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The ROMP catalysts $Mo(CO)_5PPh_3$/alkylaluminum with unstrained cyclic and linear dienes as initiators of the addition polymerisation

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Summary

We study the polymerisation of a series of unstrained cyclic and acyclic dienes with the catalytic system of $Mo(CO)_5PPh_3$/alkylaluminum. The $Mo(CO)_5PPh_3$/alkylaluminum catalyse the nonmetathesis polymerisation, through a pair of ionic complexes similar to that of Ziegler-Natta mechanism, and not through the ROMP (Ring-Opening-Metathesis-Polymerisation) mechanism followed by strained olefins. Because of the nature of these complexes the reactivity is lower with respect to that of a common Ziegler-Natta catalyst, such as $Cp_2TiCl_2/Et_3Al_2Cl_3$, as it is demonstrated, by means of kinetics and ESR measurements, in the case of the polymerisation of of 1,5-cyclooctadiene. Similarly to the Ziegler-Natta catalysts, they give cyclised products in the polymerisation of 1,5-hexadiene and 1,7-octadiene, and the 1,4-cis unit in the case of the polypentadienes. Finally we find that they are active catalysts for the polymerisation of styrene.

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 yields effective catalytic systems for the olefin metathesis reaction and for the Ring-Opening-Metathesis-Polymerisation (ROMP). One of the first cited as an effective catalyst for the ROMP of norbornene was $W(CO)_5L/\ EtAlCl_2/O_2$ (L=CO, PPh_3, $P(OC_6H_5)_3$, $P(n\text{-}C_4H_9)_3$ and pyridine) (1). Furthermore, it was shown that the catalytic system $Re(CO)_5Cl/C_2H_5AlCl_2$(2) and more recently the $Mo(CO)_5py/\ C_2H_5AlCl_2/\ R_4NCl$(3) polymerise norbomene by ROMP and olefin addition polymerisation (insertion process) simultaneously in the same chain. These results were well explained by the Ivin-Green's model (4) based on a-H migration, as it is shown below in Scheme 5 ($C \rightleftharpoons D$). More recently on the polymerisation of the highly strained monomers such as bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBDE) and bicyclo [2.2.1]hept-2-ene (norbornene, NBE) with the catalytic systems $Mo(CO)_5PPh_3$/ alkylaluminum (5) an antagonism between the ROMP mechanism and the olefin addition polymerisation mechanism in the same chain was also demonstrated. Furthemore with these last catalytic systems when the reactions were performed in a more polar solvent as dichloromethane the percentage of the olefin addition process was increased dramatically. In this last case, except the products formed, according to Ivin-Green's model, a new active center, having a cationic character, was generated as it was well demonstrated by experimental data (5).

The driving force of ROMP mechanism is the release of ring strain (6), as in the case of NBE and NBDE. In this paper we examine if the generation of the cationic center mentioned above is favoured in the polymerisation of the unstrained cyclic monomers, which present lower ring strain (6). Therefore we polymerise the cis-cis-1,5- cyclooctadiene (1,5-COD),

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which is well known to undergo the ROMP mechanism(7). The polymerisation takes place in polar and non polar solvents by the $Mo(CO)_5PPh_3$ / alkylaluminum catalysts. The results are compared to those performed in the cationic transanular polymerisation of 1,5-COD by the Ziegler-Natta catalyst, Cp_2TiCl_2/ $Et_3Al_2Cl_3$(8). In addition we examine the polymerisation with a series of unstrained cyclic dienes such as cis-cis-1,3-cyclooctadiene (1,3-COD) and 1,3-cyclohexadiene (CHD). In order to examine further the nature of the active center, we polymerise conjugated dienes such as cis-1,3-pentadiene (PE) and trans-1,3-pentadiene (PE), α,ω acyclic dienes such as 1,6-hexadiene (1,6-HD) and 1,7-octadiene (1,7- OD), and finally, styrene which undergo the cationic and Ziegler-Natta polymerisation (9-11).

Experimental

Materials

$Mo(CO)_5PPh_3$ was prepared and characterised by standard literature method(12). Organoaluminum compounds, Cp_2TiCl_2, $EtAlCl_2$, $Et_3Al_2Cl_3$ and sec-BuLi were purchased from Aldrich Chemicals and used without further purification. 1,5-COD, 1,3-COD, cis-1,3-pentadiene, trans-1,3-pentadiene, 1,6-hexadiene, 1,7-octadiene, 1,3-cyclohexadiene and styrene(Aldrich) were refluxed over CaH_2 and distilled under argon. Toluene was refluxed over metallic Na, distilled and stored under argon. Chlorobenzene and dichloromethane were distilled over CaH_2 and stored under argon. THF was purified by distillation over Na in the presence of benzoquinone and stored under argon.

Polymerisation procedure

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 between 1/50 and 1/200. The catalyst/cocatalyst ratio was 1/6. This was the best ratio found in an earlier publication(5). The end of the reaction was determined by monomer consumption. Moreover consumption was established by monitoring by GC. The reaction was stopped with methanol containing a small amount of concentrated HCl. The polymer was precipitated with excess of methanol. The precipitated polymer was collected, dissolved in a small amount of chloroform, and precipitated again as mentioned above. The methanol was poured off and the polymer was dried under vacuum for 1 day at 30°C.

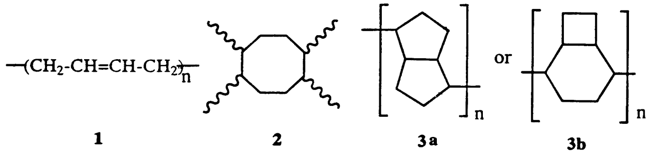
Measurements

^{1}H-NMR spectra were determined on Varian FT 80A NMR spectrometer, while ^{13}C-NMR spectra were recorded on Bruker AMX (400MHz) NMR spectrometer. Normally, $CDCl_3$ was used as the solvent, and TMS served as the internal standard for the ^{1}H-NMR spectra. Infrared spectra were recorded on a Perkin-Elmer 783B spectrometer. GC data were obtained with a Perkin-Elmer 8310B instrument equipped with an OV-101 column and a flame ionization detector. 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 for the polydienes were run according to the method applied in literature (8) and for the polystyrene 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. Thermogravimetric analysis (TGA) were performed with a Chyo Balance Corporation RDA 3 TGA in N_2 at 5°/min. DSC measurements were performed on a Du Pont 910 calorimeter equipped with a 99 thermal analyser.

Results and Discussion

Study of the polymerisation of cis-cis-1,5-COD

It is well known that cis-cis-1,5-COD offers two possibilities for homopolymerisation as shown in Scheme 1.



Scheme 1

The structure of **1** is carried out using the catalytic systems of ROMP(7) and it is identical with a polybutadiene of all-1,4 structure. The second possibility **2** involves a crosslinking process (13). The third possibility **3** is the product of the cationic transannular polymerisation of 1,5-COD(8). The polymerisation yields of 1,5-COD are shown in Table 1 in the Runs 1, 2, and 3. The ratio of Mo/alkylaluminum is taken 1/6 and it is the best ratio found for the activation of the catalytic system(5). The best yield is obtained with the more polar solvent dichloromethane.

Table 1. Polymerisation of 1,5-COD with Mo/alkylaluminum

Run No	Catalyst	Cat./cocat. ratio	Cat./monom. ratio	Solvent	Yield %	$\overline{Mw}^a$	$\overline{Mn}^a$	$\overline{Mw}/\overline{Mn}$
1.	Mo/$EtAlCl_2$	1/6	1/200	Chlorobenzene	15	920	590	1.55
2.	Mo/$EtAlCl_2$	1/6	1/70	>>	12	900	610	1.47
3.	Mo/$Et_3Al_2Cl_3$	1/6	1/200	Dichloromethane	30	943	600	1.57
4.	sec-BuLi^b	-	-	THF	-	-	-	-

$[Mo(CO)_5PPh_3]=10^{-2}$ M, T=25°C.

[a] by GPC in toluene at 25°C

[b] For the anionic polymerisation of 1,5-COD: $[\text{sec-BuLi}]=2.5\cdot10^{-4}$ mol, $[\text{1,5-COD}]=7\cdot10^{-2}$ mol, T= -75°C

The polymers obtained are soluble in organic solvents and the possibility **2** can be excluded. The IR and ^{1}H-NMR spectra show that there are no carbon-carbon double bonds in the polymer chain indicating that 1,5-COD does not undergo a ring-opening polymerisation. In the IR spectra only the methylene peaks at 2935, 2860 and 1450cm^{-1} are shown and in the ^{1}H-NMR spectra only the peaks at δ=1.27 and δ=1.52 ppm from the protons of methylene and methine exist. So the polymers obtained in Table 1 are of the structure **3.** The SEC-chromatograms obtained have a monodisperse distribution. The molar masses are small (Table 1) having narrow molecular distributions in the limits of cationic polymerisations. The DTA thermograms of poly-(1,5-COD) obtained composed of one rapid weight loss stage (433-495°C) and the total mass loss is 85%. These data are identical with these referred in literature(8).

In order to obtain further information about the kinetics of the cationic transannular polymerisation of 1,5-COD we tried to compare the poly-(1,5-COD) prepared with the

$Mo(CO)_5PPh_3/Et_3Al_2Cl_3$ (1/6) catalyst in dichloromethane with that of the literature(8) with the catalyst $Cp_2TiCl_2/$ $Et_3Al_2Cl_3$ (1/6). The latter is an original Ziegler-Natta catalyst combined with the same cocatalyst $Et_3Al_2Cl_3$ in the same solvent. We obtained the dependence of the monomer consumption(%) on the reaction time for the polymerisation initiated by $Mo(CO)_5PPh_3/Et_3Al_2Cl_3$ (1/6) and $Cp_2TiCl_2/$ $Et_3Al_2Cl_3$ (1/6) respectively, as shown in Figure 1. We used the following first order kinetic equation to describe these data:

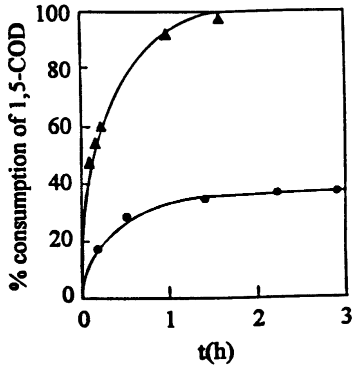


Figure 1. The effect of the nature of the catalyst on 1,5-COD consumption with the catalytic system $Cp_2TiCl_2/$ $Et_3Al_2Cl_3$ (1/6) (▲) and $Mo(CO)_5PPh_3/$ $Et_3Al_2Cl_3$ (1/6) (●) in dichloromethane. $[Cp_2TiCl_2]=$ $[Mo(CO)_5PPh_3]=$ 10^{-2}M. [Ti]/[Al]=1/6.[Mo]/[Al]=1/6.Ti/monomer= 1/200, Mo/monomer=1/200. T=25°C.

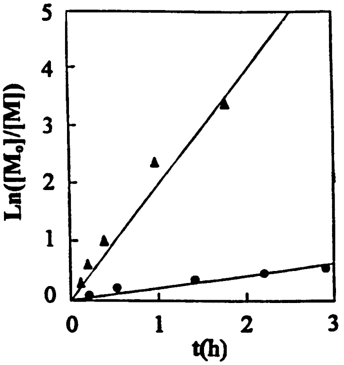


Figure 2. Plots of $Ln([M]_0/[M])$ versus reaction time for polymerisation of 1,5-COD by $Cp_2TiCl_2/$ $Et_3Al_2Cl_3$ (1/6) (▲) and $Mo(CO)_5PPh_3/$ $Et_3Al_2Cl_3$ (1/6) (●). Data from Figure 1.

$-d[M]/dt = k [M]$ or $Ln([M]_0/[M]) = kt$

In figure 2 we plot *Ln([M]$_0$/[M])* versus reaction time *t* for the two polymerisations systems initiated by $Mo(CO)_5PPh_3/Et_3Al_2Cl_3$ (1/6) and $Cp_2TiCl_2/Et_3Al_2Cl_3$ (1/6). From the slopes of the plots we obtained two values of constant *k* (noted as k_1 and k_2 for $Mo(CO)_5PPh_3/Et_3Al_2Cl_3$ (1/6) and $Cp_2TiCl_2/Et_3Al_2Cl_3$ (1/6) respectively). The result of $k_2/k_1=10$ reveals that the $Cp_2TiCl_2/Et_3Al_2Cl_3$ (1/6)-initiated polymerisation is 10 times faster than that induced by $Mo(CO)_5PPh_3/Et_3Al_2Cl_3$ (1/6). Taken into account the fact that the two systems follows a first -order kinetics and the profiles of consumption curves, we can make the assumption that the acceleration effect of the $Mo(CO)_5PPh_3/$ $EtAlCl_2$ system is lower to that of Ziegler-Natta catalyst. This must due to the nature, the solvation and low oxidation state of the transition metal. ESR studies on 1,5-COD polymerisation induced by the $Mo(CO)_5PPh_3/$ $EtAlCl_2$ catalyst, exhibited Mo(III) paramagnetic species, as it Was concluded by an ESR signal with g=1.96(14). The greater single oxidation state of metal is VI and according to literature (6) the oxidation state for the ROMP active center is mainly IV and V. From these results it is also concluded that the active center is a cationic than a ROMP one and the mechanism of this reaction is discussed below.

The homopolymerisation of the others dienes

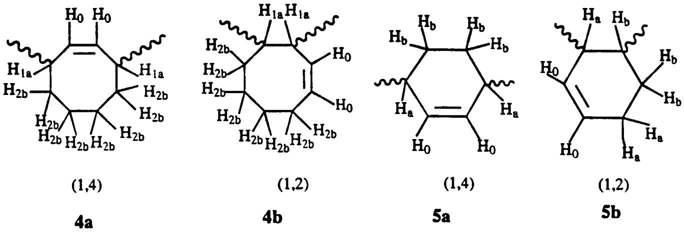
The results of polymerisation of dienes initiated by the catalyst $Mo(CO)_5PPh_3/$ alkylaluminum are summarised in Table 2.

Table 2. Conditions and results of the polymerisation of dienes by the catalytic system $Mo(CO)_5PPh_3$/alkylaluminum

Run No	Monomer	Mo/monomer ratio	Polymer yield %		$\overline{Mw}^a$	$\overline{Mn}^a$	$\overline{Mw}/\overline{Mn}$
			Amorphus	Crosslinked			
1.	1,3-COD	1/200	45 [1,2-trans(cis)]	-	2520	1530	1.65
2.	1,3-CHD	1/200	-	100	-	-	-
3.	1,3-cis-PD	1/100	71 [94%cyclic+ 6%1,4cis]	-	2330	1680	1.39
4.	1,3-trans-PD	1/100	95 [95%cyclic+ 5%1,4cis]	-	3805	2620	1.45
5.	1,5-HD	1/100	48	-	1080	585	1.84
6.	1,7-OD	1/200	-	100	-	-	-
7.	styrene	1/100	72	-	6570	2303	2.85

In Runs 1-6 the solvent was CH_2Cl_2 and in Run 7 was toluene. $[Mo]=10^{-2}$ M. [Mo]/[Al]=1/6. T=25°C. In Runs 1-6 the catalytic system was Mo/Et_3AlCl_3 and in Run 7 was $Mo/EtAlCl_2$.
[a] By GPC in toluene at 25°C.

The 1,3-COD and 1,3-CHD were polymerised by cationic catalysts (15) and the polymers obtained consisted of either 1,4 or 1,2 structural units (Scheme 2, **4a**, **4b** and **5a**, **5b** respectively). Also because of the two double bonds present in the monomer crosslinking takes place (15).

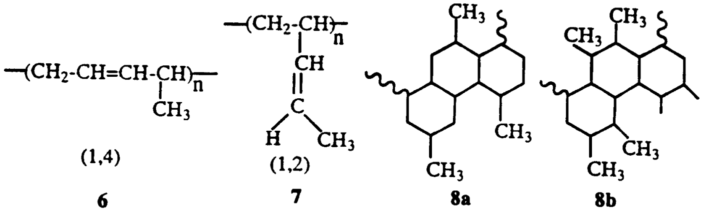


Scheme 2

In case of 1,3-COD the resulting polymer is a white amorphous powder, soluble in organic solvents, which in the IR spectra shows an absorption band at $1650cm^{-1}$ due to the carbon-carbon double bond. The ^1H-NMR spectrum of poly-(1,3-COD) exhibits broad resonances at 1.27ppm (H_{1b}) and 2.20ppm (H_{1a}) characterizing the methine protons and at 1.54ppm(H_{2b}) and 2.5ppm(H_{2a}) characterizing the methylene protons(15). The olefinic protons (H_{2b}) exhibit three resonances at 5.36ppm, 5.68ppm and 5.8ppm respectively(16). The ratio of olefinic to aliphatic protons is a measure of the degree of branching that is present in the polymer. In the present case the value of the above ratio is 1/20 which means that the degree of branching is about 70%. The ratio of allylic to the aliphatic protons is the only available intergration on the ^1H-NMR spectrum for the determination of the 1,4 or the 1,2 stuctural units. In the present case the value of the above ratio is 1/2.70 (the theoretical value for the 1,4 and 1,2 structural unit is 1/4 and 1/2.33 respectively) which means that the polymer obtained consists predominantly of 1,2 structural units. The SEC-chromatograms obtained have a monomodal molecular weight distribution (Table 2) and the DTA thermograms of poly-1,3-COD obtained composed of one rapid weight loss stage (498-588°C) and the total mass loss is 85%. The high degree of branching in cyclo-1,3-dienes by Ziegler-Natta catalysts is known in literature (17).

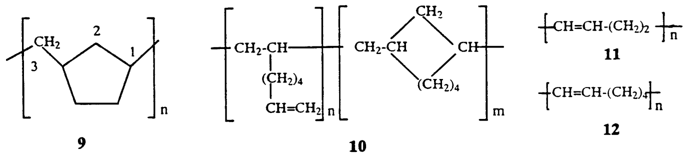
In case of 1,3-CHD the resulting polymer is a crosslinked polymer, insoluble in any organic solvent. Also in this case a cationic process of polymerisation was suggested (15).

The acyclic conjugated dienes cis and trans-1,3-pentadienes were polymerised by Ziegler-Natta and cationic catalysts(9), and the polymers obtained consisted of -1,4 and -1,2 stuctural units and a large amount of cyclic products as shown in Scheme 3. In this case the polymers formed were soluble in organic solvent. The estimated ratio of the olefinic protons to the total amount of the aliphatic protons of the polypentadienes which were found by the integration of the ^{1}H-NMR spectrum, shows that the percentage of the cyclic products for the cis-1,3-pentadiene and for the trans-1,3-pentadiene is 94% and 95% respectively. The IR spectra show an absorption band at 1660cm^{-1} due to the carbon-carbon double bond, an absorption band at 965cm^{-1} due to both 1,4trans+1,2trans structures and an absorption band at 760cm^{-1} due to the 1,4cis structure(9b). From the IR spectrum it was concluded that the unsaturated fraction of polypentadienes was consisted of 1,4-trans+1,2-trans (12%) and of 1,4-cis (88%) structure for the poly(cis-1,3-pentadiene) and of 1,4-trans+1,2-trans (19%) and of 1,4-cis (81%) structure for the poly(trans- 1,3-pentadiene), which means that the unsaturated fraction of polypentadienes consisted predominately of the 1,4-cis structure. The SEC chromatograms of polypentadienes produced display a bimodal molecular weight distribution. The one is assigned to the cyclic products and the other to the linear polymer. The DTA thermograms of polypentadienes obtained composed of two stages; the first weight loss (514-586°C) and the second (586-700°C) lead to a plateau at which point the total mass loss is 7%. From the data above was suggested that there is no incorporation of cyclic and linear structures in the same chain. Here we can mentioned that according to literature the Ziegler-Natta catalysts give rise to 1,4-cis and 1,2 units(9a). The latter favour the formation of cyclic products. The similarity of the polymers produced, from both the catalysts, confirms that the catalysts used is of the Ziegler-Natta type.



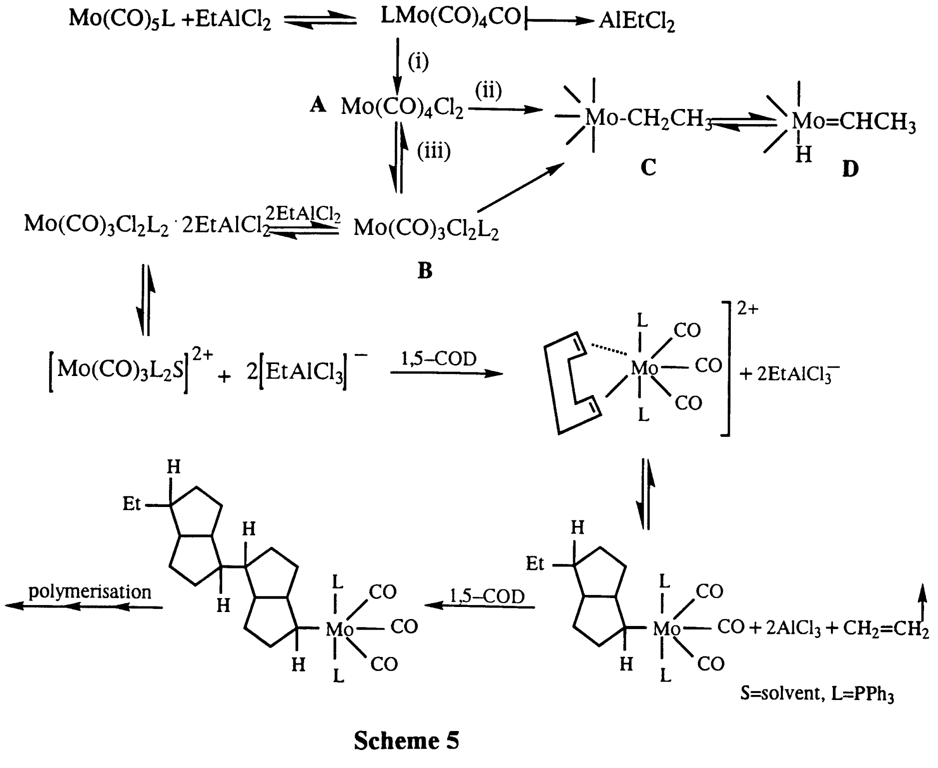
Scheme 3

The α,ω acyclic dienes, 1,5-hexadiene and 1,7-octadiene, with Ziegler-Natta catalysts give the polymes **9** and **10** respectively (10a,b) while the ROMP catalysts give the polymers **11** and **12** respectively (Scheme 4) (18). Also, crosslinked products are formed, because of the existance of the two double bonds of the monomer. The poly-(1,5-hexadiene) formed is amorphous and the ^{1}H-NMR spectrum shows no methine protons due to the double bond but the H_1 and H_3 protons are shown at 1.40 and 1.25ppm respectively due to stucture 9 (10a). The GPC chromatogram display a monomodal molecular weight disribution ($\overline{M}_w$=1080, $\overline{M}_n$=585) and the DTA thermograms composed of one rapid weight loss stage (475-700°C) and the total mass loss is 97%. From the spectroscopic data is concluded that the polymer obtained is the **9** (Scheme 4). The poly(1,7-octadiene) formed is insoluble in any organic solvent and it is a crosslinked polymer. The IR spectra of crosslinking poly(1,7-octadiene)



Scheme 4

is simple and shows the methylene absorbance at 2929 cm^{-1}, 2840 cm^{-1} and 1460 cm^{-1}. Traces of double bond at 1640 and weak absorptions of 1,4-trans, 1,2-trans and 1,4-cis at 990 cm^{-1}, 910 cm^{-1} and 710 cm^{-1} respectively assigned to the polymer **10** (Scheme 4) (10b), indicate that the resultant crosslinking polymer incorporates the polymer **10**.



Scheme 5

Finally the polymerisation of styrene was studied because this monomer is charactistically polymerised by Ziegler-Natta catalysts(11). The polystyrene formed by the catalyst Mo(CO)$_5$PPh$_3$/EtAlCl$_2$ gave in the ^{13} C-NMR spectrum the characteristic peaks of methine, methylene, and aromatic carbon at 40.8ppm, 42.3ppm and 128/129.5/148ppm respectively(19). The chromatograms display a monomodal molecular weight distribution ($\overline{M}_w$ = 6570, $\overline{M}_n$ =2303) and DSC measurements showed a single Tg value (53,6°C).

From the experimental results we conclude that the Mo/alkylaluminums catalyse nonmetathesis polymerisation in the case of unstrained cyclic and acyclic dienes contrary to the highly strained olefins as the NBE and NBDE (5). The structures of the polymer formed are similar to those obtained by a cationic polymerisation. This must be due to the stability of the unstrained cyclo-dienes used and the stability of active center formed(6). Based on the results, of all the polymerisations mentioned above, we propose a mechanism for the polymerisation of 1,5-COD by the $Mo(CO)_5PPh_3/EtAlCl_2$ catalyst (Scheme 5). After the complexation of the catalysts components (6), the formation of $Mo(CO)_4Cl_2$ (**A**), which is also detected in an earlier paper (5), and leads to metallocarbene active center of ROMP(C)(20), does not follow the process (ii), but through process (iii) is easily transformed to $Mo(CO)_3Cl_2$ (21a) (**B**). By the excess of $EtAlCl_2$ the ionic pair of $[Mo(CO)_3L_2S]^{2+}$ and $[EtAlCl_3]^-$ is formed (22b,c). According to the literature the generation of metallocarbene, from B is high when $L=AsPh_3$, while in the case of $L=PPh_3$ the results are poor (21a). This means that in the presence of unstrained olefins, and excess of $EtAlCl_2$, the formation of this pair of ionic complexes is favoured. These was suggested to be a kind of Ziegler-Natta type active intermediate of polymerisation. The species $[EtAlCl_3]^-$ produced do not play any role to polymerisation because as it is shown in Table 1 the 1,5-COD does not polymerise by an anionic method. So the coordination of 1,5-COD takes place on $[Mo(CO)_3L_2S]^{2+}$ and the series of reaction is shown in Scheme 5.

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