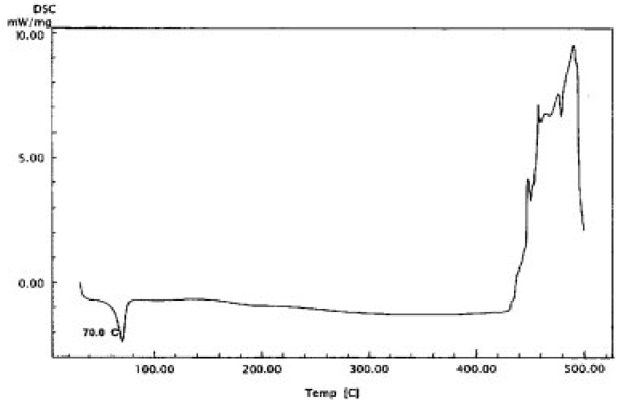
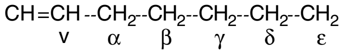


Figure 4. DSC curves of the polymers of polydodecenamer between 20.0 and 500.0 °C.



$$\underset{v}{CH{=}CH}-\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-\underset{\gamma}{CH_2}-\underset{\delta}{CH_2}-\underset{\varepsilon}{CH_2}$$

Scheme 1.

Table 1. A comparison of the polymerization results of cyclododecene using various catalyst systems

	WCl_6–e^-–Al–CH_2Cl_2	Tungsten–alkylidene[18]	Molybdenum–alkylidene[18]	Tungsten–acetylene[19]	Tungsten-based[20]	Tungsten porphyrinates[21]
Monomer/catalyst (molar ratio) ratio	70	300	300	1000	1715	3430
Reaction time	8 min	20 h	15 min	7 h	4 h	6 h
Reaction temperature (°C)	20	20	20	20	20	20
Yield[a] (%)	94	—	—	33	78	70
cis/*trans*[b] ratio	40.0/60.0	20.0/80.0	5.0/95.0	—	31.2/68.8	33.3/66.7
M_w/M_n	2.06	1.78	—	—	—	—
M_w[c]	12.0×10^3	—	—	—	—	—
T_g (°C)	19.6	—	—	—	—	—
T_m (°C)	70.0	67.2	72.0	—	—	—

[a] Determined gravimetrically.
[b] Calculated from ^{13}C NMR spectra.
[c] Determined by GPC, relative to polystyrene standard.

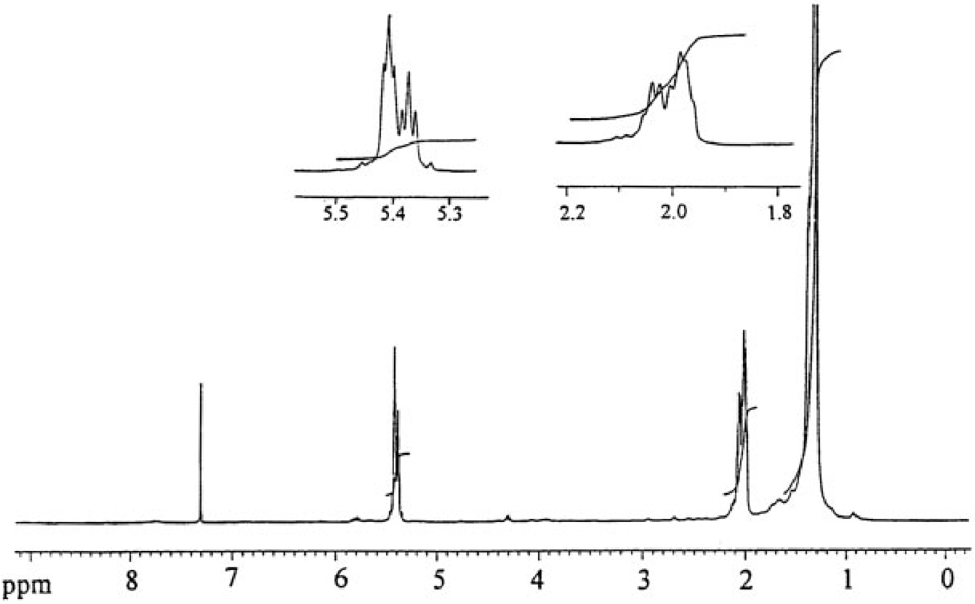


Figure 5. ^{1}H NMR spectrum of polydodecenamer.

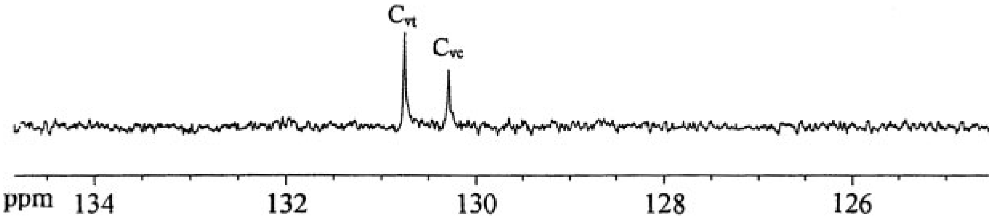


Figure 6. Olefinic region of ^{13}C NMR spectrum of polydodecenamer.

spectrum, all peaks of the polymer are in the same position as those observed previously.[14] The peak positions for the ^{13}C NMR spectrum of polydodecenamer are given in Table 2. The olefinic region (129–131 ppm) clearly confirms the formation of polymers by metathesis (Fig. 6). In the olefinic region of the ^{13}C NMR spectra of the polydodecenamer, two groups of peaks can be observed. The peaks at 130.76 and 130.30 ppm correspond to the trans and cis peaks respectively. Based on the intensities of these peaks, polydodecenamer is assigned to have a higher trans stereochemistry. For this system, the amount of trans double bonds is between 60 and 62%, which is in accordance with the cis/trans ratio calculated from the ^{13}C NMR methylene carbons (C_v and C_α), ^{1}H NMR (H_v and H_α) and IR (723 and 962 cm^{-1}) spectra. The methylene carbon atoms also give one peak for each configuration of the double bonds, with $C_{\alpha c}$, 5.403 ppm upfield from $C_{\alpha t}$, $C_{\beta t}$ 0.110 ppm upfield from $C_{\beta c}$, $C_{\gamma t}$ 0.137 ppm upfield from $C_{\gamma c}$, and $C_{\delta t}$ 0.035 ppm upfield from $C_{\delta c}$. The ε carbon gives one peak at 30.071 ppm; no other peak can be seen, because either the resolution is insufficient or the peaks overlap with other resonances (Fig. 7).

Table 2. ^{13}C NMR line position for polydodecenamer; solvent is $CDCl_3$ (positions in ppm downfield from TMS)

Assignment	Peak position (ppm)
C_{vt}	130.76
C_{vc}	130.30
$C_{\alpha t}$	33.03
$C_{\alpha c}$	27.63
$C_{\beta t}$	30.09
$C_{\beta c}$	30.20
$C_{\gamma t}$	29.61
$C_{\gamma c}$	29.75
$C_{\delta t}$	29.96
$C_{\delta c}$	30.00
C_ε	30.07

CONCLUSIONS

In this study, the ROMP of cyclododecene has been investigated using an electrochemically reduced tungsten-based

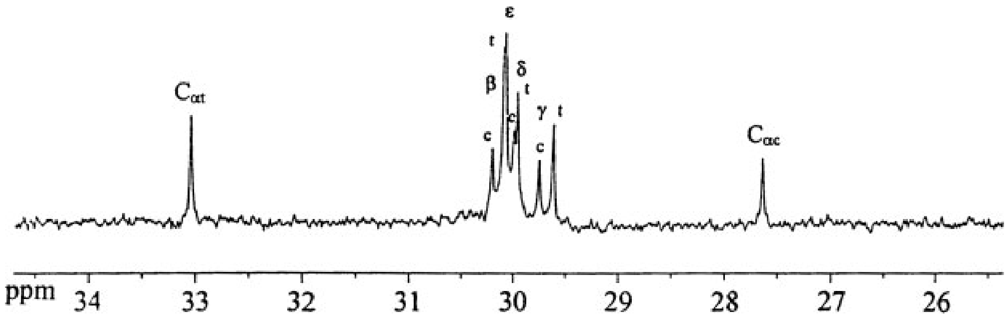


Figure 7. Non-olefinic region of ^{13}C NMR spectrum of polydodecenamer.

catalyst. This system appears to be an efficient catalyst system for the polymerization of monocyclic olefins. This system is more active than the other catalyst systems, as shown by the higher yield of polymerization and in the smaller reaction period. The goal of our next study is to investigate copolymerization reactions of several cyclic olefins by ROMP.

Acknowledgements

We would like to thank Professor F. Verpoort (Ghent University) for valuable suggestions.

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