Polymer Bulletin 38, 35–42 (1997)

Polymer Bulletin

Addition polymerisation vs. ROMP on cyclic and strained olefins with the $Mo(CO)_5PPh_3$/alkylaluminums catalysts

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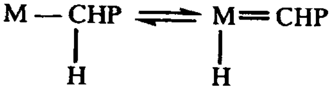
Received: 5 August 1996/Revised version: 22 October 1996/Accepted: 25 October 1996

Summary

The polymerisation of cyclic and strained monomers such as bicyclo[2.2.1)hept-2-ene (norbornene, NBE) and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBDE) with the catalytic systems $Mo(CO)_5PPh_3$/alkylaluminums was studied. From the polymers produced we demonstrate the existence of an antagonism between the ROMP (Ring-Opening-Metathesis-Polymerisation) mecanism and the olefin addition polymerisation mecanism. In addition ROMP mecanism is affected by the solvent. These catalysts also promotes the isomerisation of double bonds, as indicated by the ESR signal observed for the conjugated crosslinked polyNBDE produced by ROMP.

Introduction

It has been well established that the activation of zerovalent complexes of the type $M(CO)_5L$ (L= W, Mo and Re) with Lewis acids affords effective catalytic systems for the olefin metathesis reaction (1-8). Several catalytic systems which assist in the rationalization of the behaviour of these complexes have been reported. One of the first cited as an effective catalyst for the Ring-Opening-Metathesis-Polymerisation (ROMP) of norbornene was $W(CO)_5L/EtAlCl_2/O_2$ (L=CO, PPh_3, $P(0C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$ and pyridine) (8). Furthermore, it was shown that the catalytic system $Re(CO)_5Cl/C_2H_5AlCl_2$ (9) and more recently the $Mo(CO)_5py/C_2H_5AlCl_2/R_4NC1$ (10) polymerise norbornene by ROMP and olefin addition polymerisation (insertion process) simultaneously in the same chain. These results are well explained by the Ivin-Green's model(11) based on a a-H migration (Eq.1):



$$\underset{\displaystyle H}{M-\overset{}{C}HP} \rightleftharpoons \underset{\displaystyle H}{M=\overset{}{C}HP} \qquad (1)$$

In this work we first studied the polymerisation of norbornene with a different catalyst, the $Mo(CO)_5PPh_3$, activated with a series of alkylaluminum compounds as cocatalysts. The aim was to confirm firstly the ROMP character of these catalysts and secondly, in connection with analogous catalysts from literature, to examine the possibility of producing polymers containing structures based on both reactions: the ROMP and the olefin addition polymerisation. For this purpose we also polymerise a likely strained monomer: the bicyclo[2.2.1]hepta-2,5-diene

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(norbornadiene, NBDE). That is the first time that this monomer has been polymerised with these catalysts. Furthermore the role of the solvent in the formation of the active center is expected to be significant because of the nature of the catalysts (12).

Experimental

Materials

$Mo(CO)_5PPh_3$ was prepared and characterised by standard literature methods(13). Organoaluminum compounds, $SnMe_4$ and WCl_6 were purchased from Aldrich Chemicals and used without further purifcation. Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) and bicyclo [2.2.1]hept-2-ene (norbornene) (Aldrich) were refluxed over CaH_2 and distilled under argon. Toluene and benzene were refluxed over metallic Na, distilled and stored under argon. Chlorobenzene and dichloromethane were distilled over CaH_2 and stored under argon.

Polymerisation of norbornene

The polymerisations were conducted at room temperature in a Schlenk tube under argon. The concentration of the catalyst $Mo(CO)_5PPh_3$ was 10^{-2}M, the Mo/monomer ratio was 1/70 and the catalyst/cocatalyst ratio was in the range from 1/2 to 1/20. In a typical experiment 99.6 mg (0.2mmol) of $Mo(CO)_5PPh_3$ were added to the flask followed by injection of 16.5 ml of the chlorobenzene and 0.66 ml (1.2 mmol) of the $EtAlCl_2$. The clear homogeneous solution was stirred for two hours at ambient temperature and the colour of the mixture gradually turned to deep yellow. After the injection of (1.31g, 14mmol) of norbornene in 2.84 ml of chlorobenzene, the reaction mixture instantly turned to dark brown and became viscous. The reaction was stopped with methanol containing a small amount of concentrated HCl. The polymer was precipitated with excess of methanol and the gelled, rubbery polymer was placed in methanol and stirred overnight. The methanol was poured off and the polymer was dried under vacuum for 1 day at 60°C. It was then dissolved in refluxing deuterated chloroform. Those samples which could not be completely dissolved in refluxing chloroform (presumably crosslinked or having a very high molecular weight) were fltrated to give a clear solution for NMR studies.

Measurements

^{1}H-NMR spectra were obtained on a Bruker AMX (400MHz) spectrometer and the $CDCl_3$ solvent provided the deuterium lock frequency. Infrared spectra were recorded on a Perkin-Elmer 783B spectrometer. The IR study of the activation of the catalytic system Mo/Al took place in NaCl cells equipped with an input of Ar. GPC data were obtained using a Waters Associates 401 Liquid Chromatography apparatus equipped with both, a Varian UV-50 detector and a differential refractometer detector. The eluent was toluene and ultrastyragel (500,10^2 A^0 pore size) or Supelco LC-1 and LC-301 column in series were used. Molecular weight calibrations were run against a polystyrene standard. ESR spectra were performed on a Varian E-109 spectrometer at room temperature. The g values were estimated using 1,1-diphenyl-2-picrylhydrazyl(DDPH) as reference. DSC measurements were performed on a Du Pont 910 calorimeter equipped with a 99 thermal analyser.

Results and Discussion

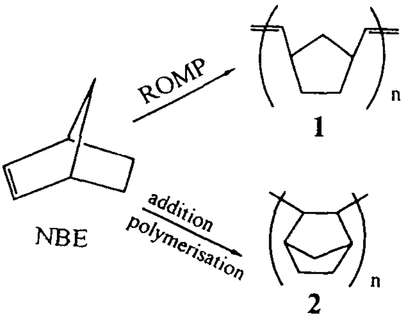
At first the activation of the catalytic systems Mo/alkylaminums was examined, and then the olefin metathesis reaction catalysed by $Mo(CO)_5PPh_3$ was investigated. A more detailed study was carried out on the polymerisation of norbornene by the catalytic system $Mo(CO)_5PPh_3$/ $EtAlCl_2$. The effect of the reaction conditions such as the ratios catalyst/cocatalyst, catalyst/monomer and the solvent on this polymerisation was examined. Finally, the best conditions found here were applied to the polymerisation of norbornadiene.

Study of the catalytic system

The activation of the catalytic system has been followed by IR spectroscopy according to a method already used by Bilhou et al. (12) for the catalytic system $W(CO)_5PPh_3/EtAlCl_2/O_2$. They have assigned the IR signals at 2050cm^{-1} and 2100cm^{-1} to the intermediate complex $W(CO)_4Cl_2$, as has been proposed by Agapiou and McNelis (14) who suggested that this compound subsequently forms a metallocarbene which promotes olefin metathesis reaction. In our work, a series of alkylaluminums such as $AlCl_3$, $EtAlCl_2$, Et_3Al, Et_2AlCl and $Et_3Al_2Cl_3$ were tested for complexation with the $Mo(CO)_5PPh_3$ in ratio Mo/Al of 1/3 and 1/6 in chlorobenzene under an inert atmosphere. From the IR spectra we observed that no complexation occured for $AlEt_3$ and Et_2AlCl. Only $AlCl_3$, $EtAlCl_2$ and $Et_3Al_2Cl_3$ gave the characteristic band of $Mo(CO)_4Cl_2$, which were similar to those obtained for the $W(CO)_4Cl_2$, after an activation period of two hours.

Study of the polymerisation of norbornene

It is well known that norbornene undergoes two different modes of polymerisation: ring-opening metathesis polymerisation (ROMP) 1 (8-10) and olefin addition polymerisation 2 (15) as shown in Scheme 1.



Scheme 1

The ^{1}H-NMR spectrum of the polyNBE produced in our work shows the vinylic resonances at δ= 5.2(cis) and δ= 5.35(trans) ppm, characteristic of the cyclopentylene vinylene unit 1 (8). The presence of this unit is also confirmed by the IR spectrum which exhibits a C=C stretch at 1680cm^{-1} and a vinylic C-H bending mode at 960 and 740cm^{-1}, characteristic for a trans and cis structure respectively(15c). Furthermore, the IR spectrum exhibits an intense absorption at 1300cm^{-1} characteristic of the bridging methylene group in C-7 position of unit 2 (15c). From the IR and ^{1}H-NMR spectra of the polyNBE produced in this work with the catalytic system $Mo(CO)_5PPh_3/EtAlCl_2$, we have concluded that in these products both structural units exist in the same chain. These conclusion is confirmed by the GPC curves (Figure 1a) of the produced polymers which display a monomodal molecular weight distribution, and by DSC measurements which show a single Tg value in the range 44-49°C suggesting random incorporation of both structures in the same chain. The results of these polymerisations and the conditions in which they were carried out are shown in Table 1. In this table the content of unit 1 (Scheme 1) in the polymer chain is expressed, according to Farona and his co-workers(10), as the percentage (%) of the ROMP polymer deduced from the proton intergration in ^{1}H-NMR spectra for the ratio of olefinic to aliphatic protons (O:A). As it is shown in Table 1 the percentage (%) of ROMP differs in each case depending on the conditions. The Mo/Al ratio was varied from 1/2 to 1/20. The best results were obtained when the ratio was 1/6 in chlorobenzene (100% of the ROMP product) and the worst when the ratio was 1/20. In the case where dichloromethane was used

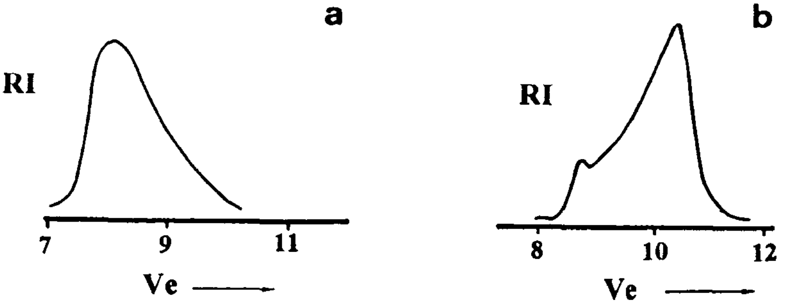


Figure 1:Indicating SEC chromatograms of polyNBE produced with the catalyst $Mo(CO)_5PPh_3/EtAlCl_2$ (1/6) in toluene (a) and polyNBDE produced with the catalyst $Mo(CO)_5PPh_3/Et_3Al_2Cl_3$ (1/6) in dichloromethane (b).

as the solvent, the polymer produced consisted of two fractions: an insoluble one (~90%w/v) even in boiling 1,2-dichlorobenzene and a soluble one in which the ROMP product was only 5%, the rest consisting of unit 2, resulting from the insertion process. The insoluble fraction must be due to ionic species discussed below.

Study of the polymerisation of NBDE

We have also tried to polymerise the NBDE which is also a strained monomer. For that we used a ratio Mo/Al of 1/6 which gave the best results for NBE. The results of these polymerisations and the conditions in which they were carried out are shown in Table 2.The polymerisation of NBDE is easily initiated by a number of catalysts and the structural units of the polymers produced are shown in Scheme 2. In most cases polymerisation produces crosslinked units, 4 (16) via ROMP and 7 (15c) via the olefin addition polymerisation, because of the two double bonds present in the monomer. An exception is the cationic transannular polymerisation in the course of which a cyclopropane ring within the 2,6-disubstituted nortricyclene repeating unit 5 is formed (17). Also in the case where the reaction takes place on one double bond, the structural units 6 (18), corresponding to an olefin addition polymerisation and unit 3 (19) corresponding to the ROMP may be formed.

Table 1. Polymerisation of norbornene with the catalytic system $Mo(CO)_5PPh_3$ /$EtAlCl_2$

Run, No	Mo/Al	Solvent	Yield %	O:A[a]	%ROMP	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$
1.	1/2	Chlorobenzene	89	1:5	83	27200	75000	2.83
2.	1/6	>>	100	1:4	100	31100	91000	2.93
3.	1/10	>>	74	1:13	35	21300	57600	2.70
4.	1/20	>>	23	1:45	11	2170	2530	1.16
5.	1/6	Toluene	91	1:5.4	78	28700	72200	2.52
6.	1/6	Benzene	81	1:6	71	26400	69900	2.65
7.	1/6	Dichloromethane	100	1:100	5	1235	2430	1.97

[a] From the ^{1}H-NMR intergration of the olefinic to aliphatic protons

All the polymerisations were carried out in ambient temperature. The ratio Mo/monomer was 1/70 and the activation time of the catalytic system was about 2h. Molecular weight calibrations were run against a polystyrene standard.

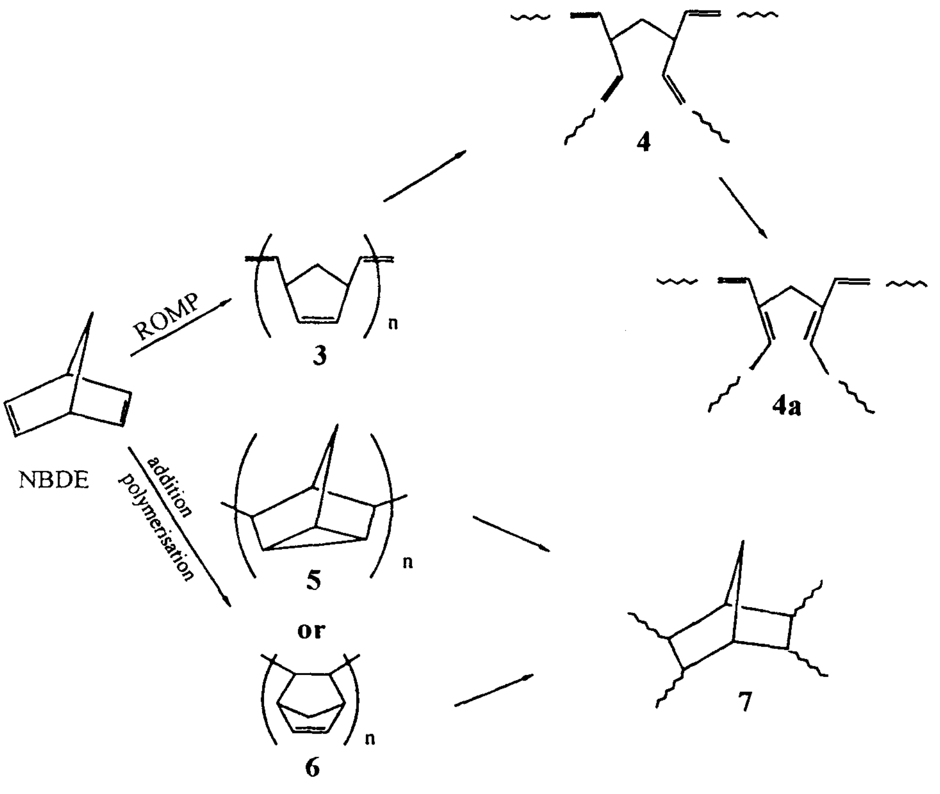
Table 2. Polymerisation of NBDE with the catalyst Mo(CO)$_5$PPh$_3$ /alkylaluminums

Run No	Catalytic system*	Mo/ monomer	Solvent	%Yield	g	ΔHpp (G)
1.	Mo/EtAlCl$_2$	1/200	Chlorobenzene	73	2.0038	15
2.	Mo/EtAlCl$_2$	1/50	>>	94	2.0038	20
3.	Mo/Et$_3$AlCl$_3$	1/200	Dichloromethane	100	2.0035	7
4.**	Mo/Et$_3$AlCl$_3$	1/40	>>	100	-	-

*The Mo/Al ratio is 1/6. All the polyNBDE produced are crosslinked except Run 4 which is amorphous with a $\overline{Mw}$=11550, $\overline{Mn}$=985 and I=11.7.

** In Run 4 only a very weak ESR signal was obtained

For our polymerisations of NBDE shown in Table 2 the polymers produced in Runs 1,2,3 are insoluble in any solvent. In the IR spectrum all of them showed the characteristic peaks at 800 and 1300cm^{-1} which can be ascribed to unit 5 (20). They also exhibited the characteristic band at 3020 cm^{-1} of =CH stretcing absorption, a broad C=C stretch centered at 1605cm^{-1}, the saturated aliphatic C-H absorptions at 2950 and 2880 cm^{-1}, the vinylic C-H bending mode at



Scheme 2

960and 740cm^{-1}, characteristic for a trans and cis structure respectively and the methylene scissor vibrations at 1450cm^{-1}. From these IR data and taking into account the insolubility of the polymers, we concluded that these polymers incorporated both repeating units **4** and **5** corresponding to ROMP and olefin addition polymerisation respectively. In the case of Run 4 (Table 2) a soluble polymer is produced. This can be attributed to the fact that the solvent used is the more polar dichloromethane which propagates the reaction in a different way than chlorobenzene. Because of the solubility of the polymer produced we cannot expect the presence of unit **4** and **7**. The IR spectra shows the characteristic peaks at 800 and 1300cm^{-1} for unit **5** and the ^{1}H-NMR spectra shows peaks at 5.12, 5.73 and 5.8 ppm which are attributed to the cyclopentylene vinylene unit **3** (19). Also there is no peak at 6.2 ppm characteristing of unit **6** (15c). So, the IR and ^{1}H-NMR data show the existence of both repeating units **3** and **5** and from the ^{1}H-NMR spectra (intergration O:A) it can be concluded that the product contains only 10.5% of unit **3**. On the other hand the GPC curves (Figure lb) present a bimodal molecular weight distribution suggesting the existence of two active centers whose character is discussed below.

Conjugation of crosslinked polyNBDE

The presence of IR absorption bands characteristic of double bond suggests that conjugation is introduced in the polymer. That is further confirmed by the observation of a ESR signal having a g-value in the area of free electrons (21). The g-values of the ESR signals of polyNBDE are shown in Table 2 and the characteristic ESR signal of Run 3 consisting of a symmetrical single line with a peak to peak width ΔHpp=7G and a g-value of 2.0035 is shown in Figure 3. Most probably the observed conjugation is due to the double bond shift in structural unit **4**, resulting to structural unit **4a** (Scheme 2), caused by the catalyst used. This type of conjugation has never been reported before for the crosslinked polyNBDE polymerised by using a series of ROMP catalysts and especially the $WCl_6/SnMe_4$ (1/2), which is the most common used catalyst, at a ratio of W/monomer=1/200 in chlorobenzene (16). For rationalizing these data we repeated the polymerisation with the catalyst $WCl_6/SnMe_4$ (1/2) and no ESR signal was observed. The IR data of this polymer were identical with those of unit **4** and no absorption at 8l0cm^{-1} characteristic of unit **5** was observed. In contrary, using the catalyst $WCl_6/EtAlCl_2$ (1/10) in a ratio of W/monomer=1/200 in chlorobenzene, which causes double bond shift on polybutadienes (22), the produced crosslinked polyNBDE also displayed a symmetrical ESR signal with a g-value 2.0035 and a peak to peak width, ΔHpp of 12G. The IR data of this polymer were identical with those of unit **4** and **5** as in the case of the catalyst $Mo(CO)_5PPh_3$ /alkylaluminums which means that the later behaves in a similar way promoting the double bond shift reaction.

Conclusion

From the results obtained it is certain that the catalytic systems Mo/alkylaluminums, in the case of the polymerisation of the strained monomers NBE and NBDE produce polymers where ROMP and olefin addition polymerisation occur simultaneously in the same chain as it is described by Ivin's model. In contrary, in a more polar solvent like dichloromethane, although ROMP polymerisation takes place, the percentage (%) of the olefin addition process becomes higher. The last result may be due to the cationic species of the transition metal formed in dichloromethane, which favour the olefin addition polymerisation and they initiate the polymerisation as a new active center. These species which are produced and rapidly consumed in the $Mo(CO)_4Cl_2$ forming process (13) leading to the metallocarbene, have a longer lifetime because of this more polar solvent. A second reason for the formation of these species can be that mentioned by Bencsze (23) in the study of the analogous system $W(CO)_3X_2L_2$, where the catalyst is easily solvated by polar solvents and in the presence of $AlCl_3$ leads to ionic species.

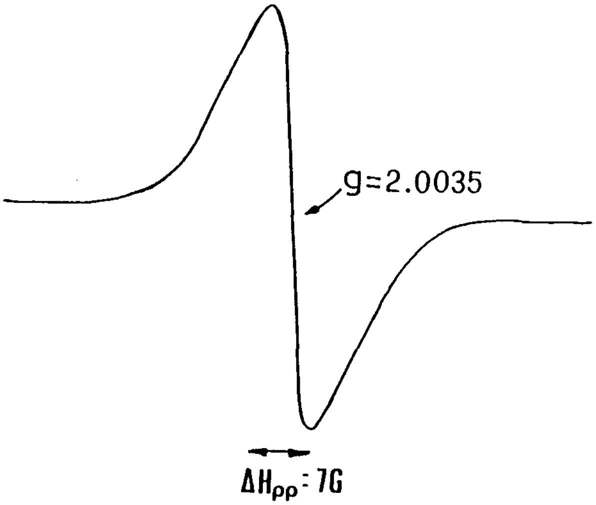


Figure 3. ESR spectra of the conjugated crosslinked polyNBDE

Therein it is also mentioned that the easily formed $W(CO)_4Cl_2$ turns into $W(CO)_3X_2L_2$. In our case for the active intermediate complex , $Mo(CO)_4Cl_2$, which is similar to that mentioned by Bencsze should occur the same transformation in the presence of a more polar solvent. These assumptions are also confirmed from the GPC curves for the polymerisation of NBDE in Run 4 (Table 2) where the existence of a second active center is observed. Also in the case of NBE in Run 7 (Table 1) the insoluble fraction produced may be due to the existence of these ionic species. The structure should be the one speculated in literature (18) forming a crosslinked structure of unit **2** (Scheme 1). Finally the double-bond-shift reactions should occur via a metal hydride $W^{\delta-}$-$H^{\delta+}$ or via the ionic species discussed above.

Acknowledgment. I wish to thank Prof. M. Kosmas (Section of Physical Chemistry, Department of Chemistry, University of Ioannina, Ioannina) and Dr. C. Mathis (Institute C. Sadron, CNRS, Strasbourg, France) for their helpful discussions. I am also greatful to Prof. I. F. Farona (Department of Chemistry, University of Akron, Acron, Ohio, USA) for a private communication.

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