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POLYMERIZATION OF ISOBUTENE INITIATED BY MAGNESIUM CHLORIDE

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Abstract—Anhydrous $MgCl_2$ has been shown to develop catalytic activity for the polymerization of isobutene when cominuted under anhydrous conditions. This activity can be explained on the basis of the electrophilic character of exposed Mg^{2+} ions. Water is a particularly effective co-catalyst. When present in excess, however, it is a very effective catalyst poison, but with little effect on polymer molecular weight. The outstanding feature of $MgCl_2$ catalyst for isobutene polymerization is its ability to produce higher molecular weight polymer under comparable conditions than any other catalyst system described in the literature. It is concluded that the polymerization is initiation controlled, and this accounts for the serious loss in catalyst efficiency with decreasing temperature, despite the increasing polymer molecular weight. Spontaneous termination makes a major contribution to the overall chain breaking process and, like initiation, it is relatively slow and responsible for the high molecular weight polymer. Studies of the copolymerization of isobutene and isoprene show the latter to be a powerful catalyst poison. In addition to its usual effects on propagation and termination reactions, isoprene obviously interferes in some way with initiation by $MgCl_2$ to such an extent that no polymer is formed at less than about $-40°$ in the presence of isoprene. Polymerization initiated by $MgCl_2$ is no less sensitive to environment than those with other cationic catalysts. Similarities exist to other cationic catalyst systems in which initiation is slow and probably rate determining.

1. INTRODUCTION

IN AN early German patent[1] $MgCl_2$ is listed among catalysts for isoprene polymerization, but no data are given to support this claim. With this exception, all literature reports consistently disclaim normal $MgCl_2$ as a catalyst for polymerization of unsaturated hydrocarbons under mild conditions.[2–6] The isomerization and polymerization of dimethallyl by $MgCl_2$ at 220° for 6 hr can hardly be regarded as active catalysis.[7] A similar comment applies to the dimerization and hydrogenation of isobutene and amylenes by a mixed $MgCl_2$/iron catalyst at 300° and 80 atmospheres.[8] Anhydrous $MgCl_2$ has been used as a support for polymerization catalysts[9,10] and as a catalyst promoter.[11–13] The hydrate has also been used to provide water as a co-catalyst in cationic polymerization,[14] but in no case has $MgCl_2$ been reported to polymerize unsaturated hydrocarbons on its own. The polymerization of vinyl ethers by anhydrous $MgCl_2$ has been described[6] but these monomers are readily polymerized by many mild reagents. $MgCl_2$ has been reported to be inactive in the polymerization of epoxides.[15] In the alkylation of aromatic hydrocarbons, $MgCl_2$ was first reported to be inactive[16] but more recent workers have found it to show an extremely low degree of activity in alkylation by olefins and alkyl halides.[2,4,5,17–19] Some catalytic activity has been found for anhydrous $MgCl_2$ in dehydrohalogenation[20,21] and oxidative dehydrogenation reactions.[22]

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To summarize the literature, it is evident that anhydrous $MgCl_2$ can only be regarded as an extremely weak Friedel–Crafts catalyst, and there is little reason to expect it to be effective in polymerizing unsaturated hydrocarbons. This is probably why the catalytic activity of $MgCl_2$, prepared by Bryce-Smith by the decomposition of non-ethereal Grignard reagent with dry HCl, was considered to be due to a special structure.[2–5] $MgCl_2$ prepared in this way polymerized styrene at room temperature, whereas Bryce-Smith stated that anhydrous $MgCl_2$ of normal structure would not polymerize unsaturated hydrocarbons.

It was discovered in these laboratories[23] that finely divided anhydrous $MgCl_2$, obtained by milling normal $MgCl_2$ under dry conditions, will in fact readily polymerize styrene at room temperature, and isobutene at its boiling point ($-7°$). Since these results are in direct opposition to expectation from the literature quoted, they were very carefully checked. It was established that $MgCl_2$ itself, rather than any impurities present initially or formed in the milling process, was responsible for the catalysis. It was also found that the activity is not a transitory phenomenon since activity is maintained indefinitely if the $MgCl_2$ is stored under rigorously anhydrous conditions; it will also survive heating to 200°. This stability shows that the activity is not of the transient defect type studied by Kargin,[24–29] who obtained polymers by milling various solids in direct contact with monomers. The metals, salts and oxides studied by Kargin lost their activity as soon as the milling was stopped.

In addition to isobutene and styrene, it has been shown[23] that milled anhydrous $MgCl_2$ will polymerize α-methyl styrene and vinyl *n*-butyl ether. Propylene oxide gives a low molecular weight oil. Conjugated dienes such as butadiene, isoprene and cyclopentadiene are polymerized in low yield by milled $MgCl_2$ to infusible and insoluble solids. Methyl methacrylate and acrylonitrile are not polymerized by milled $MgCl_2$. The general pattern of activity of milled magnesium chloride is thus seen to conform to polymerization by a cationic mechanism. This is supported by the fact that milled $MgCl_2$ has been shown to be an effective catalyst in normal Friedel–Craft alkylation reactions, and also shows positive colour reactions, like $AlCl_3$, with certain polynuclear hydrocarbons.[23]

Since isobutene is by far the most important monomer in cationic polymerizations, it was selected for further study of the polymerization activity of milled $MgCl_2$. In addition to homopolymerization, some work on copolymerization of isobutene with isoprene was desirable. This system was again chosen because of its commercial importance.

2. EXPERIMENTAL

2.1. *Materials*

No systematic study of catalyst preparation was undertaken. Most of the work detailed in this paper was done with a batch prepared as follows.

Anhydrous $MgCl_2$ was fused at 750° in a quartz beaker. After cooling in a dry atmosphere it was transferred to a dry box (argon atmosphere, < 10 ppm H_2O). The outer layers of the fused mass were cut away and discarded and the inner crystalline material charged to a ball mill. The cylindrical stainless steel mill, 3·75 in. dia. and 5 in. length, was loaded with ninety $\frac{1}{2}$ in. stainless steel balls and 110 g $MgCl_2$. The bulk volume of this ball charge is 50 per cent of the mill volume and thus the maximum for efficient milling. Sixty per cent of the void volume of the ball charge is occupied by the $MgCl_2$ when finely divided. The mill was sealed with a Teflon gasket and rotated for 164 hr at 100 rev/min. This represents an angular velocity 67 per cent of critical (centrifuging). After milling, the ball mill was emptied (in the dry box) and the catalyst stored in 20 g portions in sealed ampoules until used.

Polymerization grade isobutene was used without further purification except drying. A typical G.C. analysis showed 0·34 per cent butene-1, 0·04 per cent butadiene-1,3, and 0·02 per cent isobutane as the only significant impurities. Several drying procedures were tried; the final choice being freshly activated Al_2O_3. Water content measured on a Gilbarco Sorption Hygrometer was 18 ppm after this procedure.

Reagent grade *n*-heptane from various sources was used. Olefins, aromatics and oxygenated impurities were removed by treatment with conc. H_2SO_4. After washing with dilute alkali and water the solvent was percolated through activated Al_2O_3. Gas-chromatographic analysis showed only ethyl cyclohexane (0·05 per cent) and dimethylhexane (0·02 per cent) as impurities.

Ethyl chloride was used direct from the cylinder and simply dried by passing through a column of 4A molecular sieve. Gas chromatographic analysis showed it to be 99·98 per cent pure. Methylene chloride was redistilled and dried over activated Al_2O_3.

Pure grade isoprene from various sources was used. Various purification procedures were tried when it was suspected to contain some poison. These treatments made no difference to copolymerization and the isoprene was simply dried (with freshly activated Al_2O_3) and used without even removing the stabilizer (*tert*-butylcatechol, nominal 50 ppm). Gas chromatographic analysis detected a large number of impurities at the trace level, the major ones being isopentane (0·1 per cent), 2-methylbutene-1 (0·12 per cent) and 2-methylbutene-2 (0·05 per cent).

2.2. *Polymerization procedure*

All glassware was dried and stored in the oven at 150° until required for use. Teflon sleeves were used on all joints, and all taps and stirrer glands were Teflon lubricated. Polymerizations were carried out in an atmosphere of dry nitrogen (< 5 ppm H_2O). Liquids were measured by volume at room temperature or at their boiling points (for isobutene and ethyl chloride). Catalyst was weighed in the dry box and transferred to the apparatus in a small stoppered glass tube. With a rapid stream of nitrogen issuing from the reaction flask, the unstoppered tube containing $MgCl_2$ was added to the flask equipped with stirrer, thermometer pocket, and cold finger condenser. After addition of diluent, the previously condensed and measured monomer was run into the reaction flask as rapidly as possible maintaining the required temperature. Runs were continued until no further polymerization took place (1–3 hr). Polymer was precipitated by pouring into excess ethanol. The polymer was redissolved in heptane, shaken with water to remove catalyst residues and finally reprecipitated by ethanol. After polymers had been dried *in vacuo* at 50°, molecular weights were determined from viscosity measurements on cyclohexane solutions. The isoprene content of the copolymers was determined by measuring unsaturation (iodine number).

3. RESULTS

3.1. *Homopolymerization of isobutene*

3.1.1. *Preliminary experiments.* Preliminary experiments showed isobutene to be polymerized to relatively high molecular weights by milled $MgCl_2$ but the reaction was very erratic. At any given temperature the most consistent feature of the polymerization was the molecular weight of the polymer produced. Thus at $-10°$ four repeat polymerizations, which gave conversions ranging from 2 to 41 per cent, gave products of molecular weight in the relatively narrow range 110,000–140,000.

It was found that extreme water sensitivity was the chief cause of the difficulties and after careful attention to drying procedures greater consistency was obtained. The effect of adding water to the initial reaction mixture can be seen in Fig. 1. Addition of 2 μl water slightly increases the polymer yield, but larger additions cause pronounced poisoning.

The molecular weights of polymer formed in these experiments are not available, but it had previously been established[30] that, contrary to its effect on conversion, the molecular weight of polymer is relatively insensitive to water content. In addition it was shown for copolymerization that the molecular weight is little affected by catalyst concentration.[32]

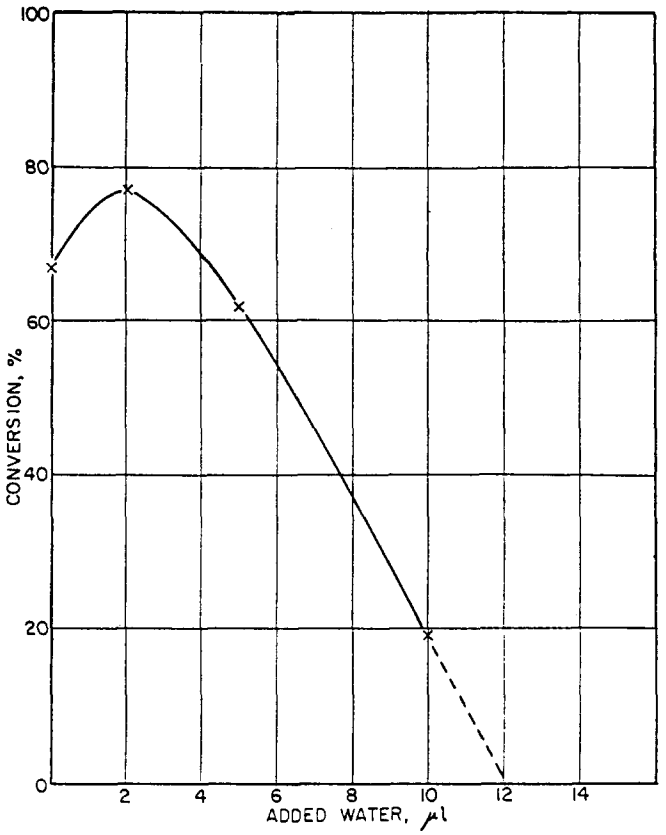


FIG. 1. Effect of added water on polymerization of isobutene. 100 ml isobutene, 140 ml *n*-heptane, 0·5 g $MgCl_2$.

3.1.2. *Effect of temperature.* These preliminary experiments indicated that the outstanding property of this catalyst is the ability to polymerize isobutene to higher molecular weights than other catalyst systems under comparable conditions. In common with other polymerizations of this type, the molecular weight increases as the polymerization temperature is reduced, as seen in the Arrhenius type plot of Fig. 2, curve A.

The yields of polymer corresponding to curve A are shown in Fig. 3. It can be seen that as the temperature is decreased the conversion is drastically reduced. A different batch of catalyst gave a similar decrease in catalyst activity as the temperature is reduced (curve B). Molecular weights corresponding to curve B are seen in Fig. 2 to be somewhat lower than previously obtained.

If water is the putative co-catalyst, then one explanation of the reduced yield of polymer is that at the lower temperatures water may not be in a physical state capable of acting as co-catalyst. For this reason an alternative, viz HCl which cannot "freeze out" at the temperatures involved, was tried. Addition of co-catalytic amounts of HCl gave no improvement in polymer yield, however, at $-78°$. It was also shown at a later stage in isobutene–isoprene copolymerizations that *tert*-butyl chloride cannot function as a co-catalyst at $-10°$.

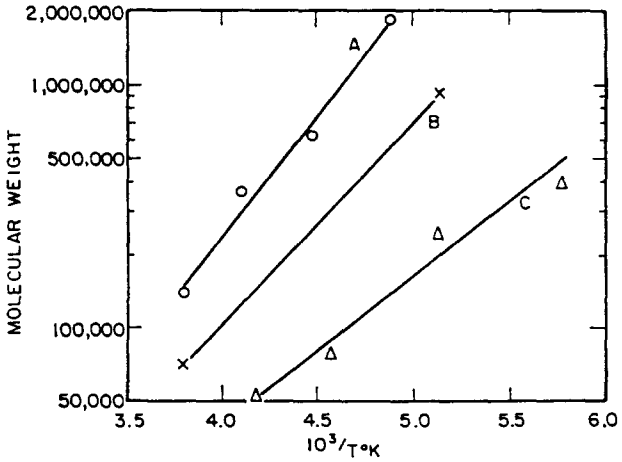


FIG. 2. Temperature effect on polymerization of isobutene. A—isobutene 100 ml, *n*-heptane 140 ml, $MgCl_2$ 0·1 g. B—isobutene 100 ml, *n*-heptane 140 ml, $MgCl_2$ 0·5 g. C—56 mole % isobutene in *n*-pentane, $AlCl_3$ catalyst.

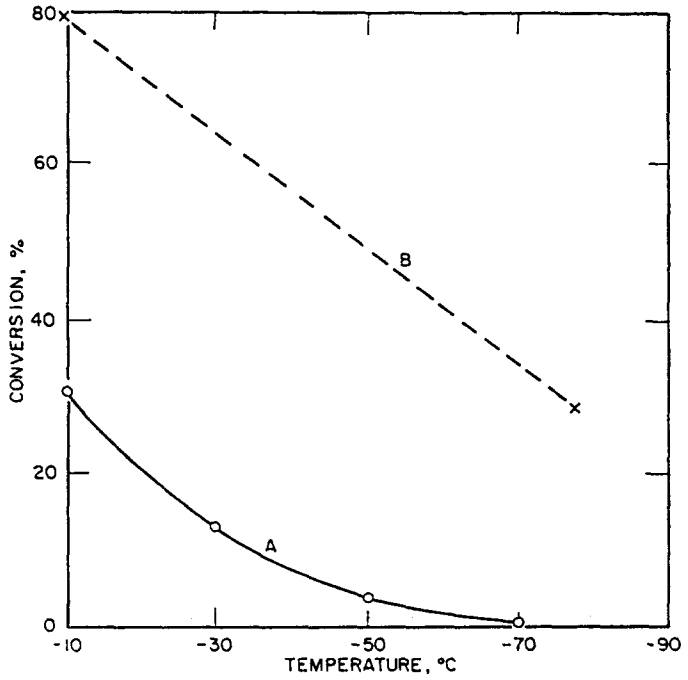


FIG. 3. Temperature effect on polymerization of isobutene. A—isobutene 100 ml, *n*-heptane 140 ml, $MgCl_2$ 0·1 g. B—isobutene 100 ml, *n*-heptane 140 ml, $MgCl_2$ 0·5 g.

The polyisobutene formed with $MgCl_2$ at the low temperatures (−78°) is of sufficiently high molecular weight to be insoluble in the reaction mixture. Entrainment of catalyst in the precipitated polymer could account for reduced activity at the lower temperature. To examine this possibility a polymerization was started at −78°.

After 2 hr at −78°, during which time a little polymerization occurred, the reaction mixture was allowed to warm to −10°. At the lower temperature the small amount of polymer was insoluble and was readily visible in the clear mixture of excess monomer and solvent. On raising the temperature the reaction mixture became cloudy, which was taken as an indication that high molecular weight polymer had dissolved allowing the catalyst to form a suspension. However, the overall yield of polymer was only 1 per cent and no greater than an equivalent run at −78° alone. This result indicates that entrainment of catalyst by insoluble polymer is not the primary reason for low catalyst activity at low temperatures.

3.2. *Copolymerization of isobutene and isoprene*

3.2.1. *Hydrocarbon diluent.* If $MgCl_2$ catalyst loses its activity at low temperature due to some fundamental mechanistic difficulty, rather than a physical reason as suggested above, then commercially it is unlikely to be of any real interest for the production of butyl-type elastomers. Study of isobutene–isoprene copolymerization might have enabled this point to be resolved since copolymers formed at these temperatures would be expected to be of low enough molecular weight to be soluble in the hydrocarbon diluent.

Initial attempts at copolymerization of 40 vol. % of a mixture of monomers (97·4 mole % isobutene, 2·6 mole % isoprene) in *n*-heptane at −78° gave no polymer. Even at −10° only 6 per cent conversion to polymer resulted. These runs were bracketed

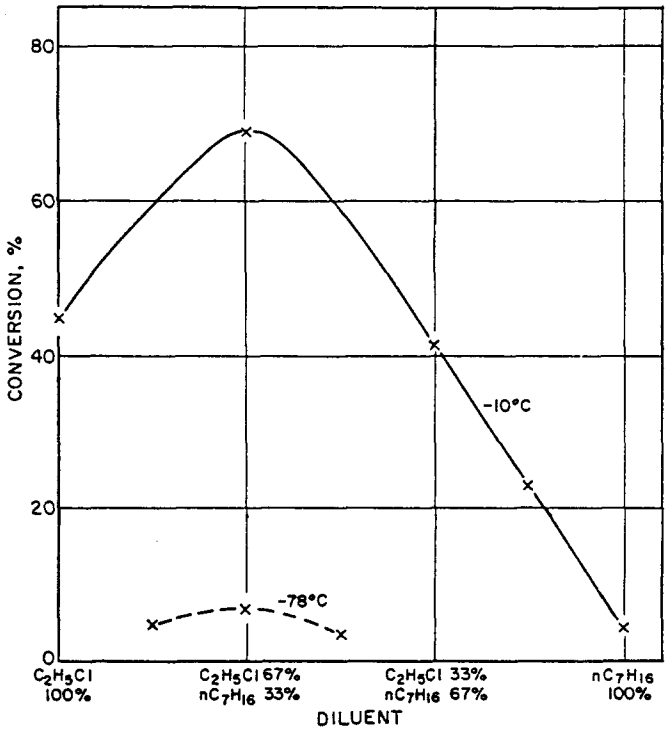


FIG. 4. Diluent effect on copolymerization of isobutene–isoprene. Monomers—2·6 mole % isoprene in isobutene, 100 ml. Diluent—ethyl chloride and/or *n*-heptane, 150 ml. Catalyst—$MgCl_2$, 1·0 g.

by similar runs in the absence of isoprene, which gave conversions of 28/20 per cent at $-78°$ and 79/78 per cent at $-10°$ showing that there had been no deterioration in the materials or the experimental technique. No impurities which would account for such inhibition were found in the isoprene. Different purification procedures and changing the source of supply of the isoprene gave no improvement and it is evident that isoprene itself is the cause of inhibition.

3.2.2. *Alkyl halide diluent.* In more polar diluents, such as ethyl chloride, polymerization was found to occur readily even in the presence of isoprene. The conversion to polymer of 40 vol. % mixed monomer (2·6 mole % isoprene in isobutene) can be seen in Fig. 4 for various diluents. It can be seen that at $-10°$ with all hydrocarbon diluent only 4·3 per cent conversion to polymer is obtained. Replacing the hydrocarbon diluent with ethyl chloride gave a rapid increase in the extent of polymerization up to a maximum of 69 per cent at about 2/1 ratio of ethyl chloride to *n*-heptane. Further increase in the more polar diluent decreases the conversion to 45 per cent in 100 per cent ethyl chloride. At $-78°$ the yields were very low but there is an indication of a maximum in the same region. In comparison to the effect on conversion, the effect of diluent on molecular weight of polymer produced is rather less, as seen in Fig. 5. In Fig. 6 there

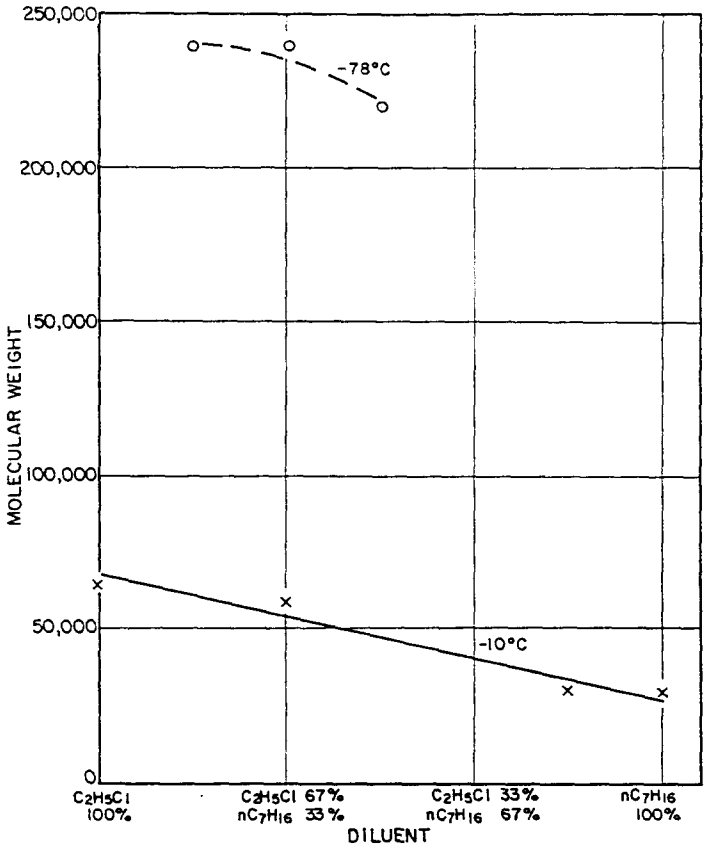


FIG. 5. Diluent effect on copolymerization of isobutene–isoprene. Monomers—2·6 mole % isoprene in isobutene, 100 ml. Diluent—ethyl chloride and/or *n*-heptane, 150 ml. Catalyst—$MgCl_2$, 1·0 g.

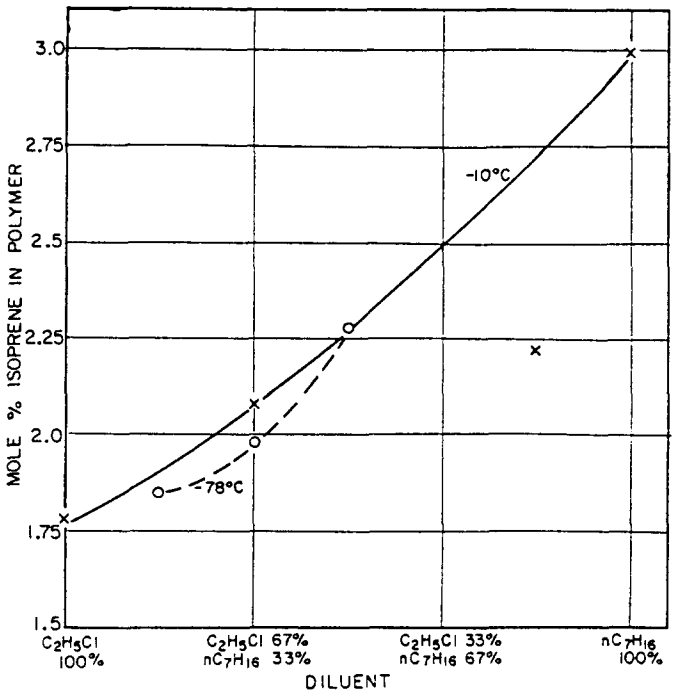


FIG. 6. Diluent effect on copolymerization of isobutene–isoprene. Monomers—2·6 mole % isoprene in isobutene, 100 ml. Diluent—ethyl chloride and/or *n*-heptane, 150 ml. Catalyst—$MgCl_2$, 1·0 g.

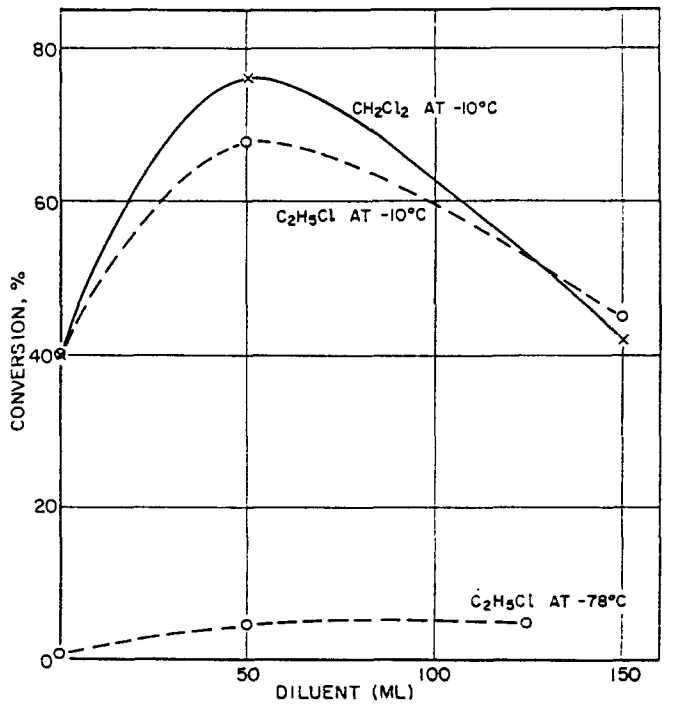


FIG. 7. Diluent effect on copolymerization of isobutene–isoprene. Monomers—2·6 mole % isoprene in isobutene. Diluent—ethyl chloride or methylene chloride. Total volume 250 ml. Catalyst—$MgCl_2$, 1·0 g.

can be seen to be a considerable continuous increase in the isoprene incorporation as the non-polar diluent is increased.

The effect of varying the monomer concentration in simple binary mixtures with alkyl halide diluents can be seen in Figs. 7–9. When the diluent content is plotted against conversion, as in Fig. 7, there is a pronounced maximum for polymerization at $-10°$ at about 80 vol. % monomer in ethyl chloride or methylene chloride. At $-78°$ the conversions were too low to establish any effect of diluent. The molecular weight of the copolymer increases as the monomer concentration is reduced at $-78°$ as seen

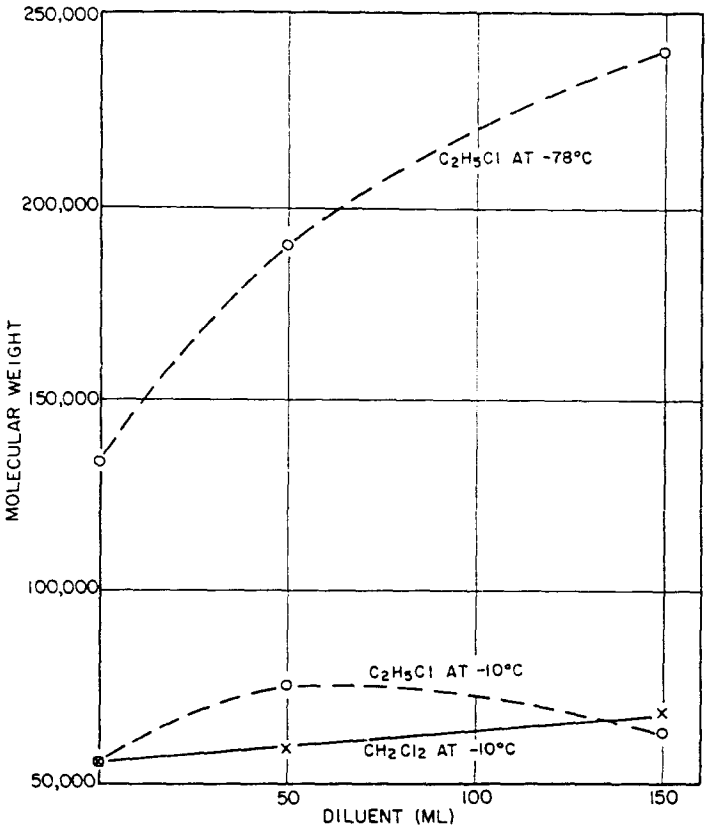


FIG. 8. Diluent effect on copolymerization of isobutene–isoprene. Monomers—2·6 mole % isoprene in isobutene. Diluent—ethyl chloride or methylene chloride. Total volume 250 ml. Catalyst—$MgCl_2$, 1·0 g.

in Fig. 8. At $-10°$ in both diluents the effect on molecular weight is small. In methylene chloride at $-10°$ and in ethyl chloride at both 10° and $-78°$, the effect of monomer concentration on degree of isoprene incorporation is similar. Increasing dilution reduces the isoprene copolymerization as seen in Fig. 9.

3.2.3. *Effect of temperature.* The effect of temperature on conversion to polymer can be seen in Fig. 10 for 40 vol. % monomer (in mixed ethyl chloride/*n*-heptane) and 80 vol. % monomer (in ethyl chloride). These are the conditions at the maximum of the conversion curves of Figs. 4 and 7. The drastic reduction in polymerization as the temperature is reduced is apparent. The effect of temperature on molecular weight is shown in Fig. 11 and on the extent of copolymerization in Fig. 12.

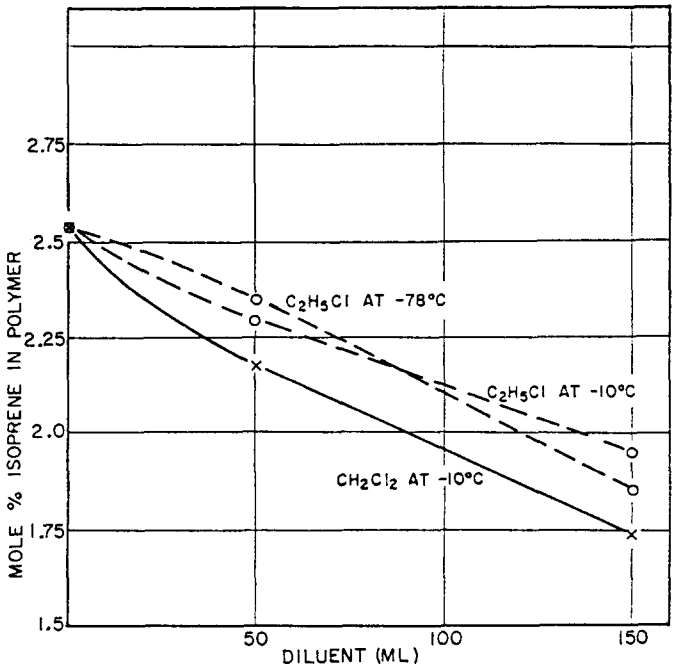


FIG. 9. Diluent effect on copolymerization of isobutene–isoprene. Monomers—2·6 mole % isoprene in isobutene. Diluent—ethyl chloride or methylene chloride. Total volume 250 ml. Catalyst—$MgCl_2$, 1·0 g.

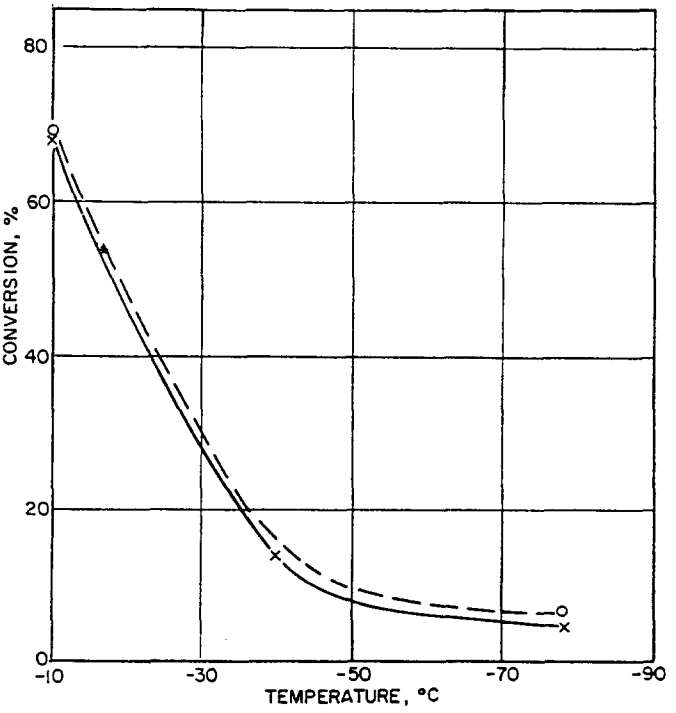


FIG. 10. Temperature effect on polymerization of isobutene–isoprene. X—isobutene 194 ml, isoprene 6 ml, EtCl 50 ml, $MgCl_2$ 1·0 g. O—isobutene 97 ml, isoprene 3 ml, EtCl 100 ml, nC_7H_{16} 50 ml, $MgCl_2$ 1·0 g.

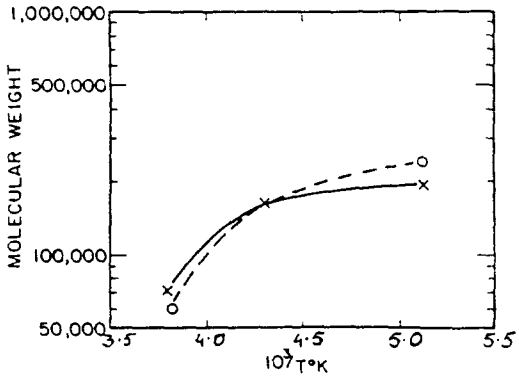


FIG. 11. Temperature effect on polymerization of isobutene–isoprene. X—isobutene 194 ml, isoprene 6 ml, EtCl 50 ml, $MgCl_2$ 1·0 g. O—isobutene 97 ml, isoprene 3 ml, EtCl 100 ml, nC_7H_{16} 50 ml, $MgCl_2$ 1·0 g.

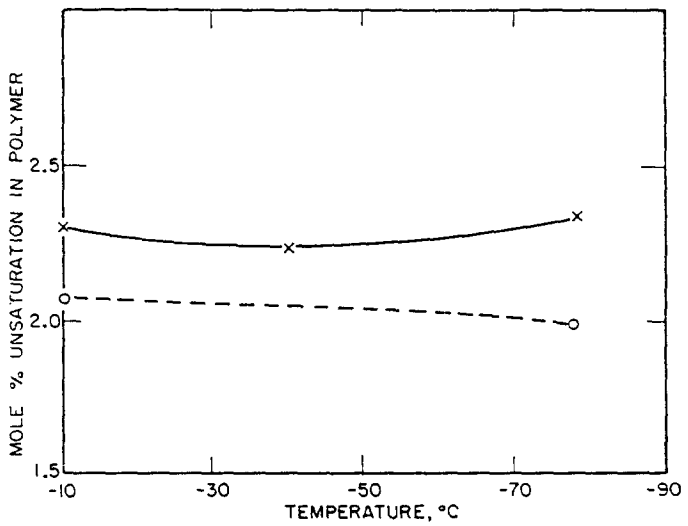


FIG. 12. Temperature effect on polymerization of isobutene–isoprene. X—isobutene 194 ml, isoprene 6 ml, EtCl 50 ml, $MgCl_2$ 1·0 g. O—isobutene 97 ml, isoprene 3 ml, EtCl 100 ml, nC_7H_{16} 50 ml, $MgCl_2$ 1·0 g.

4. DISCUSSION

4.1. *Catalytic activity of milled* $MgCl_2$

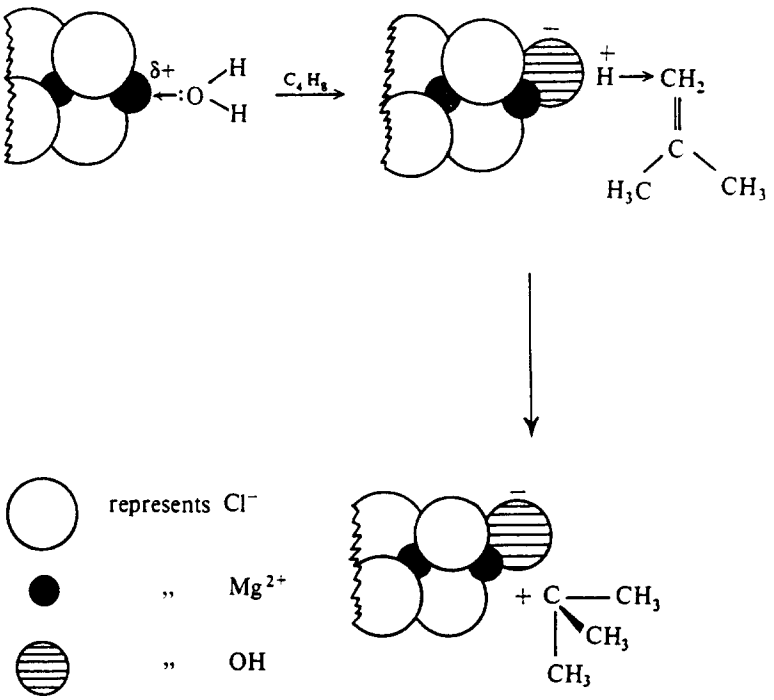
The overall pattern of reactivity of milled $MgCl_2$ is undoubtedly that of a Friedel–Crafts catalyst; the milling process produces a spectacular increase in the level of activity. $MgCl_2$ is completely insoluble in hydrocarbons and therefore the activity must be associated with electrophilic sites on the $MgCl_2$ crystal surface. $MgCl_2$ has a layer lattice structure of the $CdCl_2$ type in which planar layers of close-packed Cl^- ions lie on either side of Mg^{2+} ions to form a sandwich.[31] A large increase in the number of exposed Mg^{2+} ions will occur on milling as a result of fracture of the lamellar crystals.

These exposed Mg^{2+} ions will have a small net positive charge, and in addition magnesium ions show considerable electrophilic character in, for example, the formation of hydrates, alcoholates and ammoniates of the halides.

If this interpretation of the catalytic activity of milled $MgCl_2$ is correct, other halides of the same crystal structure should show similar activity. It was in fact demonstrated[32] that milled $FeCl_3$, $MnCl_2$, $NiCl_2$, $CoCl_2$ and $CdCl_2$ would initiate polymerization of styrene or isobutene.

4.2. *Effect of water*

Isobutene is not polymerized by Friedel–Crafts metal halides unless an ionogenic substance, the co-catalyst, is present.[43] Water can be an extremely effective co-catalyst, and in view of the known ease of formation of hydrates of $MgCl_2$, it can be expected to function as a co-catalyst in this case also. The initiation is then represented diagrammatically as follows:



The observed effect of water on catalyst efficiency, with relatively little effect on polymer molecular weight, explains why in the preliminary experiments very erratic yields of polymer were obtained but with consistent molecular weights. The occurrence of a maximum yield with increasing amounts of added water is similar to that observed with Wichterle's heterogeneous catalyst.[36, 37] The amounts of water involved are similar, but quantitative comparison is not worth while since initial concentrations of water (in catalyst + isobutene + diluent) are not known in either case. The inhibition by water is easily explained, however, since co-ordination of a second H_2O molecule with an exposed Mg^{2+} ion will first shield the active position, and co-ordination of further molecules will eventually lead to disruption of the original crystal structure at the surface.

The possibility that water reacts to give basic chlorides such as Mg(OH)Cl which might be the initiating species is eliminated since basic magnesium chloride (either milled or unmilled) shows no ability to polymerize isobutene.[23]

The relative insensitivity of polyisobutene molecular weight to $MgCl_2$ concentration and water concentration is taken as evidence that spontaneous or unimolecular chain breaking occurs, and that propagation is via ion pairs rather than free ions.[38] This is not unreasonable in a heterogeneous system where it would have been surprising if free ions had been involved. Two spontaneous termination processes could operate:

(a) Proton expulsion to associated counter-ion. Formally this regenerates the initiating co-catalyst/catalyst complex and gives a terminal double bond on the polymer.

(b) Combination of carbonium ion with OH^- from counter-ion.

Process (b) would lead to co-catalyst depletion. Attempts to test this by adding water to "dead" polymerizations did not give conclusive results,[32] and need to be repeated with more refined techniques and with end group analysis. The first process (a) undoubtedly occurs and unsaturation has been detected in low molecular weight homopolymers of isobutene.

4.3. *Homopolymerization of isobutene*

The most notable feature of milled $MgCl_2$ as a catalyst for isobutene polymerization is that it gives higher molecular weight than other catalyst systems under comparable conditions. Included in Fig. 2 (curve C) is a plot of data of J. P. Kennedy[33] for the polymerization of 56 mole % isobutene in *n*-pentane with $AlCl_3$ catalyst. The molecular weight given by $MgCl_2$ is even higher than obtained with Wichterle's catalyst[37] which had previously been considered to give higher molecular weight polyisobutene than any other catalyst system under comparable conditions.[43]

The increase in molecular weight with decreasing temperature is common to this type of polymerization and means that the activation energy of propagation (usually considered to be approximately zero) is less than the activation energy of chain breaking reactions. The linear relation between log MW and $1/T$ means that either no chain transfer occurs or that it has approximately the same activation energy as the termination reaction.

The decreasing yield of polymer as the temperature is lowered, accompanied by increasing molecular weight, can only mean that the initiation process is failing at the lower temperatures. It is suggested that, in the case of $MgCl_2$, the overall rate of polymerization is initiation controlled. It has already been deduced that unimolecular termination makes a major contribution to the overall chain breaking process, and, since this is formally the reversal of initiation, slow initiation would be expected to be accompanied by slow termination. Since molecular weight is dependent on the relative rates of propagation and chain breaking, this would account for the high molecular weight polyisobutene produced with $MgCl_2$ catalyst.

4.4. *Copolymerization of isobutene and isoprene*

In contrast to the linear plots for homopolymerizations, the plot of log MW vs. $1/T$ for copolymerization of isobutene with isoprene shows marked curvature as seen in Fig. 11. The molecular weights of copolymers at the lower temperature are not as high as would have been predicted. Deviations from linearity of this type are not new in cationic polymerization. With $AlCl_3$ catalyst for the homopolymerization of isobutene,

the plots are linear down to about $-100°$ in many different diluents.[34, 39] Below this temperature deviations to lower molecular weight occur and a suggested explanation[39] is that increasing viscosity of the reaction medium results in the degree of polymerization becoming diffusion controlled. This explanation is unlikely since the polymerization is reported to be instantaneous even at $-185°$. In any case this explanation cannot apply with $MgCl_2$ since the plots for homopolymerization do not show any deviation such as that obtained in copolymerizations with isoprene.

Similar deviations from linearity have been observed for isobutene homopolymerization with other catalyst systems and are discussed by Plesch *et al.*[40] They believe that the departure from linearity occurs at the temperature at which free cations begin to play a dominant part in the reactions, which at higher temperatures proceed via ion-pairs. It is highly unlikely that in the case of heterogeneous catalysis by $MgCl_2$ we are dealing with propagation by free cations. Hence in the temperature range of interest, it is probable that only ion-pairs are involved since the Arrhenius type plot is linear for isobutene homopolymerization. To use Plesch's terminology, the polymerization is monoeidic.

Obviously in the case of copolymerizations, the reaction must be enieidic since propagation is through more than one type of active chain end. However, it has been shown that the extent of copolymerization is relatively little affected by temperature, which makes this unlikely to be the cause of the anomalies in the molecular weight of copolymers at the lower temperatures. If then this effect is not due to competing propagation reactions, it must be due to competing termination or chain breaking reactions, the relative importance of which changes with temperature. Obviously in any copolymerization, this possibility exists. However, it does not occur in the case of $AlCl_3$ catalyst where there is ample evidence that the log MW vs. $1/T$ plot is linear over the same temperature range as for isobutene homopolymerization.

The catalyst poisoning produced by isoprene at the higher temperatures with $MgCl_2$ is similar to that observed in the case of initiation by $AlCl_3$.[35] However, from this work of Kennedy and Squires, the increased inhibiting efficiency of isoprene as the temperature is reduced could not be foreseen. There is in fact a threshold temperature at about $-40°$, below which very little polymerization takes place in the presence of isoprene, even in the more favourable diluents. The increase in inhibition by isoprene with reducing temperature is greater than the increase in molecular weight poisoning efficiency. This suggests that, in addition to its effect on propagation and termination (which determine MW), isoprene in some way interferes with the initiation process and this interference becomes progressively more important as the temperature is reduced.

The effect of diluent and monomer concentrations on the copolymerization of isobutene and isoprene is no less complicated in the case of $MgCl_2$ as catalyst than with other catalyst systems. The observed increase in relative reactivity of isoprene with increasing hydrocarbon content of the diluent would account for the small observed reduction in molecular weight, due to a reduction in propagation rate. This results from the greater stability of the growing carbonium-ion with a terminal isoprene residue, relative to an isobutene residue.

4.5. *Comparison of $MgCl_2$ with other catalyst systems*

Attention has already been drawn to the similarity between isobutene polymerizations initiated by milled $MgCl_2$ and by Wichterle's catalyst. We have concluded that

the main features of polymerization of isobutene with $MgCl_2$ result from slow initiation. A similar situation, where it has been concluded that the polymerization of isobutene is initiation controlled, is with $SnCl_4$ as catalyst.[41, 42] In this case polymerization is relatively slow and very high molecular weights are obtained provided the water content is low (~600,000 MW at $-78°$ without added water). The molecular weight is not as high as with $MgCl_2$ at this temperature, but considerably higher than obtained with $AlCl_3$, $TiCl_4$, etc. under comparable conditions. Despite this superficial similarity, the parallel ends here since the kinetics show[41, 42] that in the case of $SnCl_4$ propagation is via free cations, and termination involves bimolecular reaction with the free counter-ion. This follows from the large molecular weight depression observed with increasing water content. The basic difference therefore between these two systems is that the soluble $SnCl_4$ involves propagation via free ions whereas the heterogeneous $MgCl_2$ involves propagation via ion-pairs.

Solubility *per se* is not the chief reason for the difference, since there is considerable similarity between $MgCl_2$ and the soluble $AlEt_2Cl$[44] system as initiators for isobutene polymerization. The overall rate of polymerization with $AlEl_2Cl$ is slow compared to that with $AlCl_3$. Catalyst efficiency decreases with decreasing temperature. The effect of temperature on molecular weight is complicated and depends on the co-catalyst used in conjunction with the $AlEt_2Cl$. The effect is also complicated in the case of copolymerization of isobutene with isoprene; in some cases the plot of log MW vs. $1/T$ is linear down to about $-100°$, but in others it shows marked deviations to lower molecular weight from temperatures as high as $-35°$. This variability is probably due to the presence of adventitious traces of co-catalysts. In general it appears that initiation with this system is slow and, under certain circumstances, can be rate determining. Kennedy[44] has suggested that under some conditions (e.g. low temperature) propagation is slow because molecular weight of polymer can increase with increasing polymerization time. This, however, is not conclusive evidence, since such an observation could also be explained by gradual consumption of chain-breaking agents during a slow, initiation controlled polymerization. It is suggested that this system also gives high molecular weights because of the sluggish initiation and consequent slow termination reaction.

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Résumé—On montre que le $MgCl_2$ anhydre possède une activité catalytique pour la polymérisation de l'isobutène lorsqu'il est ajouté en petites quantités dans des conditions anhydres. Cette activité peut s'expliquer par le caractère électrophile de l'ion Mg^{2+}. L'eau est un co-catalyseur extrêmement efficace. Un excès d'eau empoisonne le catalyseur mais n'a que peu d'effet sur la masse moléculaire du polymère. La caractéristique principale du catalyseur $MgCl_2$ dans la polymérisation de l'isobutène est de donner naissance à un polymère de masse moléculaire beaucoup plus élevée que tout autre système catalytique connu dans des conditions comparables. On conclut que la vitesse de polymérisation est contrôlée par la vitesse d'amorçage et ceci rend compte de la perte d'efficacité du catalyseur lorsqu'on abaisse la température, malgré une augmentation de la masse moléculaire. Une terminaison spontanée contribue de façon décisive au processus général de terminaison des chaînes et, de même que l'amorçage, cette réaction est assez lente ce qui explique les valeurs élevées des masses moléculaires des polymères obtenus. Une étude de la copolymérisation de l'isobutène avec l'isoprène a montré que ce dernier est un poison très puissant du catalyseur. En dehors de ses effets habituels sur la propagation et la terminaison, l'isoprène perturbe de manière évidente le processus d'amorçage à tel point que la polymérisation est totalement inhibée en dessous de $-40°$ environ en présence d'isoprène. La polymérisation amorcée par $MgCl_2$ est au moins aussi sensible à la nature du milieu que les polymérisations amorcées par d'autres catalyseurs cationiques. La réaction présente des ressemblances avec les polymérisations observées avec d'autres systèmes catalytiques cationiques dans lesquelles l'amorçage est lent et contrôle probablement la vitesse globale.

Sommario—Si é trovato che il $MgCl_2$ anidro esplica un'attività catalitica nella polimerizzazione dell'isobutene se si opera in condizioni anidre. Questa attività può essere spiegata in base al carattere elettrofilo dello ione Mg^{+2}. L'acqua é un catalizzatore particolarmente efficace. Se presente in eccesso danneggia notevolmente il catilazzatore mentre influenza poco il peso molecolare del polimero. La caratteristica principale del cloruro di magnesio, come catalizzatore per la polimerizzazione dell'-isobutene, é la sua capacità di far formare polimeri a più alto peso molecolare in condizioni paragonabili con quelle di tutti gli altri sistemi catalitici riportati in letteratura. Si conclude che la polimerizzazione

é a iniziazione controllata, ciò spiega la notevole diminuzione dell'efficacia del catalizzatore, con la diminuzione della temperatura, nonostante aumenti il peso molecolare del polimero. La terminazione spontanea dà il maggior contributo al processo di rottura delle catene e, come l'iniziazione, é relativamente lenta e responsabile dell'alto peso molecolare del polimero. Ricerche sulla copolimerizzazione dell'isobutene e dell'isoprene mostrano che quest'ultimo avvelena notevolmente il catalizzatore. Oltre ad influenzare, nel solito modo, le reazioni di propagazione e di terminazione, ovviamente l'isoprene interferisce in qualche modo con l'iniziazione del $MgCl_2$ al punto che in presenza di isoprene non si forma polimero al di sotto dei $-40°$.

La polimerizzazione iniziata del $MgCl_2$ non é meno sensibile alle condizioni di reacione di quanto lo siano altri catalizzatori cationici. Presenta caratteristiche simili a quelle di altri sistemi catalitici cationici nei quali l'iniziazione é lenta e determina probabilmente la velocità della reazione.

Zusammenfassung—Es wird gezeigt, daß wasserfreies $MgCl_2$ bei der Polymerisation von Isobuten unter wasserfreien Bedingungen katalytische Aktivität entwickelt. Diese Aktivität lässt sich durch den elektrophilen Charakter verfügbar Mg^{2+} Ionen erklären. Wasser ist ein besonders wirksamer Cokatalysator. Liegt das Wasser jedoch im Überschuß vor, so ist es ein sehr wirksames Katalysatorgift, beeinflußt aber das Molekulargewicht des Polymeren nur wenig. Ein charakteristisches Merkmal von $MgCl_2$ als Katalysator bei der Isobuten-Polymerisation ist seine Fähigkeit, unter vergleichbaren Bedingungen höhermolekulare Produkte zu bilden als irgendein anderes in der Literatur beschriebenes Katalysatorsystem. Es wird daraus geschlossen, daß die Polymerisation durch die Startreaktion kontrolliert wird. Dies erklärt auch den starkren Verlust der katalytischen Wirksamkeit bei abnehmender Temperatur, trotz zunehmendem Molekulargewicht des Polymeren. Der spontane Kettenabbruch stellt den Hauptanteil an Kettenabbruchreaktionen und ist, wie die Initiierung relativ langsam und verantwortlich für das hohe Molekulargewicht des Polymeren. Bei Untersuchungen der Copolymerisation von Isobuten und Isopren erweist sich letzteres als starkes Katalysatorgift. Außer seinem üblichen Einfluß auf Wachstums- und Abbruchsreaktionen stört Isopren offenbar auf gewisse Weise die Initiierung durch $MgCl_2$ derart, daß bei Gegenwart von Isopren unterhalb etwa $-40°$ kein Polymeres gebildet wird. Die durch $MgCl_2$ initiierte Polymerisation ist ebenso empfindlich gegenüber dem umgebenden Milieu wie diejenige mit anderen kationischen Katalysatoren. Es bestehen Ähnlichkeiten zu anderen kationischen Katalysatorsystemen, bei denen die Initiierung langsam und vermutlich geschwindigkeitsbestimmend ist.