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Some Problems Concerning the Mechanism of the Isotactic Polymerization of Methyl Methacrylate Initiated by Organomagnesium Compounds in Toluene Solution—Application of Modified Dilatometer and NMR Methods

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Some Problems Concerning the Mechanism of the Isotactic Polymerization of Methyl Methacrylate Initiated by Organomagnesium Compounds in Toluene Solution—Application of Modified Dilatometer and NMR Methods

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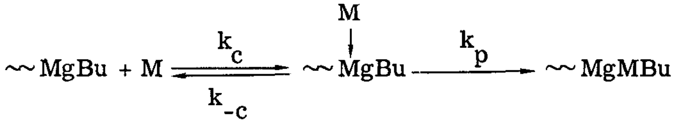
ABSTRACT

A dilatometer capable of being rapidly filled with monomer and initiator solutions mixed under carefully controlled conditions and a modification of an NMR T_1 program, adapted to store and display on recall the results of frequent sweeps at 30-s intervals of relevant proton resonances of a polymerizing mixture, are reported. These techniques have been applied to the identification of the optimum conditions for efficient initiation of isotactic polymerization and investigation of the mechanism of propagation. It is shown that heat treatment does not remove the coordinated THF (1 molecule per RMg group) when toluene-soluble "tBuMgBr" or "PhMgBr" initiators are prepared and that the optimum THF concentration is slightly in excess of this. The nature of the solute in the toluene-soluble initiator solutions is discussed. The kinetics of the polymerization change from internal zero order to internal order of one with respect to monomer as the temperature increases from 225-275 K. This is consistent with a previously proposed mechanism in which propagation proceeds through a complex between monomer and the active center.

INTRODUCTION

Allen and Bateup [1, 2] have proposed that the polymerization of methyl methacrylate (MMA) initiated by n-butylmagnesium bromide or di-n-butylmagnesium in tetrahydrofuran (THF)-toluene solution is an insertion reaction proceeding through a complex between monomer and active center:



$$\sim\!\sim\mathrm{MgBu} + \mathrm{M} \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} \sim\!\sim\overset{\overset{\mathrm{M}}{\downarrow}}{\mathrm{MgBu}} \xrightarrow{k_p} \sim\!\sim\mathrm{MgMBu} \qquad (1)$$

The most compelling evidence in support of this mechanism was kinetic [1]. Yerusalimskii had proposed a similar mechanism for acrylonitrile polymerization [3]. The polymers produced by nBuMgBr and $\mathrm{nBu_2Mg}$ are syndiotactic-like at low temperature and high THF concentration and of the short stereoblock type at low THF concentration. We have investigated tBuMgBr and PhMgBr which at low THF concentration give isotactic polymers to see if these stereospecific polymerizations follow a similar mechanism.

Reactions which lie at the fast end of the classical chemical kinetic domain, but which are too slow for modern fast-reaction techniques, are a problem. Polymerization of methyl methacrylate initiated by phenyl- or tertiary butyl-magnesium compounds lies in this awkward region. One answer would be a flow method, but with air- and moisture-sensitive reagents this involves elaborate manipulations. Flow techniques have been developed for similar polymerizations [4, 5], but we preferred the convenience and safety of the sealed-tube experiment. Adiabatic reaction calorimetry has been used successfully with highly air-sensitive cationic polymerizations [6]. However, in our systems the polymerization reaction was masked, in the early stages, by the exothermicity of the initial complex formation and side reactions of initiator [1]. The solution was found in modifications to traditional methods: dilatometry and NMR measurements on sealed reaction tubes.

We have reported elsewhere [7, 8] that the molar-mass distribution and chain configuration of polymers of methyl methacrylate initiated by organomagnesium compounds are often critically dependent on the temperature prevailing during the initiation step. In a classic dilatometer experiment, initiator solution is run into the bulb, frozen by liquid nitrogen, and monomer distilled on top. Initiation occurs at an uncontrolled temperature somewhere between the boiling point of liquid nitrogen and the melting point of the initiator solution. Controlled mixing of the required volumes of monomer and initiator solution cannot be obtained within the bulb of a conventional dilatometer. Neither can a conventional dilatometer be easily and quickly filled with a premixed polymerizing solution. These problems have been solved by a modification of the traditional design.

Dilatometry is a blind method; it gives an indirect measure (though capable of precise calibration) of monomer and polymer concentrations but none at all of initiator, side products, and other substances that may be present in a complex mechanism. In systems such as these it is often prudent to follow the changes of the integrated intensities of relevant NMR peaks in a sealed-tube experiment. When the reaction is slow [9], no special problems are involved, but these polymerizations require special techniques to collect and store the data.

EXPERIMENTAL

Reagents

Tetrahydrofuran (THF) was refluxed over lithium aluminum hydride and distilled on a high-vacuum line onto sodium benzophenone. Toluene was refluxed and stored over calcium hydride. Methyl methacrylate (MMA) was destabilized by alkaline wash, washed to neutrality, dried successively with anhydrous magnesium sulfate, calcium hydride, and sodium benzil, being distilled from this last reagent as soon as the onset of a slow polymerization was manifest. The final purification stage of all liquid reagents was carried out, and the reagents distilled as required into baked dispensing capsules, on a high-vacuum apparatus.

Magnesium (BDH "for Grignard reactions") was cleaned by refluxing for 15 h in a toluene-THF mixture. Phenyl and alkyl halides used for Grignard reagent syntheses were dried with calcium hydride. Under these conditions the reaction proceeded readily in THF without the use of a promoter. t-Butylmagnesium bromide, iso-butylmagnesium bromide and sec-butylmagnesium bromide were prepared from magnesium and t-butyl bromide (2-bromo-2-methylpropane), iso-butyl bromide (1-bromo-2-methylpropane) and sec-butyl bromide (2-bromobutane), respectively. Since the stereospecificity of butylmagnesium halides is critically dependent on the structure of the butyl group [10], the alkyl halides used in the Grignard syntheses were checked by gas chromatography and NMR to ensure the structural purity of the alkyl group.

Three basic classes of Grignard reagent solution were used as initiator.

Grignard reagents in toluene-THF solutions were made by appropriate adjustment of the initial filtered solution obtained from the preparation in THF. Analysis for halide (Volhard's method) showed that the solute conformed to the Grignard stoichiometry (RMgX).

"Toluene-soluble Grignard reagents" were prepared by pumping the solvent from solutions in THF under high-vacuum with warming up to 313 K. The residues were treated with toluene and filtered from toluene-insoluble material.

"Toluene-soluble, heat-treated Grignard reagents" were prepared in the same way except that the residues were heat treated at 353 K. The most drastic treatment, that reported by Tsvetanov [11], used 8 h heating, but we found that 20 min sufficed to give the same result.

Dialkyl and diaryl magnesiums were prepared from an appropriate Grignard reagent solution. Excess dioxane was added and magnesium halide precipitated. The dioxane soluble material was separated by filtration and the solvent changed as described above. The solutions were tested for halide by Volhard's method. None could be detected.

Solutions of organomagnesium compounds in deuterated solvents were prepared using the same solvent-change procedures, with or without heat treatment as appropriate. When d^8-toluene solutions were prepared, a solvent change from THF to toluene was carried out before changing to the deutero solvent.

A Quick-Filling Twin Tube Dilatometer

This is shown in Fig. 1. Monomer and initiator solutions are dispensed through burette A, controlled by a modified J. Young greaseless high-vacuum tap B, into the mixing vessel C. In this way temperature of initiation can be controlled and, if necessary, rate of addition of monomer to initiator and vice versa. A portion of the polymerizing solution is then poured into dilatometer D through capillary E. Capillary F (of the same calibrated bore) permits escape of vapor from the bulb (essential for easy and rapid filling) and allows for any overfill to be quickly remedied by pouring back into C. C can be a large bulb if necessary, in which case the dilatometer may be used to monitor the conversion of a large-scale preparative run.

NMR Measurements

These were made using a Bruker HX90E spectrometer. The kinetic data were obtained using a modified version of the BNC-12 computer program T1PRGM/II, version 74. The program was modified to wait for a hardware flag before the acquisition of each block of f.i.d. This hardware signal was generated by our modified B-GD 1 gated decoupling unit and was applied to the SENSE 1 input of the BNC-12. The timing of this signal could be set to better than 10 μs so we could initiate blocks of scans of the proton resonances of molecules of interest at predetermined time intervals with an error of less than 100 μs. The predetermined time interval could be varied from 0.1 to 9990 s.

Initiator and monomer solutions were frozen into an NMR tube which was then sealed. The solutions were melted by immersion in a bath, set at the chosen initiation temperature, and rapidly mixed with the assistance of a glass ball sealed into the tube. The tube was

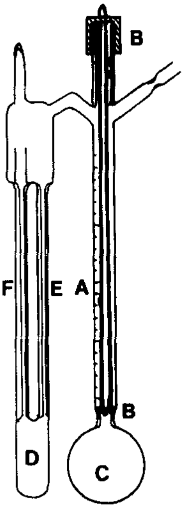


FIG. 1. Rapid filling twin-tube dilatometer (DEF) attached to dispensing burette A and initiation mixing vessel C.

quickly transferred to the spectrometer probe which was set at the chosen polymerization temperature. At the appropriate time the hardware flag allowed the acquisition of the first set of f.i.d. The accumulated signal of a predetermined number of scans was then automatically stored on disk, various housekeeping tasks performed, and the spectrometer allowed to idle until the end of the next time interval when the acquisition process was repeated.

Once all data had been acquired, Fourier transformation, plotting, and peak-picking could be performed at any time. Figure 2 shows the plot of the time-dependent spectrum of a polymerizing solution initiated by t-butylmagnesium bromide. For quantitative kinetic measurements the printout of the integrated peak intensities of monomer, polymer, and initiator is used. It should be noted that the peak heights of toluene and vinyls in Fig. 2 increased between the second and third minutes. This occurred in some but not all runs. It arose from fluctuations in T_2^*. The effect was not apparent in the integrated intensities which remained constant from the first accumulation in the case of toluene and declined monotonically (see Figs. 3 and 4) in the case of the consumable vinyl group.

Care must be taken to watch for the effects of the automatic peak-picking. A peak is picked and integration started when the signal departs by more than twice the root-mean-square error from the mean base-line. Integration stops when the signal returns to the mean base-line or begins to increase again by more than twice

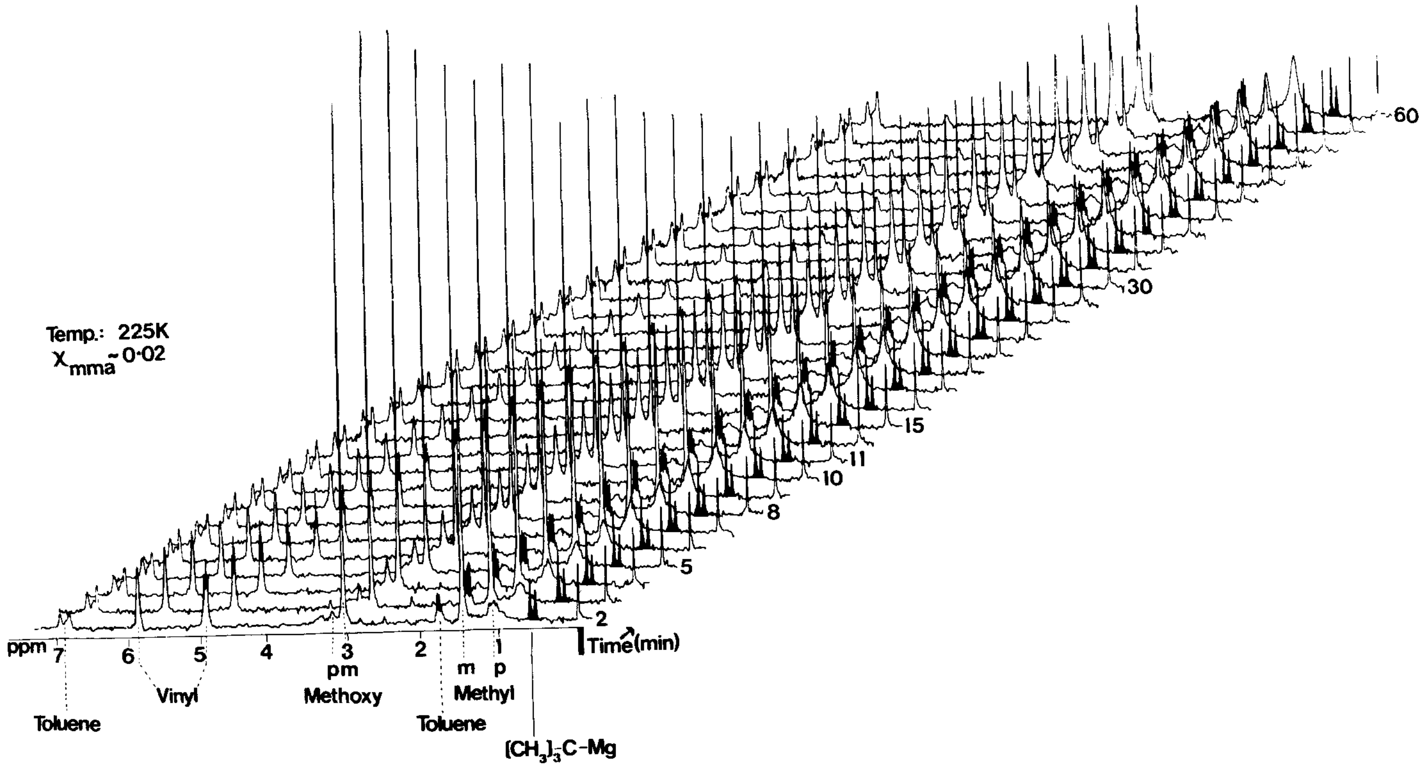


FIG. 2. Proton resonances in the alkyl, vinyl, and aromatic region during a polymerization initiated by "tBuMgBr" in d^8-toluene (the toluene resonances are protonated impurities): $X_{mma} = 0.02$, $X_{d^8\text{-toluene}} = 0.98$, $X_{THF} \sim 0.003$, initiated and polymerized at 225 K. The symbols m and p indicate the polymer and monomer αCH_3 and OCH_3 resonances. The chemical shift is given in ppm from tetramethyl silane.

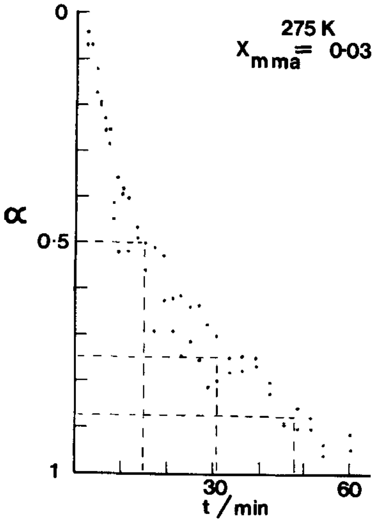


FIG. 3. Conversion curve determined from the monomer vinyl proton resonances: α = fraction conversion, t = midpoint time of the accumulated scans at each acquisition. At a given t the two values of α are the integrated intensities of the two vinyl peaks (see Fig. 2) relative to their extrapolated values at t = 0. The polymerization was initiated and polymerized at 275 K, initiated by "tBuMgBr" in d^8-toluene solution: $X_{\text{mma}} = 0.03$, $X_{d^8\text{-toluene}} = 0.97$, $X_{\text{THF}} \sim 0.003$.

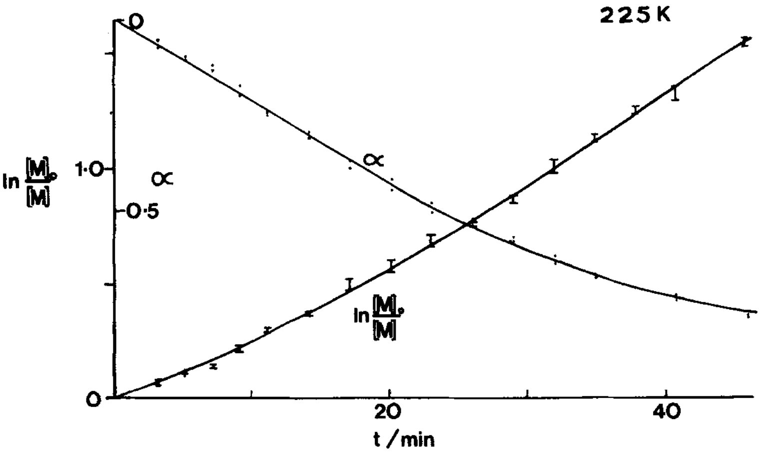


FIG. 4. Conversion curve (dots) and integrated first-order plot, ln $[M]_0/[M]$ (bars), against time, t, for run shown in Fig. 2.

r.m.s. error. The deviations between the integrals of the two vinyl peaks, which is most apparent in Fig. 3, arose from departures of the local base-line from the mean. The integrals of the disappearing monomer methoxy and the appearing polymer methoxy, which look so striking in Fig. 2, are not in perfect stoichiometric relationship. This is because the peaks overlap and the peak-picking procedure does not deconvolute them correctly. Part of the problem may be the presence of side-product methoxy peaks in this region, and a coordinated THF peak just downfield of the polymer peak.

The method is restricted, by viscosity broadening, to low monomer concentrations or low conversion. It has also been applied to a radical polymerization. Apart from the not-insuperable problem in an above-ambient temperature experiment of solvent refluxing to the upper part of the tube, the results were satisfactory. The method would seem to have widespread applicability, particularly to the addition reactions of unsaturated compounds, because vinyl and conjugated diene resonances lie in a sparsely inhabited region of the field.

RESULTS AND DISCUSSION

Initiation Conditions

The stereochemistry of the chain growth reaction is strongly dependent on the temperature prevailing when the chains are initiated. This is consistent with the hypothesis [2, 7, 8, 10] that active centers are formed during the initiation stage and retain their identity and independence throughout the growth stage. Generation of isotactic growth centers is favored by high temperatures but other factors limit the optimum range to 225-275 K. It must be remembered that initiation and propagation are exothermic reactions and, depending on the size of the vessel, the reaction mixture may be several degrees above the nominal bath or probe temperature. It is essential to have either a temperature sensor in the reaction vessel, or if this is inconvenient, as it certainly is in an NMR experiment, calibration experiments must be performed. This point was first noticed by Nishioka [12] whose findings have not received the attention they warrant. In our experiments, where the volume of vessels rarely exceeded 20 cm^3, the temperatures rarely exceeded bath temperature by more than 2 K.

A variable, previously undetected, is order of addition of reagents. For efficient initiation, under some conditions [7], monomer must be added to initiator solution. When initiator solution was added to monomer, polymerization, if it occurred at all, was very slow and the concentration of unreacted tBuMg groups was very low. Unreacted BuMg groups which survive initiation and persist throughout the polymerization are characteristic of these mechanisms [2, 13]. They amount to between 20-50% of those present initially. They can be seen in Fig. 2. All tBuMg groups consumed in initiation and the formation of side products have reacted within the first 2 min; the concentration then remained constant throughout the polymerization. The stereodirecting influence of the butyl group, as manifest in the influence of its isomeric structure on the stereospecificity, means that one must be attached to every growth center throughout the propagation of a stereoregular chain [2]. The formation of a stereospecific growth center is only a very minor component of the reactions occurring during the initiation step; the concentration of growth centers is very much lower than that of residual BuMg groups [10]. When the two reagents are added in different orders, the local concentrations of solvent and monomer prevailing during the mixing stages will be different. This must affect the balance of competitive reactions, leading to large differences in the yield of the very minor product: the isotactic growth center.

Initiation by phenyl magnesium bromide was less reproducible. As well as abortive experiments, abnormally fast polymerizations (complete within 2 min) were encountered. We suspect that with this initiator there is a variable affecting the initiation efficiency that remains undefined.

The Nature of the Initiator

It is apparent that the isotactic content of the polymers is reduced as the proportion of THF in the solvent mixture is increased [2, 10]. This is the case even with the isotactic-favoring initiators tBuMgBr and PhMgBr [7]. On the other hand, tBu_2Mg does not yield isotactic polymers even when THF is absent (Fig. 5). It might be concluded then that the isotactic initiator is tBuMgBr or tBuMgCl (Fig. 5) (or PhMgBr) in toluene solution. This, however, is not an exact specification as the details of the NMR spectra of the best initiator solutions revealed.

The NMR spectrum of tBuMgBr in THF is complicated (Fig. 6). It consists of four main peaks. At lower resolution these can appear as a doublet [14] which goes through a classic broadening and coalescence at higher temperatures. This has been attributed to two peaks, tBuMgBr and tBu_2Mg, coalescing as the Schlenk equilibrium becomes more labile. However, at high resolution this was revealed to be an artifact. We could find no evidence for kinetic behavior manifest in the 90 MHz proton spectrum between 210-330 K (Fig. 7). The complex phenomena observed are most readily explained in terms of chemical shifts of two pairs of 2 singlets or four unrelated singlets. Of the butyl magnesium bromides, only isobutyl magnesium bromide showed classical coalescence. This is illustrated in Fig. 8 where the two sets of doublets of the α-CH_2 spectrum can be seen broadening and coalescing as the temperature is increased. If each doublet can be assigned to either iBuMgBr or iBu_2Mg, then, in this case, the Schlenk equilibrium

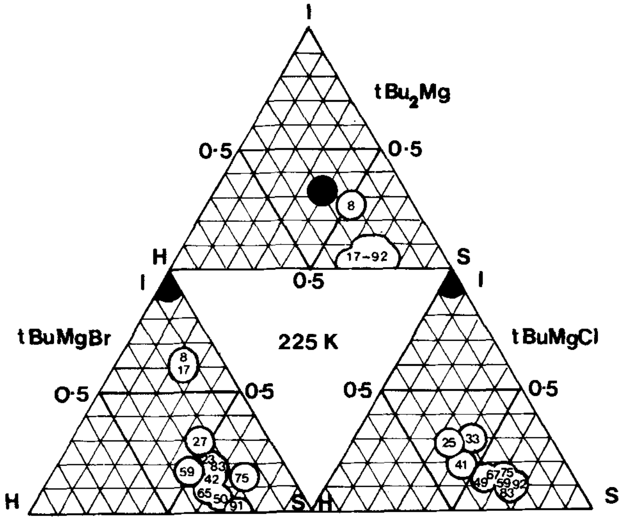


FIG. 5. Steric triad composition of polymers produced at 225 K by (top) ditertiary butylmagnesium, (left) tertiary butylmagnesium bromide, and (right) the corresponding chloride. The apex I of each triangle represents pure isotactic, S = pure syndiotactic and H = pure heterotactic polymer. The fractional content of isotactic triads in a polymer is represented by the number of horizontal gradations from the base opposite the I apex. The filled circles refer to "toluene-soluble" initiators in toluene solution. The open circles refer to THF-toluene solution with the percent THF specified within.

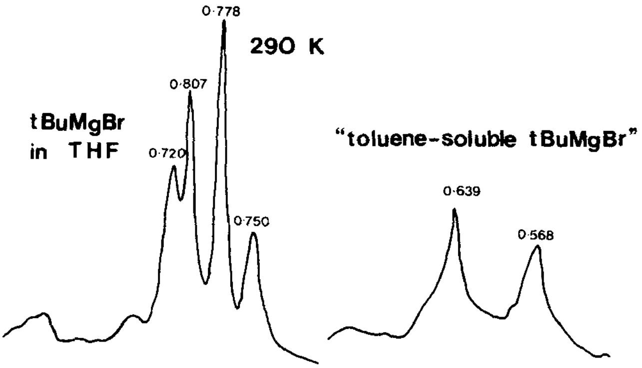


FIG. 6. 90 MHz proton NMR spectra of tBuMgBr in THF and "toluene-soluble tBuMgBr" in toluene at 290 K. The field positions are given in ppm from tetramethyl silane.

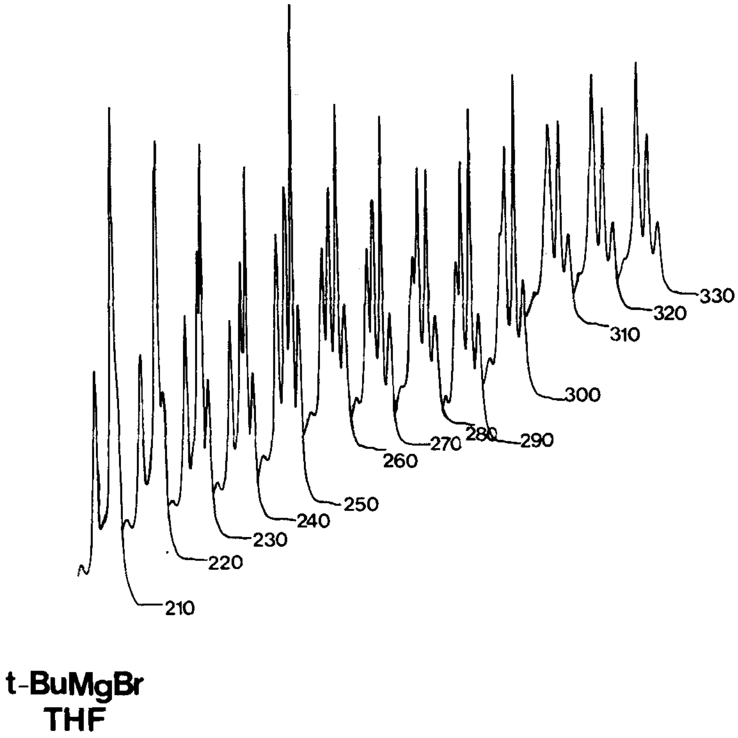


FIG. 7. The temperature dependence of the NMR spectrum of the CH_3 protons of tBuMgBr in THF. Temperature in K is given.

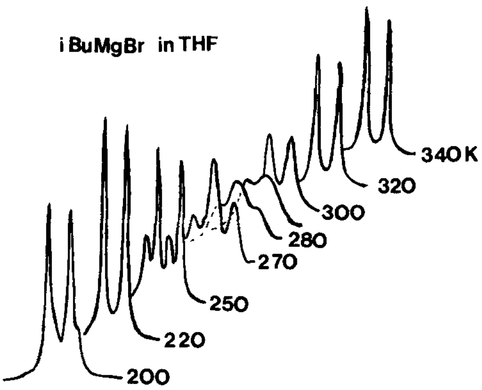


FIG. 8. The temperature dependence of the α-CH_2 proton resonances of iBuMgBr in THF.

$$2iBuMgBr \rightleftharpoons iBu_2Mg + MgBr_2 \qquad (2)$$

is labile and above ca 290 K the exchange life-time is shorter than 10 ms. In the case of the other reagents the spectra formally give no evidence about the lability or otherwise of the Schlenk equilibrium. However, the number of lines to be accounted for with tBuMgBr (a tBu group in a single chemical environment has only a singlet proton resonance) suggests that in this case the equilibrium has an exchange time >1 ms between 210-330 K. The lability of the Schlenk equilibrium is important in the initiation state because the competition between the addition of tBuMgBr and tBu_2Mg to monomer and the relaxation of the equilibrium will determine the proportions of the different active centers and possibly the efficiency of initiation relative to inactive side products.

The spectrum of "toluene-soluble tBuMgBr" in toluene was very different from that of tBuMgBr in THF (Fig. 6). It resembled much more closely that of tBu_2Mg in toluene, which also showed two peaks in very similar positions (0.574 and 0.644 ppm at 290 K) and intensities. This, coupled with the very significant deficiency in halide, raised the question whether "toluene-soluble tBuMgBr" should not be regarded as tBu_2Mg. However, as an initiator, it cannot be. It has quite different stereospecificity as can be seen from Fig. 5 (black spots).

Solution State of the Toluene-Soluble Initiators

In a series of experiments we have measured the residual THF concentrations in toluene solutions of toluene-soluble "tBuMgBr" and "PhMgBr" prepared by heat treatment of increasing duration. Figure 9 shows the proton resonances of tetrahydrofuran in the

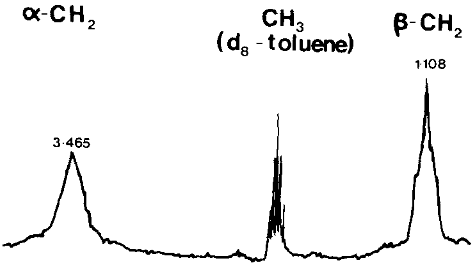
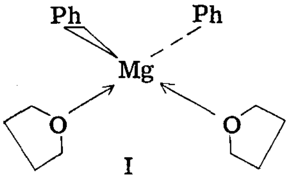


FIG. 9. The chemical shift of the ^1H NMR resonances of the residual THF (ppm from TMS) in d^8-toluene solution of PhMgBr heated under high vacuum at 383 K for 10 h. The CH_3 peak is the isotopic impurity in the solvent.

filtered d^8-toluene solution of PhMgBr heated for 10 h under high-vacuum at 353 K. The integrated intensity relative to that of PhMg indicated that the solution contained 1.2 THF molecules for every PhMg group. This ratio was reached at much shorter heating times than 10 h or the recommended 8 h [11]. It was concluded that it was close to the limiting residual value.

Magnesium is believed to exist in solution in a tetrahedral coordination state. The amount of THF present was therefore sufficient to maintain this state provided the solute, if monomeric, was Ph_2Mg (I).



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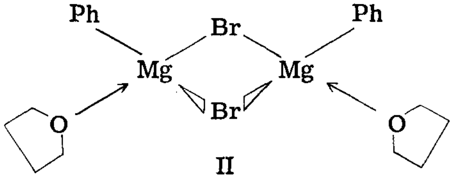


II

This is to assume that the bromide did not pass into solution. If on the other hand the solute was PhMgBr, or a Schlenk equilibrium mixture, tetrahedral coordination can only be assured by this amount of THF if dimers, e.g., II, are present.

The chemical shift of the limiting residual THF (Fig. 9) confirms that it is predominantly coordinated. In bulk THF the chemical shifts of the α- and β-methylene resonances are 3.58 and 1.73 ppm, respectively.

The toluene-soluble initiators prepared without heat treatment, but merely warmed, had residual THF around twice the PhMg concentration. The results were similar, but not so well defined, in the case of toluene-soluble "tBuMgBr."

In the case of initiators based on tBuMgBr and tBuMgCl, polymers, which within the sensitivity of our analysis were 100% isotactic, were produced by using only brief warming and hard pumping to remove THF before making the toluene-soluble initiator solution. In the polymerization mixtures, e.g., those of Figs. 3, 4, and 5, the mole fraction of THF would have been ca. 0.003. Toluene-soluble heat-treated tBuMgBr was much less efficient as initiator. In the case of PhMgBr the toluene-soluble heat-treated intiator in some instances gave a less isotactic product than those that had not been heated above 313 K.

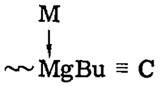
Heat treatment at 353 K does not cause any irreversible decomposition. The residues were redissolved in THF, and the NMR spectra shown to be indistinguishable from those of the original THF solution.

Mechanism of Polymerization: Kinetic Evidence

The Bateup-Yerusalimskii mechanism (1), established for the stereoblock polymerization initiated by nBuMgBr in THF-toluene solution, depended on kinetic arguments [1]. The internal order of reaction with respect to monomer was shown to be zero. This is a limiting case which occurs when

$$\frac{k_{-c}+k_p}{k_c[M]} \longrightarrow 0 \tag{3}$$

In the steady-state solution the complexed form of the growth center



$$\overset{\displaystyle M\downarrow}{\sim\!\sim\text{MgBu}} \equiv C \tag{4}$$

becomes predominant and the second step of the mechanism (k_p) becomes rate controlling. The limiting rate equation is

$$-d[M]/dt = k_p f[\text{BuMgX}]_0 \tag{5}$$

since initiation of growth centers is effectively instantaneous but of low efficiency f. With n-butylmagnesium bromide, f depended on monomer concentration, but since this is <u>initial</u> monomer concentration $[M]_0$, Eq. (5) is independent of the time-dependent monomer concentration [M] and is formally of internal order: zero.

The data for tBuMgBr in toluene-solution at 275 K (Fig. 3) fitted a first-order monomer decay curve. This could be interpreted as representing a normal bimolecular propagation reaction not involving complex formation, or the other limiting case of the Bateup-Yerusalimskii mechanism ([M] being lower by a factor of 10 compared with Bateup's experiments [1]):

$$\frac{k_c[M]}{k_{-c}+k_p} \longrightarrow 0 \tag{6}$$

where

$$-\frac{d[M]}{dt} = f\frac{k_c k_p}{k_{-c}+k_p}[\text{BuMgBr}]_0[M] \tag{7}$$

The discrimination between these alternatives came with kinetic measurements at lower temperatures, 225 and 250 K, where the data deviated from first order into an intermediate kinetic domain between zero and first order, consistent with a Bateup-Yerusalimskii mechanism between its two limiting states. At 225 K (Fig. 4) the first-order plot was clearly a misfit. The conversion-time curve could not be distinguished from a zero-order plot over the first 40% but did not fit overall. At 250 K the data were nearer to a first-order fit than zero order.

The application of the new data-handling techniques has enabled us to obtain sufficient data points, particularly in the important early stages, to distinguish differences in internal order of less than one unit and discriminate between mechanisms.

CONCLUSIONS

1. The toluene-soluble initiators which give highly isotactic polymers are not entirely ether-free or de-etherated, even when heat treated.
2. Neither can they accurately be described as Grignard reagents in the sense that they have the stoichiometry RMgX.
3. Despite the similarity of their NMR spectra to the species R_2Mg, they are distinguished as initiators by their exclusive ability (when R ≡ tBu or Ph) to yield isotactic polymer.
4. The traces of THF appear to have a vital role in the formation of the isotactic growth center since, when THF is reduced to the minimum residue necessary to maintain tetrahedral coordination of R_2Mg, there is a loss of efficiency in forming isotactic centers.
5. Since the presence of THF in greater than trace amounts is deleterious to isotactic stereospecificity, the optimum amount is delicately balanced and this may account for difficulties in obtaining efficient stereospecific polymerizations with these systems.
6. The removal of bulk THF, with or without heat treatment, is reversible so that any partition, rearrangement, or decomposition of the initiator when it goes into toluene solution takes place at this stage, not during the THF removal.
7. The role of traces of THF in isotactic polymerization in toluene solution is to solubilize sufficient halide to form an adequate concentration of isotactic growth centers.
8. The isotactic polymerization initiated by tBuMgBr in toluene follows the same basic monomer-complex propagation mechanism as the syndiotactic-like, stereoblock nBuMgBr/THF/toluene system. However, differences in the stability of the complexes lead to variation in the order of reaction. At higher temperatures the complex is weaker and first-order kinetics prevail; as the temperature is lowered the complex stability is increased and the order of reaction drifts toward zero.

ACKNOWLEDGMENT

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