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Active Centers for the Stereospecific Polymerization of Methyl Methacrylate by Organomagnesium Compounds

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Active Centers for the Stereospecific Polymerization of Methyl Methacrylate by Organomagnesium Compounds

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ABSTRACT

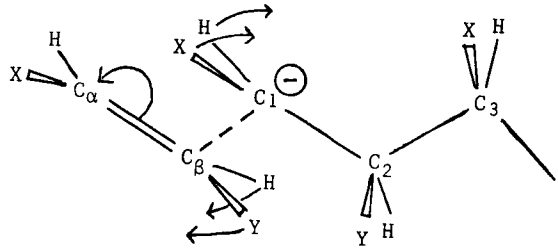
New evidence on the polymerization kinetics of methyl methacrylate and molar mass distributions is presented which together with earlier work on the stereochemistry of the polymerization of α,β-dideuteroacrylates shows that these are not typical anionic polymerizations. The persistence and stability of the active centers, together with evidence that the α-carbon of the monomer assumes the tetrahedral configuration it takes in the polymer chain as it becomes the active chain end, suggests that the active centers are covalent magnesium-carbon bonds. Existing hypotheses about the mechanism of steric control in homogeneous polymerizations are examined. Kinetic evidence confirms that complexing of the monomer to the active center does occur. However, intramolecular complexing of the penultimate or antepenultimate chain carbonyl group to the metal is not a prerequisite for isotactic polymerization though it may be involved in controlling the in-chain configuration of the β-carbon. Gel-permeation chromatography shows that in some systems more than one active center operates independently. These centers are established in the initiation stages and persist. The proportions of active centers of different reactivity and stereospecificity are determined by conditions prevailing during

initiation and it is these that primarily determine the structure of the polymers formed. Evidence is reported that confirms this.

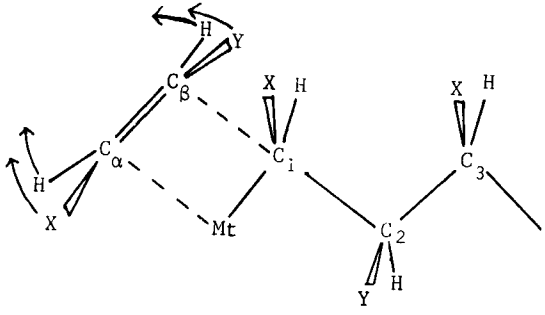
INTRODUCTION

The origins of the stereospecificity of polymerizations on solid catalysts is sought in the chemical structure and topology of the surface of the catalyst which are believed to steer the monomer on to the active center in such a way that the direction of delivery, rotation of the active endgroup, aspect of presentation, and mode of bond opening are controlled. The same factors must be controlled in a homogeneous stereospecific polymerization and it is usual to assume that this control is exerted by complexes of appropriate structure and symmetry. The absence of established cases of stereospecific polymerization of nonpolar vinyl monomers in homogeneous solution for many years gave encouragement to this belief. Although aryl and allyl hafnium and zirconium initiators for stereospecific polymerization of α-olefins have since been claimed to be genuinely homogeneous [1], there are still doubts. The polymerizations are very slow, and it has been suggested that the true initiators are the products of reaction with adventitious traces of dissolved water [2]. Alternatively, initiation might occur on the vessel walls at sites created by the reaction of the organometallic reagent with chemisorbed water. Notwithstanding the nature of the initiator, it is interesting to note that the mechanisms proposed still assume coordination of the monomer to the active site.

The prerequisites for steric control depend very much on whether the active center of the growing chain is trigonal or tetrahedral [3, 4]. If the active center is trigonal, as might be the case if it were a free anion as in I, the tetrahedral symmetry this carbon atom assumes in the chain is not established until the next monomer unit has added. In I the monomer is approaching the active center C_1 in a direction trans to the C_2–C_3 bond. C_1 will assume the same configuration as C_3 and C_β as C_2. For this to occur, rotation of the C_1–C_2 bond prior to addition must be prevented, and the monomer must be restrained from attacking C_1 along a direction cis to the C_2–C_3 bond. Rotation of C_1–C_2 through 180° inverts the symmetry of C_1 in the chain. Cis approach of the monomer inverts the symmetry of C_1 and C_β in the chain. If C_β is to replicate the symmetry of C_2, the monomer itself must be restrained from



I



II

rotating its plane of symmetry through 180°. In the case of C_α, the ultimate configuration in the chain can be "corrected" if the monomer presents the "wrong" side by rotation about the C_α–C_β bond after addition but before the addition of the next monomer [5a]. An elegant model explaining the stereospecificity of the polymerization of α,β-dideuteroisopropyl acrylate makes use of this effect [6].

The requirements for steric control at a tetrahedral active center, such as a covalent metal-carbon bond or an intimately paired ion, are much less stringent, provided the configuration is stable and persistent [3, 4]. If this is so, the symmetry of the active center is established when it is formed (II). The configurations of C_α and C_β in the chain are both fixed as the monomer adds to C_1, the controlling factors being the aspect the monomer presents to the active center and the mode of opening of the π-bond (II). If successive monomers are constrained to present the same side to the active center, then cis-opening, as in II, leads to replication of the α-carbon configuration in the chain but alternation of the β-carbon configuration.

If there is rapid inversion of a tetrahedral active center, as would be the case with a paired ion participating in a labile free ion-paired ion equilibrium, the steric requirements are similar to that of a trigonal center. It is therefore important to establish the

type of active center or centers operating in any particular initiator-monomer-solvent system at a particular temperature. There is little prospect of obtaining direct evidence on this point. Solutions of Grignard reagents have small but significant conductances, but this is attributed to low concentrations of complex ions of the types RMg^+ and $RMgX_2^-$ [7, 8] and is not evidence for dissociation to carbanions and magnesium cations. However indirect kinetic and mechanistic evidence is presented which can be brought to bear on this problem and the related ones of the role of intramolecular and monomer complexes.

EVIDENCE FOR COMPLEXING

Petiaud and Quang-Tho Pham [9] have obtained direct evidence for complex formation between methyl methacrylate (MMA) and magnesium chloride in tetrahydrofuran (THF). Their NMR measurements indicate that the predominating equilibrium is

$$2MMA + MgCl_2,4THF \rightleftharpoons MgCl_2,2MMA + 4THF \qquad (1)$$

There is little prospect of using these methods to investigate monomer complexing to the active center. In a recent analysis of rate and molar-mass data of polymerizations initiated by a number of Grignard reagents and dialkyl magnesium compounds, we have shown that the concentration of active centers lies in the micromolar to millimolar concentration range [10].

However, indirect evidence is available; the rate and molar mass equations of these polymerizations (2) are very different from those obeyed by typical anionic mechanisms (3) [11, 12].

$$v_p = k[\text{Initiator}]_0[\text{MMA}]_0$$

$$\overline{DP}_n = k'\alpha/[\text{Initiator}]_0 \qquad (2)$$

$$v_p = k[\text{Initiator}]_0[\text{MMA}]$$

$$\overline{DP}_n = k'\alpha[\text{MMA}]_0/[\text{Initiator}]_0 \qquad (3)$$

where α = fraction conversion and $[\text{MMA}]_0$, $[\text{Initiator}]_0$ denote initial concentrations. The kinetic abnormalities can be explained if the propagation is a two-step process:

$$\sim\sim M\text{–}Mg\text{–}X + M \rightleftharpoons \underset{\underset{M}{\uparrow}}{\sim\sim M\text{–}Mg\text{–}X} \longrightarrow \sim\sim MM\text{–}Mg\text{–}X \qquad (4)$$

III

The complex postulated (III) manifests itself kinetically only if the second step of reaction (4) becomes rate-controlling. In the systems we investigated it is, and so we obtained evidence for the existence of what has been postulated for many years [6, 13].

In most mechanisms for homogeneous stereospecific polymerizations of acrylate monomers the role of the surface in heterogeneous catalysts is assumed by a cyclic intramolecular complex of the endgroup formed by chelation of the penultimate [6] or antepenultimate [14, 15] carbonyl to the metal of the active center. The formation of cyclic β-keto ester endgroups under conditions where termination is favored [16] is the only evidence that intramolecular complexes may exist. The Bovey mechanism [6] based on chelation of the penultimate carbonyl, with monomer or polar solvent complexed to the vacant site on the lithium ion, provides a convincing explanation of the stereospecificity of the anionic polymerization of β-monodeutero acrylates. For systems initiated by organomagnesium compounds, the only evidence recorded concerns α,β-dideuteroisopropyl acrylate initiated by 1:1 mixtures of phenylmagnesium bromide and magnesium bromide in 9·5:1 toluene/diethyl ether solutions [17]. The first two monomer units incorporated in the chain have random configurations at C_β (CHD) but thereafter a regular configuration is established. On the other hand, the regular configuration of C_α (CDCOOiPr) in the chain is established with the first monomer unit incorporated and persists therefrom. Intramolecular complexing of the penultimate or a more remote carbonyl to the active center is clearly not, in this case, a prerequisite for the formation of an isotactic chain.

EVIDENCE FOR THE STABILITY AND PERSISTENCE OF THE ACTIVE CENTERS

The NMR spectra of poly-α,β-dideuteroacrylates provide evidence on the apparent mode of opening of the monomer bond, that is, whether the monomer is incorporated in the chain as if it opened in a cis or trans manner. Yoshino has shown that the apparent mode of bond opening is established in the initial stages of the polymerization and persists throughout [18]. This is the case both with phenyl magnesium bromide and diphenyl magnesium as initiator. Depending on conditions, one mode or a 1:1 mixture of both may prevail. The controlling conditions are temperature and solvent composition, and in the case of temperature it is that prevailing during initiation which is the

critical factor, not that during the subsequent propagation stages. Further experiments [19] demonstrated that the α-methine endgroup (C_1) of a growing isotactic polyacrylate chain reacts stereospecifically with water and hydrochloric and acetic acids, and in the case of D_2O the preferred position of attachment of the D atoms on C_1 is the same as that for a monomer unit. It seems therefore that not only does the stereospecific active center remain stable and persistent once it is formed in the initial stages of the polymerization, but it carries in itself the configuration that the C_1 atom assumes in the chain. In some cases more than one active center would seem to be operating, a conclusion also reached by Bovey [5b].

We have been able to confirm the existence of different active centers operating independently and without interchange by examining the gel-permeation chromatographs of poly(methyl methacrylates) initiated by various butylmagnesium compounds [10]. The polymers become more syndiotactic as the ether component (tetrahydrofuran in this case) of the solvent mixture is increased. This is very common in anionic polymerization and is readily explained by assuming that a solvated form of the active center is syndiotactic-favoring, while a lower or unsolvated state is isotactic-favoring [5]. Such equilibria are normally assumed to be labile. Strictly speaking this means that their relaxation time is shorter than the lifetime of a propagation reaction step, but for practical purposes it may be taken that it is significantly shorter than the lifetime of a propagating chain.

Gel-permeation chromatographic analysis of the molar mass distributions of the polymers shows they are polymodal. A particularly complex case occurs when sec-butylmagnesium bromide is used. This is shown in Fig. 1. The distribution of the methanol-insoluble polymer exhibits two and probably three peaks. As the solvent composition changes, these peaks remain at the same molar mass but the amount of polymer present in each changes. This means that the polymer in each peak is produced at an independent active center. The solvent dependence arises from changes in the concentration of the different active centers or in their relative reactivities or both. The active centers are stable and persistent, and there is little or no interchange of growing chains between them. If this were not the case the distributions would be very broad but not polymodal. It is probable that the solvent dependence of the steric triad composition of the polymers produced is governed in the same way by solvent-dependent changes in the concentrations or activities of independent active centers.

Confirmation that the proportions of the different active centers is predominantly determined in the initiation stages comes from work using tert-butylmagnesium bromide. Depending on the conditions under which the initiation step is carried out, the distribution of molar mass may be polymodal, including peaks at very high molar mass ($> 10^6$) [10], or of moderate molar mass with a unimodal distributions. The key difference in conditions is whether the monomer is distilled on to frozen initiator solution cooled by

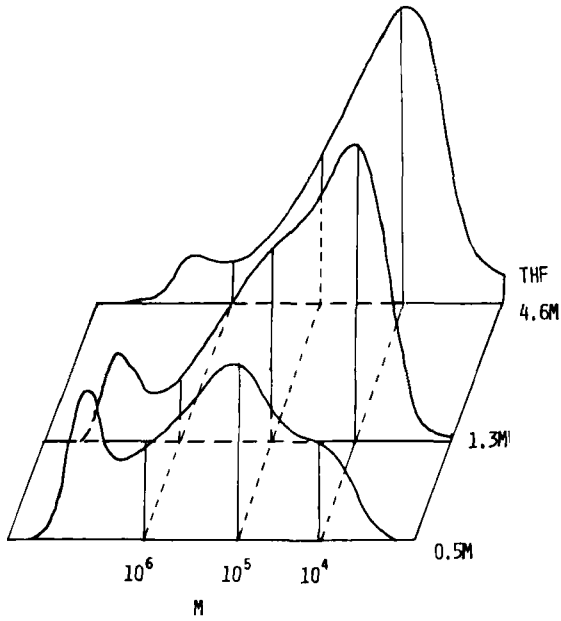


FIG. 1. Gel-permeation chromatographs (one linear Styragel column) of chloroform solutions of the methanol-insoluble polymer produced by initiating 0.96 M methyl methacrylate with 0.02 M sec-butylmagnesium bromide in toluene containing tetrahydrofuran at three different concentrations. The molar mass (M) is dependent on universal calibration against standard polystyrene samples.

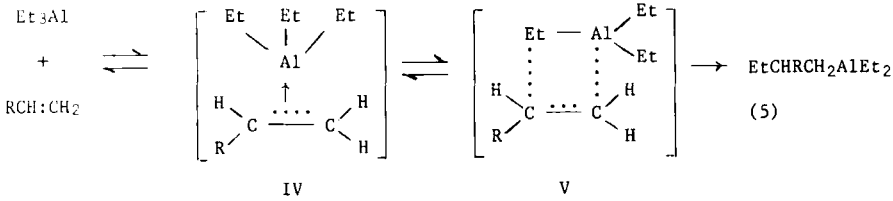
liquid nitrogen or whether initiator solution and monomer are both cooled to 230°K and then mixed. The experimental details are described elsewhere [20]. In the first instance, mixing occurs at the melting temperature of the solution, in the second at 230°K or a few degrees above, depending on the exothermicity and rate of mixing. There is an equally striking effect on the chain configuration of the polymers. In toluene solution at 230°K a steric triad composition of i:h:s ≈ 1:1:1 is produced if initiation occurs at the melting point of toluene solution, while i:h:s ≈ 99:0:1 if monomer and initiator solution are mixed at 230°K [20].

Control of the polymer structure by a particular distribution of independent and persistent active centers set by the conditions prevailing during initiation does not mean that it is absolutely preordained. Conditions prevailing during propagation can introduce modification. If a polymerization initiated at 230°K in toluene is fed with further monomer and tetrahydrofuran to bring toluene:THF to 1:1, i:h:s changes

to 70:10:20, and the gel-permeation chromatograph shows that different types of active center have appeared in the system [20]. Another way in which the conditions of propagation can influence the stereochemistry is if an active center interchanges between two states of different stereospecificity (a Coleman-Fox mechanism [21]). We have seen this happening in n-butylmagnesium bromide initiated systems [12].

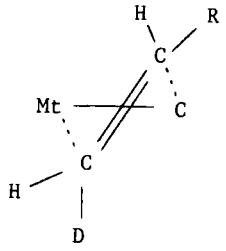
MECHANISM OF THE INSERTION STEP OF THE PROPAGATION

The evidence that, except possibly in very polar solvents, the active center is a magnesium-carbon bond (II) has been discussed elsewhere [10]. The prime reason for believing this is evidence that C_α assumes its in-chain tetrahedral configuration as it becomes the active end of the chain and then remains stable with respect to inversion. The reaction is therefore an organometallic insertion mechanism. The best characterized of these reactions is the bimolecular reaction between n-1-alkenes and triethylaluminum for which the established mechanism [22] is



The reaction proceeds through a π-complex (IV), which may be intermediate or the transition state, and then through a four-center orientation (V), which may be the transition state or, if IV is the transition state, an orientation through which IV must pass as it rearranges to form products. This mechanism is a good model for reaction (4), except that the complex III is believed to be a carbonyl complex rather than a vinyl π-complex (IV). If however the reaction passes through a four-center transition state of the type shown in II and V the double bond would be expected to open in a cis mode as shown in II. Yoshino's work on α,β-dideuteroacrylates has demonstrated that an apparent trans mode prevails under some conditions with organo-magnesium initiators particularly when halide is present [18]. This raises a problem but it does not mean that an insertion-at-a-covalent-bond mechanism can be ruled out. The cis-trans isomerization of the α,β-dideutero monomer, which could occur in the complex III prior to the passage through the four-center transition

state, would lead to apparent trans addition being observed when the actual opening mode was cis. Alternatively, both real and apparent trans modes would occur if the four-center transition state, instead of being planar as in II and V, was skewed as in VI. Skewed four-center



VI

transition states have been postulated to explain trans opening observed in the insertion reactions of acetylenes at metal hydride bonds [23].

CONCLUSIONS

The polymerization of acrylate esters initiated by organomagnesium reagents, despite many apparent similarities to the typical anionic polymerizations initiated by organic compounds of the alkali metals, proceeds by a different mechanism. This pseudo-anionic mechanism involves the complexing of monomer to an active center which is believed to be a covalent magnesium-carbon bond. An analogous difference in mechanism between acrylonitrile polymerizations initiated by organolithium and organomagnesium compounds has been observed by Yerusalimskii [24, 25]. In some systems more than one active center is operating independently–a so-called eneidic mechanism. The stereochemistry and molar mass distribution of the polymer produced is controlled primarily by the relative reactivities and concentrations of these independent active centers. Since the concentrations of the active centers are established during initiation, this explains the prime influence of initiation conditions on the structure of the polymer produced.

The detailed structures of the active centers remain elusive and so no detailed stereomechanism can be proposed. However some specifications can be laid down for those propagating isotactic chains. The inner coordination shell of the magnesium must include the active chain end and a halide atom. Halide is an essential component of highly isotactic initiators and we have shown that its essential presence cannot be explained on the hypothesis that its steric role lies in the formation of MMA $\rightarrow MgX_2$ complexes and so it must be present in the active center [10]. Yoshino [26] has demonstrated

a correlation between the concentration of unreacted Ph-Mg bonds in the polymerizing mixture and the apparent mode of bond opening, so some active centers must include an unreacted R (alkyl or aryl) group from the initiator. If all three groups: chain, halide, and R are present in any active center, then it must contain at least two magnesium atoms. If some active centers are associated organomagnesium halide molecules, this would explain the very low concentrations [10], particularly of the isotactic favoring centers. The vacant coordination sites on magnesium can be filled by monomer, solvent or chain carbonyl. The steric restrictions imposed on a monomer approaching a magnesium atom in an associated molecule could be quite as drastic as those imposed by intramolecular chelation and it could be this that enacts the role played by the surface in heterogeneous catalysts.

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