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Synthesis and characterization of polyoctenamer with WCl_6–e^-–Al–CH_2Cl_2 catalyst system via ring-opening metathesis polymerization

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A typical low-strain monomer, cyclooctene, was polymerized via ring-opening metathesis polymerization with electrochemically produced active species. The structural properties of the polyoctenamer were determined by NMR, gel-permeation chromatography and differential scanning calorimetry. Analysis of the polyoctenamer microstructure by ^1H and ^{13}C NMR spectroscopy indicates that the polymer contains a highly cis stereoconfiguration of the double bonds ($\sigma_c = 0.75$). The resulting polymer is of low molecular weight and has a reasonably broad molecular weight distribution ($M_w = 18\,000$, PDI = 1.9). The glass transition temperature and melting point of the polyoctenamer are −11.3 °C and 36.5 °C respectively. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: electrocatalysis; cyclooctene; ROMP; tungsten hexachloride; electrochemistry

INTRODUCTION

In the field of polymers, ring-opening metathesis polymerization (ROMP) of cycloalkenes is an attractive process for making polymers possessing special properties. Several industrial processes involving ROMP have been developed and brought into practice, such as the ROMP of cyclooctene, norbornene and dicyclopentadiene, leading to useful polymers, because these monomers are quite cheap and readily available.[1,2] The properties of the resulting polymers depend on the monomer structure, the initiating system and the reaction conditions.[3] The development of well-defined initiators allows the use of living ROMP in the synthesis of polymers with novel well-defined topologies. It has been established that ROMP using well-defined initiators allows control over several important parameters, such as molecular weight and molecular weight distribution, sequence and distribution of cis/trans vinylenes, tacticity and mechanical, thermal, conductivity, dielectric, etc.[4–7]

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. The catalyst produced electrochemically emerges as a powerful tool for olefin metathesis carbon–carbon transformation reactions. The major advantages of this electrochemically generated catalyst system are low expense of preparation, high efficiency and selectivity.[8–12] The WCl_6–e^-–Al–CH_2Cl_2 system (easily obtained) 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. A facile route for the electrochemical generation of an alkene metathesis catalyst from methylene chloride solution of WCl_6 was described by Düz and co-workers.[13] The monomers, norbornene and cyclododecene, have each been homopolymerized previously by ROMP techniques, yielding polynorbornene and polydodecenamer respectively. As a class of catalyst, it functions accordingly in the production of polynorbornene and polydodecanamer while exhibiting similar characteristics to those seen in previous ROMP systems based on WCl_6.[14,15] Here, we present a detailed study on the ROMP of a typical low-strain olefin, cyclooctene, by electrochemically generated active species. Characterization of the polyoctenamer is also investigated and discussed.

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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 pure and dry nitrogen (99.9%)

atmosphere.[10] Cyclooctene was supplied from Aldrich and used as received. Dichloromethane (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. Tefrahydrofuran (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 at constant potential (+0.9 V). Reductive electrolysis at 0.9 V was performed without a supporting electrode because of 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 to a minimum.

Generation of the 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

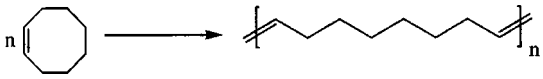
All reactions were carried out in an inert atmosphere with Schlenk techniques under nitrogen. 1 ml of the catalytic solution was added to 1.6 mmol of monomer. The mixture was kept at room temperature under vigorous stirring. The reaction was quenched by methanol addition after 24 h. The polymer was further 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. Polymerization reactions were repeated for different reaction times and monomer/catalyst ratios to optimize reaction conditions. The polymerization yield in percentage terms was calculated as the weight fraction of converted monomer over the total monomer.

Polymer characterization

^1H and ^{13}C NMR spectra of the polyoctenamer 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 analysis was performed with a Shimadzu LC-10AD*V*P liquid chromatograph equipped with a Shimadzu SPD-10A*V*P UV detector, relative to polystyrene standards. Samples were prepared in THF (w/v, 1%) as eluent and passed through a Nucleogel GPC M-5 μ-styragel column. A constant flow rate of 1 ml min^{-1} was maintained at 25 °C. Glass transition temperature was measured using a Shimadzu DSC-60 differential scanning calorimeter (10 °C min^{-1}).

RESULTS AND DISCUSSION

Cyclooctene, a typical low-strain olefin, was polymerized at room temperature with the WCl_6–e^-–Al–CH_2Cl_2 catalyst system. The polymerization process is illustrated as follows:



(1)

For a quantitative estimation of polymer yield, a series of polymerizations was carried out by varying the monomer/catalyst ratio and reaction time (Figs 1 and 2). The dependence of the monomer/catalyst ratio on the polymerization yield was analysed. The polymerization yield increases with monomer/catalyst ratio and the yield after 24 h reaches 90% when the monomer/catalyst ratio is 80. Figure 2 displays the influence of polymerization time on the polymerization yield. Polymer yield increases with time, and two distinct periods can be observed. In the first period there is a rapid increase of the yield with time observed. In the second period, the polymer yield increases slightly and tends to a constant value (at 30 min polymerization time) as a consequence of a significant decrease of the polymerization rate. From this result, it is noticed that low-strain monomers are converted with excellent

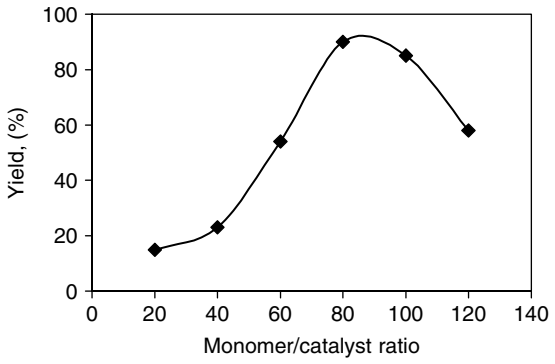


Figure 1. Influence of monomer/catalyst ratio on polymerization yield. Reaction conditions: reaction time, 24 h; temperature, 20 °C.

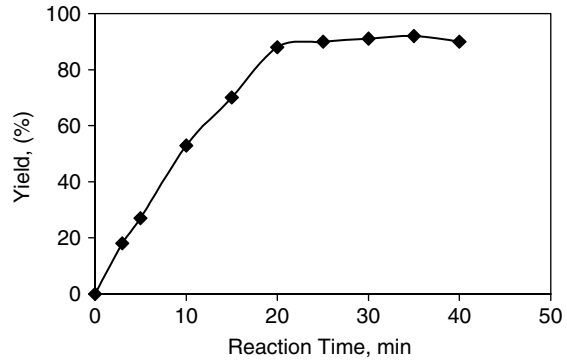


Figure 2. Influence of reaction time on polymerization yield. Reaction conditions: monomer/catalyst ratio, 80; temperature, 20 °C.

yields with the electrochemically produced metathesis catalyst.

A comparison of the polymerization results of cyclooctene is reported in Table 1 using various catalyst systems with WCl_6–e^-–Al–CH_2Cl_2. The differential scanning calorimetry (DSC) curve for polyoctenamer is shown in Fig. 3. The melting point of polymer is 36.5 °C. This compares favourably with experimental values for the T_m of 15.5 °C and 40.1 °C at cis contents of 90% and 30% respectively and 54.1 °C for the polyoctenamer with 20% cis content.[16] The glass transition temperature of polyoctenamer is −11.3 °C. The polymer was of low molecular weight and had a reasonably broad molecular weight distribution (M_w = 18 000, PDI = 1.9). The molecular weight of polymer produced using the electrochemical catalyst is relatively lower than that of obtained using a ruthenium-based catalyst. It appears that

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

	Monomer/ catalyst	Reaction time (h)	Temp. (°C)	Yield (%)	Cis/trans ratio[a]	M_w/M_n	[b]M_w	T_m (°C)	T_g (°C)
WCl_6–e^-–Al–CH_2Cl_2	80	0.5	20	90	75/25	1.90	18 000	36.5	−11.3
W-alkylidene[19]	300	20	40	—	90/10	1.39	—	15.5	—
Mo alkylidene[19]	300	20	40	—	30/70	1.50	—	40.1	—
Ru vinylidene[16]	5000	0.5	60	54		1.66	629 000	—	—
Ru allenylidene[17]	303	16	80	65	60/40	1.81	173 300	—	—
Ru carbene[18]	200	24	25	90	—	—	—	—	−60

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

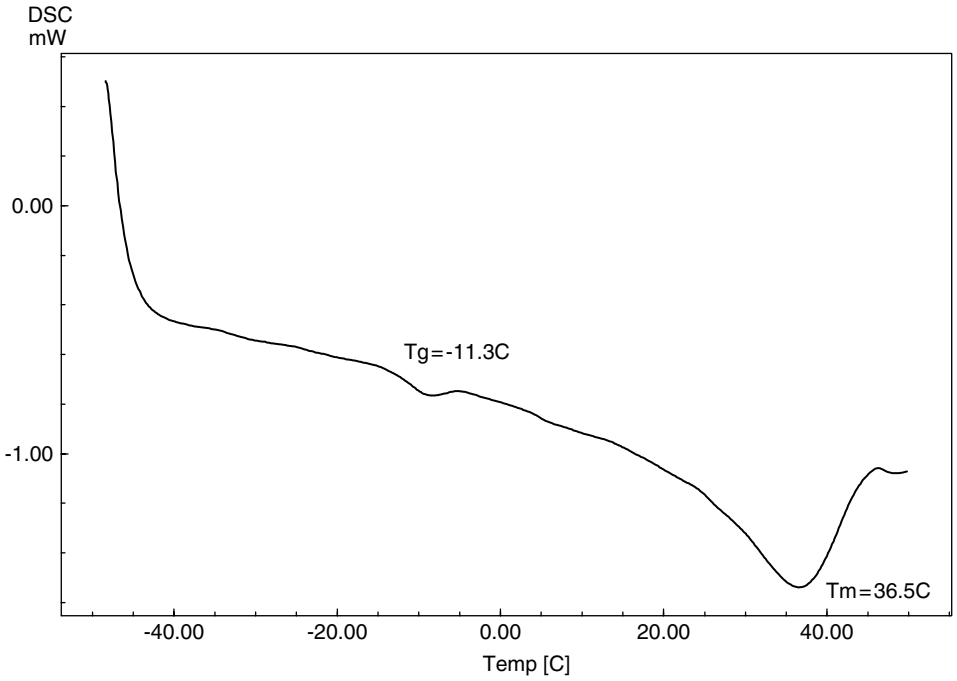


Figure 3. The DSC curve for polyoctenamer obtained by electrochemically generated metathesis catalyst.

Table 2. Assignment of carbon lines in the ^{13}C NMR spectrum of polyoctenamer (solvent: $CDCl_3$)[a]

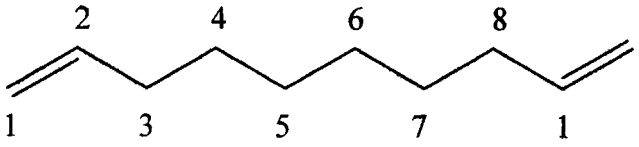
Carbon	Peak position (ppm)
$C_{1,2}$	130.73 (ttt) 130.26 (ccc)
$C_{3,8}$	32.99 (t) 27.61 (c)
$C_{4,7}$	30.14 (c) 30.03 (t)
$C_{5,6}$	29.61 (cc) 29.57 (ct) 29.48 (tc) 29.43 (tt)

[a] t: trans; c: cis.

inefficient stirring due to increased viscosity prevents the formation of high molecular weight samples.

Investigation of the stereochemistry of the ROMP of the cyclooctene reaction was made by ^{13}C and ^{1}H NMR in $CDCl_3$. The microstructure of the resulting polyoctenamer was deduced from the ^{13}C NMR spectrum (Figs 4 and 5). The carbon atoms in the polyoctenamer are numbered from 1 to 8, as indicated in Scheme 1 and Table 2.

The spectrum of the olefinic carbon atoms is shown in expanded form in Fig. 4. The ^{13}C NMR spectrum shows three resolved signals for both the cis and trans olefinic



Scheme 1.

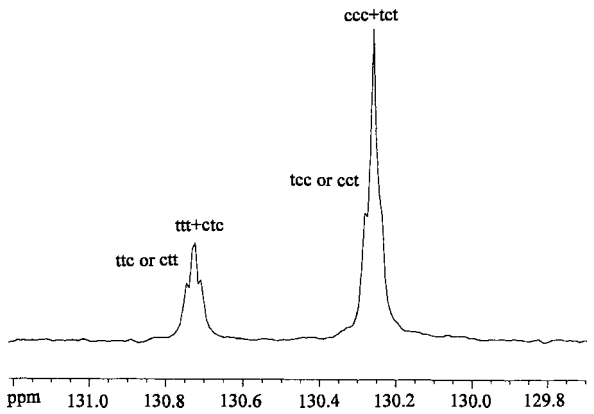


Figure 4. Expansion of the olefinic region of the ^{13}C NMR spectrum of the polyoctenamer.

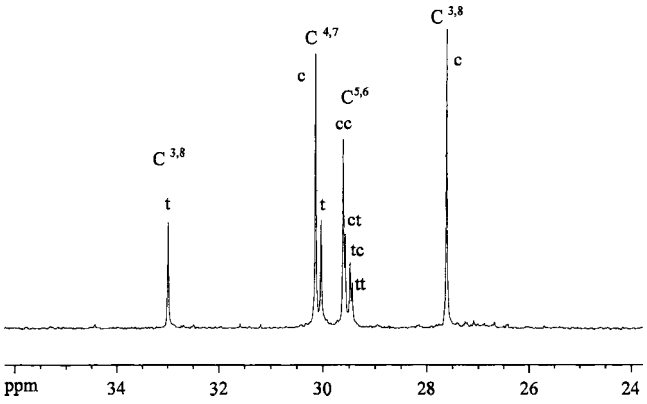


Figure 5. Expansion of the non-olefinic region of the ^{13}C NMR spectrum of the polyoctenamer.

carbon atoms. Adjacent double bonds in the polyoctenamer chain are close enough to affect each other and triad splitting of the cis and trans olefinic signals is observed. The assignment of these peaks is based on the observation that the splitting pattern for this effect generally appears to consist of one intense peak and two smaller peaks of equal intensity on either side, for both the cis and trans signals. Assignments of the C_4 to the double bonds indicates that the polyoctenamer was highly blocky and the more intense peak is assigned as trans, trans, trans (ttt) or cis, cis, cis (ccc). The ttc (or cct) and ctt (or tcc) peaks should have the some intensities since the presence of a ttc carbon requires the presence of a ctt carbon. The ctc and tct peaks should be relatively low intensity and be overlapped by the ttt and ccc peaks respectively.[19] An expanded spectrum of the C_3–C_8 regions is shown in Fig. 5. The C_3 and C_4 atoms are only subjected to the effect of the nearest double bond, giving one peak for both cis and trans with C_3c upfield from C_3t by 5.38 ppm and C_4t upfield from C_4c by 0.11 ppm. The $C_{5,6}$ shows a four-line splitting pattern in the cc, ct, tc and tt sequence of environments. The relative intensities of cis and trans olefinic peaks at the C_2 region and of the cis and trans non-olefinic peaks at the C_3 region give similar cis-contents of the polyoctenamer, i.e. 75%. Cyclooctene polymerized at room temperature using an electrochemically produced catalyst gave a high cis polymer, whereas polymerization using the molybdenum-based initiators gave high-trans polymers, as can be seen in Table 1.[19]

The results obtained by ^{13}C NMR agree well with the ^{1}H NMR spectrum. The ^{1}H NMR spectrum of the polyoctenamer has olefinic proton signals at 5.51 ppm and 5.55 ppm corresponding to cis and trans peaks respectively and non-olefinic proton signals between 2.19 ppm and 1.47 ppm (Fig. 6). The relative intensities of the olefinic peaks at 5.51 and 5.55 ppm give a cis/trans ratio of 75/25. Additionally, the relative integrated peak areas of the two signals at 2.19 and 2.14 ppm indicate a similar cis-content of the polymer.

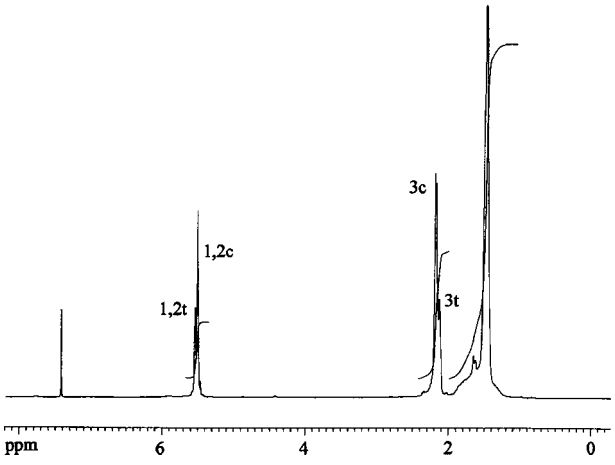


Figure 6. ^{1}H NMR spectrum of the polyoctenamer.

CONCLUSIONS

This study shows the application of the $WCl_6-e^- -Al-CH_2Cl_2$ catalyst system to the ROMP of a type of low-strain olefin, i.e. cyclooctene. It appears that electrochemically reduced catalyst is an active system toward ROMP, because a near quantitative yield of 90% for cyclooctene is obtained, % depending on the monomer/catalyst ratio and reaction time. A high cis proportion polyoctenamer was obtained by this catalyst system with high yields in a short period. The aim of the next study is to investigate copolymerization of cyclic olefins by ROMP using this catalyst.

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