APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 997–1001
Materials, Nanoscience and Catalysis AOC
Published online 20 July 2005 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.921

Electrochemically reduced tungsten-based active species as catalysts for metathesis-related reactions: ring-opening metathesis copolymerization of cyclopentene with cyclooctene

Solmaz Karabulut, Sevil Çetinkaya and Yavuz İmamoğlu*

Hacettepe University, Department of Chemistry, 06532 Beytepe, Ankara, Turkey

Received 7 January 2005; Accepted 5 March 2005

The ring-opened metathesis copolymerization of cyclopentene with cyclooctene by an electrochemically generated WCl_6-based catalyst has been prepared and ^{13}C NMR spectroscopy used to analyse in detail the nature of the homo- and hetero-dyad units. This copolymer was characterized by gel-permeation chromatography (M_n = 12 900, PDI= 2.2) and differential scanning calorimetry analysis. The glass-transition temperature T_g of the copolymer was −18.7 °C. Homopolymerization of cyclopentene is also reported to compare with copolymers produced in this work. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: ring-opening metathesis copolymerization; cyclopentene; cyclooctene; reduction; WCl_6; electrocatalyst

INTRODUCTION

The study of copolymerization by ring-opening metathesis may provide a new route to tune material properties through combinations of various monomers and reaction stoichiometry.[1] Copolymers can be synthesized by various polymerization methods. However, copolymerization of monomer mixtures by ring-opening metathesis polymerization (ROMP) is rare. Also, much of this scientific work has been done on the homopolymerization of cycloolefins,[2–5] and only very few publications have been devoted to the copolymerization of these cycloolefins,[6–8] especially monocycloolefins.[9,10] Some of the unsaturated copolymers can be synthesized using Schrock-type catalyst systems.

This study deals with the copolymerizations of cyclopentene (CPE) with cyclooctene (COC) catalysed by an electrochemically reduced tungsten-based catalyst. The electrochemical reduction of WCl_6 and $MoCl_5$ produces metathetically active species.[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 the complexation with the olefin.[13] We previously reported the homopolymerization of cyclododecene[14] and cyclooctene[15] by a WCl_6–e^-–Al–CH_2Cl_2 catalyst system. We subsequently focused our efforts on the formation of copolymers by this catalyst. Here, we report the synthesis of copolymer of cyclopentene with cyclooctene via ROMP and interpret the results to give a large amount of information concerning not only the composition and cis double bond content, but also the proportions of compositional dyads and cis–trans double bond pair sequences.

*Correspondence to: Yavuz İmamoğlu, Hacettepe University, Department of Chemistry, 06532 Ankara, Turkey.
E-mail: imamoglu@hacettepe.edu.tr
Contract/grant sponsor: Hacettepe University.

EXPERIMENTAL

Chemicals

WCl_6 was purified by sublimation of the more volatile impurities (WO_2Cl_2 and WCl_4O) under nitrogen at about 200 °C and kept under nitrogen atmosphere. COC was supplied from Aldrich and used as received. CPE was distilled before use. CH_2Cl_2 (Merck) was washed with concentrated H_2SO_4, water, an aqueous solution of Na_2CO_3 (5 wt%) and water again. It was dried over anhydrous $CaCl_2$ and then distilled over P_2O_5 under nitrogen. Tetrahydrofuran

(THF) and methanol were supplied from Merck and used as received.

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 a nitrogen atmosphere in a three-electrode cell having a jacket through which water from a constant-temperature bath was circulated. In the electrochemical experiments, 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. Experiments were carried out in an undivided cell with a macro working platinum foil electrode (2.0 cm^2) and aluminium foil (2.0 cm^2) counter electrode. Electrolysis was carried out without a supporting electrode because of its deleterious effect on the catalyst system. For this reason, the distance between the platinum working electrode 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.

Activation of catalyst

Electrochemical experiments were performed under a nitrogen atmosphere. WCl_6 (0.2 g, 0.50 mmol) was introduced into the electrochemical cell containing CH_2Cl_2 (25 ml) and a red solution was observed. The electrodes were introduced into the deep-red solution and reductive electrolysis at +0.9 V was applied to the solution for 3 h. The colour of the solution darkened progressively. Aliquots from this catalytic solution were used in copolymerization reactions.

Polymerization reactions

Reactions were carried out in a flask equipped with a nitrogen gas inlet and a magnetic stirrer. A typical reaction was as follows: the monomer solution (55 mg CPE and 88 mg COC) was put into the reactor. In copolymerization reactions, a mixture of equimolar amounts of CPE and COC was used as a monomer solution. Then, 1 ml of the catalytic solution was added to the reactor. The mixture was kept at room temperature under vigorous stirring. The reaction was quenched by methanol addition after 24 h. The polymer was further purified to remove the catalytic residues by dissolving it in THF and reprecipitating it with methanol and drying it overnight in a vacuum at room temperature. The polymerization yield as a percentage was calculated as the weight fraction of converted monomer over the total monomer.

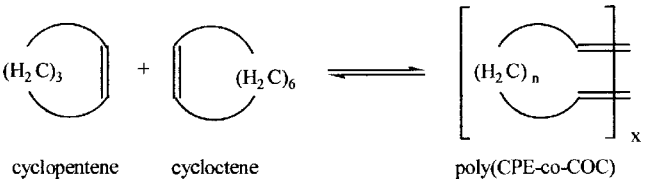
Polymer characterization

^{1}H NMR and ^{13}C NMR spectra of the polymers were recorded with a Bruker GmbH 400 MHz high-performance digital FT-NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane as the reference.

Average molecular weight M_w was determined by gel-permeation chromatography (GPC). GPC analyses were performed with a Shimadzu LC-10AD*VP* liquid chromatograph equipped with a Shimadzu SPD-10A*VP* UV detector, relative to polystyrene standards. Samples were prepared in 1% THF as eluent and passed through a μ-styragel column. A constant flow rate of 1 ml min^{-1} was maintained at 25 °C. Glass transition temperatures were measured by Shimadzu DSC-60 (10 °C min^{-1}).

RESULTS AND DISCUSSION

Ring-opening metathesis homopolymerization has been investigated for some decades now.[2–5] Nevertheless, there are only a few copolymers made by ROMP using molybdenum, tungsten and ruthenium compounds.[6–8] We used a new technique to study the copolymerization reactions by ROMP. Metathesis reaction of CPE (M_1) with COC (M_2) in the presence of an electrochemically reduced tungsten-based active species resulted in the formation of poly(CPE-co-COC) polymers, as shown in Eqn (1). The homopolymerization reaction of CPE was also studied to compare with the copolymerization reactions. The monomer COC has been homopolymerized previously by ROMP techniques, yielding a polyoctenamer.[15]



(1)

Table 1 summarizes the results obtained from the homopolymerization and copolymerization of CPE and COC under the same conditions. The glass transition temperatures T_g of polypentenamer and poly(CPE-co-COC) are −20.8 °C and −18.7 °C respectively. Both peaks remain after repeated heating cycles. Differential scanning calorimetry (DSC) measurements show that the copolymer T_g is lower than that of polypentenamer, but higher than polyoctenamer (Table 1). The copolymer shows an intermediate behaviour compared with both homopolymers and only a single glass transition, which confirms the absence of phase-separated blocks of the monomers.

A single GPC peak was observed, illustrating a homogenous product rather than a blend of homopolymers. The CPE and COC polymerized with electrochemically reduced WCl_6-based catalyst yielded poly(CPE-co-COC) having a weight-average molecular weight M_w and a polydispersity index (M_w/M_n, PDI) of 12 900 and 2.2 respectively. This system is more active than the other catalyst system, due to higher yield of copolymerization and in a smaller reaction period.[9]

Table 1. A summary of polymerization results synthesized by electrochemically produced tungsten-based catalyst (catalyst/monomer$_{CPE}$/monomer$_{COC}$, 1 : 40 : 40)

	CPE (M_1)	COC (M_2)	CPE : COC
Yield[a] (%)	82	90	75
Cis/trans ratio[b]	17/83	75/25	15/84 M_1M_1 35/62 M_2M_2
M_w/M_n	2.4	1.9	2.2
M_w[c]	4100	18 000	12 900
T_g (°C)	−20.8	−11.3	−18.7

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

$$\underset{1}{=CH-}\underset{2}{CH_2-}\underset{3}{CH_2-}CH_2-CH=$$

Scheme 1.

We first examine the ^{13}C NMR spectra of the polypentenamer as a means of determining the carbon atoms in the polypentenamer and then go on to analyse the spectra of poly(CPE-co-COC). In the NMR analysis of polypentenamer presented subsequently, the number (1) indicates a vinylic hydrogen atom, and other numbers indicate the methylene units related to the vinylic unit (Scheme 1).

In the olefinic region of the ^{13}C NMR spectra of the homopolymer of CPE, two groups of peaks can be seen (Fig. 1). The peaks at 130.71 ppm and 130.20 ppm correspond to trans and cis peaks respectively.

Based on the intensities of these peaks, the polypentenamer is assigned with a higher trans (cis/trans: 17/83) stereochemistry. In the non-olefinic region of the polypentenamer the C^1 carbon atoms give four lines at 32.56, 32.43, 27.29 and 27.14 ppm and the C^2 carbon atoms give three lines at 30.25, 30.10 and 29.96 ppm, as shown in Fig. 2. The polypentenamer has the same structure as those obtained using different catalyst systems.[2,3] A detailed ^{13}C NMR study of the polyoctenamer was previously reported.[15]

In copolymers of the two monomers, M_1 (CPE) and M_2 (COC), the compositional dyads may be M_1M_1, M_1M_2, M_2M_1 or M_2M_2 (Scheme 2). The structural evidence of copolymerization lies in a detailed NMR analysis of poly(CPE-co-COC), which is additive for the homopolymer. Figure 3 shows the olefinic region of the ^{13}C NMR spectrum of the copolymer of CPE (M_1) and COC (M_2) obtained with electrochemically produced tungsten-based catalyst. The olefinic region of the copolymer clearly confirms the formation of copolymers. Whereas the ^{13}C NMR spectrum for each homopolymer possesses only two signals (cis and trans stereochemistry), the spectra of copolymers exhibit seven signals. These seven signals are due to the presence of additional linkages in the copolymer. The first (131.0 ppm), third (130.5 ppm), fourth (130.4 ppm) and seventh peaks (130.0 ppm) are assigned to the two olefinic carbons atoms in M_1M_2 and M_2M_1 heterodyads. The other three (130.7, 130.3 and 130.2 ppm) of these are related to the M_1M_1 and M_2M_2 homodyads. The peak at 130.7 ppm is interpreted as having two components, i.e. M_1M_1 and M_2M_2 homodyads. All the upfield peaks of homopolymers in the M_1M_1 and M_2M_2 dyads in Fig. 4 are in the same position as those observed previously for the homopolymers.[3,4] The peak positions for the ^{13}C NMR spectrum of CPE (M_1)–COC (M_2) copolymers are given in Figs 3 and 4. Assignments and peak positions are recorded in Table 2. In the light of all of this, the overall intensity pattern corresponds to 33% M_1 and 67% M_2 units distributed in the copolymer. The cis/trans ratios of M_1M_1 and M_2M_2 in the copolymer are 15/84 and 35/62 respectively.

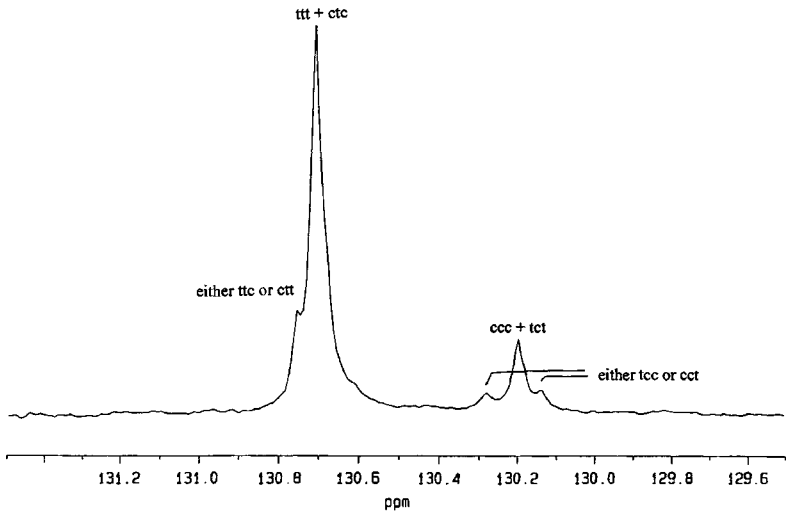


Figure 1. Olefinic region of the ^{13}C NMR spectra of the polymers of the polypentenamer.

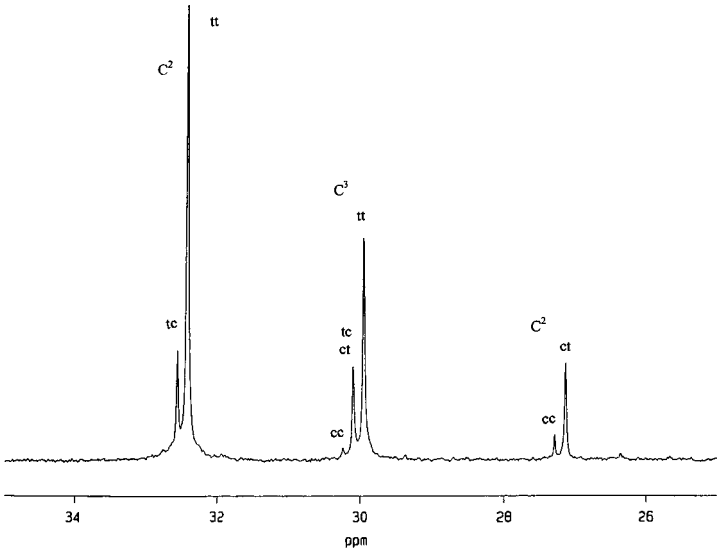
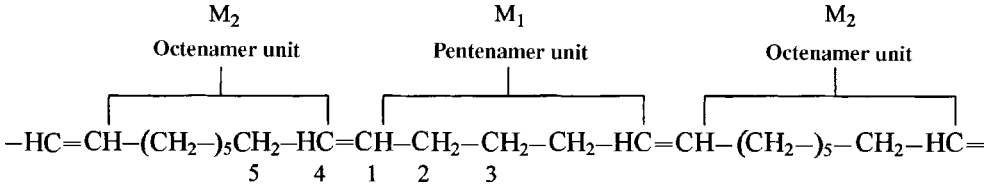


Figure 2. ^{13}C NMR spectra of the non-olefinic carbon atoms in the polymers of the polypentenamer.



Scheme 2.

Table 2. Assignment of lines in the ^{13}C NMR spectrum of CPE (M_1) — COC (M_2) copolymers (solvent: $CDCl_3$)

Peak position (ppm)	Assignment
131.0 (t)	$C^4M_2M_1$
130.5 (c)	
130.7 (t)	$C^4M_2M_2$
130.3 (c)	
130.7 (t)	$C^1M_1M_1$
130.2 (c)	
130.4 (t)	$C^1M_1M_2$
130.0 (c)	
32.43 (tt)	$C^2M_1M_1$
27.28 (cc)	
27.11 (ct)	$C^3M_1M_1$
32.98 (t)	$C^5M_2M_2$
30.02 (t)	
29.56 (ct)	
29.43 (tt)	
27.61 (c)	
30.12	$C^{2,3,5}M_1M_2$ or M_2M_1
28.21	
26.98 (t/c)	
26.38	
25.69	

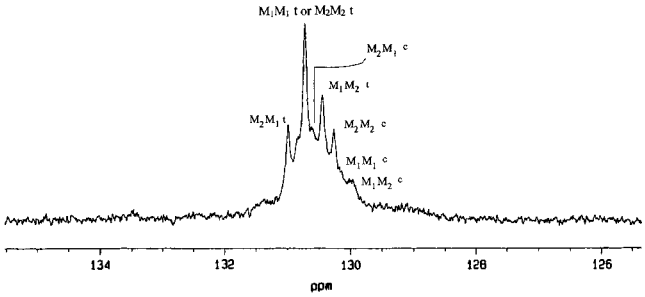


Figure 3. Olefinic region of the ^{13}C NMR spectra of the polymers of poly(CPE-co-COC).

The ^1H NMR spectrum of the polypentenamer had olefinic proton signals at 5.37–5.42, α-proton signals at 2.00 ppm and β-proton signals at 1.28–1.74 ppm (Fig. 5). In the ^1H NMR spectrum of poly(CPE-co-COC) there are two groups of peaks, corresponding to the non-olefinic proton signals at 2.84 and 2.60 ppm and a second group of peaks relating to the olefinic proton signals at 5.32 ppm (Fig. 6). These spectra are the proof of the occurrence of copolymerization in the presence of tungsten-based active species. This comes from a comparison of the ^1H and ^{13}C NMR spectra of the copolymer with the spectra of the homopolymers of CPE and COC.[15]

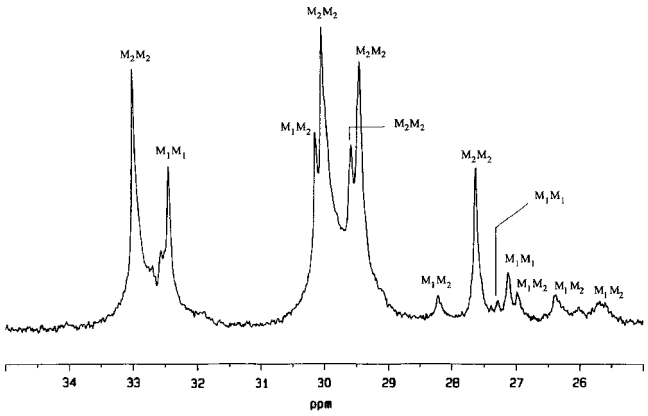


Figure 4. ^{13}C NMR spectra of the non-olefinic carbon atoms in the polymers of poly(CPE-co-COC).

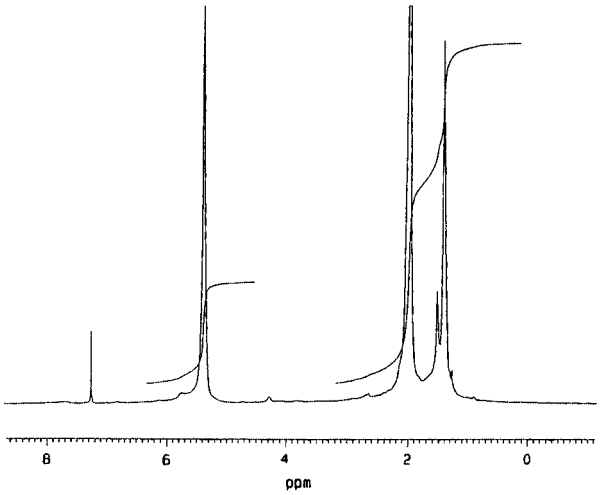


Figure 5. ^{1}H NMR spectra of the polymers of the polypentenamer.

CONCLUSIONS

Electrochemically generated tungsten-based active species have proven to be an effective metathesis catalyst in the synthesis of poly(CPE-co-COC). The detailed ^{13}C NMR spectra of the ring-opened copolymers of CPE with COC were given and information derived concerning the dyad distribution and cis–trans double bond distribution. All these GPC, DSC and NMR spectroscopy observations manifest that the product of this copolymerization is a copolymer and not a mixture of homopolymers. In the future we aim to broaden the scope of copolymerization further, to prepare a variety of copolymers based on known unsaturated homopolymer structures, and to examine the possibility of copolymerizing olefins of unequal reactivity.

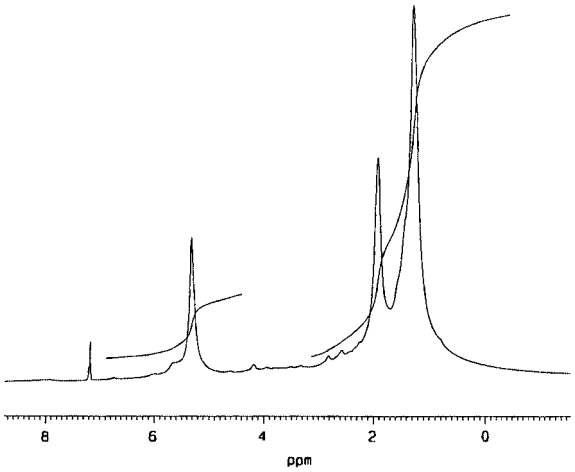


Figure 6. ^{1}H NMR spectra of the polymers of poly (CPE-co-COC).

Acknowledgements

We thank the Hacettepe University Foundation for their support of this work.

REFERENCES

1. Ivin KJ, Mol JC. *Olefin Metathesis and Metathesis Polymerization*. Academic Press: London, 1997.
2. Johnston JA, Farona MF. *Polym. Bull.* 1991; **25**: 625.
3. Jan D, Delaude L, Simal F, Demonceau A, Noels AF. *J. Organometal. Chem.* 2000; **606**: 55.
4. Dounis P, Feast WJ, Kenwright AM. *Polymer* 1995; **36**: 2787.
5. Dimonie M, Coca S, Teodorescu M, Popescu L, Chiapara M, Dragutan V. *J. Mol. Catal.* 1994; **90**: 117.
6. Ivin KJ, Lapienis G, Rooney JJ. *Makromol. Chem.* 1982; **183**: 9.
7. Amir-Ebrahimi V, Carvill AG, Hamilton JG, Rooney JJ, Tuffy C. *J. Mol. Catal. A: Chem.* 1997; **115**: 85.
8. Al Samak B, Amir-Ebrahimi V, Corry DG, Hamilton JG, Rigby S, Rooney JJ, Thompson JM. *J. Mol. Catal. A: Chem.* 2000; **160**: 13.
9. Dall'Asta G, Motroni G. *Eur. Polym. J.* 1971; **7**: 707.
10. Ivin KJ, Lapienis G, Rooney JJ, Stewart CD. *Polym. Commun.* 1979; **20**: 1308.
11. Gilet M, Mortreux A, Nichole J, Petit F. *J. Chem. Soc. Chem. Commun.* 1979; 521.
12. Gilet M, Mortreux A, Folest JC, Petit F. *J. Am. Chem. Soc.* 1983; **105**: 3876.
13. Düz B, Pekmez K, İmamoğlu Y, Süzer Ş, Yildiz A. *J. Organometal. Chem.* 2003; **684**: 77.
14. Karabulut S, Çetinkaya S, Düz B and İmamoğlu Y. *Appl. Organometal. Chem.* 2004; **18**: 375.
15. Çetinkaya S, Karabulut S, Düz B and İmamoğlu Y. *Appl. Organometal. Chem.* 2005; **19**: 347.