

Ring-opening polymerization of cycloolefins with MgCl_2

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Abstract

Until now polymerization catalysis was linked to transition metal chemistry with only few exceptions. However, in our work we will show that the main group metal salt MgCl_2 can give rise to oligomerization and polymerization of olefins. Since the late 1960s MgCl_2 has been used as support material for commercial Ziegler–Natta catalysts in many variations. Although the influence of this ‘inert’ support on the structure and properties of the resulting polymers is known, investigations of the reactivity of MgCl_2 with olefins are rare. Surprisingly MgCl_2 polymerizes strained olefins like norbornene, norbornadiene, 5,6-dichloronorbornene and bistrifluoromethyltricyclo[4.2.2.0]decatiene in high yield to high molecular weight products. The polymers are characterized by FT-IR, NMR, size exclusion chromatography (GPC) and thermoanalytical methods. The properties and structure of these polymers correspond to those prepared by ring-opening metathesis polymerization (ROMP). The characterization of different MgCl_2 phases is carried out by the use of powder diffraction measurements, electron microscopy, measurements of the specific surface (BET), simultaneous thermal analysis (STA), and atomic absorption spectroscopy (AAS).

Keywords: Polymerization; Norbornene; Heterogeneous catalyst; Magnesium dichloride

1. Introduction

The development of heterogeneous Ziegler–Natta catalysts for the polymerization of α -olefins can be described in terms of different ‘catalyst generations’ [1,2]. Each generation is marked by an increase in activity and stereospecificity. The catalysts of the so-called first generation were based on TiCl_3 or TiCl_4 and alkylaluminium compounds, those of the second generation included also a Lewis base and were described as ‘self-supported systems’.

In these heterogeneous Ziegler–Natta catalysts only about 1% of the titanium atoms of the transition metal compound are involved in the polymerization process [3], and account for their moderate activity compared to modern catalyst systems.

A major development of heterogeneous Ziegler–Natta catalysis occurred in the late 1960s. Many support materials were investigated to improve catalyst activity and control the properties of the resulting polyolefins such as molecular weight distribution, morphology and stereochemistry. ‘Active’ MgCl_2 proved to be the best for titanium compounds which are almost exclusively used for α -olefin polymerization [4,5]. Because of their similar crystal

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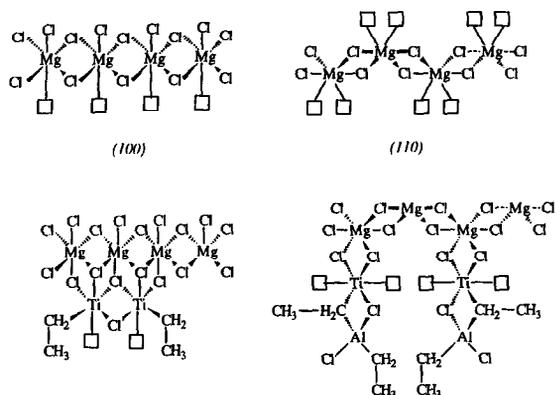


Fig. 1. Acidic centres on different MgCl_2 surfaces.

structure the titanium atoms in TiCl_3 are strongly bound at the MgCl_2 surfaces by acidic centres (Fig. 1). This bonding weakens the bonding between the growing polymer chain and the Ti-centres. In this way activity of the catalyst system is increased – but not the stereospecificity in propylene polymerization [6].

Further improvements of Ziegler–Natta catalysis were achieved with suitable Lewis bases e.g. esters, organic amines or alkoxysilanes as internal and external donors [7–9]. According to the variety of bases with different functionalities, basic strength and steric hindrance, both the rate of reactions, and the stereochemistry of the resulting polymers can be modified [10]. Compared to the original heterogeneous Ziegler–Natta catalysts the modern systems are very complex consisting of the transition metal compound, MgCl_2 as support, Lewis bases as internal and external donors and alkylaluminium compounds as co-catalysts. The most crucial step in the construction of these catalyst systems is the preparation of ‘active’ MgCl_2 .

‘Active’ always refers to the activity of the final catalyst with incorporated TiCl_3 or TiCl_4 and means amorphous MgCl_2 with a disordered structure prepared in various ways documented in the patent literature [11–14].

The simplest way is to mill commercially available anhydrous MgCl_2 under dry condi-

tions for 12 to 360 h to provide high active surface areas.

Further increase in surface area is obtained by adding electron donors like ethylbenzoate or organic amines to the milling process. These substances are partly incorporated in the MgCl_2 structure and thus break up its crystal lattice.

Grignard–Wurtz coupling reactions of alkyl- or aryl-chlorides in different solvents lead to structurally strong disordered MgCl_2 phases. The degree of distortion and the properties of the resulting support depend on the nature of the solvent. If diethylether is used as solvent a crystalline MgCl_2 -etherate results, whereas in the case of nonpolar solvents like *n*-octane, an amorphous material with many crystal defects is obtained.

A major part of the commercially applied MgCl_2 supports is synthesized via MgCl_2 alcohol adducts. This permits better control of the particle size and the crystallinity of the support. Organic alcohols like ethanol and 2-ethylhexanol intercalate in the crystal structure of the MgCl_2 . Spherical amorphous MgCl_2 particles of homogeneous size can be obtained either by precipitating the alcoholic solutions of MgCl_2 alcohol adducts in cold hydrocarbons [15] or by spray drying. The formed particles can be treated with TiCl_4 to produce Ziegler–Natta catalysts with Ti-alcoholates on MgCl_2 . Alternatively the MgCl_2 alcohol particles treated with $(\text{C}_2\text{H}_5)_3\text{Al}$ or SiCl_4 provide the amorphous support. The resulting Al- and Si-alcoholates must be removed by extensive washing.

MgCl_2 is regarded as an ‘inert’ support material for Ziegler–Natta catalysts and investigations on its reactivity are rare. However, we investigated the reactions of ‘active’ MgCl_2 , prepared in various ways, with cycloolefins, and found it to be active in the polymerization of strained cycloolefins [16]. Very little is reported about similar reactivities of main group salts in the literature. However, a single report showed that anhydrous ZnCl_2 polymerizes propylene without further cocatalysts [17]. Recently magnesium diacetate was found to be active in

polymerizing propylene but in that case a cocatalyst was necessary [18]. Finally it has been reported that aluminiumalkyls which are mainly used as cocatalysts in Ziegler–Natta and metathesis polymerizations can polymerize strained cycloolefins in a similar way to ROMP without any transition metal compound [19].

This is the first time that a magnesium compound without any cocatalyst is shown to be active in catalytic polymerization of strained bicycloolefins.

2. Experimental

2.1. Synthesis of amorphous $MgCl_2$

The preparation of amorphous $MgCl_2$ via ball milling was carried out under dry conditions in a glove box. The synthesis of the amorphous $MgCl_2$ via Grignard–Wurtz coupling reactions and also via the decomposition of $MgCl_2$ alcohol adducts were performed with dried reagents under argon using the Schlenk technique.

2.1.1. Ball milling of commercially available anhydrous $MgCl_2$ with / without ethylbenzoate

Commercially available $MgCl_2$ was milled in an agate ball mill for 3 days either directly or as a mixture with ethylbenzoate (1:1 or 1:0.5 mol).

2.1.2. 'Active' $MgCl_2$ via Grignard–Wurtz coupling reactions in diethylether

$Mg_{met.}$ (2.55 g/0.105 mol) was placed in a 250 ml two-necked flask and etched with a small crystal of iodine. Then 20 ml of diethylether were added.

While heating, a solution of benzylchloride (26.62 g/0.212 mol) in diethylether (100 ml) was added slowly. After the reaction had started the $Mg_{met.}$ was dissolved and $MgCl_2$ precipitated. The reaction was kept under reflux for 2 h. The $MgCl_2$ powder was filtered under inert atmosphere, washed extensively with dieth-

ylether to remove the coupling product (diphenylethane) and dried.

2.1.3. 'Active' $MgCl_2$ via Grignard–Wurtz coupling reactions in *n*-octane

$Mg_{met.}$ (3.0 g/0.123 mol) was placed in a 250 ml two-necked flask and etched with a small crystal of iodine. Then 20 ml of diethylether were added. While heating this suspension a solution of *n*-butylchloride (22.1 g/0.238 mol) in *n*-octane (100 ml) was added slowly. The reaction mixture was kept under reflux till the $Mg_{met.}$ was completely dissolved. $MgCl_2$ began to precipitate after the reaction had started. The $MgCl_2$ powder was filtered from the solution, washed several times with *n*-octane to remove the *n*-butylchloride and dried.

2.1.4. 'Active' $MgCl_2$ via formation and activation of $MgCl_2$ alcohol adducts

(a) To a suspension of $MgCl_2$ (6 g/0.063 mol) in *n*-pentane (80 ml) 2-ethylbutanol (24 ml/0.196 mol) was added dropwise. After 2 h of stirring at room temperature a voluminous powder resulted. This product was dried overnight to give a $MgCl_2$ alcohol adduct.

(b) Anhydrous $MgCl_2$ (6 g/0.063 mol) was stirred in ethanol (25 ml/17.42 mol) at room temperature. After 2 h the alcohol was completely incorporated in the $MgCl_2$ powder. The product was dried over night to give $MgCl_2 \cdot xEtOH$.

The additional activation of these powders was carried out in two different ways:

(i) With $Al(C_2H_5)_3$: $MgCl_2 \cdot xEtOH$ (2.55 g) was stirred for 3 h with 16 ml of a 1.01 mol/l solution of Et_3Al in *n*-hexane. The mixture was diluted with *n*-hexane (50 ml), heated up to 80°C and stirred for 4 h. After filtration and extensive washings with *n*-hexane the powder was dried.

(ii) With $SiCl_4$: $MgCl_2 \cdot xEtOH$ (3.0 g) was refluxed over night in 50 ml $SiCl_4$. The mixture was filtered, washed with toluene to remove the Si alcoholates and dried.

2.2. Polymerizations

All of the polymerization experiments were carried out at room temperature in a glove box. The monomers were either used directly or as a solution in toluene with addition of 10–30 wt% of MgCl_2 (relative to the monomer).

2.2.1. Polynorbornene from solution with 'active' MgCl_2

To a suspension of MgCl_2 (e.g.: 30 mg in 0.5 ml toluene) 1 ml of a 1M solution of norbornene in toluene was added. The mixture was slowly stirred at room temperature. Polymerization started immediately and the mixture became very viscous. After 20 min the mixture was dissolved in THF. The polymer was precipitated in ethanol and was stirred for 1 h to remove the MgCl_2 . The product was dried under vacuum. According to the different MgCl_2 phases the yield varied from 10 to 80%.

2.2.2. Polynorbornadiene from solution with 'active' MgCl_2

To a suspension of MgCl_2 (e.g.: 50 mg in 0.5 ml toluene) 1 ml of a 50 vol.% solution of norbornadiene in toluene was added. The solution was stirred at room temperature. The reaction was as fast as the norbornene polymerisation reaction. After 20 min the mixture was dissolved in THF, the polymer precipitated in ethanol, and stirred extensively to remove the MgCl_2 . According to the activity of the MgCl_2 used the yield rose up to 65%. After precipitation the polymer could not be redissolved in common organic solvents due to crosslinking.

3. Results and discussion

Our investigation reveals that amorphous MgCl_2 phases are active for the ring-opening polymerization of strained cycloolefins. The morphology and the reactivity of the resulting MgCl_2 changes, depending on the preparation method.

Commercially available anhydrous MgCl_2 that is milled in an agate ball mill for 72 h under dry conditions exhibits a moderate polymerization reactivity with cycloolefins. If donor substances like ethylbenzoate are added to the milling process the MgCl_2 powder shows no activity at all. Although this additive enhances the disorder of the crystal lattice it is able to coordinate to the active centres on the MgCl_2 surface.

The most active MgCl_2 phases for the polymerization of cycloolefins are among those prepared by Grignard–Wurtz coupling reactions. According to the solvent used and its coordinating ability inactive as well as highly active MgCl_2 can be obtained.

If the polymerization is carried out in ethers like THF or diethylether MgCl_2 ether complexes are formed.

The coordination of THF to the active centres on the MgCl_2 surface is much stronger than that of diethylether and explains why MgCl_2 prepared in THF is absolutely inactive for the polymerization of cycloolefins whereas that synthesized in diethylether is highly active. Grignard–Wurtz coupling reactions in hydrocarbon solvents like decaline or *n*-octane also give MgCl_2 powders with high activity. In these cases the MgCl_2 surface should be free from coordinating agents. The alkylchlorides used are benzylchloride when ethers are used and *n*-butylchloride when hydrocarbons are used as solvents for catalyst preparation. To remove the coupling products from the surface, the resulting MgCl_2 has to be washed with non-coordinating solvents like hydrocarbons or CH_2Cl_2 .

Organic alcohols form crystal alcoholates with MgCl_2 . The decomposition of these alcohol adducts with $(\text{C}_2\text{H}_5)_3\text{Al}$ or SiCl_4 gives active MgCl_2 powders with a very distorted structure. Their activity is comparable to the phases synthesized via Grignard–Wurtz coupling reactions if the Al- and Si-alkoxy compounds formed are completely removed by extensive washing. The reactivity of the MgCl_2 -phases depends, to a large extent, on their crys-

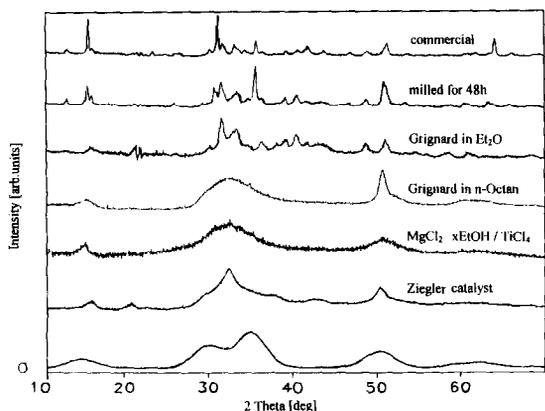


Fig. 2. X-ray powder diffractograms of differently synthesized MgCl_2 with decreasing crystallinity.

tallinity and on the preparation method used. Fig. 2 shows the X-ray powder diffractograms of differently synthesized MgCl_2 with decreasing crystallinity. The last curve in this figure is a calculated spectrum based on JCPDS-data (Joint Committee of Powder Diffraction Scattering) with a simulated degree of crystallinity. The morphological properties of the synthesized MgCl_2 phases were also determined by electron microscopy.

The absence of a transition metal in the MgCl_2 phases was proved by atomic absorption spectroscopy (AAS) and energy dispersive X-ray analysis (EDX). The MgCl_2 phases which were

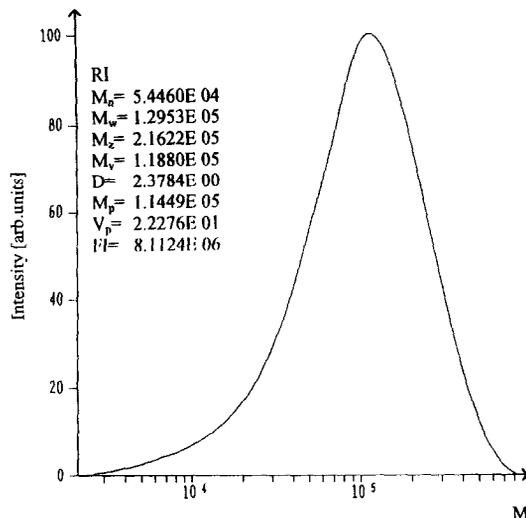


Fig. 3. Size exclusion chromatogram of polynorbornene from the reaction of a norbornene solution with MgCl_2 .

characterized before the reactions contained no other metal than magnesium.

Nonpolar strained cycloolefins like norbornene react quickly with MgCl_2 . The reaction with norbornene was carried out in a 1M solution of norbornene in toluene under dry conditions and at room temperature. The reaction time was dependent on the nature of the MgCl_2 surface ranging from minutes (phases prepared by Grignard–Wurtz couplings) to half an hour (commercially available anhydrous MgCl_2).

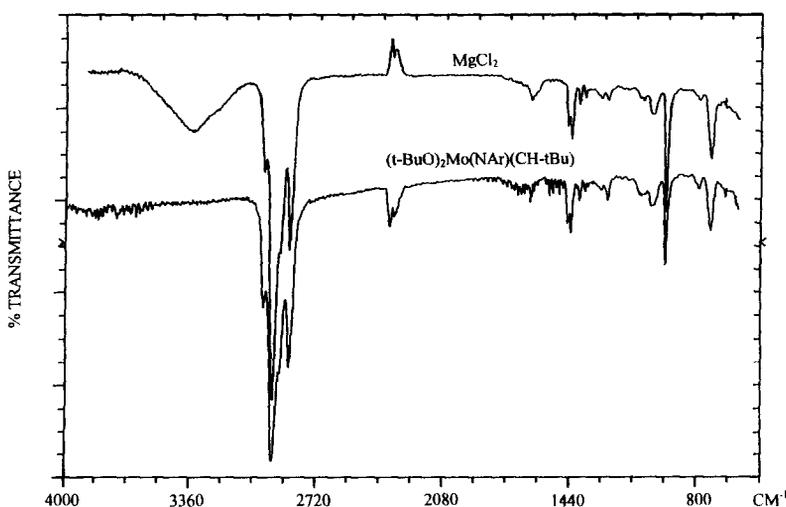


Fig. 4. FT-IR Spectrum of polynorbornene in comparison with a ROMP-polynorbornene synthesized with $(t\text{-BuO})_2\text{Mo}(\text{NAr})(\text{CH-tBu})$.

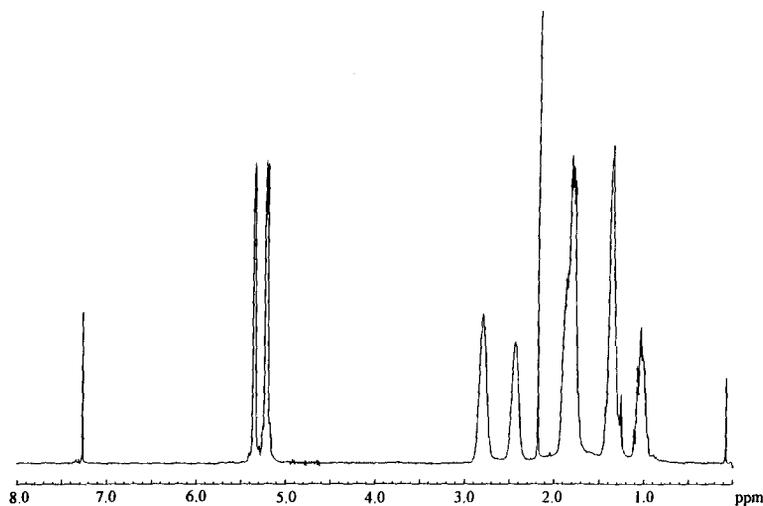


Fig. 5. $^1\text{H-NMR}$ Spectrum of polynorbornene obtained with MgCl_2 .

According to the differences in activity and morphological properties of the various MgCl_2 phases it cannot be totally excluded that a polyaddition of norbornene occurs as a side reaction to a minor degree.

Fig. 3 shows a GPC curve of a polynorbornene from the reaction of a norbornene solution with MgCl_2 . The high molecular weight with a comparatively narrow size distribution can be seen. To check the structure of the

polymer spectroscopic investigations were carried out. A film of the polymer obtained was cast on NaCl . Fig. 4 shows the FT-IR spectrum of this polymer in comparison with a polynorbornene synthesized with $(t\text{-BuO})_2\text{Mo}(\text{NAr})(\text{CH-}t\text{Bu})$.

The spectra are almost identical, which indicates that the polynorbornene obtained with MgCl_2 has a similar structure as that with the molybdenum carbene catalyst. Importantly,

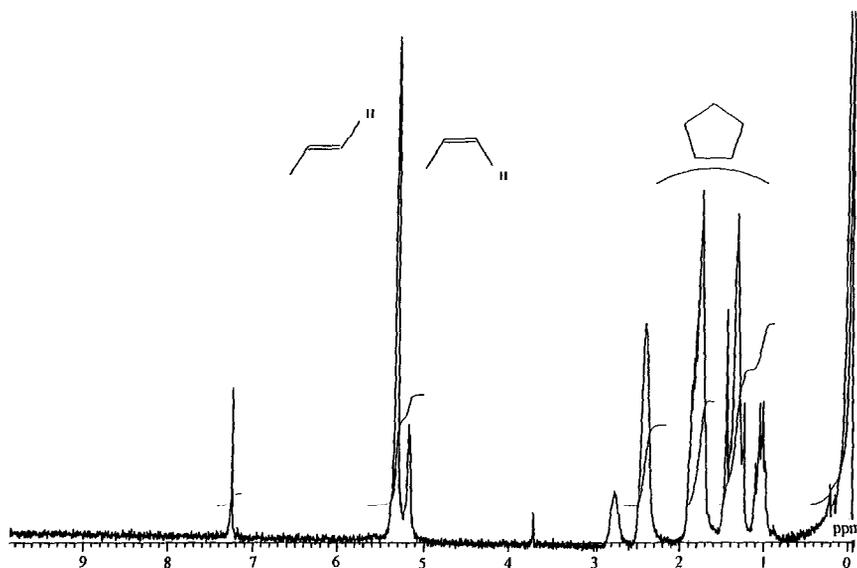


Fig. 6. $^1\text{H-NMR}$ spectrum of metathesis-polynorbornene obtained with $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$.

bands at 960 cm^{-1} and 736 cm^{-1} can be seen, indicating the presence of both *trans*- and *cis*-double bonds.

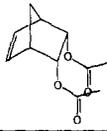
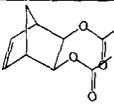
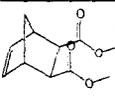
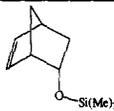
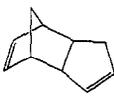
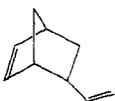
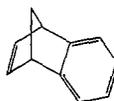
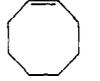
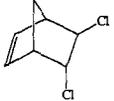
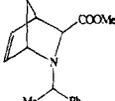
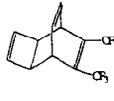
The $^1\text{H-NMR}$ spectrum shows two double bond-H signals corresponding to a *cis*-*trans* ratio of approximately 1 for the polynorbornene obtained with MgCl_2 (Fig. 5). The structure resulting from the spectroscopic investigations corresponds well to the data taken from literature for polynorbornene prepared via metathesis (e.g. the NMR shown in Fig. 6) [20].

In addition the DSC measurement indicates a glass transition temperature in the region from

37 to 50°C (measured on a Perkin Elmer DSC 4 instrument, heating rate $10^\circ/\text{min}$). Polynorbornene synthesized with a typical metathesis catalyst has a glass transition in the same temperature range, depending on the *cis*/*trans* ratio. No other significant phase transitions were indicated.

The reaction of norbornene with MgCl_2 is so fast that it can be performed in a fixed bed reaction. A solution of 1M norbornene in toluene or chlorobenzene is pumped through a column filled with MgCl_2 . The GPC of the resulting polymer is shown in Fig. 7. Because of the high

Table 1
Reactivity of MgCl_2 with various cycloolefins

monomer	reactivity on $\text{MgCl}_2^{*)}$	monomer	reactivity on $\text{MgCl}_2^{*)}$	monomer	reactivity on $\text{MgCl}_2^{*)}$
	++		++		-
	-		-		+/-
	-		-		-
	-		+/-		+/-
	+		-		++

(The ++ means high rate of reaction and a yield above 50%, +/- means slow rate of reaction and yields about 10–30% and – means no precipitable polymer.

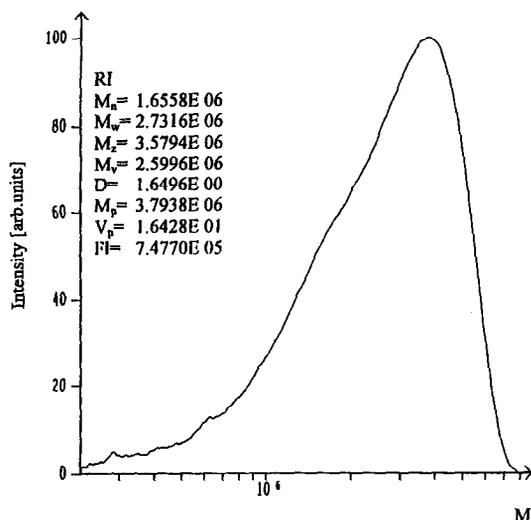


Fig. 7. Size exclusion chromatogram of polynorbornene from the reaction of a norbornene solution with MgCl_2 in a fixed bed reaction.

viscosity of the polymer solution the yield of this reaction is low, but the molecular mass is extremely high.

Norbornadiene also react with MgCl_2 to form high molecular weight products. The structure is again identical to polynorbornadiene synthesized by ROMP when the reaction is carried out in a 50% solution of norbornadiene in toluene.

Because of the high insolubility of the polymer, $^1\text{H-NMR}$ -investigation of its structure can only be carried out during the polymerization process. ^1H -signals arising from the main chain-double bonds at 5.4 ppm and from the double bonds in the ring at 5.6 ppm can clearly be detected.

Table 1 gives an overview about the monomers tested in this work.

An interesting detail of these investigations is, that benzonorbornene, vinylnorbornene and dicyclopentadiene did not react with MgCl_2 . At present we can not rationalize this, but we suppose that the π -systems opposite to the norbornene double bond may in some way inhibit access of that bond to the MgCl_2 surface. It is however surprising that norbornadiene can be polymerized in spite of its second double bond. It may be that since double bonds in norborna-

diene are equivalent both can be activated. Due to the much higher ring strain of the norbornadiene ring and a weaker coordination ability compared to the other monomers a polymerization may be favoured.

Unstrained cycloolefins give oligomers or polymers after reaction times of days in very low yield. There is no evidence for the presence of double bonds in the oligomeric products derived from cyclooctene and 1,5-cyclooctadiene, we therefore suggest a cationic mechanism for this polymerization. The mechanism of the ring opening polymerization of strained cycloolefins with MgCl_2 is not clear at the moment.

We suggest a coordinating/cationic mechanism as a provisional hypothesis; MgCl_2 surfaces possess acidic centres that can be blocked by donors like esters or solvents such as THF. These centres must be involved in the polymerization of cycloolefins with MgCl_2 initiation because donating reagents inhibit the reaction. The correspondence of our data with that of the ROMP of polynorbornene indicates that the bicyclic monomers which are polymerizable with MgCl_2 are also ring opened. There is no evidence whether the double bond, as in the case of ROMP reactions, or a single allylic bond is opened.

4. Summary and conclusion

Since the late 1960s MgCl_2 has been used as a support for heterogeneous Ziegler–Natta catalyst systems and was supposed to be inert. In our work we have shown that ‘active’ MgCl_2 is not inert at all. ‘Active’ MgCl_2 , prepared by the various ways documented in patent literature, is able to polymerize strained cycloolefins like norbornene and norbornadiene to high molecular weight products with conservation of double bonds without an apparent requirement for addition of another activating agent. This was confirmed by NMR and FT-IR spectroscopy. These polymers have the same structure as those ob-

tained using conventional organometallic metathesis initiators.

A variety of monomers was investigated. We only obtained high molecular weight polymers from monomers with high ring strain and minor polar substituents.

We found a relationship between the MgCl_2 phases used and the rate of reactions. The more amorphous the MgCl_2 -phases the faster the reaction. If the preparation was carried out in the presence of coordinating substances, like THF or esters, the polymerization reaction was inhibited. This may be a hint that acidic centres on the MgCl_2 surface are involved.

The very surprising fact that a main group salt like MgCl_2 can give rise to polymerization reactions is remarkable and might be useful in many respects.

After more than forty years of research side reactions are still a problem in Ziegler–Natta catalysis. Considering the self activity of MgCl_2 not only the transition metal, and the alkylaluminium, compounds but also the catalyst support can be responsible for these side reactions. A technical application of MgCl_2 as initiator especially for the polymerization of norbornene offers several advantages. Since ‘active’ MgCl_2 has been used as support for Ziegler–Natta catalysts for about thirty years various preparation methods are already known. Polymerization of norbornene with the heterogeneous MgCl_2 is carried out at room temperature and normal pressure; and MgCl_2 is non-toxic and very cheap.

Up to the present polymerization catalysis was linked to transition metal chemistry. However our studies reveal another example of a non-transition metal compound which is able to polymerize olefins. At the moment only the observed facts can be presented, further investigations above all concerning the mechanism of

the polymerization reactions remain to be carried out.

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