Elastomer Stereospecific Polymerization

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Symposium Chairmen

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FOREWORD

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PREFACE

In recent years the use of organometallic compounds for stereoregulated polymerization of monomers to form elastomers and plastics has grown from the research stage to large scale commercial production. The degree of stereoregularity obtained in these polymerization systems varies with the monomer in question, with the metal used in the catalyst, and even with the nature of the solvent. The desire and practical need to understand these relationships has led to intensive investigation of the mechanism of polymerization in these systems and of the polymeric structure and properties of the polymers.

As a result, polymerization systems have been developed which are optimum for each type of monomer and for producing polymers for specialized end usage. The papers presented at the Symposium on New Aspects of Elastomer Stereospecific Polymerization cover many of these various types of polymerization systems.

For instance, in the field of elastomers, alkyllithium catalyst systems are used commercially for producing butadiene homopolymers and copolymers and, to a somewhat lesser extent, polyisoprene. Another class of important, industrial polymerization systems consists of those catalyzed by alkylaluminum compounds and various compounds of transition metals used as cocatalysts. The symposium papers reported several variations of these polymerization systems in which cocatalysts are titanium halides for isoprene or propylene and cobalt salts for butadiene. The stereospecificity and mechanism of polymerization with these monomers were compared using the above cocatalysts as well as vanadium trichloride. Also included is the application of Ziegler-Natta catalysts to the rather novel polymerization of 1,3-pentadiene to polymeric cis-1,4 stereoisomers which have potential interest as elastomers.

The second part of this symposium, conducted jointly by the Division of Rubber Chemistry and the Division of Polymer Chemistry of the American Chemical Society, was devoted to methods for measuring the tacticity and the kinetics of polymerization of a variety of materials such as the higher aldehydes, polypropylene oxide, and 4-methylpentene-1. High resolution nuclear magnetic resonance has been particularly valuable in characterizing the structures of polyacetaldehyde and polyisopropyl acrylate.

The intense interest in this field, as illustrated both by the variety of polymerization systems and products that were discussed in this symposium and by the broad representation in it of major academic and world-wide industrial laboratories, assures the continued growth in understanding and in the number and quality of stereospecific polymers.

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1

The Nature of Organometallic Polymerization—A Review

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Elucidating the mechanism of stereospecific polymerization by Ziegler-Natta–type organometallic catalysts has been unusually challenging owing to difficulty in establishing the exact nature of the active species in these heterogeneous systems. Considerable success has been achieved, however, with homogeneous systems involving organolithium initiators. It is concluded that the chain growth process in these systems is not a result of simple molecular collision but involves an intermediate complex formation between the carbon—metal bond and the monomer. This is confirmed by the few available kinetic measurements which indicate that the propagation reaction has a low energy but a very high entropy, and may help to explain the occurrence of stereospecific polymerization in the case of certain monomers.

Addition polymerization, initiated by organometallic compounds, has in recent years aroused widespread interest mainly because of the stereospecific character of many of these systems. It soon became apparent that the chain propagation reaction in these systems differed markedly from that of the well-known free radical polymerizations in that it involved an orientation of the incoming monomer instead of a more random reaction. However, elucidating the detailed mechanism of this important step has been difficult owing to lack of knowledge about the exact structure of the organometallic compound as well as the heterogeneous nature of most such systems. The available knowledge of stereoregular polymerization (*1*), anionic propagation kinetics (*13*), and organolithium polymerization (*2*) has recently been reviewed. Based on presently available knowledge, therefore, it is now possible to sketch some general guide lines toward a better understanding of these phenomena.

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In his early work on the reaction of dienes with the alkali metals and organoalkali compounds, Ziegler (*18*) described the polymerization process as a series of consecutive stepwise additions where the two components of the organometallic, RM, add either 1,4 or 1,2 to the diene. More recently, such reactions have been viewed as proceeding by an ionic mechanism where the growing chain is considered as a carbanion, as proposed by Higginson and Wooding (*5*) for the polymerization of styrene by sodium amide in liquid ammonia (a homogeneous system). However, the occurrence of stereospecificity rules out a mechanism based on a "free" carbanion especially since it was found that the nature of the metal (*7*) and even the type of solvent present (*16*) profoundly affect the structure of the polymer. Hence, the more realistic view has been that the chain growth mechanism involves the interaction of the incoming monomer unit with the carbon—metal bond as such.

Since, most of the stereospecific polymerizations involving the Ziegler-Natta type of catalysts are heterogeneous in character, studying the rate processes is very difficult, if not impossible, and cannot readily be used to elucidate the actual mechanism. However, the organolithium systems are homogeneous in nature and have lent themselves more readily to kinetic analysis (*9*, *17*). From these studies much important information has become available concerning the basic mechanisms involved. In these systems it is known (*16*) that isoprene (but not butadiene) can be polymerized to a high cis-1,4 structure in hydrocarbon media, but even traces of ethers, such as tetrahydrofuran, completely disrupt the stereospecificity. Furthermore, kinetic studies (*10*) have shown that the following schemes can explain the effect of reaction variables on the rate of the propagation reaction.

In tetrahydrofuran

$$R_p = k_p\,[\mathrm{RLi}]\,[\mathrm{M}] \tag{1}$$

In hydrocarbons

$$R_p = k_p^{1/2}\,K_e^{1/2}\,[(\mathrm{RLi})_2]^{1/2}\,[\mathrm{M}] \tag{2}$$

R_p is the propagation rate, k_p is the propagation rate constant, RLi represents the propagating organolithium species. K_e is the equilibrium constant for the following equilibrium which governs the association of the organolithium species in hydrocarbon media.

$$(\mathrm{RLi})_2 \overset{K_e}{\rightleftharpoons} 2\,\mathrm{RLi}$$

RLi represents the active "free" organolithium while $(\mathrm{RLi})_2$ is in the inactive, associated form. Since K_e is generally very small, $[(\mathrm{RLi})_2]$ can be taken as representing the total organolithium concentration.

Recently it was found possible (*10*) actually to determine the value of K_e from physical measurements, and Equation 2 could be resolved for the two systems—isoprene (hexane) (*10*) and styrene (benzene). Typical data obtained in the latter system are shown in Table I. By measuring K_e at different temperatures, it is possible to determine the actual concentration of active species,

Table I. Ethyllithium Polymerization of Styrene in Benzene

$[C_2H_5\,Li] = 1.1 \times 10^{-3}\ ML^{-1}$

	30° C.	*40° C.*	*50° C.*
Degree of Association	1.973	1.954	1.923
K_e ($\times 10^6$)	1.56	4.90	14.2
[RLi] ($ML^{-1} \times 10^5$)	2.97	5.06	8.5
k_p ($LM^{-1}S^{-1}$)	17.3	21.4	26.0
ΔE_a(kcal./mole)	3.8(ave.)		
ΔH_e(kcal./mole)	21.8(ave.)		

RLi, and obtain a value for the true activation energy. In addition these measurements yield a value of ΔH_e—the heat of dissociation of the associated organolithium.

From such data it is then possible to derive the absolute values of the propagation rate constants representing the interaction of the growing chain with the incoming monomer unit. These are shown for isoprene and styrene in Table II. Obviously these propagation rate constants are all characterized by a low activation energy as well as an extremely low frequency factor. This is true both for the non-stereospecific polymerization of isoprene in THF as well as for the stereospecific case of isoprene in hexane (although it seems somewhat more extreme in the latter and for the styrene in benzene).

The abnormally low values of the frequency factors in Table II reflect a very high entropy of activation, strongly indicating that the activated state consists of a very specific complex formation between the propagating chain end and the incoming monomer. This is a striking illustration of the difference in mechanisms between these organometallic systems and free radical polymerizations which also exhibit moderately low activation energies but much higher frequency factors—ca. 10^8—as expected for ordinary bimolecular reactions. Unfortunately, an explanation of the presence or absence of sterospecificity in organolithium polymerizations must await a more detailed knowledge of the structure of the lithium—carbon bond in different media.

Table II. Absolute Propagation Rate Constants in Organolithium Systems

	Isoprene		*Styrene*
	THF	*Hexane*	*(benzene)*
[a]k_p (30° C.)	0.14	5.0	17
[b]ΔE_a	7.0	4.2	3.8
[a]A ($\times 10^{-3}$)	15	5.2	11

[a] k_p and A in $LM^{-1}S^{-1}$.
[b] ΔE_a in kcal./mole.

However, the above type of data clearly indicate the need for new approaches outside the usual scope of polymerization kinetics. Such approaches should be aimed at learning more about the intermediate activated complex between the organolithium and the monomer, perhaps by using monomers that do not polymerize in organolithium systems. In this regard, it should be remembered that organoalkalies in general are effective only for monomers containing the conjugated double bond and are ineffective for simple olefins.

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The importance of specific complex formation between monomer and organolithium is illustrated in copolymerization studies (*6*, *8*, *12*). Thus, it is well known that in hydrocarbon media the organolithium species show a high degree of selectivity leading to long sequences of one monomer to the exclusion of the other. On the other hand, in the presence of coordinating solvents such as amines or ethers, this selectivity is largely destroyed, presumably by lack of formation of the intermediate complex between the growing chain and the monomer. This is strikingly illustrated by the copolymerization reactivity ratios in Table III where the marked differences between the r_1 and r_2 values are very obvious as well as the dramatic effect of the solvents on these ratios.

Table III. Alkyllithium Copolymerization of Styrene and Dienes (*8*)

Monomer 1	*Monomer 2*	*Solvent*	r_1	r_2	*Ref.*
Styrene	Butadiene	Toluene	0.1	12.5	*11*
Styrene	Butadiene	THF	8	0.2	*11*
Styrene	Isoprene	Toluene	0.25	9.5	*12*
Styrene	Isoprene	Triethylamine	0.8	1.0	*12*
Styrene	Isoprene	THF	9	0.1	*11*
Butadiene	Isoprene	*n*-Hexane	3.4	0.5	*8*

Some progress in this regard has also been made in the case of the Ziegler-Natta catalysts despite the heterogeneous nature of the polymerization system. Cossee (*3*, *4*) has recently proposed a mechanism to account for the stereospecificity in the polymerization of propene by α-$TiCl_3$ + $Al(C_2H_5)_3$ catalyst. This mechanism is based on a crystalline α-$TiCl_3$ coordinated with the aluminum trialkyl: the active center is the octahedrally coordinated titanium, with partly empty t_{2g} orbitals, attached to the alkyl group and having one vacant octahedral position. According to this mechanism, the titanium—alkyl bond must be sufficiently destabilized when an olefin molecule is coordinated in the vacant position to lead to its rupture and to form a new bond between the titanium and the CH_2 group of the incoming monomer. This requires only slight nuclear displacements and can be considered in the class of electronic rearrangements. Accordingly, the activation energy of this propagation step is also quite low, ca. 10 kcal./mole (*11*).

It is becoming increasingly clear that polymerizations by organometallic compounds involve intermediate coordination complexes between the incoming monomer and the metal of the organometallic. The monomer unit can then become interposed between the metal and the organic moiety by a simple electronic rearrangement. Such a process could account for the low activation energy and high entropy of the overall reaction step. It is obvious, therefore, that any real explanation of the stereospecificity of such propagation processes might best be obtained by more information concerning the energetics of the complex formation reaction, as well as from a more detailed knowledge of the bond structure of the organometallic.

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2

Preformed Alkylaluminum-Titanium Tetrachloride Catalysts for the Polymerization of Isoprene

Effect of Groups Attached to the Aluminum on Catalytic Performance

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Catalysts prepared from $TiCl_4$ and C_1 to C_8 trialkylaluminum compounds showed higher activity for cis-1,4 polymer formation with increasing chain length or branching of the alkyl group. Diisobutylaluminum hydride and triisobutylaluminum behaved similarly while diisobutylaluminum monochloride was a less efficient cocatalyst. Aging of catalysts prepared from the higher alkyls improved their stereospecificity. Separated and thoroughly washed solids (β-$TiCl_3$) from preformed catalysts of 0.8–1.3 Al/Ti mole ratios exhibited catalytic activities which in most instances surpassed those of the corresponding unseparated catalysts. The variability in activity of catalysts examined in this study is explained in terms of the reducing power and adsorption characteristics of the various organoaluminum compounds toward $TiCl_3$.

The use of Ziegler-type catalysts prepared from triisobutylaluminum and titanium tetrachloride for the polymerization of isoprene has been explored in great detail over the past few years (*1, 5, 6, 11, 13, 14, 17*). Several papers and patents mention cursorily the use of organolithium compounds other than triisobutylaluminum, but there has been, to our knowledge, no systematic comparison of catalysts made from these various cocatalysts. Results given in the first part of this study have shown that the nature of substituents attached to the aluminum has a considerable bearing on the catalytic behavior of the resulting preformed catalysts. The period of aging of these catalysts also markedly affects their performance.

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Early polymerization work with Ziegler-type catalyst systems has shown (*8, 11, 12, 17, 18*) that both the solid and liquor phase of preformed R_3Al-$TiCl_4$ catalysts play an important role in determining the catalytic activity. In the second part of the present study we have attempted to correlate the differences in catalytic action encountered with the various alkylaluminum cocatalysts examined to either the solid or liquid portion of the preformed catalysts.

Experimental

Materials. Alkylaluminum compounds, supplied by Texas Alkyls, Inc., were used without further purification. Analytical data supplied by the manufacturer showed all alkyls to be of greater than 90% purity. The diisobutylaluminum hydride was prepared by heating the commercial triisobutylaluminum at 130° C. and pumping off the gases evolved. Analysis of the product showed 16.8% aluminum as compared to the theoretical value of 18.97%.

Titanium tetrachloride ($TiCl_4$) was supplied by Columbia Southern Chemical Corp. and used as received.

Heptane—ASTM grade and pentane—99% pure were obtained from Phillips Petroleum Co. These were washed with concentrated sulfuric acid, flash distilled, and stored over sodium wire.

Isoprene was supplied by Goodyear Chemicals Division and had a purity of 99% or higher.

Catalyst Preparation. Details of the equipment and procedures used were described earlier (*13*). Essentially, a 2*M* solution of the alkylaluminum compound in heptane was added gradually to a vigorously stirred 0.38*M* solution of titanium tetrachloride in a 2-liter Morton-type flask at 20° C. After a desired molar ratio of Al/Ti was reached, an aliquot of the catalyst slurry was withdrawn for testing. The addition of the aluminum compound was then resumed, and the operation was repeated at successive Al/Ti ratios.

Polymerization and Product Evaluation. A catalyst aliquot containing 0.132 mmole of titanium was syringed into a 4-ounce bottle containing 10 grams of isoprene diluted with 40 grams of pentane. The bottles were placed in a 50° C. bath and left tumbling for the specified length of time.

The procedures used in polymer product isolation and evaluation were the same as presented earlier (*13*). Basically, the dried polymers were extracted with a 50:50 by volume mixture of hexane and isopropyl alcohol to remove low molecular-weight material, herein called extractables. Physical properties such as inherent viscosity, % gel, and polymer microstructure were determined on the solid polyisoprene residue.

Separated Catalysts. The procedures used by Saltman (*12*) in his study of separated catalysts were adopted here with few modifications. The supernatant liquor of a preformed catalyst (prepared as described above and transferred to 8-ounce bottles) was removed, and then the solid was washed six times with deaerated heptane. Finally, enough heptane was added to re-attain the original volume. All removals of liquors were performed as follows. The 8-ounce bottles, capped with perforated metal screw-caps fitted with self-sealing rubber gaskets and Teflon liners, were first centrifuged for 10–15 minutes at 1500 r.p.m. Most of the supernatant liquor (approximately 65% by weight of the total liquor) was then removed by using nitrogen pressure to force the liquor into a 100-ml. syringe which was equipped with a Luer-lock stopcock and 6-inch No. 18 gauge needle. After an equal volume of the purified heptane was added, a new cap was put on the bottle (under nitrogen), and the bottle was shaken vigorously for several minutes. Then the entire procedure was repeated until the solid had been washed six times. During all the operations extreme care was taken to exclude air or moisture from the system.

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By this technique a calculated 99.9% plus of the original liquor was removed. The last wash, after evaporation, contained no weighable residue. Thus, it appears that no further removal of aluminum could be obtained by washing. The analytical data, however, show that a small amount of aluminum may still be present in the washed solids. For example, analyses of solids from triisobutylaluminum (i-Bu_3Al)-$TiCl_4$ catalysts of 0.9 and 1.0 Al/Ti mole ratio showed that possibly 5–10% of the original aluminum was left in the solid. In the case of a solid from a triethylaluminum (Et_3Al)-$TiCl_4$ preparation which was washed 11 times, an indicated 5% of the original aluminum was retained in the solid. The Cl/Ti mole ratios in the above washed solids were quite close to 3.0 as would be expected under the experimental conditions (*2, 4, 11*).

The separated solids were evaluated for polymerization as described for the unseparated catalysts. The solids were also evaluated in combination with alkylaluminum compounds added in situ to the polymerization bottle. In all cases, the alkylaluminum compound was added first followed by the solid slurry in heptane. This procedure will be referred to as modification or, if the resulting system has a higher catalytic activity than the solid alone, as activation.

Results

The catalysts studied here were preformed by the gradual addition of the alkylaluminum compound to a solution of titanium tetrachloride. This preparation method was found earlier (*13*) to give highly reproducible results. An Al/Ti mole ratio range of 0.60 to 2.0 or higher was usually covered. Each

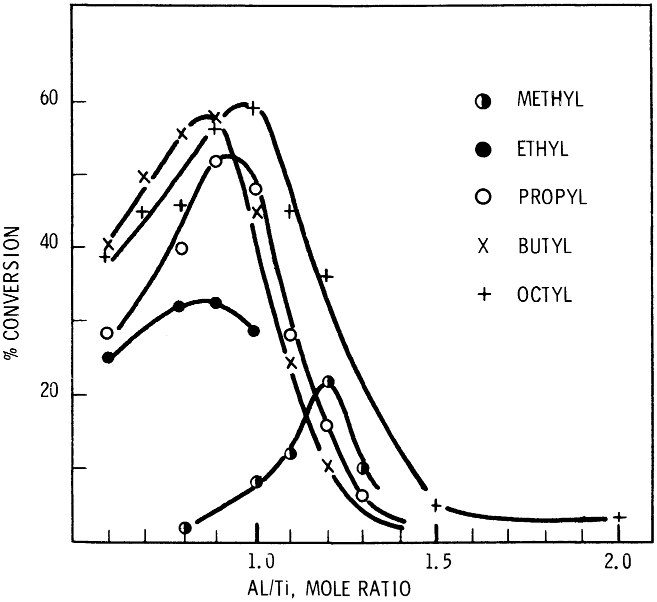

Figure 1. Conversion of isoprene to solid polymer as a function of Al/Ti molar ratio and alkyl size in tri-n-alkylaluminum cocatalyst; polymerization time—22 hours

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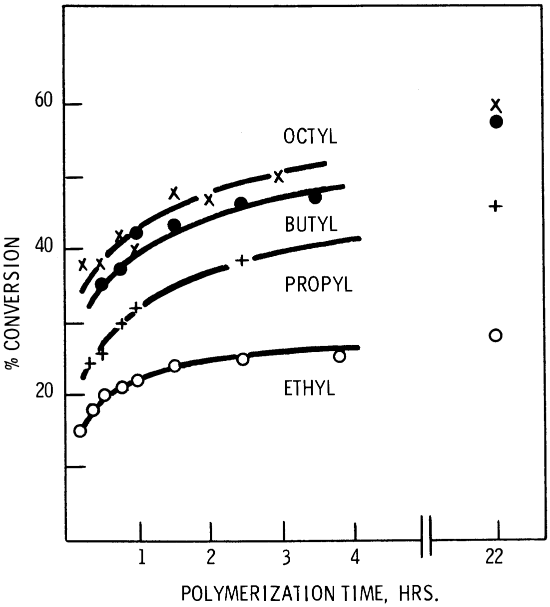

Figure 2. Effect of alkyl size in tri-n-alkylaluminum cocatalyst on activity as measured by bottle polymerization rates

catalyst was evaluated for the polymerization of isoprene within 10 minutes after its preparation. The same catalyst preparations were tested again after one and five weeks of aging at room temperature. Several other catalyst preparations were separated into the liquid and solid fractions for a study of the catalytic contribution of each phase.

Unseparated Catalyst. UNAGED CATALYSTS. Our previous work (*13*) with the triisobutylaluminum-titanium tetrachloride catalysts preformed at 20° C. had shown that the optimum Al/Ti ratio for *cis*-1,4 polyisoprene formation is about 0.9 to 0.1. The yields of solid polymer fell off rapidly on either side of this ratio. Lower ratios led to mixed leathery-rubbery products of high gel, whereas higher ratios (above 1.3) produced increasing amounts of low molecular weight oily materials, so-called extractables.

When catalysts prepared from tri-*n*-alkylaluminum compounds were employed, the above polymerization pattern still prevailed (Figure 1). The optimum Al/Ti mole ratio was close to 1.0 for all cocatalysts with the exception of trimethylaluminum which required a slightly higher ratio. At Al/Ti ratios above 1.3, up to 40–60% of the isoprene was converted into low molecular weight extractables. Most interesting is the gradual increase in polymer yields observed with catalysts prepared from alkylaluminum compounds with an alkyl chain length increasing from C_1 to C_8. The increase in activity is particularly great in passing from trimethyl-to triethyl- and tripropyl-aluminum; thereafter the improvement is relatively small. Natta and co-workers (*9*),

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in a study of propylene polymerization with $R_3Al-TiCl_4$ systems, found that in the same group of alkyls, trimethylaluminum produced the most active combination with $TiCl_4$. This divergency from our data is probably related to the high Al/Ti (about 2.0) requirement for optimum polymerization of propylene.

Rate studies which were carried out with preformed catalysts of or near the optimum Al/Ti ratio also confirmed that the higher alkylaluminum compounds result in the more active preparations (Figure 2). It is significant that the rate differences encountered with the various catalysts show up mainly in the initial phase of polymerization. A noticeable break occurs in all curves at about the same reaction time, beyond which the curves show almost identical slopes. This break in the rate curves was observed in earlier studies by us (*13*) and by other workers (*7, 17*), and a likely explanation for this was offered (*13*).

Physical properties such as inherent viscosity, % gel, and % cis-1,4 content of the polyisoprenes produced with the above catalysts are given in Table I. The differences from one system to another are small and do not suggest any particular trend.

Table I. Polymer Properties Obtained with Unaged Catalysts Prepared from Different Tri-*n*-Alkylaluminum Compounds

(Polymerization: 22 hours)

Aluminum Compound	*Al/Ti*	*Yield, %*	*Inherent Viscosity*	*Gel %*	*Cis-1,4 %*
Methyl	1.1	12	4.4	16	
	1.2	22	3.2	15	94.6
	1.3	10	2.3	15	
Ethyl	0.8	32	2.2	21	
	0.9	31	2.6	16	95.0
	1.0	29	2.5	13	
Propyl	0.8	40	2.1	28	
	0.9	52	2.4	18	96.5
	1.0	47	2.5	14	96.5
Butyl	0.8	55	3.1	19	
	0.9	58	3.2	12	96.8
	1.0	45	3.6	12	
Octyl	0.8	46	2.3	13	
	0.9	56	2.4	11	
	1.0	59	2.7	8	94.0

When the bulkier, branched aluminum compounds such as triisohexylaluminum and diisobutylaluminum hydride were used as cocatalysts, we found (Figure 3) the same polymerization pattern as before with the tri-*n*-alkylaluminums. The polymer yields at optimum Al/Ti ratio, though, are significantly higher with these systems as compared to the yields obtained with the most active unaged *n*-alkylaluminum preparations.

By comparison with triisobutylaluminum and diisobutylaluminum hydride, diisobutylaluminum chloride required higher Al/Ti mole ratios for good activity, at least 2.0 and above (Figure 4). This must be owing, at least in part, to the lower active aluminum—carbon bond content of the halide. The halide system was also considerably less active over the entire Al/Ti range tested as compared to the corresponding triisobutylaluminum catalysts.

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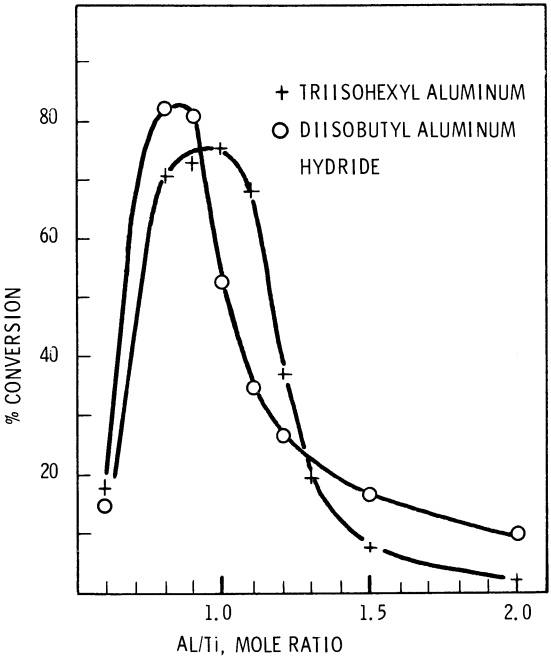

Figure 3. Conversion of isoprene to solid polymer as a function of Al/Ti molar ratio and groups in alkylaluminum cocatalyst; polymerization time—22 hours.

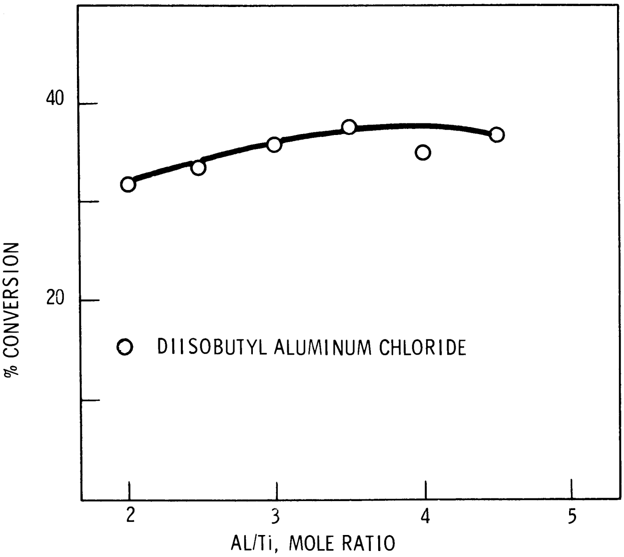

Figure 4. Conversion of isoprene to solid polymer as a function of Al/Ti molar ratio; polymerization time—22 hours.

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The physical properties obtained with the latter catalysts (Table II) vary little from one system to another. As noted before with *n*-alkylaluminum preparations, no particular trends could be established from the obtained results.

Table II. Polymer Properties Obtained With Unaged Catalysts Prepared from Different Organoaluminum Compounds

(Polymerization: 22 hours)

Aluminum Compound	*Al/Ti*	*Yield %*	*Inherent Viscosity*	*Gel %*	*Cis-1.4 %*
Triisobutyl	0.8	76	3.1	19	
	0.9	78	3.3	13	
	1.0	33	3.7	10	
Triisohexyl	0.8	70	2.5	30	
	0.9	72	2.3	26	
	1.0	75	2.7	21	95.1
Diisobutyl hydride	0.8	85	2.6	15	95.4
	0.9	81	2.7	12	93.9
	1.0	53	2.8	20	
Diisobutyl chloride	2.0	32	3.4	25	
	2.5	33	2.8	19	
	3.0	37	3.0	19	94.0
	3.5	38	2.9	27	94.3
	4.0	35	2.8	17	94.4
	4.5	37	3.1	23	95.1
	5.0	39	2.9	24	

AGED CATALYSTS. In our study of preformed catalysts prepared from triisobutylaluminum and titanium tetrachloride, we observed (*14*) that these catalysts on aging at room temperature improved their stereospecificity. In this instance, aged catalysts of about 1.2 to 2.0 Al/Ti gave increasing yields of solid *cis*-1,4 polyisoprene and simultaneously lower yields of extractables. The same behavior was generally observed with catalysts prepared in this study, particularly so with the higher alkyl preparations. Figure 5, for example, illustrates the polymerization results obtained with triisohexylaluminum catalysts when unaged and after aging for one and five weeks, respectively, at room temperature. A very significant improvement in solid cis-1,4 yields was achieved after one week of aging over the entire Al/Ti range, including the region of optimum performance (0.8–1.1). Further improvements, although less pronounced, were observed after a total of five weeks of aging. This improvement goes hand in hand with a reduction in formation of extractables.

The same behavior was noticed with aged catalysts which were prepared from tri-*n*-octylaluminum and diisobutylaluminum chloride. All other catalyst preparations examined by us showed relatively small changes in cis-1,4 polymer production after a one and five week aging period.

The action of aged catalysts was also followed in polymerization rate studies. Again we see a distinct improvement in activity with five-week aged catalysts prepared from triisobutyl-, triisohexyl-, and tri-*n*-octylaluminum (Figures 5, 6, 7). The previously mentioned break in the polymerization curves obtained with unaged catalysts is missing or considerably attenuated with the latter catalysts. A similar change related to catalyst aging was

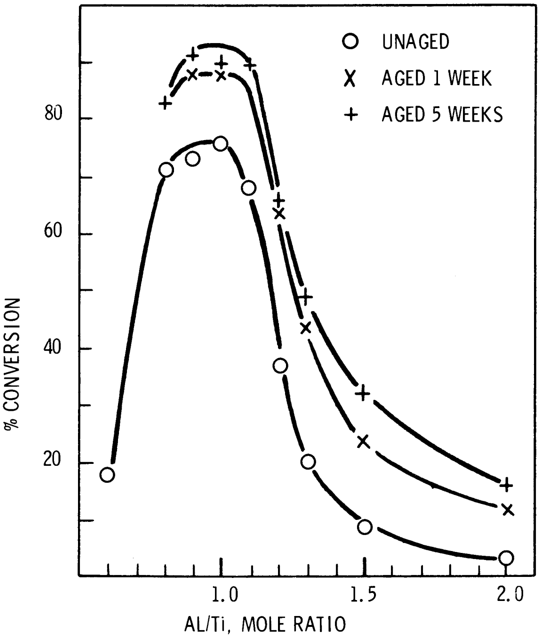

Figure 5. Conversion of isoprene to solid polymer as a function of Al/Ti molar ratio and catalyst aging; triisohexylaluminum-$TiCl_4$ catalyst system; polymerization time—22 hours.

reported earlier (*13*) for preformed triisobutylaluminum catalysts, and an explanation for this was then proposed.

The properties of polymers produced with five week old catalysts are listed in Table III. Compared with the results from unaged catalysts (Tables I, II), we notice a trend of increasing polymer inherent viscosities after aging for most of the catalysts tested. The viscosity increase, about 0.5 unit, is more evident with those systems which have also shown considerable improvement in solid yields upon aging as was the case with tri-*n*-octyl- or triisohexylaluminum catalysts.

Separated Catalysts. Since considerable differences in activity were encountered for the various catalysts employed in this study, it was of interest to correlate these differences with either the solid or liquor portion of the preformed catalysts. The triisobutylaluminum (i-Bu_3Al)-$TiCl_4$ and triethylaluminum (Et_3Al)-$TiCl_4$ catalyst systems, found to vary widely in activity, were chosen for a more detailed study. The solids of the following catalysts were separated:

i-Bu_3Al-$TiCl_4$ preparations of 0.9 and 1.0 Al/Ti mole ratio
Et_3Al-$TiCl_4$ preparations of 0.8, 0.9, 1.0, and 1.3 Al/Ti mole ratio

The above separated solids will be referred to as 0.9, 1.0 i-Bu_3Al- and 0.8, 0.9, 1.0, 1.3 Et_3Al-solids, respectively.

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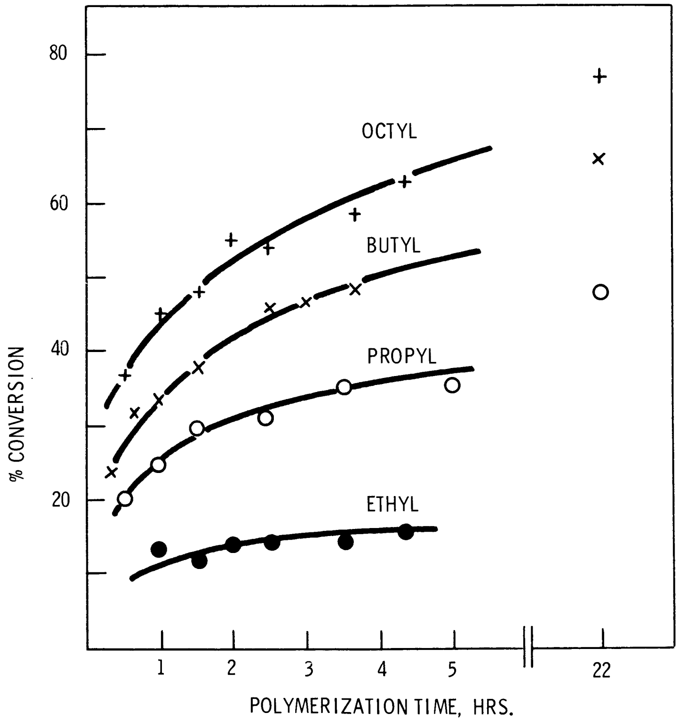

Figure 6. Effect of alkyl size in tri-n-alkylaluminum on activity of aged catalyst preparations; catalysts aged for five weeks at room temperature.

Catalytic Activity of Separated Solids. Although a calculated 99.9% plus of the original liquor was removed, the above solids possessed surprisingly high activity. Other investigators (*8*, *12*) reported no catalytic activity for isoprene or butadiene polymerization with washed solids in the above Al/Ti range.

Figure 8 compares the polymer yields obtained with i-Bu_3Al–$TiCl_4$ catalysts and their separated solids. Although the 0.9 i-Bu_3Al solid is less active than its unseparated counterpart, it still shows considerable activity as is demonstrated by the 22-hour conversions. However, in the case of the solid separated from a 1.0 Al/Ti preformed catalyst, the washed solid is much more active than the unseparated preparation. Indeed the activity of the 1.0 i-Bu_3Al solid compares favorably with that of the optimum unseparated catalyst from the i-Bu_3Al–$TiCl_4$ system—namely the 0.9 Al/Ti one. The observed scatter in polymerization data is believed to be caused by the sensitivity of the separated solids to traces of impurities such as oxygen or water. We have noticed that solids which were left standing for several weeks lost their activity, most likely because of slow poisoning. These solids could, however, be reactivated readily through the addition of minute amounts of alkylaluminum compounds.

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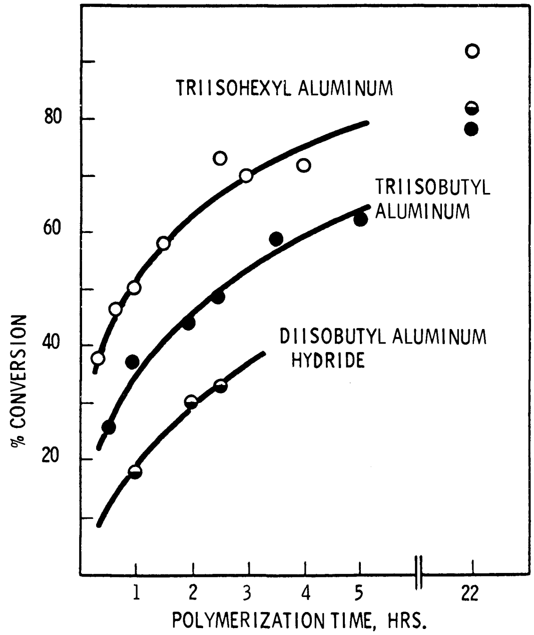

Figure 7. Effect of groups in alkylaluminum cocatalyst on activity of aged catalyst preparations; X*—diisobutylaluminum chloride; catalysts aged for five weeks at room temperature.*

Table III. Polymer Properties Obtained With Five-Week Aged Catalysts Prepared from Different Organoaluminum Compounds

(Polymerization: 22 hours)

Aluminum Compound	*Al/Ti*	*Yield %*	*Inherent Viscosity*	*Gel %*	*Cis-1,4 %*
Tri-*n*-propyl	0.8	40	2.6	5	
	0.9	48	3.1	7	95.7
	1.0	40	3.1	10	94.6
Tri-*n*-butyl	0.8	66	3.3	14	
	0.9	59	3.0	10	96.8
	1.0	49	3.3	13	96.8
Tri-*n*-octyl	0.9	80	3.6	28	
	1.0	77	3.4	25	
Triisohexyl	0.8	83	3.2	24	95.5
	0.9	91	3.1	27	95.8
	1.0	90	3.1	20	94.4
Diisobutyl hydride	0.8	82	2.5	18	
	0.9	73	2.6	13	
	1.0	55	2.5	7	
Diisobutyl chloride	2.0	21	3.6	16	
	2.5	36	3.8	18	
	3.0	56	3.4	15	
	4.0	54	3.3	14	

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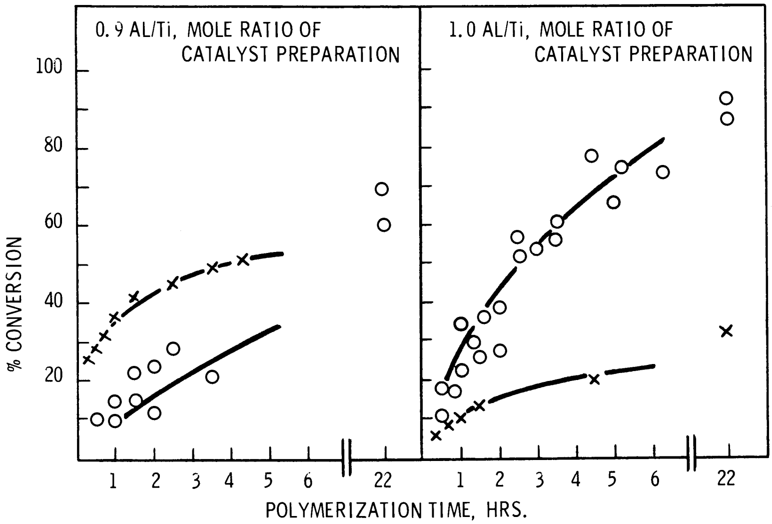

Figure 8. Comparison of the activity of i-Bu_3Al*–*$TiCl_4$ *unseparated catalysts and their separated solids. Solid polymer yields at variable polymerization times;* X*—unseparated catalysts;* O*—separated solids.*

Table IV. Comparison of the Activity of Et_3Al–$TiCl_4$ Catalysts and Their Separated Solids

	% Polymer Yield			
	2.5 Hours		*22 Hours*	
Al/Ti[a]	*Unseparated Catalyst*	*Separated Solid*	*Unseparated Catalyst*	*Separated Solid*
0.8	25	48	30	80
0.9	25	50	27	70
1.0	15	40	21	70
1.3	2	25	5	55

[a] Mole ratio of catalyst preparation.

The activity of separated solids stands out even more markedly in the case of solids separated from Et_3Al-$TiCl_4$ preparations (Table IV). For this system, at the four Al/Ti mole ratios examined, all solids were considerably more active than their unseparated counterparts. In one instance, a solid from a 1.0 Al/Ti ratio catalyst was subjected to five more washings (a total of 11) without further loss of activity.

MODIFICATION OF SOLIDS. Our next step was to investigate the behavior of washed solids when recombined with various alkylaluminum compounds. A 0.9 *i*-Bu_3Al solid with relatively little residual activity was chosen for this purpose. Figure 9 illustrates a typical polymerization curve for the solid upon activation with triethylaluminum. The addition of only minute amounts, in the range of 0.025–0.075 mole per mole Ti in the solid, was needed to regain or surpass the original activity of the unseparated catalyst. The same procedures were used to study the activation of the above brown $TiCl_3$ solid with other organoaluminum compounds. From the yields (maximum on the polymerization curve) listed in Table V we see that all compounds were capable of reactivating the solid to where it equalled, and in most cases, out-performed the unseparated catalyst. The different trialkyls—about equivalent among themselves—were more efficient cocatalysts then the corresponding dialkylaluminum halides. Alkylaluminum dichlorides were not capable of activating the solids at all.

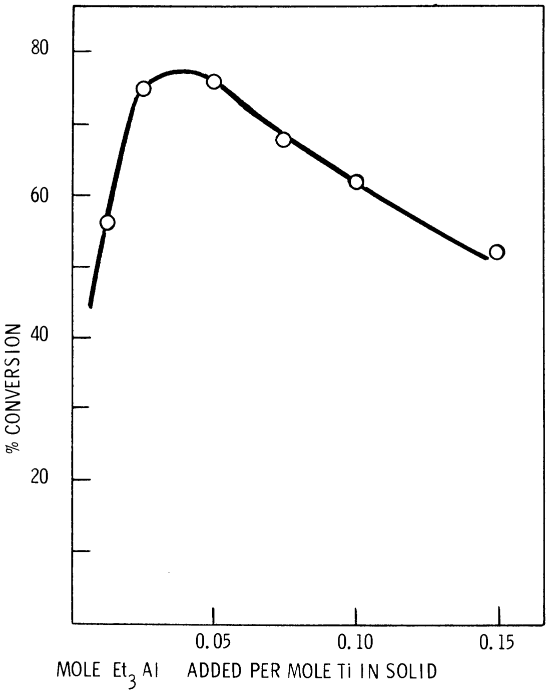

Figure 9. Activation of a 0.9 i-Bu_3Al–$TiCl_4$ separated solid with Et_3Al added in situ; polymerization time—2.5 hours.

Table V. Optimum Activation of 0.9 *i*-Bu_3Al–$TiCl_4$ Separated Solid with Various Organoaluminum Compounds

Organoaluminum Compound[a]	*% Yield* 2.5 Hours	*% Yield* 22 Hours
Trimethyl	64	88
Triethyl	76	96
Tri-*n*-propyl	74	92
Tri-*n*-butyl	69	89
Tri-*n*-octyl	79	93
Triisobutyl	72	89
Diisobutyl chloride	56	88
Diethyl chloride	42	72
Diisobutyl hydride	65	92
Unseparated catalyst[b]	44	71

[a] The amounts of activator used were $> 0.013 \times 10^{-3}$ and $> 0.033 \times 10^{-3}$ mole aluminum for the trialkyls (including the hydride) and the dialkylhalides, respectively.
[b] No activation used.

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The same type of experiments were conducted with the Et_3Al-$TiCl_4$ washed solids using a smaller number of alkylaluminum compounds. Figure 10 shows the modification of these solids with triethylaluminum. None of the solids could be activated to give a polymer yield exceeding that obtained with the separated solid alone, in contrast to the behavior of the 0.9 i-Bu_3Al solid. Experiments along the same line showed that the highest polymer yields obtainable upon modification of Et_3Al solids with variable amounts of other organoaluminum compounds were always below that observed with the separated solid alone.

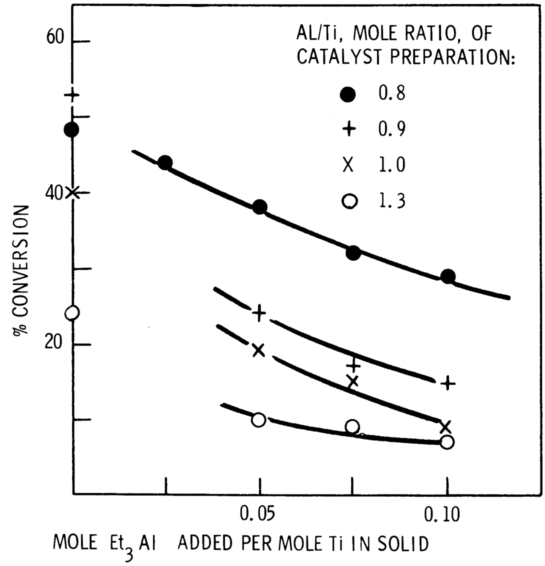

Figure 10. Modification of Et_3Al-$TiCl_4$ separated solids with Et_3Al added in situ; polymerization time—2.5 hours.

To complete the picture, a detailed study was made of the effect on activity of recombining increasing amounts of diisobutylaluminum chloride (i-Bu_2AlCl) or diethylaluminum chloride (Et_2AlCl) with 0.9 i-Bu_3Al and 0.9 Et_3Al solids. These halides are known to be the main constituents found in the liquor of unseparated catalysts. The results (Figures 11, 12) confirm that the i-Bu_3Al solid can be activated with either alkyl halide whereas the Et_3Al solid cannot. In addition, we see that with the i-Bu_3Al solid, i-Bu_2AlCl is a better activator than the Et_2AlCl and that the latter can be tolerated only in small amounts. Thus, when Et_2AlCl is added to the i-Bu_3Al separated solid in amounts equal to that present in the unseparated catalyst, the catalytic activity approximates quite closely that of an unseparated Et_3Al-$TiCl_4$ catalyst, as shown by both 2.5-and 22-hour polymerization data (compare with data in Table IV).

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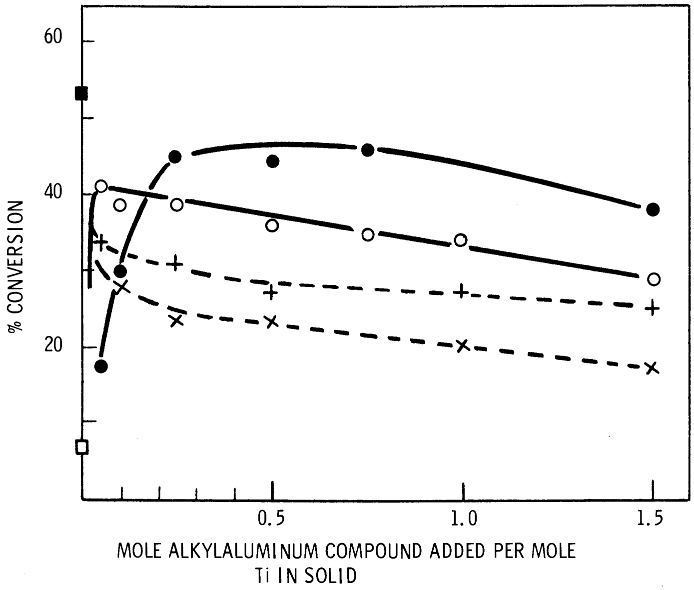

Figure 11. Catalytic activity of 0.9 Al/Ti separated solids and their combinations with dialkylaluminum halides. I. i-Bu$_3$Al–TiCl$_4$ solid; □ without activation; ● activated with i-Bu$_2$AlCl; ○ activated with Et$_2$AlCl. II. Et$_3$Al-TiCl$_4$ solid; ■, without modification; +, modified with i-Bu$_2$AlCl; X, modified with Et$_2$AlCl; polymerization time—2.5 hours.

The physical properties of polyisoprenes produced with separated *i*-Bu$_3$Al solids and their modified versions are listed in Table VI. These systems appear to give polymers with somewhat higher inherent viscosities than observed before with unseparated catalysts. No significant changes in micro-structure of the polymers were noticed between the various systems.

Discussion

One of the most important observations of this study is the high catalytic activity for isoprene polymerization encountered with separated solids from 0.8–1.3 Al/Ti preformed catalysts. Previously (*12*), these ratios were reported to give solids which, when thoroughly washed, were inactive. Only solids of high ratios exhibited catalytic activity which, however, was rather low. In our case, the washed solids from 1.0 ratio *i*-Bu$_3$Al–TiCl$_4$ and 0.8–1.0 ratio Et$_3$Al-TiCl$_4$ catalysts were all superior in activity to the unseparated preparations.

A possible explanation for the discrepancy between our findings and those of others must first be sought in terms of both the solid treatment and the purity of the polymerization system. It is generally accepted (*3*) that an organometallic bond (whether in form of Al—C or Ti—C) is essential for polymerization. The amount of organometallics in a separated solid is very

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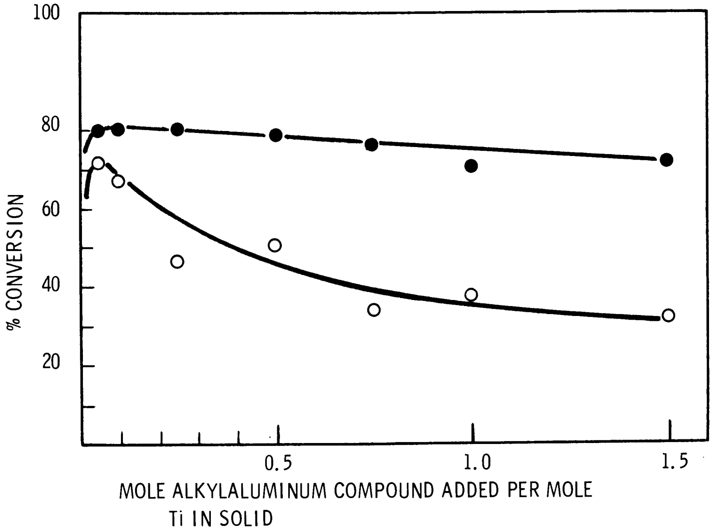

Figure 12. Catalytic activity of 0.9 i-Bu_3Al–$TiCl_4$ separated solid activated with dialkylaluminum halides. ●, modified with i-Bu_2AlCl; ○, modified with Et_2AlCl; polymerization time—22 hours.

Table VI. Polymer Properties Obtained with Separated and Activated *i*-Bu_3Al–$TiCl_4$ Catalyst Solid

(Solid of 0.9 Al/Ti; 22-hour polymerization)

Activator[a]	*Yield %*	*Inherent Viscosity*	*Gel %*
Trimethylaluminum	88	3.1	20
Triethylaluminum	94	3.8	15
Tri-*n*-propylaluminum	89	3.4	46
Tri-*n*-butylaluminum	88	3.6	14
Tri-*n*-octylaluminum	88	3.6	12
Triisobutylaluminum	90	4.3	42
Diisobutylaluminum hydride	90	3.8	16
Diisobutylaluminum chloride	87	3.1	51
Separated solid[b]	72	3.3	10
Unseparated catalyst[b]	71	3.1	16

[a] 0.013×10^{-3} mole aluminum (i.e., 0.1 mole Al/mole of Ti in solid).
[b] No activation employed.

low and will be easy prey for any impurities such as oxygen, water, etc, with the net result of inactivation of such a solid. We believe that the introduction of impurities via repeated washings and through the polymerization mixture very likely caused the inactivation of solids studied by others. When precautions were taken to reduce the amount of damaging impurities to a minimum, a solid (Et_3Al-type) could be washed as many as 11 times without loss in activity. Theoretically these washings should have removed all soluble organoaluminum compounds quantitatively. Even if further washings had ended in a loss of the activity, this would have to be attributed to a reaction with impurities rather than to a desorption of the organometallic compound.

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The differences in activity found for the various separated solids prepared by us can be best interpreted from the changes in composition which take place in the course of the reaction of a R_3Al with $TiCl_4$. In our case, where triisobutylaluminum is added gradually to $TiCl_4$ at 20° C., a maximum heterogeneity in reaction products is expected at low Al/Ti mole ratios. At a ratio below 0.75, we may expect the catalyst to contain, besides brown $TiCl_3$, the alkylaluminum-monohalide, -dihalide, and perhaps some $AlCl_3$. Polyisoprenes obtained with low Al/Ti ratio catalysts indeed are of mixed composition (*13*). As a ratio of 0.9 is approached, the catalyst mixture becomes more homogeneous and will essentially consist of brown $TiCl_3$ and the alkyl monohalide with possible traces of trialkylaluminum. At this ratio we also see maximum activity and stereospecificity for cis-1,4 polymerization. This ratio is a critical one; any trialkyl added thereafter is not used up for equilibration (with $RAlCl_2$) but will act directly on the $TiCl_3$, be adsorbed onto it, eventually alkylate, and reduce it further to $RTiCl_2$ and $TiCl_2$, respectively. The net result is a loss in both activity and stereospecificity. The activity of washed solids can then be interpreted in either of two terms:

(1) Alkylated Ti species such as R_2TiCl_2 and $RTiCl_2$ which are formed on the solid surface are not desorbed by repeated washings. These species then constitute the active sites as proposed by one school of authors (*3*). At higher Al/Ti mole ratios, more of the alkylated Ti compounds are to be expected; hence the high residual activity.

(2) R_3Al is preferentially adsorbed on the solid and cannot be removed by washing. More saturation occurs with R_3Al at higher Al/Ti ratios, hence the increased activity. In support of this hypothesis is the fact that with $TiCl_4$ and β-$TiCl_3$ the trialkylaluminum produces a more active system than the dialkylmonohalide as observed by us for isoprene polymerization and by others (*10, 16*) for olefin polymerization. Only excesses of R_3Al are damaging, probably owing to over-reduction of the titanium.

In the case of triethylaluminum, both further alkylation of the Ti and/or adsorption of the trialkyl onto the solid would be achieved at lower Al/Ti ratios, because triethylaluminum is a stronger reducing agent and is required in lesser amounts to reach this stage.

From our studies with solids it clearly emerges that separation of the solids or separation plus recombination of the solid with a trialkylaluminum provides a system which is more active than the corresponding unseparated catalyst. The trialkylaluminum is a substantially better activator (for β-$TiCl_3$ with low residual activity) than the corresponding dialkylaluminum halide. Saltman (*12*) reported that the maximum activity obtained with β-$TiCl_3$ solids was about the same using either AlR_3 or AlR_2Cl. He considered only long polymerization times where the differences in optimum polymer yields were slight. Van Amerongen (*15*), similarly, found that both Et_3Al and Et_2AlCl gave the same maximum activation when combined with a low Al/Ti ratio Et_3Al-$TiCl_4$ preparation. In the latter case, the trialkyl aluminum probably was converted to the monohalide before initiation of polymerization. Yamazaki and coworkers (*17*), surprisingly, reported that combination of β-$TiCl_3$ with diethylaluminum chloride failed to provide an active catalyst for *cis*-1,4 isoprene polymerization. The source of the β-$TiCl_3$ used by Yamazaki was not given, and their solid could possibly have been rich in $AlCl_3$ and thus explain the ineffectiveness of the monohalide activation.

The solid studies have also shown that all trialkylaluminum compounds are more or less equivalent as cocatalysts. Thus with a "good" solid, such as the 0.9 i-Bu_3Al solid, trialkyls—as far apart as the trimethyl- and trioctylaluminum—are essentially equivalent. This indicates that the poorer activity of unseparated catalysts prepared from the lower alkyls (trimethyl-, triethylaluminum) must be directly related to the resulting reaction products with $TiCl_4$, i.e., the reduced and/or alkylated Ti species (expected to be found in the solid phase) and the alkylaluminum chlorides (unless strongly adsorbed, expected to be found in the liquid phase).

The activation of the 0.9 i-Bu_3Al solid with diisobutylaluminum- and diethylaluminum chloride, (Figures 11, 12) shows that although the two chlorides are about equivalent activators, an excess of the diethylchloride has a much greater inhibiting effect than an excess of the diisobutylaluminum chloride. In this respect diethylaluminum chloride almost approaches the action of triisobutylaluminum itself. The exact nature of the "damage" done by an excess of diethylaluminum chloride is not known, but it could be caused by several factors such as the excess halide: (1) is strongly adsorbed on the solid and prevents the monomer coordination on the active site; (2) it forms poisons; (3) it alkylates and reduces the $TiCl_3$ further during the polymerization at 50° C. Diisobutylaluminum chloride would be expected to show a less severe action with respect to items listed under (1) and (3).

Although there is no doubt that an excess of diethylaluminum chloride—equal to that formed in an unseparated catalyst—is harmful, we note also that the catalyst solid obtained from triethylaluminum has been "damaged" irreversibly. Such a solid can not achieve the activity obtainable with triisobutylaluminum-type solids no matter what technique (separation or activation) is applied to it. The "damage" noted in the triethylaluminum-type solids is attributed to further alkylated or reduced Ti species produced by the stronger reducing power of ethylaluminum compounds. With the higher alkyls the "damage" appears to be minimized as long as the Al/Ti ratio is below 1.0.

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3

Polymerization of 1,3-Pentadiene to cis-1,4 Stereoisomers

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By polymerizing the trans isomer of 1,3-pentadiene two different types of crystalline cis-1,4 polymers have been obtained, one with an isotactic, the other with a syndiotactic structure. The isotactic polymer was obtained by homogeneous systems from an aluminum alkyl chloride and a cobalt compound, the syndiotactic one by homogeneous systems from an aluminum trialkyl and a titanium alkoxide. Some features of the polymerization by Ti and Co catalysts are examined. IR and x-ray spectra, and some physical properties of the crystalline cis-1,4 polymers are presented. The mode of coordination of the monomer to the catalyst, and possible mechanisms for the stereospecific polymerization of pentadiene to cis-1,4 stereoisomers are discussed.

The polymers of 1,3-pentadiene, whatever their structure, exhibit two sites of isomerism per monomeric unit. The number of stereoisomers foreseeable for polypentadiene is therefore higher than for polybutadiene or polyisoprene, these two exhibiting only one site of isomerism per monomeric unit. Thus, although polybutadiene or polyisoprene can each have only one stereoisomer with trans-1,4 or cis-1,4 structure, in the case of pentadiene, owing to the presence of an asymmetric carbon atom in each 1,4 unit, three different trans-1,4 or cis-1,4 polymers are possible—namely, isotactic, syndiotactic, or atactic polymers. Of all the possible stereoregular polymers of 1,3-pentadiene only three types have been obtained and characterized up to now—namely, the trans-1,4 isotactic (*5*), the cis-1,4 isotactic (*6*, *7*), and cis-1,4 syndiotactic (*8*) polymers. Polymers, which are predominantly cis-1,4 or trans-1,4, but which are amorphous because of insufficient order in the configurations of the asymmetric carbon atoms are also known (*5*, *7*).

In Elastomer Stereospecific Polymerization; Johnson, B., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

The cis-1,4 stereoisomers of polypentadiene are interesting as potential elastomers. This paper will report briefly their synthesis, examine their properties, and discuss the mechanism of their formation.

Polymerization

The cis-1,4 syndiotactic polypentadiene has been obtained by soluble catalysts prepared from an aluminum alkyl chloride and a cobalt compound. Only the trans isomer of pentadiene has been polymerized by these catalysts. However, mixtures of the cis and trans isomers can be used, the cis isomer remaining seemingly unaltered. The presence of the cis isomer was found to have no appreciable influence on the stereospecificity when its percentage in the mixture of the two isomers is lower than about 30%. For higher percentages a decrease in the stereoregularity of the syndiotactic polymer obtained was observed.

The soluble catalysts from an aluminum alkyl chloride and a cobalt compound are well known since they have long been used, even on an industrial scale, for polymerizing butadiene to cis-1,4 polymer. The features of pentadiene polymerization by these catalysts are more or less similar to those of butadiene polymerization. Since the latter has been widely investigated and has already been the object of various papers (*See* e.g. *3, 4*), we shall limit ourselves here to underlining the more significant differences that we have observed between the polymerization of butadiene and pentadiene.

It is known that the cobalt catalysts for polymerizing butadiene can be prepared from $Al(C_2H_5)_2Cl$, from $Al_2(C_2H_5)_3Cl_3$, or from $Al(C_2H_5)Cl_2$. From the polymerization of pentadiene, on the contrary, somewhat different results are obtained depending on the particular aluminum compound employed. Catalysts prepared from $Al(C_2H_5)_2Cl$ yield polymers which are predominantly cis-1,4 and exhibit a crystallinity of syndiotactic type. The reproducibility of the results, however, was rather low; the cis-1,4 content of the crude polymers obtained in different runs varied from about 50 to about 80%. These systems are probably rather sensitive to impurities present in the solvent and monomer. On the other hand, catalysts prepared from $Al(C_2H_5)Cl_2$ or $Al_2(C_2H_5)_3Cl_3$ give rise to a cationic polymerization, with formation of amorphous polymers having a low molecular weight and a high 1,2 unit content. The different behavior of pentadiene is caused by its higher sensitivity to the cationic initiation. If, however, a Lewis base, such as thiophene, is added to the catalysts prepared from $Al(C_2H_5)Cl_2$, catalysts are obtained which no longer exhibit cationic activity and which yield, from pentadiene, polymers having a cis-1,4 syndiotactic structure. These catalysts prepared from $Al(C_2H_5)Cl_2$ complexed with a Lewis base were found to be the most reliable for preparing the cis-1,4 syndiotactic polypentadiene, the reproducibility of the results being fairly good. The two systems we have used most in our work are those prepared from $Al(C_2H_5)Cl_2$ complexed with pyridine or thiophene. In these systems the thiophene/aluminum molar ratio can be varied from about 0.5 to about 5 or even more, while the pyridine/aluminum ratio can be varied within a narrower range, from about 0.5 to about 0.9. This is related to the different basicity

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of the two electron donors. For ratios lower than those indicated, a cationic polymerization occurs, while for higher ratios no polymerization occurs at all.

Another observed difference between the polymerization of butadiene and pentadiene concerns the influence of the solvent on the type of polymer obtained. In polymerizing pentadiene, cis-1,4 polymers have been obtained only in aromatic solvents, while in aliphatic solvents, at least with catalysts prepared from $Al(C_2H_5)_2Cl$, polypentadienes having a 1,2 syndiotactic structure have been obtained (*9*). (The catalyst systems prepared from $Al(C_2H_5)Cl_2$ complexes with pyridine or thiophene are practically insoluble in aliphatic solvents and yield only small amounts of low molecular weight polymer, probably of cationic origin.)

However, it is known that in the case of butadiene, polymers predominantly cis-1,4 can be obtained both in aromatic and in aliphatic solvents, although the polymers obtained in the latter solvents have a somewhat lower cis-1,4 unit content.

Table I reports the results of typical polymerization runs of pentadiene by cobalt catalysts prepared from $Al(C_2H_5)Cl_2$ complexed with thiophene or pyridine. The crude polymerization products obtained by these systems have a cis-1,4 content of about 75–80%. Fractions having a higher cis-1,4 content (about 85%) could be isolated by dissolving the crude polymers in benzene and reprecipitating with methylethyl ketone (MEK). This solvent dissolves only the low molecular weight polymers, which, in this case, have also a low cis-1,4 unit content.

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Table I. Polymerization of 1,3-Pentadiene Acetonate and $Al(C_2H_5)Cl_2$ Complexed

Run	*$Co(acac)_2$*[c] *moles × 10^5*	*Solvent (benzene) ml.*	*Monomer*[d] *grams*	*Polymerization temp., ° C.*	*Polymerization time, hrs.*
1	5.1	350	28	20	24
2	1.5	50	10.5	20	6
3	0.34	15	3.1	20	12
4	0.68	30	5	0	20
5	0.5	30	3	20	8
6	0.15	15	3.5	0	48
7	0.5	30	3	0	12

[a] Runs 1–6; Al/Thiophene molar ratio:1.
[b] Runs 7 and 8; Al/Pyridine molar ratio:0.53.
[c] Al/Co molar ratio: ~500. Catalyst prepared by introducing first the Co compound and the Lewis base, then the $Al(C_2H_5)Cl_2$ and finally, after a few minutes, the monomer.

Shortly after the cis-1,4 syndiotactic polypentadiene was obtained and characterized, it was observed that the homogeneous systems prepared from an aluminum trialkyl and a titanium tetralkoxide can polymerize pentadiene to polymers predominantly cis-1,4. Both the cis and trans isomers of pentadiene are polymerized by these systems. However, while the crude polymers obtained from the cis isomer were found to be amorphous by x-ray examination, those obtained from the trans isomer were found to be crystalline. The type of crystallinity of these polymers appeared different from that of the polymers

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obtained by the cobalt catalysts. On the basis of x-ray analysis, a cis-1,4 isotactic structure was attributed to these new crystalline polypentadienes (*6, 7*).

Some data concerning the polymerization of pentadiene by the $Al(C_2H_5)_3$-$Ti(O\text{-}n\text{-}C_4H_9)_4$ system are reported in Table II.

The crude polymerization products obtained from the trans isomer have a cis-1,4 unit content of about 75%. Fractionation of the crude products by dissolving them in benzene and reprecipitating with MEK has permitted isolation of fractions (insoluble in MEK) having a cis-1,4 unit content of about 85%.

The crude polymerization products obtained from the cis isomer have also a high cis-1,4 unit content (about 75%), but as mentioned above, they appear amorphous on x-ray examination. However, by fractionating them, fractions could be isolated exhibiting a very low degree of crystallinity of isotactic type.

Mixtures of the cis and trans isomers yield polymers which are also predominantly cis-1,4 but which are less crystalline than those obtained from the pure trans isomer, the crystallinity being lower for those products obtained from a mixture richer in the cis isomer.

In polymerization runs performed with pure cis isomer and terminated with CH_3OH after a 10–15% conversion, it was found that the unreacted monomer, recovered under vacuum from the polymerization medium, was a mixture of the cis and trans isomers, the latter predominating. Therefore, isomerization of the cis isomer occurs during the polymerization. It is possible that only the trans isomer formed by isomerization polymerizes. In this case, the absence or the very low degree of crystallinity observed in the polymers from the cis isomer could depend on the influence of the unaltered cis isomer on the polymerization of the trans isomer formed through isomerization. Disturbing influences of this type, caused by nonpolymerizable unsaturated compounds, upon the stereospecificity of a polymerization by coordination catalysts have been already observed. (It has been reported, for example, that in the polymerization of butadiene by the $Al(C_2H_5)_3$-vanadium triacetyl-

by Catalysts Prepared from Cobalt Diacetyl with Thiophene[a] or Pyridine[b]

Crude Polymer			MEK Insoluble Fraction[e]		
	IR Analysis %		IR Analysis %		
yield, grams	cis-1,4	trans-1,4	cis-1,4	trans-1,4	[η] dl. g^{-1}
23	77	23	84	16	2.8
8	72	28	85	15	. . .
2.3	73	27	83	17	2.9
4	81	19	86	14	2.3
2.6	77	23	83	17	1.9
3.2	71	29	85	15	. . .
1.7	76	25	86	14	. . .

[d] Trans isomer, 99.5% pure.

[e] Crystalline by x-ray examination (polymer annealed 4 hrs. at 35° C.)·[η] was determined in toluene at 30° C.

Table II. Polymerization of 1,3-Pentadiene by

			Polymerization		Crude Polymer			
						IR Analysis (%)		
Run	*Titanium Compound moles × 10^3*	*Al/Ti molar ratio*	*temp., ° C.*	*time, hrs.*	*yield, grams*	*cis-1,4*	*trans-1,4*	*3,4*
1	1.6	5	0	35	6	80	14	6
2	1.4	5	−15	45	6.5	79	15	6
3	2.1	7	0	14	5	73	17	10
4	1.5	6	0	24	5.5	74	14	12
5	1.4	7	0	24	5.8	78	12	10
6	1.4	5	0	60	1.5	75	15	10
7	2.3	7	−15	30	1.2	76	15	9

[a] Polymerization conditions: solvent (benzene or toluene), 100 ml.: monomer, 15 grams [runs 6 and 7, cis isomer (99.9%): other runs, trans isomer (99%)]—$Al(C_2H_5)_3$ was 96% pure.

acetonate system, the impurities present in the monomer strongly influence the stereospecificity of the polymerization (*11*).)

It could be, however, that the cis isomer is also able to polymerize slightly, given trans-1,4 or 1,2 units which disturb the formation of cis-1,4 sequences.

That the polymers obtained from the cis isomer are actually formed through isomerization of the monomer is confirmed by the results of polymerizations performed with optically active systems. It has been reported that by polymerizing the trans isomer with the $Al(C_2H_5)_3$-titanium tetramenthoxide system, optically active cis-1,4 polypentadienes are obtained (*10*). The cis isomer, utilizing the same system, yields polymers which are also optically active (Table III). The optical activity of these polymers is of the same sign as that of the polymers obtained from the trans isomer. This is in accordance with the fact that the cis-1,4 sequences actually originate from the trans isomer formed through isomerization. In effect, if the cis isomer were able to give cis-1,4 polymers without isomerization, one would expect these to have an optical activity of opposite sign to that of polymers from the trans isomer.

Table III. Optical Activity of the cis-1,4 Isotactic Polypentadiene Obtained by the Aluminum Triethyl-Titanium Tetramenthoxide[a] Catalyst System

Monomer	*Cis-1,4 Content of the Polymer*	α_D^{18}[b]	$[\alpha]_D^{18}$	$[\eta]$ dl./gram[c]
trans isomer[d]	79	−0.25	−21.6	6.5
trans isomer	75	−0.21	−19	4.1
trans isomer	72	−0.17	−16.3	. . .
cis isomer[e]	75.2	−0.205	−18	4.7
cis isomer	72.5	−0.104	−17.5	4.2

[a] $(-)Ti(OC_{10}H_{19})_4$: $[\alpha]_D^{18}$ − 98.3 (c = 5.54 grams/100 ml., benzene); optical purity 98–99%.
[b] Determined in *n*-hexane solution (l = 4 dm).
[c] Determined in toluene at 30° C.
[d] 99.1% pure.
[e] 99.8% pure.

The fact that the polymers obtained from the cis isomer are optically active also proves that these polymers, notwithstanding that they are amorphous by x-ray, are not atactic. In fact if they were atactic in the proper meaning of the word—that is if the configurations of the asymmetric carbon

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the $Al(C_2H_5)_3$-$Ti(O\text{-}n\text{-}C_4H_9)_4$ Catalyst System [a]

MEK Insoluble Fraction[b]			
IR Analysis (%)			*X-ray Examination*[c]
cis-1,4	*trans-1,4*	*3,4*	
85	10	5	crystalline
87	9	4	crystalline
82	12	6	crystalline
86	9	5	crystalline
84	8	8	crystalline
79	13	8	amorphous
84	10	6	crystalline traces

[b] 30–40% of the crude polymer –[η]: 5–7 dl. gram^{-1} (determined in toluene at 30° C.).

[c] The polymers were annealed 4 hrs. at 35° C. before examination.

atoms were randomly distributed—no optical activity should be noted when they are produced by an optically active system. The presence of an optical activity proves that these polymers possess a certain stereoregularity of isotactic type. The fact that they are amorphous indicates that they are constituted of cis-1,4 isotactic sequences which are not sufficiently long to give rise to crystallinity detectable by x-ray.

Characterization and Structure of the cis-1,4 Polypentadienes

IR spectra of the cis-1,4 isotactic or syndiotactic polymers, in the molten state or in solution, and of the amorphous polymers are practically identical. All are characterized by an intense band at 751.8 cm.$^{-1}$ (cis double bonds). In the spectra of the solid isotactic or syndiotactic polymers, however, new bands appear which are typical of the crystallinity of the polymers (Figure 1 and 2). The positions of the most intense of these bands are as follows: (1) isotactic polymers: 746.2; 843.8; 925.9; 1005 cm.$^{-1}$; (2) syndiotactic polymers: 757.5; 854.7; 925.9; 1000; 1136 cm.$^{-1}$ It is interesting to observe that the band of the

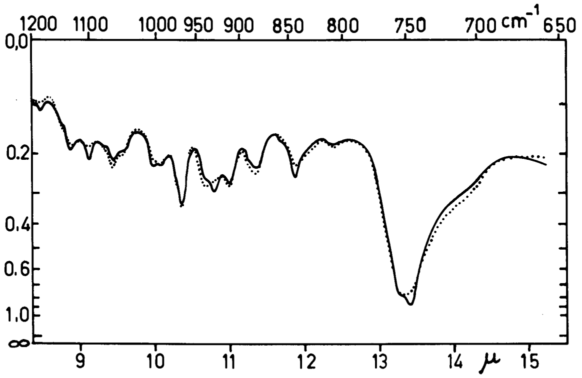

Figure 1. IR spectrum of a sample of cis-1,4 isotactic polypentadiene; continuous line—crystalline polymer; dotted line—molten polymer.

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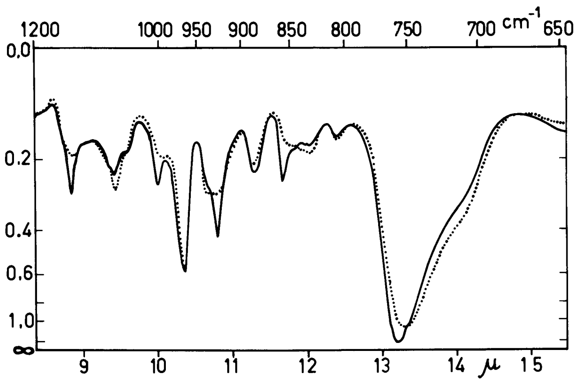

Figure 2. IR spectrum of a sample of cis-1,4 syndiotactic polypentadiene; continuous line—crystalline polymer; dotted line—molten polymer.

cis double bonds, which is at 751.8 cm.$^{-1}$ in the spectra of the molten or dissolved cis-1,4 stereoregular polymers (and also in that of the amorphous polymers), shifts to 746.2 cm.$^{-1}$ in the spectrum of the isotactic, and to 757.5 cm.$^{-1}$ in the spectrum of the syndiotactic polymers in the solid state. This difference in the positions of the bands of the cis double bonds in the IR spectra of the two polymers in the solid state is the best criterion for distinguishing between the isotactic and the syndiotactic cis-1,4 polypentadiene.

The x-ray spectra, registered by a Geiger counter, of the isotactic and syndiotactic cis-1,4 polypentadienes are reported in Figure 3. One can see from these spectra that the degree of crystallinity is not high, and this can be easily accounted for if we consider that the polymers do not have a very high cis-1,4 content. Evidently they consist of macromolecules containing cis-1,4 stereoregular sequences sufficiently long to give rise to crystallinity and interspersed with units of other types.

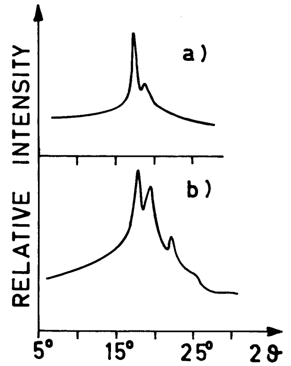

Figure 3. X-ray spectra (CuKα), registered by a Geiger counter, of (a) isotactic and (b) syndiotactic cis-1,4 polypentadiene

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Some properties of the polymers are reported in Table IV. The identity periods observed for the two polymers are rather close—i.e., 8.1 and 8.45 A. Conformational analysis of the chain of the cis-1,4 polypentadiene led us to attribute the syndiotactic structure to the polymer having an identity period of 8.45 A. and the isotactic structure to that having an identity period of 8.1 A. The correctness of this attribution is confirmed by the observed distribution of the diffracted intensity on the first and second layers in the fiber spectra (*6, 8*). The chain conformations of the two cis-1,4 polypentadienes in the crystalline state are reported in Figure 4. It is interesting that the chain conformation of cis-1,4 syndiotactic polypentadiene is identical with that of cis-1,4 polybutadiene and cis-1,4 polyisoprene (*12*) (except, obviously, for the absence of the methyl groups in polybutadiene and the different positions of these groups in polyisoprene and polypentadiene).

Table IV. Some Physical Properties of the Stereoregular cis-1,4 Polypentadienes

Polymer	*Melting Temp., ° C.*	*Identity Period A.*	*Density Grams/Ml.*
Isotactic	43–47	8.1	0.924
Syndiotactic	50–53	8.4	0.915

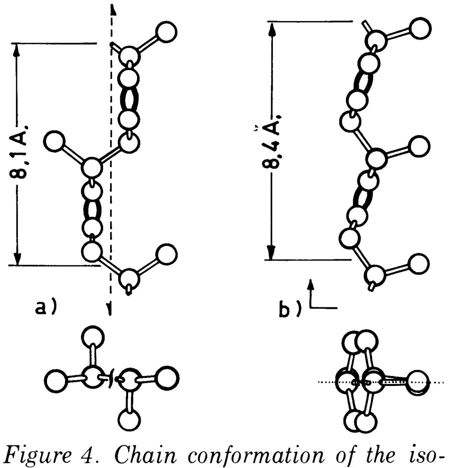

Figure 4. Chain conformation of the isotactic, (a), and the syndiotactic, (b), cis-1,4 polypentadienes in the crystalline state

Mechanism of Formation

The possibility of obtaining, from the same monomer, different stereoregular polymers having an isotactic or a syndiotactic structure is, perhaps, the most challenging feature of the stereospecific polymerization.

We wish to discuss, in the following, the factors which could determine, in the polymerization of pentadiene by Ti or Co catalysts, the formation of cis-1,4 isotactic or syndiotactic sequences, respectively.

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Mode of Coordination of the Monomer. It is now generally admitted that in the case of Ziegler catalysts, incorporation of the monomer into the growing polymer chain is preceded by coordination of the monomer to the transition metal of the catalyst. Some information concerning the mode of coordination of the monomer to Ti can be derived from the following experimental findings: (1) butadiene and isoprene are polymerized by titanium catalysts to 1,2 and 3,4 polymers, respectively (*13*); (2) both the cis and the trans isomers of pentadiene are polymerized, cis-1,4 polymers being obtained from each isomer.

The above findings suggest the hypothesis that in the case of Ti catalysts, the monomer coordinates to the active center by the vinyl group only. This hypothesis seems quite reasonable in the case of butadiene and isoprene since 1,2 and 3,4 polymers, respectively are formed from these monomers. The situation could seem different in the case of pentadiene which yields cis-1,4 polymers. On could suppose that in this case the formation of cis-1,4 units is caused by the fact that pentadiene coordinates to Ti by the two double bonds in the cis conformation before it is incorporated into the growing chain.

Let us examine separately the case of the cis and trans isomers of pentadiene. For the trans isomer the cis conformation is permissible so that one cannot assume *a priori* that this isomer won't coordinate to Ti by the two double bonds. This hypothesis, however, can be easily rejected by the following considerations. If the steric situation around Ti during the polymerization were to permit the coordination of the trans isomer of pentadiene by the two double bonds, in the cis conformation, butadiene or isoprene should also coordinate the same way. In this case, however, cis-1,4 units should be obtained both from butadiene and isoprene, and not 1,2 and 3,4, respectively, as observed. It seems reasonable to conclude, therefore, that the trans isomer of pentadiene coordinates to Ti by the vinyl group only, as butadiene or isoprene, before it is incorporated as a cis-1,4 unit.

The same conclusions can be reached for the cis isomer. As already mentioned, isomerization of this isomer occurs in the polymerization medium. If we admit that only the trans isomer formed through isomerization polymerizes, we fall under the case examined above. If we admit also that the cis isomer can polymerize to cis-1,4 units, we must assume that also in this case the coordination occurs only through the vinyl group and not through the two double bonds, in the cis conformation. The cis isomer, in fact, cannot assume the cis conformation for steric reasons. On the other hand, coordination by the internal double bond, both for the cis and trans isomers, appears less probable (for steric reasons) than the coordination by the vinyl group.

The case of the Co catalysts appears different. Some information concerning the mode of coordination of pentadiene to these systems can be derived from the following points:

(1) The Co catalysts polymerize only the trans isomer of pentadiene.

(2) They give polymers which are prevalently cis-1,4 (at least 70%) from all the common hydrocarbon diolefins (butadiene (*3*, *4*), isoprene (*14*), pentadiene (*8*), 1,3-dimethyl-butadiene (*14*)).

(3) When they are used in aromatic solvent (and in the case of pentadiene polymerization they must be used in aromatic solvent in order to obtain cis-1,4

polymer), two molecules of arene are coordinated by Co. Furthermore, evidence exists that the coordination of the diolefin occurs through displacement of the arene.

The coordination of the arene to Co can be proved by the following: when the reaction between $Al(C_2H_5)_2Cl$ and a cobalt compound is performed in benzene saturated with hexamethylbenzene (the latter, being a solid melting at 166° C. cannot be used by itself as solvent) the cation $\{Co[(C_6CH_3)_6]_2\}^+$ can be isolated from the reaction products (*14*). This cation, as already known (*1*, *15*), has sandwich structure and is stable in H_2O, from which it can be precipitated by anions such as $B(C_6H_5)_4^-$, PF_6, etc. From solutions of the catalyst in pure benzene, the cation $[Co(C_6H_6)_2]^+$ could not be isolated, owing to its instability in H_2O (it decomposes giving equivalent amounts of metallic Co and $CoCl_2$). It is obvious, however, that a cation of this type exists in the catalyst solution in benzene. The much higher stability of the cation containing $C_6(CH_3)_6$ is caused by the fact that $C_6(CH_3)_6$ is a much stronger electron donor than C_6H_6. The fact that coordination of the diolefin occurs by displacing the arene is shown by following: the rate of polymerization of butadiene by the $Al(C_2H_5)_2Cl$ cobalt compound system depends on the type of solvent, and more precisely, is lower in those solvents having a higher basicity. In fact, the rate of polymerization decreases in the order: benzene > toluene > xylene > 1,3,5-trimethylbenzene (*14*). Furthermore, adding hexamethylbenzene to a benzene solution of the catalyst slows down the rate of, and high concentration completely stops, polymerization. All these facts are interpretable assuming that during the polymerization there is a competitive coordination of the diolefin and arene to Co. When the arene is $C_6(CH_3)_6$, the polymerization does not occur because the diolefin cannot displace this arene.

All the findings reported under 1,2, and 3 suggest the hypothesis that, in the case of Co catalysts, the monomer coordinates to the active center in the cis conformation before it is incorporated into the growing chain. This hypothesis easily explains why the cis isomer of pentadiene is not polymerized, the cis conformation being prohibited for this isomer. It also explains why all the common conjugated hydrocarbon diolefins yield predominantly cis-1,4 polymers by these catalysts. In fact, if all the different diolefins coordinate to Co predominantly in the cis conformation (by the two double bonds), predominantly cis-1,4 polymers will be obtained in every case.

The fact that coordination of the diolefin occurs by displacing the arene also favors the hypothesis that the diolefin coordinates in the cis conformation by the two double bonds. Displacement reactions of this type are well known in organometallic chemistry (*See* e.g. (*2*)) and, in the cases already clarified, it has been shown that diolefin coordinates in the cis conformation by the two double bonds. This is not surprising if we consider that the diolefin, coordinated in this way to a transition metal, has a quasi-aromatic character owing to the complete delocalization of the π-electrons.

The conclusions we can draw from the above facts concerning the mode of coordination of pentadiene to Ti and Co, respectively are as follows: coordination to Ti most probably occurs by the vinyl group only, while coordination to Co occurs by the two double bonds, with the monomer in the cis conformation. Furthermore, we have seen that the Co catalysts contain two sites of

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coordination per Co, which, in the absence of monomer, are occupied by two molecules of arene.

Models for the Stereospecific Polymerization. The different modes of coordination of pentadiene to Ti and Co catalysts, respectively suggest two possible schemes for polymerizing this monomer to cis-1,4 isotactic or syndiotactic polymer.

A scheme for forming cis-1,4 syndiotactic sequences is presented in Figure 5. In this figure, (a) represents the last polymerized unit, bonded to the transition metal and a molecule of pentadiene coordinated to it by the two double bonds; (b) represents the transition state; (c) represents the transition metal with the monomer which was coordinated in (a) already incorporated and a new monomer coordinated. It is easily seen that (c) represents a situation which is the enantiomorph of that represented in (a). Therefore, the monomer which is coordinated in (c) will give, after incorporation into the growing chain, a unit having the opposite configuration of the preceding one. Hence, by this mechanism, cis-1,4 syndiotactic sequences will be formed.

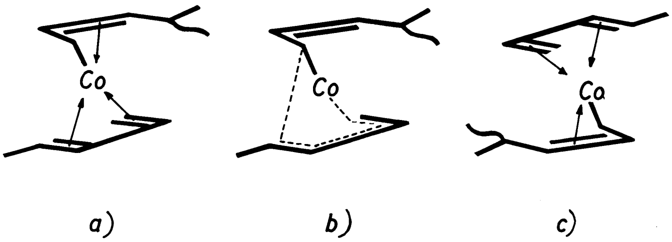

Figure 5. Possible scheme for formation of cis-1,4 syndiotactic polypentadiene

A possible scheme for forming cis-1,4 isotactic sequences is represented in Figure 6. In this figure, (a) represents the Ti, with the last polymerized unit bonded to it and a monomer coordinated through the vinyl group. The three bonds of (a) could be part of a tetrahedron, of a trigonal bipyramid, or of an octahedron. Only the angles between the three bonds vary depending on the type of coordination. What the type of coordination around Ti actually is during the polymerization is not yet known. However, the scheme of polymerization discussed here is valid independently of the type of coordination actually existing around Ti. It is clear, that in Figure 6 (a) the transition metal lies on the plane of the paper, while the coordinated monomer and the last polymerized unit are above that plane. Figure 6 (b) represents the transition state, and Figure 6 (c) represents the monomer which was coordinated in (a), already incorporated into the growing chain and a new monomer coordinated to Ti by the vinyl group. It is easily seen that Figure 6 (c) represents a situation which is identical with that represented in Figure 6 (a). Therefore, the monomer coordinated in (c) will give, after incorporation, a monomeric unit having the same configuration as the preceding one. Hence, by this mechanism, cis-1,4 isotactic sequences will be formed.

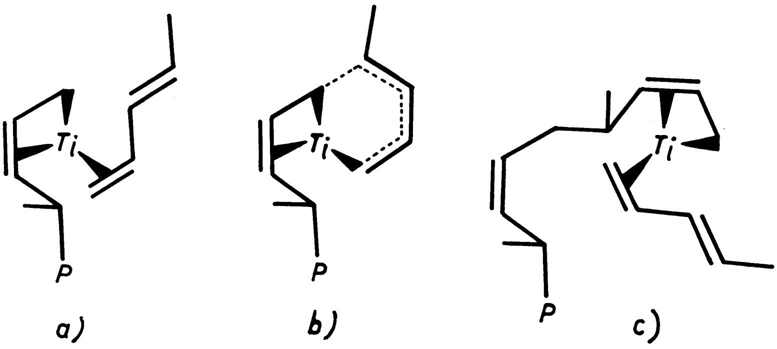

Figure 6. Possible scheme for formation of cis-1,4 isotactic polypentadiene.

Obviously, the schemes of Figures 5 and 6 will not represent a complete interpretation of the phenomena actually occurring during the polymerization, which are presumably rather complex. They are used only as models to try to interpret how the different mode of coordination of the monomer and the existence, in the case of Co catalysts, of two sites of coordination could give rise to a different stereospecificity.

We wish also to point out that the fact that in the above schemes only the transition metal, the last polymerized unit, and the coordinated monomer are represented does not mean that the catalysts prepared from $Al(C_2H_5)_3$ and a titanium alkoxyde or from $Al(C_2H_5)_2Cl$ and a Co compound are pure organometallic compounds of Ti or Co, respectively. These catalysts are presumably complexes containing Al and the transition metal, the latter probably being part of a cation, the Al of an anion. In the above schemes we have represented only the transition metal for the sake of simplicity.

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4

Polymerization Mechanism of Nonpolar Monomers by Lithium Alkyls

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In lithium alkyl-initiated polymerizations only chain initiation and propagation steps need be considered in hydrocarbon solvents. Both reactions are strongly influenced by extensive association of all lithium compounds. The reactive species in chain propagation is the small amount of dissociated material which probably exists as an ion pair. Association phenomena disappear on adding small amounts of polar additives, and the aggregates are replaced by solvated ion pairs. In polar solvents of relatively high dielectric constant (e.g. tetrahydrofuran), some dissociation of the ion pairs to free ions occurs, and both species contribute to the propagation step. The polymerizations are often complicated in tetrahydrofuran by two side reactions, namely carbanion isomerization and reaction with the solvent.

With lithium alkyls it is possible to initiate the polymerization of many vinyl monomers containing electron-attracting groups. The behavior of the polymerizations studied so far seem to fall into two groups. With polar monomers such as methylmethacrylate or acrylonitrile, complications arise because reactions can occur with the polar group as well as with the vinyl double bond. The behavior of hydrocarbon monomers such as styrene, butadiene, or isoprene is more straightforward, and the reaction mechanisms discussed in this paper are restricted to this latter class of monomers.

The general characteristics of these polymerizations are those of the so-called "living polymer" (*24*). Under suitable conditions every lithium alkyl molecule will initiate one chain, and there is no evidence for chain transfer or termination (*14, 27*). The molecular weight distributions will be narrow—$\bar{M}_w/\bar{M}_n$ of 1.3 or less according to the relative rates of chain initiation and

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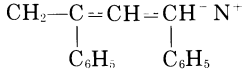
chain propagation—and can approach unity if the former rate is much larger than the latter. The number average degree of polymerization, when all initiator is consumed, is the molar ratio of added monomer to initiator.

The initiation reaction is thought to be the addition of the lithium alkyl across the vinyl double bond to give another organolithium compound. This will then propagate the polymer chain by adding further monomer in a stepwise reaction each time re-forming the same type of carbon—lithium bond. There has been some speculation about the nature of this carbon—lithium bond, particularly in the case of the polymers derived from diene monomers (*22*, *25*). It has been suggested that in hydrocarbon solvents this bond is largely covalent, but that in more polar media the bond becomes more ionic in nature. This change has been suggested as being responsible for the change in microstructure observed in the polymerization of isoprene and butadiene in different solvents.

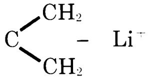
Some information may be gained about this bond by measuring the ultraviolet absorption spectra of these polymer-lithium compounds. The carbon—lithium bonds are adjacent to double bonds in the diene polymers and a phenyl ring in polysytrene. If the bond is ionic, resonance stabilization of the carbanion should occur, and molecular orbital calculations suggest that there would be an absorption in the visible or near ultraviolet roughly in the same position as the corresponding cation (*12*). A covalent metal—organic bond would not absorb appreciably in this region. It is found that the spectra of these polymer-lithium compounds do have appropriate absorption bands under all conditions. It is found, moreover, that differences in position of these bands are small when either a hydrocarbon solvent or an ether such as tetrahydrofuran is used. The change in peak position is also small if the counter ion is changed to sodium or potassium (*3*). These results suggest that the nature of the bond in the bulk of the material is very similar under different conditions and is presumably ionic. Conductivity measurements in tetrahydrofuran (*26*) indicate that for polystyrylsodium, the major part exists as ion pairs with a small equilibrium concentration of free ions. It can be shown that polystyryllithium behaves in a similar way in tetrahydrofuran, the proportion of free ions being somewhat similar. In hydrocarbon solvents the polymer-lithium compounds are largely associated, and the measured spectra refer to this state of aggregation. There remains the possibility that the unassociated material, active in the polymerization process, is more covalent in the absence of the stabilizing effect of self-solvation; however, this does not seem too likely.

The study of the spectra of "living polymer" systems is valuable from a more practical point of view and indicates that the term has some limitations. At room temperature all the polymer-lithium compounds in hydrocarbon solvents show spectra which are stable for considerable time intervals. At elevated temperatures spectral changes occur at least for polystyryllithium, which indicate that isomerization reactions are occurring (*4*). Most of them display instability in solvents containing appreciable amounts of more polar constituents such as tetrahydrofuran. This effect was first noticed for polystyrylsodium (*11*) and has been attributed to the elimination of sodium hydride, followed by a subsequent reaction to form the more stable substituted allyl anion (*21*).



$CH_2-\underset{C_6H_5}{C}=CH=\underset{C_6H_5}{CH^-}\ N^+$

Similar reactions occur with polystyryllithium and are particularly noticeable at high dilution. Isomerization of polyisoprenyllithium is quite a rapid process in tetrahydrofuran even at moderate concentrations since the original absorption at 287 mμ is converted to absorption at 330 mμ during the polymerization process at room temperature. It is seemingly a reversible reaction and becomes conspicuous at low monomer concentrations. The original absorption band is re-formed on the addition of more isoprene. It was suggested (*3*) that the observed changes are caused by isomerization to the more stable symmetrical anion shown below:



This type of reaction is not observed with polybutadienyllithium as expected from this mechanism, but this and other carbanions react slowly with tetrahydrofuran to form colorless species which are inactive in polymerization.

Chain Initiation

In hydrocarbon solvents the chain initiation step is relatively slow, and the lithium alkyl competes for monomer with the growing polymer chains. Indeed, at high initiator concentrations frequently all the monomer has been consumed before complete reaction of the lithium alkyl has occurred. Most investigators, therefore, now take precautions to ensure that chain initiation is complete (*14*, *20*, *23*, *27*) before studying the propagation step although some of the earlier reports refer to polymerization rates under conditions where both initiation and propagation were taking place simultaneously.

In benzene solution, measurements have been made of the rate of reaction of butyllithium with styrene (*27*), 1:1-diphenylethylene (*6*), and with fluorene (*7*). In each case the reaction was first order in olefin and close to one-sixth order in butyllithium. This latter, fractional order has been attributed to the sixfold association of lithium alkyls in hydrocarbon solution. The actual species active in initiation is the monomeric butyllithium in equilibrium with the hexamer.

In cyclohexane solution, however, the reaction mechanism appears to be more complex. Under sufficiently rigorous conditions, the initiation reaction has a sigmoidal rate curve. The rate of growth of active centers accelerates in the early stages of reaction in contrast to the behavior observed in benzene (Figure 1). If the maximum rate is taken as the typical rate, the reaction appears to be between one-half and first order in butyllithium, but this result probably has little real significance. The maximum initiation rate for styrene is nearly 100-fold lower in cyclohexane than in benzene solution at 10^{-4} molar initiator and equal monomer concentration, whereas the propagation reaction is only about three times slower. It is possible that the simple bimolecular reaction to give the polymer ion pair is not favored in aliphatic solvents, and

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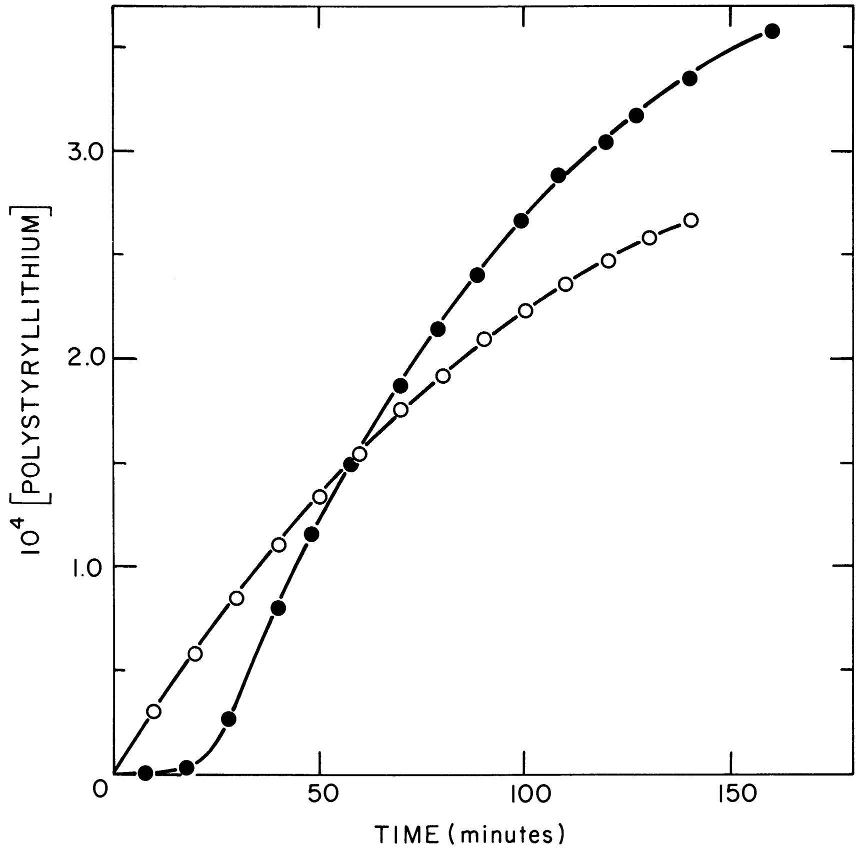

Figure 1. Rate of formation of polystyryllithium at about 7 × 10^{-4} molar butyllithium; o—benzene at 30° C., [styrene] = 0.0067M; ●—cyclohexane at 40° C., [styrene] = 0.253M. Note the much higher styrene concentration required in cyclohexane to produce a similar rate.

the presence of more polar material accelerates the reaction. Thus, the reaction would be autocatalytic. This explanation is supported by the fact that with butadiene and isoprene, incomplete drying of the monomer or addition of traces of air eliminates the period of slow initiation. This does not, however, seem to be true in the polymerization of styrene which suggests that in cyclohexane at least, the initiation reaction is complex and not yet fully understood.

The initiation reaction is particularly susceptible to the presence of trace amounts of impurity or added polar substances. Small amounts of tetrahydrofuran accelerate the rate, which becomes too fast to measure by conventional methods at quite low tetrahydrofuran concentrations. This behavior is presumably connected with the dissociation of the hexamer of butyllithium and its replacement by solvated free butyllithium. The addition of salt produces different and perhaps specific behavior in different systems. So far only the effect of lithium *tert*-butoxide has been investigated. In benzene the initiation rate

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of styrene is depressed, and at sufficiently high salt concentrations the reaction order in butyllithium increases to about one-half (*18*). Presumably this is caused by the formation of mixed aggregates containing butyllithium and butoxylithium. It is more difficult to compare the results in cyclohexane, but in agreement with the above results the period of slow initiation is still present and is perhaps lengthened. It would seem likely that this might not be the case for isoprene and butadiene in view of the observations on additions of traces of air.

Chain Propagation

The propagation reaction in hydrocarbon media has been found by most authors to be very much affected by association phenomena. In the three monomers considered here the propagating species are ion pairs; to stabilize themselves in nonpolar solvents, they are forced to form aggregates. It appears that the small concentrations of free ion pairs in equilibrium with the aggregates are the active moieties, and the propagation reactions are fractional order in active chain ends because of this. The degree of association is in some dispute for isoprene and butadiene but not for styrene. In the latter case dimerization of the active centers was postulated from kinetic evidence (*27*) and inde-

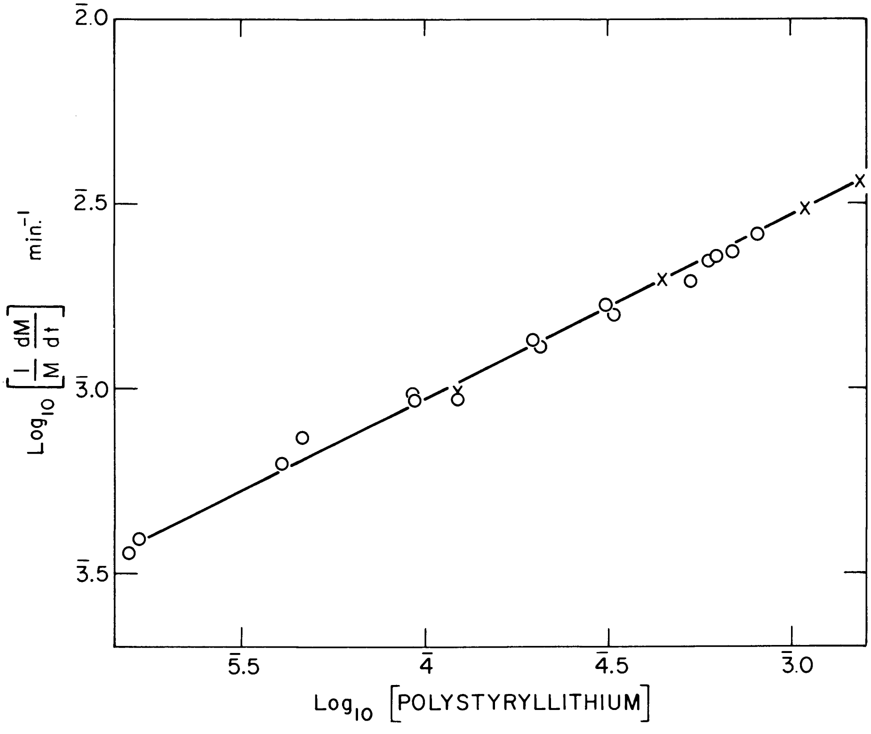

Figure 2. Variation of the propagation rate with concentration of polystyryllithium in benzene at 20° C., o—Worsfold and Bywater (27); •—Morton and co-workers (16).

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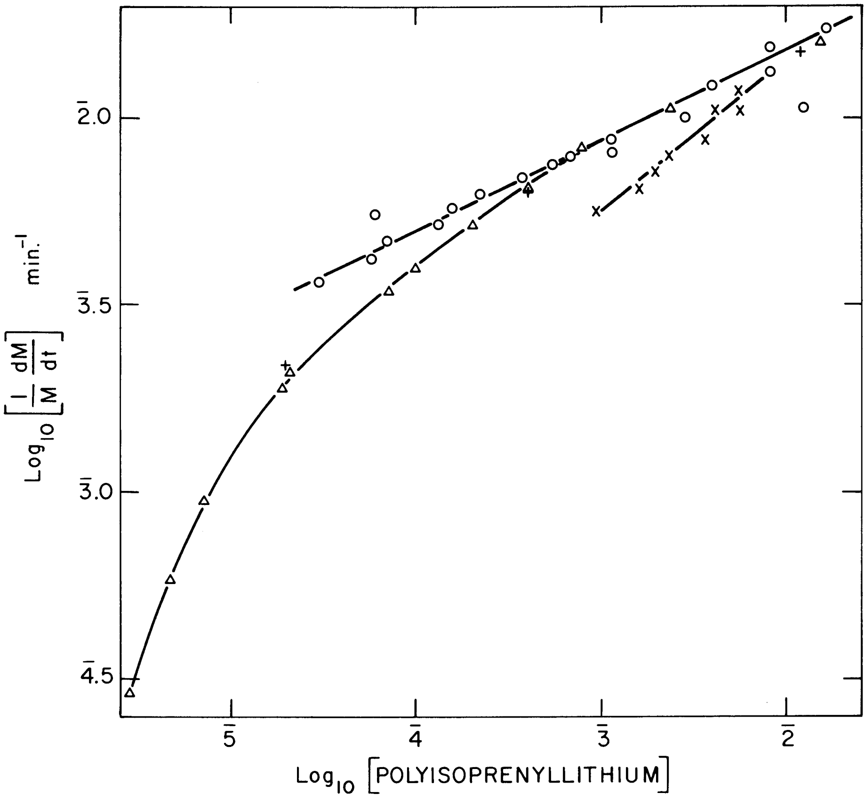

Figure 3. Variation of the propagation rate with concentration of polyisoprenyllithium at 30° C., o—Worsfold and Bywater (29); Δ—Sinn and co-workers (19); +—Spirin and co-workers (23); ×—Morton and co-workers (15).

pendently from measurements of the decrease in viscosity on removal of the charged species from the chain ends (*14*). The observed rates are close to half order in active center concentration in benzene (Figure 2). For isoprene both rates and measurements of degree of association vary significantly. Figure 3 shows a collection of propagation rates reported by various workers (*15, 20, 23, 29*). (Hsieh's results (*J. Polymer Sci.*, **A3**, 175 (1965)) are about 15% higher than in reference (*29*) at all concentrations below 10^{-2} molar, but deviate rapidly at higher concentrations.) The results agree reasonably closely at 10^{-2} molar concentration of polyisoprenyllithium but deviate as the concentration is lowered. The majority of the results are consistent with a degree of association of about four at millimolar concentrations. This interpretation is confirmed by physical measurements (*19, 29*) although at lower concentrations Sinn's results suggest that the degree of association decreases. Morton's results—both kinetic and by viscosimetric determination of the association number—suggest dimeric association. It is surprising that such differences are found for isoprene (and butadiene), whereas with the same experimental techniques agreement is found for styrene. The discrepancies observed would suggest that the degree of association with the dienes is extremely sensitive to the presence of traces of low molecular weight lithium compounds.

It is found that adding unreactive but comparatively polar compounds, such as ethers or amines, to the reaction mixture in hydrocarbon solvents modifies the reaction markedly. If a small amount of tetrahydrofuran is added, in all cases the initiation reaction rate is increased immensely while the propagation rate increases only a few times. The tetrahydrofuran causes the aggregates in the propagation reaction to be replaced by etherates. The other additives presumably produce similar effects. In the case of polystyryllithium, first a monoetherate and then a dietherate appear to form, and essentially none of the polymer ion pairs are in aggregates in the presence of 0.4% tetrahydrofuran. The reaction is then first order with respect to polystyryllithium. The aggregates in the case of polyisoprenyllithium in hydrocarbon solvents require considerably more tetrahydrofuran to break them down completely, and even with 1% of additive, the order with respect to chain ends is close to one-half. For both polystyryllithium and polyisoprenyllithium, the solvated ion pair seems to have a much smaller reactivity in a predominantly hydrocarbon solvent than does the free ion pair. The increase in rate observed on the addition of small amounts of tetrahydrofuran is caused largely by an increased concentration of free ion pairs.

Very little work has been reported on the influence of salts on the propagation reaction in hydrocarbon solvents although these are probably the major impurity in the system and may influence the results obtained. Something is known about the influence of lithium-*tert*-butoxide on the propagation rate of polystyryllithium (*18*). In benzene it causes a decrease in the propagation rate to about one-half its initial value at a 1:1 ratio of salt to active center concentration. Larger amounts have little additional effect. The reaction order remains one-half in polystyryllithium which suggests that this salt does not act by destroying the dimerization of active centers as does tetrahydrofuran. Viscosity measurements confirm that these remain dimerized. The salt must add to the polystyryllithium and thus modify the reactivity. In cyclohexane the salt has little effect on the propagation reaction.

When the higher dielectric solvent tetrahydrofuran is used, it has been found by Szwarc (*1*) that deviations from kinetics first order in organolithium once more occur. With polystyryllithium the order is between first and one-half. This is caused by a small amount of dissociation of the ion pairs into free ions. The free polystyryl ion has been found to have a very high reactivity and although it is present in quite small amounts, it can carry much of the reaction. In addition, the solvated ion pair itself has a higher reactivity in tetrahydrofuran than in less polar solvents so that the reaction rates are extremely fast. It is possible to show that the free ion has a measurable effect on the reaction rate in mixed solvents also, even in a 50% mixture of benzene and tetrahydrofuran. With butadiene and isoprene in tetrahydrofuran, Morton (*15*) has reported that the polymerization rate is first order in organolithium concentration above 3×10^{-3} molar. This observation suggests that the contribution of free anions is not important at relatively high concentrations of organo-lithium. Experiments carried out over a wider concentration range,

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however, show that the apparent k_p drifts with concentration, so the free anion again cannot be neglected.

Stereospecificity

Much of the interest in polymerization initiated by lithium compounds is caused by the formation of highly specific products in nonpolar solvents. Under these conditions a highly *cis*-1,4-polyisoprene is formed, and methyl methacrylate is polymerized to a largely isotactic product. It is reported that isotactic polystyrene can be formed at low temperatures (*2*, *9*), but this seems to form only in the presence of lithium hydroxide formed by catalyst destruction (*28*).

For isoprene there is much data in the literature concerned with the microstructure of polyisoprene and its variation with solvent and alkali metal. The analysis of microstructure is normally carried out using standard methods of infrared analysis. Chen (*5*) has shown how it is possible to measure the microstructure of polyisoprenes by means of NMR spectra. This method appears to differentiate more clearly between the cis- and trans-1:4 structures than do the standard infrared methods. Moreover, it is better able to measure the 1:4 content in the presence of large amounts of 3:4 structures. The NMR spectra suggest that the polyisoprene, formed with about 3×10^{-4} molar butyllithium in cyclohexane, contains as much as 15% trans-1:4 structures as well as about 5% 3:4 in the predominantly cis-1:4 polymer. In the presence of low concentrations of tetrahydrofuran the major effect is to replace cis-1,4 groups in the polymer by 3,4 although the trans-1,4 content also increases somewhat. At 10% tetrahydrofuran in cyclohexane the cis-1,4 structures have disappeared completely and some 1,2 is present. In the presence of larger amounts of tetrahydrofuran the trans-1,4 groups are replaced gradually by 1,2. According to the NMR method, therefore, in pure tetrahydrofuran the polymer structure is mostly 3,4 with about 25% 1,2 groups. The infrared methods suggest appreciable amounts of trans-1,4 structures under these conditions (*25*). In contrast the effect of adding small amounts of lithium hydroxide or butoxide is to increase the trans-1,4 content without changing the amount of 3,4. If the NMR results are valid, the homogeniety of microstructure is no greater in hydrocarbons than it is in tetrahydrofuran, and postulating a highly specific transition state for the hydrocarbon systems becomes less plausible. In addition, the generally accepted mechanism in these systems involves covalent bonding of lithium which is doubtful in view of the arguments put forward in the earlier sections. The microstructure of the polymer would seem to be primarily determined by nonbonding interaction between chain end and incoming monomer, the effects of which would depend on the size of the counter ion itself and the presence or absence of complexing agents at the ion pairs.

Copolymerization

The copolymerization of monomer pairs such as butadiene and styrene follows a different course in hydrocarbon solvents than in more polar solvents such as ethers. The copolymerization in tetrahydrofuran is fairly straightforward, but the behavior in hydrocarbon solvents is often considered anomalous. The initial copolymer is rich in butadiene in the latter case and proceeds at about the rate of the homopolymerization of butadiene, whereas the homopolymerization of styrene is considerably faster. This has been explained in terms of preferential absorption of butadiene around the growing chain end (*10*), whereas others (*17*) suggest that this assumption is not necessary. In this system it is found from the ultraviolet spectra that initially the vast majority of the chains end in the polybutadienyl anion. This is because butadiene reacts very rapidly with the polystyryllithium many times faster than does styrene with either anion (*13*). Under these conditions, the copolymerization rate must approximate to that of the homopolymerization of butadiene, and the initial copolymer must be rich in this monomer (*8*). By spectroscopic methods it is possible to measure the reaction rate of styrene with polybutadienyllithium in both the presence and absence of butadiene. It is found that the rate is the same in both cases (*8*) which suggests there is no preferential absorption of the butadiene at the chain end. It is probable that the high rate of one of the cross-propagation reactions is responsible for the similar behavior observed with other monomer pairs such as isoprene-styrene or isoprene-butadiene.

The reactivity ratios observed are markedly different in polar and non-polar solvents. These differences appear to be determined mainly by the nature of the solvation at the active chain end. Most of the change occurs at quite low concentrations of polar solvent in a primarily hydrocarbon medium; hence, the bulk dielectric constant of the solution is not an important factor under conditions where most of the reaction is carried by ion pairs. In solvents such as tetrahydrofuran it might be possible to detect changes in reactivity ratios at different concentrations of active polymer chains as the proportion of free anions increases with dilution. No experiments have been reported yet to check this point.

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5

Electron Donors in Diene Polymerization

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The effects of donors in the polymerization of isoprene by $AlEt_3$ and VCl_3 and of butadiene by $AlEt_2Cl$ and cobalt salts have been studied. In the former, strong donors such as pyridine inhibit polymerization, but with diisopropyl ether the rate passes through a maximum with increase in ether concentration. Measurements of active center concentrations indicate that the main effect of the donor is to increase the number of sites from which polymerization can proceed. The structure of the trans-1:4-polymer is unaffected. In the latter system tertiary amines in low concentration reduce the polymerization rate, molecular weight, and the cis-1:4 content of the polymer, giving ultimately liquid, nonstereoregular products. Two amines (NMe_3 and NEt_3) give new catalytic species which result in the formation of high trans-1:4-polybutadiene.

Using electron donors to modify coordination catalysts dates back to the earliest days of the subject, and patents from 1956 to 1958 refer to advantages gained by adding regulated amounts of polar compounds such as ethers and amines (*1, 3, 9, 12, 14, 19, 21, 27*). The use of these additives was essentially empirical; claims were made for decreased gel, improved stereospecificity and the like without any idea of the way in which the donors operated. Since 1960 the role of these compounds gradually has become clearer. One of the first observations was that adding certain donors retarded the polymerization of propylene. Vesely (*32*) suggested that these donors removed $AlEt_3$ from active participation in the polymerization by complexing with it. The effect was shown to be related to the strength of the donor, and Vesely recognized that there would be some competition for the donor molecule between the alkyl-

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metal and the transition metal halide. Kodama (*15*) and Razuvaev (*28*) noted that donors increased the rate of polymerization of propylene and changed the molecular weight and stereospecificity of the polymer. Similar effects in styrene polymerization were observed by Murahashi (*22*). Boor (*2*), using a catalyst from alkylzinc and $TiCl_3$ found that the polymerization rate of propylene passed through a minimum with increasing concentration of an amine such as triethylamine. Stronger donors, such as pyridine, retarded the polymerization (the reaction stopping at a 1:1 molar ratio) while bulky amines, such as tribenzylamine, were without effect. From the concurrent influence on stereospecificity Boor concluded the the donor first deactivated nonstereospecific sites, but as the proportion of amine was increased, its adsorption near active sites caused an increase in their activity. The polymerization was inhibited at very high donor concentrations. The fact that alkylaluminums and alkylzincs behaved similarly in spite of their different complexing abilities was taken to show that the donor reacted with the surface of the transition metal compound. The contrasts with Natta's view that the control of stereospecificity depends on the nature of the alkylmetal and that the various forms of $TiCl_3$, with or without $AlCl_3$ in solid solution, give the same type of active site (*23*). Zambelli (*33*) studied the effect of anisole and other donors on the formation of syndiotactic polypropylene using a catalyst from diethylchloride aluminum and vanadium tetrachloride. The effect was in line with previous work. Strong donors inhibited the reaction; weaker ones accelerated the rate at low concentrations but inhibited at higher concentrations, and the yield of stereospecific polymer passed through a maximum.

Turov *et al.*(*30*) studied the influence of ethers on the polymerization of butadiene with a $TiCl_4$-$Al(i\text{Bu})_3$ catalyst. The cis content of the polymers fell to a limiting value with increase in ether concentration, dependent on the structure of the ether. Limits of 30% cis structure were observed with Me_2O, 50% with MeOEt, and 70% with Et_2O, but higher homologues were relatively ineffective. Lewis bases, such as ethers and amines, added to AlH_3—$TiCl_4$ catalysts for butadiene have little effect on the polymerization at low concentrations. However, in larger amounts, they reduce both the cis content and the polymerization rate (*18*).

Donors have been added to the cobalt catalysts used to polymerize butadiene (*20*). Cobalt chloride-pyridine complexes gave a soluble catalyst with $AlEt_2Cl$ which was effective for cis polymerization of butadiene, but at the low concentrations of pyridine employed (Al/Co/py = 1000/1/1 to 4), there was no effect on the polymer structure. However, it was observed that the molecular weight fell as the ratio of pyridine to cobalt was increased. Isopropyl ether in the cobalt octoate-methylaluminum sesquichloride catalyst had a similar effect, although at the highest ether concentrations (typical ratios employed were $Al/Co/iPr_2O$ = 160/1/3.5 to 8), a reduction in cis content and polymerization

The inorganic complex $Co(AlCl_4)_2$ polymerizes butadiene, according to Scott *et al.* (*29*), to nonstereoregular polymers, but adding thiophene results in high cis polymer. It is suggested that a charge transfer complex is formed between the thiophene and the complexed aluminum halide giving a σ Al—C bond at the 2-position in the thiophene ring. The cobalt is considered to coordinate with the displaced halogen atoms but not to coordinate either with donor or monomer, and no organocobalt intermediate is produced. This catalyst seems to be quite distinct from those prepared with organometal compounds.

Organocobalt compounds are undoubtedly formed in the reaction of cobalt salts with Grignard or organoaluminum compounds. It is possible to reduce the cobalt salt to the metal under certain conditions; there is also the possibility of cobalt (I) compounds being produced although Kovalevskaya (*17*) has found no change in the valence state of the cobalt in the catalyst complex. It is well known that butadiene stabilizes the catalyst against reduction, and it is reasonable to assume that this occurs by coordination of the π-electrons of the monomer with the cobalt. Following insertion of the monomer into the complex and formation of the growing chain, stabilization could occur either by the coordination of another monomer unit or back coordination of the adjacent ethylenic bond in the polymer chain. It is not known whether the growing polymer molecule is attached to the cobalt or to the aluminum atom or shared between them in a bridge ring complex, but it would be attached to the catalyst site as a carbanion. Attempts have been made to confirm or disprove this by terminating the polymerization with alcohols labelled with C^{14} or tritium. These experiments should distinguish between clear-cut cationic and anionic mechanisms, but they are unlikely to indicate the correctness of the mechanism proposed by Duck (*10*) or Uelzmann (*31*) where although initial reaction with the monomer is regarded as cationic, the polymer molecules became attached to metal atoms and thus would analyze as carbanions. In fact, as far as the cobalt systems for butadiene are concerned, the experimental evidence is inconclusive.

Childers (*5*) found that a cobalt-catalyzed polymerization terminated with C^{14} labelled alcohol resulted in activity in the polymer, whereas H^3 hydroxyl labelled alcohol gave inactive polymer. He deduced, therefore, that the mechanism was cationic. The organometal compound used in this catalyst was ethylaluminum sesquichloride, and his observations have been confirmed (*26*). We carried out virtually the same experiment as Childers except that $AlEt_2Cl$ was used instead of $Al_2Et_3Cl_3$ with the opposite conclusion—namely, the growth was anionic (*8*).

Natta *et al.* (*24*) also came to this conclusion but reported a "contamination" which indicated that a proportion of the radioactivity did not arise from termination of active polymer chains. There are several possible explanations for this contamination. It could result from addition of diethylaluminum chloride to the double bond, but this is not likely to be significant under the polymerization conditions (triethylaluminum does not show any such addition reaction). Another alternative is that oxidation could have occurred with the formation of carbonyl or hydroxyl groups which, after reacting with $AlEt_2Cl$ followed by ROH^3, would give rise to H^3 in the polymer chain. It was found, however, that some contamination occurred even in the absence of oxygen. It was suggested to one of the authors (by Prof. Porri, Milan Polytechnic Institute) that H^3Cl from the decomposition of $AlEt_2Cl$ by ROH^3 may have added to ethylenic bonds in the polymers. Following this suggestion we prepared $AlEt_2Cl^{36}$ which was used as a component of the catalyst, and after terminating with alcohol, the polymers were assayed for Cl^{36}. The results are summarized in Table I.

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Table I. Butadiene/Cobalt Naphthenate/$AlEt_2Cl^{36}$/H_2O

Solvent	Benzene
Al/Co	1000
Polymerization temperature	20° C.
Conversions	6–20%
Cobalt concentration (Co)	$1.59–4.55 \times 10^{-5}$ mole/liter
Metal-carbon bonds (M–C) (H^3 count)	$2.15–5.15 \times 10^{-5}$ mole/liter
(Co)/(M–C)	0.6–1.23
Chlorine content (Cl) (Cl^{36} from $AlEt_2Cl^{36}$)	$0.04–0.53 \times 10^{-5}$ mole/liter

The average level of contamination by halogen is of the order 2.5×10^{-6} mole/liter. If we allow for the isotope effect, it is calculated that about 20–40% of the observed activities in tritiated polymers would arise from this source. This is of the same order as observed by Natta *et al.* (*24*). Some data in this paper also confirm these results. Normal polymerizations were terminated by a slight excess of inactive methanol. A quantity of $AlEt_2Cl$ was then added after removing unpolymerized monomer to ensure that no further polymerizations occurred. Addition of ROH^3, isolation, and assay of the polymer gave the results in the second column of Table II. The first column gives the results which would have been expected for one reactive polymer molecule per cobalt atom, which is of the order observed for an ROH^3-terminated polymerization. The fraction of radioactivity resulting from side reactions (column three) is substantial.

Table. II. Contamination by Side Reaction

Expt.	*Assay Expected for 1 Chain/Co (c/m/mg.)*	*Assay Found c/m/mg.*	*% Interference*
1	91.0	19.8	22
2	84	33	39
3	33.6	13.4	40
4	25.6	3.3	13
5	32.9	12.2	37

These results, though not entirely conclusive, show that cobalt catalysts prepared with $AlEt_2Cl$ result in the majority of polymer chains attaching themselves to metal atoms as carbanions. In this respect at least they resemble the coordination catalysts based on other transition metals. An important question which arises is whether the polymerization mechanism is changed by the presence of a donor molecule. It will be shown later in this paper that in several catalyst systems for diene polymerizations, the majority of polymer molecules are linked to metal atoms as carbanions. Therefore, we consider that the donors influence the catalyst stability, rate of polymerization, and polymer structure by competing with coordination sites on the transition metal or organometal components rather than by changing the mechanism of initiation or propagation.

On this basis we shall consider in detail the influence of donors on two catalyst systems; (a) VCl_3-$AlEt_3$ with isoprene, and (b) CoX_2-$AlEt_2Cl$ (H_2O or MeOH) (X = Cl or naphthenate) for butadiene.

VCl_3/$AlEt_3$/iPr_2O/Isoprene

The general characteristics of the polymerization and the experimental methods used have been discussed previously (*7*). Adding strong donors (e.g., amines), stops the reaction, but weaker donors (isopropyl ether) cause an increase in the rate to a maximum (Figure 1). At high concentrations of ether the rate falls; this can be prevented by proportionately increasing the concentration of $AlEt_3$ (Figure 2). At any fixed VCl_3/iPr_2O ratio the rate shows the usual maximum as the Al/V ratio is increased (Figure 3).

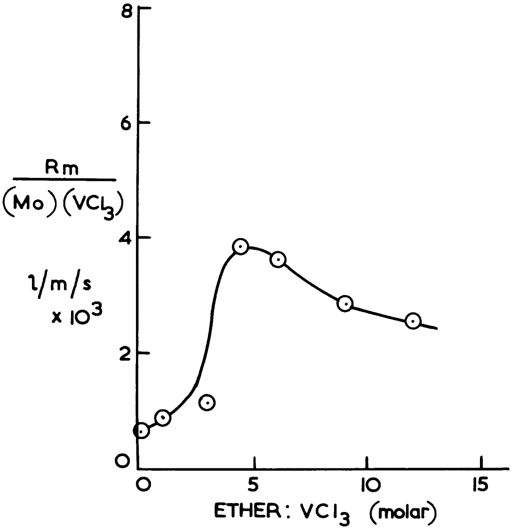

Figure 1. Effect of iPr_2O/V ratio at Al/V-2 = 1 at 50° C.

These observations can be explained by competing interactions of monomer, donor, and alkylmetal for the VCl_3 surface. Strong donors complex with the active sites even at low concentrations and thus inhibit the polymerizations; the same effect is observed with weaker donors at higher concentrations. An increase in the ratio of alkylmetal to donor counteracts the inhibiting effect of excess donor by complexing it in the solution rather than at the surface. Soluble species do not appear to be formed. Complexes of VCl_3 with ethers, thioethers, and amines have been obtained (*6*, *11*); although they are soluble in an excess of the donor, they do not dissolve appreciably in aliphatic hydrocarbons. At the relatively low concentrations of donor at which polymerization will occur, the system is completely heterogeneous (*7*). The increased rate of polymerization at low donor concentrations could arise from changes in the

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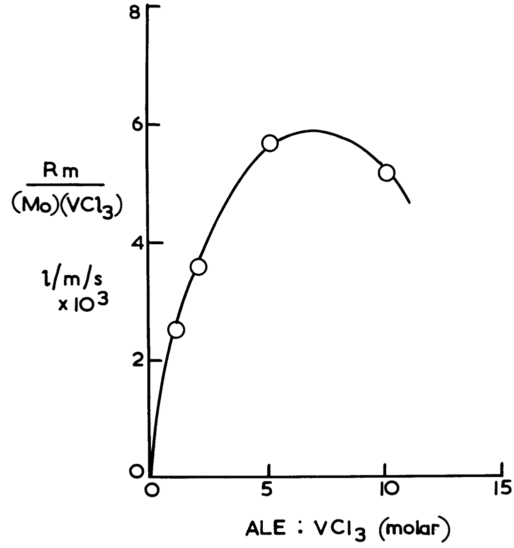

Figure 2. Influence of Al/V ratio at Al/iPr$_2$O = 1/3 at 50° C.

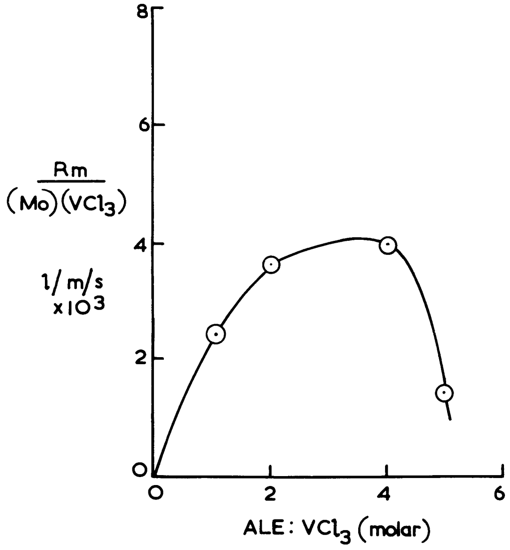

Figure 3. Influence of Al/V ratio at V/iPr$_2$O = 1/6 at 50° C.

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nature of the propagating sites or in their number. The former might result from the change in polarizability of the metal-carbon bonds involved in the polymerization brought about by complexing the donor either at the vanadium or the aluminum with subsequent increase in the propagation rate. A measure of the propagation constant (*kp*) is given by $R_f = k_p M_f N_f$ where R_f is the rate of polymerization, M_f the monomer concentration, and N_f the concentration of metal-polymer bonds when the polymerization is terminated. Values of k_p at low conversions are shown in Table III.

Table III. Relative Propagation Constants

Catalyst	$k_p \times 10^{-2}$ *at 50° C.*
VCl_3-$AlEt_3$	9.2 ± 5.6
VCl_3-$AlEt_3$-iPr_2O	4.3 ± 2.2
VCl_3-$AlEt_3$-$n$$Bu_2S$	4.9 ± 0.1

These values are not absolute velocity constants since transfer to alkylaluminum occurs during the reaction. However, the transfer reactions will be proportional to the concentration of active centers. Hence, at similar conversions the fractions of active alkylmetal bonds are likely to be approximately the same, and the constants will be proportional to the true velocity constants. Determining relative propagation velocity constants is complicated by the participation of a termination reaction. At low temperatures the polymer is insoluble and the catalyst is embedded in a semi-solid mass, resulting in very slow rates of polymerization. At temperatures of 41°–60° C. reasonably good first-order reactions with respect to monomer are found, but at higher temperatures there is a rapid fall-off in reaction rate with time (Figure 4). The velocity constants in Table III were calculated from the linear portion of the rate-time curve, and no account was taken of termination reactions.

Since the effect of electron donors, if any, is to decrease k_p to some extent, their effect in increasing the polymerization rate is attributed to the formation of increased numbers of active centers, although it is not clear how this occurs. We have observed a remarkable development of color intensity (bright purple) as the reaction proceeds, corresponding to a marked reduction in particle size. In the presence of donors even distribution of catalyst throughout the mass occurs more readily and at an earlier stage in the polymerization; further, reactions are more uniform and reproducible as can be seen from Table III. Although soluble complexes of the type previously referred to are not produced, the donor appears to facilitate cleavage of the vanadium chloride crystals by partly solubilizing the catalyst fragments and possibly by cleaving the crystals at surface defects, and it may well stabilize the organovanadium complexes produced.

It is important to note that the ether had little or no effect on the stereospecificity of the polymer produced even at iPr_2O/V ratios of 20/1. This in itself is significant in suggesting that the active center is not drastically changed by the presence of the donor.

It is highly probable that an alkylated vanadium complex is the site at which polymerization occurs. In the case of coarsely powdered VCl_3 the amount of alkylation as judged by divalent vanadium in the catalyst is very small

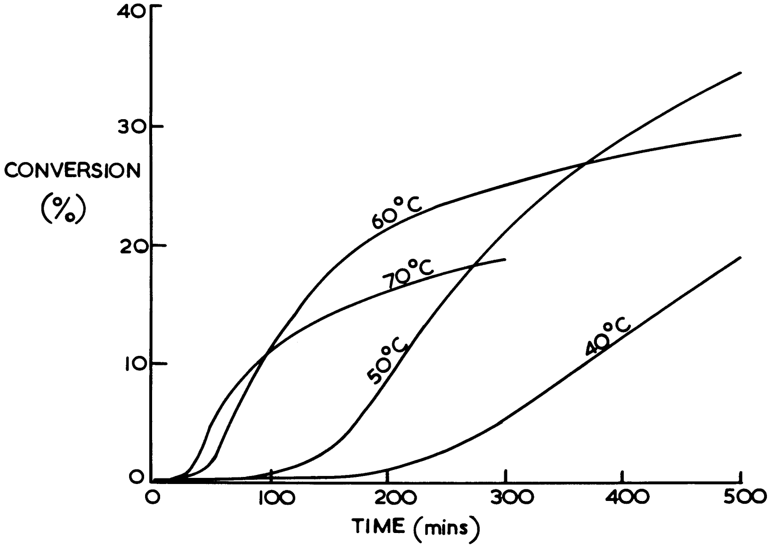

Figure 4. Dependence of polymerization rate on temperature

(1–2% reduction has been observed in some cases, but in others negligible reduction has been found). However, from the number of metal-carbon bonds produced, reduction to the extent of 1–2% could account for the number of active sites formed. If finely divided VCl_3 is prepared (by reducing VCl_4 using organometalic compounds or by ionizing radiation), much larger amounts of divalent vanadium are produced (as high as 40–60%) by reaction with triethyaluminum, and the rates of polymerization are higher by a factor of 10. Vanadium chloride itself is inactive as a catalyst, so presumably a V(II) catalyst complex is not involved. More probably the catalyst is alkylated vanadium trichloride, $RVCl_2$, which gives rise to V(II) on analysis. These alkylated compounds with the associated alkylaluminum chloride or alkyl chloride are located on the catalyst surface since, as mentioned above, no soluble species were found. (We cannot, however, exclude the possibility that a $V(II)Cl_2$-$RV(III)Cl_2$ complex is involved in the reaction). Termination, either by concerted bimolecular or homolytic decomposition, to give an inactive V(II) site probably causes the fall-off in rate observed at elevated temperatures.

In considering the nature of the catalyst site, some account should be taken of the role of the alkylaluminum. It has been found that active catalysts from VCl_3 are not formed with alkylmetals such as $ZnEt_2$, Ph_2Hg, or RMgCl. Only when $AlEt_3$ was added to VCl_3, alone or in conjunction with the other alkyls, did polymerization occur.

$AlEt_2Cl/CoX_2NR_3/(MeOH)/$Butadiene

When triethylamine is added to cobalt salts in hydrocarbon solvents, bright blue complexes are produced which are soluble in solvents such as benzene. With cobalt chloride, adding diethylaluminum chloride increases the solubility slightly but does not change the color unless a large excess is employed or if reduction to metal occurs, when a brown-black color is produced. The effect of an amine such as triethylamine on the polymerization of butadiene is to slow down the reaction and to modify the polymer microstructure. Several cobalt compounds and a number of amines have been examined, and the results are given below.

Cobalt Chloride. The effect of triethylamine is to decrease the yield of polymer, the molecular weight, and the cis content until, at 7.5/1/10 ratio of $\text{NEt}_3/\text{Co}/\text{Al}$, liquid nonstereospecific polymer was produced. Above this ratio high trans 1:4 polymer was produced with an increase in polymer yield. This is shown in Table IV and Figures 5 and 6. With still larger amounts of amine the structure remained unchanged but the rate fell until, at a ratio NEt_3/Co of 18/1, polymerization was completely inhibited. The rates are generally quite

Table IV. Structure of Polymer at Different Donor Levels*

Al/Co/NEt₃	*cis*	*trans*	*1:2*
10/1/0	87	3	10
10/1/2.2	34	39	27
10/1/7.5	23	49	28
10/1/10	0	94	6

* $\text{CoCl}_2 = 1.91 \times 10^{-2}$ moles/liter

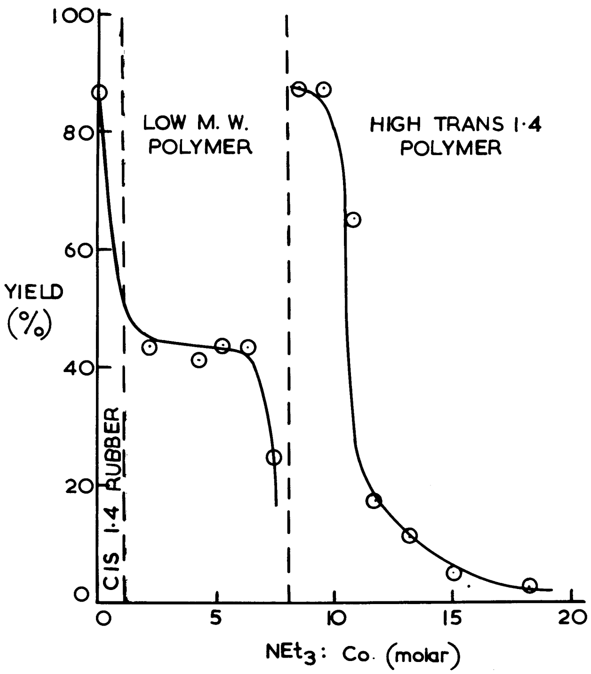

Figure 5. Influence of NEt_3/Co ratio on polymer yield; ($\text{CoCl}_2 = 1.9 \times 10^{-2}$ moles/liter, Al/Co = 10/1)

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low for both the low molecular weight and the trans polymers compared with those in which no triethylamine is present.

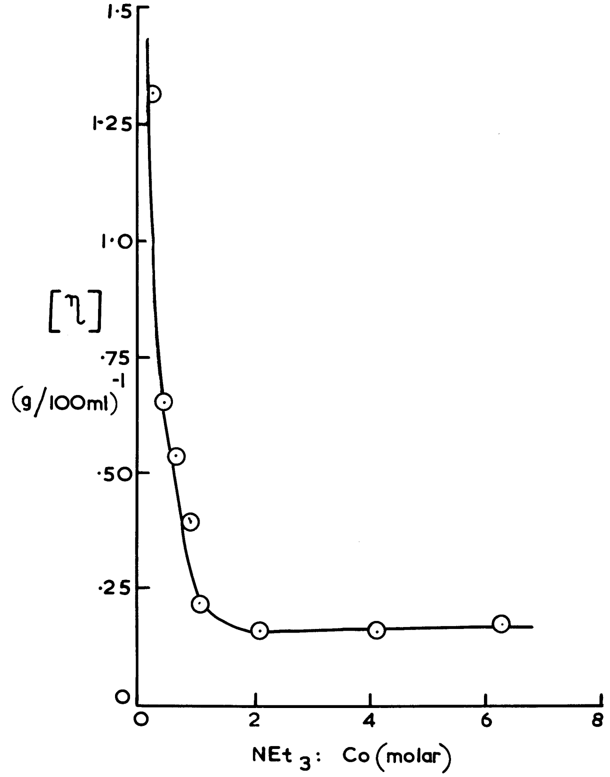

Figure 6. Influence of NEt$_3$/Co ratio on molecular weight; (CoCl$_2$ = 1.9 × 10^{-2} moles/liter, Al/Co = 10/1)

Polymerizations are characterized by an induction period which may be prolonged, and the reaction may cease at relatively low conversions (Figure 7). Figure 8 shows the influence of cobalt chloride concentration on the formation of trans polymer, which shows also the prolonged induction period. For low molecular weight polymers the minimum concentration of cobalt chloride for reasonable conversion (ca. 50%) at 50° C. is about 1%, which gives polymers with cis contents of 42–46%. At 20° C. comparable results were found, but somewhat higher cis contents were recorded (52–63%) at similar NEt$_3$ levels. Methanol or water was found to be necessary for polymerization to occur. The exact concentration of methanol or water was not very important, but since the reaction was more sensitive to water concentration, methanol was preferred. Its concentration was in the region of 3% calculated on the cobalt chloride. Neither cocatalyst had any influence on polymer structure.

The yield of trans polymer fell as the ratio of Al/Co was reduced below 10/1. The yield of polymer was greatest at 50° C. (Figure 9), but temperature had little effect on polymer structure.

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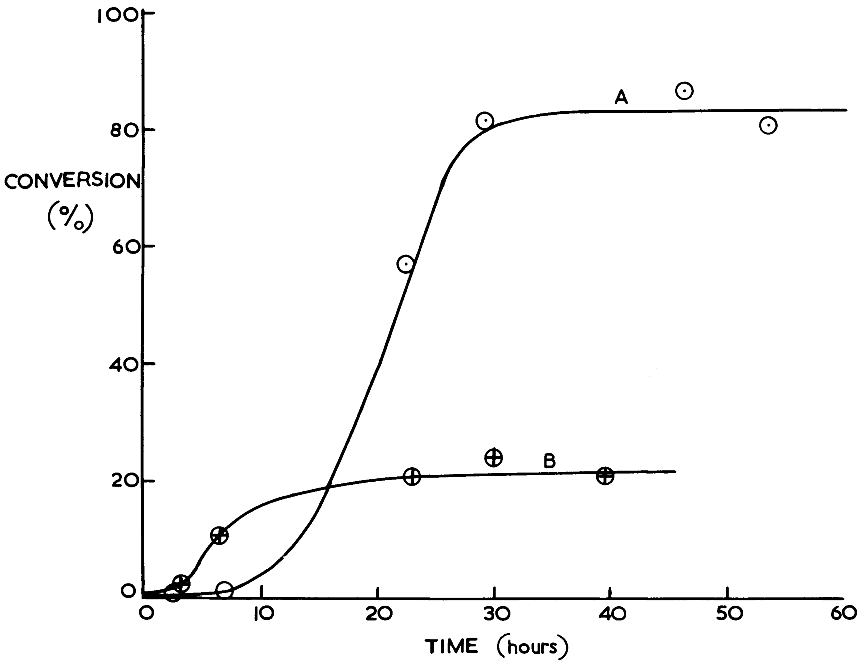

Figure 7. A: low molecular weight polymer, Al/Co/NEt$_3$ *= 10/1/0.7; B: trans polymer, Al/Co/NEt*$_3$ *= 10/1/8; (CoCl*$_2$ *=* 1.9×10^{-2} *mole/liter)*

In the presence of diethyl ether the concentration of triethylamine required to give polymer of high trans structure was greatly reduced (Figure 10).

Other amines reduced the molecular weight of the polymer (Table V) but only with triethylamine and trimethylamine was high trans polybutadiene formed.

The critical ratio of NEt_3/Co at which high trans polymers were produced increased with increase in the Al/Co ratio as can be seen from the data in Table VI.

Cobalt Naphthenate. Cobalt naphthenate behaved in much the same way as cobalt chloride, but at equivalent metal concentrations the soluble salt gave much faster rates. As the triethylamine concentration was increased, the 1:2 contents increased from 21 to 39% at the expense of cis structure. The trans contents remained constant at 30 ± 3% (Table VII) until a ratio of NEt_3/Co of about 4 was reached (dependent on the cobalt concentration (Table VIII)) when high trans polymer was obtained.

At constant Al/Co/NEt_3 ratios the molecular weight increased with increase in concentration of cobalt, and at the same time the 1:2 structure increased at the expense of the trans content (Table IX).

Other Cobalt Compounds. Catalysts prepared from cobalt oleate, octoate, and acetyl acetonate have also been examined. The characteristics of the reactions were the same as with cobalt chloride and naphthenate. The results are shown in Table X.

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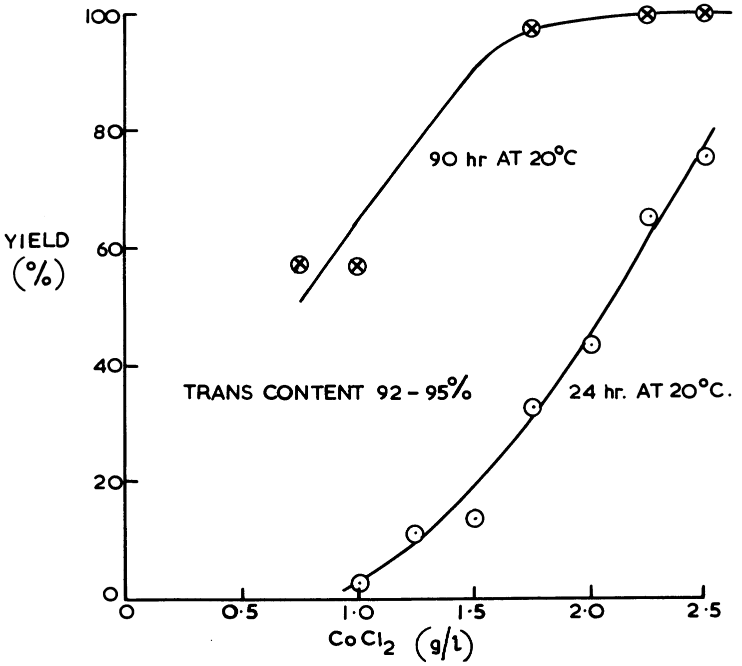

Figure 8. Catalyst concentration and yield of trans-polybutadiene; $Al/Co/NEt_3 = 10/1/8.5$

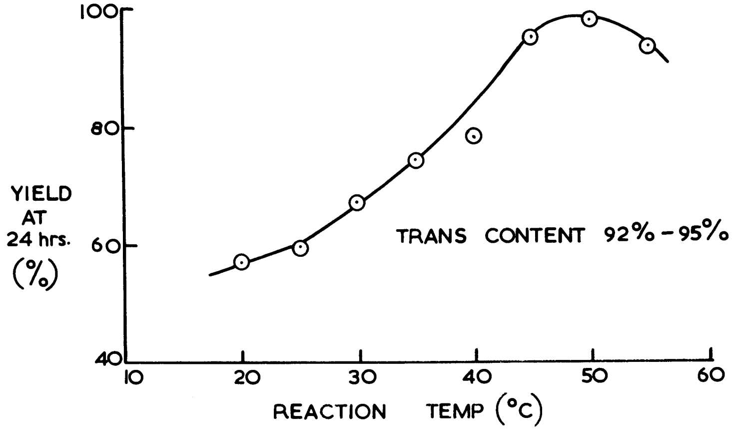

Figure 9. Effect of temperature on yield of trans-polybutadiene $Al/Co/NEt_3 = 10/1/9.5$; $CoCl_2 = 2.5$ grams/liter

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Metal—Carbon Bonds in Cobalt-Catalyzed Polymerization. Concentrations of metal-carbon bonds were determined (using tritium labelled alcohol) with increase in conversions. Experiments were made in two solvents (petrol and benzene) with two cobalt salts (chloride and naphthenate) under conditions giving rise either to liquid mixed structure or to high trans polybutadiene. The data are summarized in Table XI. Table XII and Figure 11 shows optical properties of some cobalt salts and complexes.

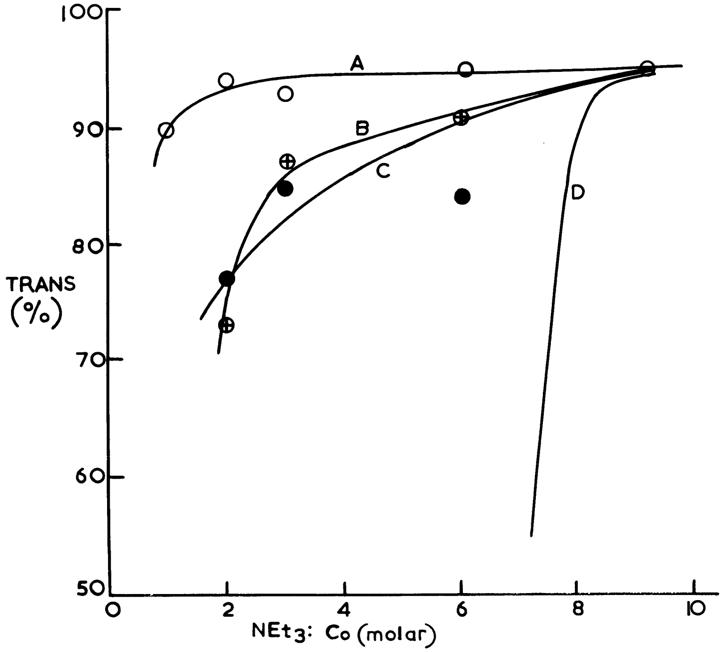


Figure 10. Dependence of structure on solvent composition; ether/benzene; A—1:1; B—1:2; C—1:5; D—no ether

Experimental

$VCl_3/AlEt_3/Pr_2O$/Isoprene. Polymerizations were carried out in a mixed hydrocarbon solvent (SBP 5 Shell Chemicals Ltd.) b.p. 90°–105° C. consisting of paraffins (60%), naphthenes (30%), and aromatics (4%), purified by washing with sulfuric acid and water, and dried over alumina. A closed, stirred dilatometer reactor described previously (7) was used at 50° C. except where stated. Monomer concentrations were varied over the range 0.94–2.82 moles/liter with VCl_3 concentrations between 0.34–2.35 grams/liter. Electron donors, pyridine, di-*n*-butyl sulfide and diisopropyl ether were purified by fractionation and dried over alumina. Details of the labelling technique, polymer purification, and radioactive assay have been described elsewhere (7).

$AlEt_2Cl/CoX_2NR_3$/(MeOH)/Butadiene. All polymerizations were carried out in 250-ml. crown-capped pressure bottles with perbunan/aluminum foil seals. The bottles were dried before use by heating overnight at 120° C. and

Table V. Influence of the Nature of the Donor

Amine	*Polymer Yield %*	$[\eta]$	*Amine/Co**
None	97	1.87	. . .
NEt_3	54	0.16	2.1
NPr_3	77	0.17	1.6
NBu_3	81	0.18	1.2
$N(Hex)_3$	76	0.15	2.5
$N(CH_2Ph)_3$	54	0.21	2.0
$NMe(C_4H_80)$	44	0.37	2.6
C_5H_5N	50	0.15	6.6

* Cobalt concentration 2×10^{-2} mole/liter

flushing with dry argon or nitrogen. The dry, inert-gas filled bottles were charged in a dry-box with benzene (150 ml.), cobalt salt, diethylaluminum chloride, cocatalyst, and amine. The relative proportions and amounts of the components are given in the Tables. The catalyst mixture was then shaken for 15 minutes. The pressure bottles containing the catalyst mixtures were cooled in a solid CO_2/alcohol bath to about −30° C., and dry butadiene (18.5 grams) was added. The bottles were then capped and shaken for 48 hours in a water bath maintained at 20° C. At the end of the experiment the catalyst was destroyed by adding a benzene-methanol mixture containing 1% phenyl 2-naphthylamine as antioxidant, the solution of polymer extracted with hydrochloric acid and washed with water until free from acid. The polymer was then isolated by freeze drying or by precipitation. In the samples labelled with H^3, C^{14}, or Cl^{36} the polymers were isolated by precipitation from solution and repeated dissolution and freeze drying until the radioactive counts were constant.

Discussion

Structure of the Catalyst. Until a pure complex is isolated, no definite structure can be given, but from the polymerization behavior some conclusions can be drawn as to its likely composition. The initial complex (which forms cis polymer) from cobalt chloride and $AlEt_2Cl$ is likely to have the structure $CoCl_2 \cdot AlEt_2Cl$, or $Co(AlEt_2Cl_2)_2$ by analogy with the known complex $Co(AlCl_4)_2$. This complex is stabilized by the presence of monomer, and at the ratios of Al/Co normally employed there will be a substantial excess of uncomplexed $AlEt_2Cl$ in solution. Both the components of the catalyst form strong complexes with tertiary amines, and it is clear that there will be competition between them for added base. At a given ratio of Al/Co there is a level of NEt_3 which results in a change from a yellow to blue colored complex, the level increasing with increasing Al/Co ratio (Table VI). The yellow catalyst gives low molecular weight nonstereoregular polymer, whereas the blue catalyst gives a polymer of high trans content.

From the optical properties of the solutions it is clear that the blue color is associated with cobalt complexing (Table XI and Figure 11). At low concentrations of $AlEt_2Cl$ the blue color of the cobaltamine complex persists, but at the higher concentrations of $AlEt_2Cl$ when the color is yellow it is reasonable

Table VI. Dependence of Polymer Structure on Al/Co Ratio*

Molar Proportions of Catalyst Components			*Color of Catalyst*	*Polymer*
Al	*Co*	*NEt_3*		
2	1	1	Blue	Cryst. (92% trans, 8% 1:2)
2	1	5	Blue	Cryst. (95% trans, 5% 1:2)
5	1	1	Yellow	Liquid (55% cis)
5	1	2	Yellow	Liquid
5	1	5	Green/Blue	Cryst. (86% trans, 14% 1:2)
5	1	10	Blue	Crystalline polymer
10	1	up to 7.5	Yellow	Liquid polymer
10	1	8	Blue	Crystalline polymer
20	1	1	Yellow	Liquid polymer
20	1	5	Yellow	Liquid polymer
20	1	10	Yellow	Liquid polymer
20	1	20	Yellow	Liquid polymer

* Cobalt = 1.67 grams/liter

Table VII. Influence of Added Triethylamine on the Cobalt Naphthenate/$AlEt_2Cl$ System*

NEt_3/Co	*% cis*	*% trans*	*% 1:2*	*[η] dl/gram*
1.05	47	32	21	0.63
1.60	46	28	26	0.35
2.10	40	34	26	0.28
2.60	40	32	28	0.24
3.20	34	35	31	0.23
4.20	30	31	39	0.14

* Al/Co = 10/1: cobalt concentration = 7.6×10^{3} moles/liter.

Table VIII. Dependence of Critical NEt_3/Co Ratio on Cobalt Concentration*

Cobalt Concentration (moles/liter) × 10^3	*Critical NEt_3/Co*	*Structure of polymer*	
		% 1:2	*% 1:4 trans*
19.0	5.0	22	78
9.5	4.2	19	81
5.7	3.5	10	90
3.8	3.6	14	86
1.9	4.1	17	83

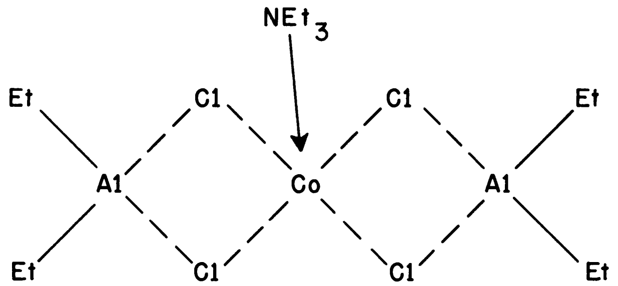
* Al/Co = 10/1

to assume that the amine is associated entirely with the alkylaluminum. In this concentration range it would seem that the donor interferes with coordination of the monomer with the catalyst and so reduces both the rate and the stereoregularity of the polymerization in proportion to its amount. It would not be unreasonable to expect further additon of donor to give progressively reduced yields of low molecular weight nonstereoregular polymer. However, the abrupt change in rate and polymer structure with the transition to a complex of different color indicates the formation of a new catalytic entity with at least one of the coordination sites of cobalt occupied by an amine molecule.

The complexing power of cobalt with trimethylamine or pyridine is variable; mono-, di-, and tetra-amine complexes have been obtained, but there are

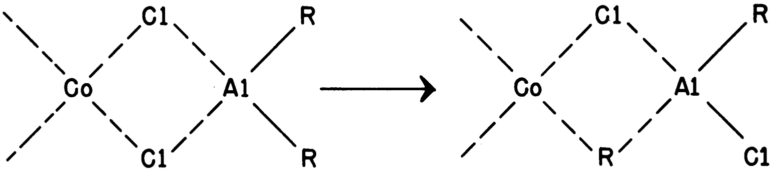
In Elastomer Stereospecific Polymerization; Johnson, B., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

no reports of complexes with tertiary amines having coordination numbers of six other than an unstable complex $Co(Py)_6I_2$ (*13*). The latter have however been achieved with ammonia or ethylene-diamine. The coordination of one or two amine molecules with the cobalt would clearly leave some power of coordination for monomer. In the absence of direct evidence proposals for the structure of the catalyst complex are pure speculation, but it is not unreasonable to suggest that with large concentrations of amine in the blue trans polymer producing complex the cobalt possesses octahedral coordination. A possible structure is I.

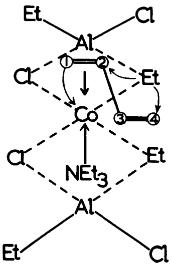


I

The amine, by blocking one coordination point, prevents two-point coordination of the butadiene in the cis configuration, and monomer enters with only one double bond coordinated to the cobalt atom. It is presumed that in the active intermediate an organic group is in the bridge of the complex (II) (*16*), and we would represent the polymerization as indicated by III.



II



III

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(In suggesting mechanism III no attempt has been made to take into account the influence of the cocatalyst in forming more complex, possibly condensed, catalytic entities.)

The monomer coordinates at a vacant coordination site on the cobalt atom. It assumes the trans form since the second coordination attachment on the other side of the cobalt is blocked by an amine molecule. The organic group in the bridge is favorably located for attack either on the C_2 or C_4 positions of the complexed monomer molecule to give 1:2 or trans 1:4 addition. A sigma bond is formed between the Co and C_1 atom of the monomer, and after bond rotation into the bridge, the coordination site is then once more available for monomer insertion.

Table IX. Change in Structure and Molecular Weight with Cobalt Naphthenate Concentration*

Cobalt Concentration (mole/liter) × 10^3	*% cis*	*% trans*	*% 1:2*	*[η] dl/gram*
9.5	45	37	18	0.94
7.6	47	32	21	0.63
5.7	47	31	22	0.45
3.8	46	26	28	0.28
1.9	56	19	25	0.21
1.5	48	22	30	0.18

* Al/Co/NEt_3 ratio = 10/1/1

Table X. Effect of Cobalt Salt on Butadiene Polymerization*

Cobalt Salt	*Cobalt Concentration (moles/liter) × 10^3*	*NEt_3/Co*	*Structure %* *1,4 cis*	*1,4 trans*	*1,2*	*[η] dl/gram*
Acetylacetonate	6.7	2.1	43	22	35	0.15
	6.7	6.3	0	84	16	0.87
Octoate	22.6	7.4	36	24	40	0.09
	22.6	8.4	0	95	5	0.25
Oleate	4.5	4.7	0	91	9	1.85

*Al/Co = 10/1; solvent, benzene

With amines other than NMe_3 or NEt_3 the polymerization rate is reduced and stereoregularity destroyed, but at high concentration trans polymer is not produced; presumably bulky amines prevent coordination of the monomer in the trans conformation, and its approach involves one double bond to the vacant site with the remainder of the molecule directed away from the complex. Adding further quantities of donor does not change the structure of the polymer, but by occupying sites at which monomer can be coordinated, it reduces the polymerization rate ultimately to zero. Adding a second donor such as diethyl ether reduces the competition for the amine by the $AlEt_2Cl$, and high trans structure is observed at lower ratios of amine to cobalt. With the catalyst which produces cis and nonstereoregular polymer, different complexes of cobalt, possibly of the planar type as suggested by Scott *et al.* (*29*), may be involved.

Table XI. Metal-carbon Bonds in Cobalt-Catalyzed Polymerization[1]

$Al/Co/NEt_3$ (molar ratio) and polymer type	*Co. mole/liter × 10^3*	*Time, hrs.*	*Polymer Yield, %*	*$N \times 10^4$ moles/liter*
Cobalt chloride[2]				
10/1.6/0.9 liquid	14.3	4.2	2.1	0.65
		21.1	52.5	4.65
		25.5	64	4.50
		28.9	67	4.10
		45.5	70	2.94
		52.0	70	. . .
10/1.4/1.0 liquid	11.4	2.7	0.5	0.52
		6.7	0.9	1.25
		22.5	57.6	20.4
		29.1	79	23.4
		46.2	84	17.2
		53.7	85	8.8
10/1.1/3.3 liquid	11.3	5	5.1	1.96
		23.4	46	12.4
		29	52	10.9
		46	46	13.8
10/1.2/3.3 liquid	12.3	8.8	4.3	4.8
		78.5	21.2	12.9
		78.8	28.5	12.5
		85.7	45.7	. . .
10/1.2/6.5 liquid	10.7	3.7	4.3	0.57
		31.0	21.8	12.9
		33.3	28.2	11.3
		38.5	45.2	. . .
10/1.0/8.15 trans	9.4	0.4	2.0	. . .
		1.1	5.3	. . .
		3.5	21.5	0.58
		5.5	28.6	1.03
		8.6	45.5	0.95
10/1.0/8.6 trans	11.0	1.9	3.0	0.28
		10.4	6.3	0.52
		21.0	23.0	0.38
		21.5	30.0	1.57
		22.0	39.7	1.29
10/1.0/4.7 liquid[3]	10.8	2.4	1.0	1.38
		5.7	3.0	4.52
		44	20.7	5.21
		49	27	6.61
		52	44	. . .
10/1.0/14.2 trans[3]	10.8	0.7	1.0	0.66
		3.2	2.8	2.54
		15.2	21	5.45
		24.2	26.8	. . .
		46	46	4.05
Cobalt naphthenate[2]				
10/0.82/3.3 liquid	16.5	2	48	64
		18.7	43	38.6
		24.1	77	57.0
		42.6	86	80.5
		66.6	83	30.3

[1] It will be noted that the concentrations of metal-carbon bonds are 10–100 times larger than those observed with a typical cis-producing catalyst (cf. Table II). Such concentrations clearly demonstrate the presence of carbonization in the polymerization and dispose of the view that activity arises from side reactions.

[2] Petrol SBP 5 as solvent unless otherwise noted.

[3] Benzene as solvent.

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Attempts to isolate the complex which forms trans polymer have been made, but no pure compounds have yet been isolated. From cobalt chloride, solid or liquid products were obtained which have variable composition. (Co = 5.7–15%, Al = 5.2–10.6%, Cl = 20.6–26.2%, N = 4.5%, and replaceable ethyl groups 1.2–16.9%). It seems probable that in certain of these products some of the amine cobalt chloride complex is present without coordinated $AlEt_2Cl$. The corresponding products from cobalt octoate have all undergone decomposition to a greater or lesser extent during isolation, but by suitably protecting the catalyst with other donors such as ethers or nonpolymerizable dienes, it may be possible to isolate a stable product.

Table XII. Optical Properties of Catalyst Complexes

Sample	*Composition Solvent*	*Absorptions*
Hydrated $CoCl_2$	Aqueous	510
Anhydrous $CoCl_2$	Nujol mull	580–590
Anhydrous $CoCl_2$	Isopropyl alcohol	575 610 650
Anhydrous $CoCl_2$	Acetone	575 640 675
Anhydrous $CoCl_2$	T.H.F.	590 630 670
$CoCl_2/NEt_3$	Benzene	596 634 660
$CoCl_2/NEt_3/AlEt_2Cl$	Benzene	595 632 660
$CoCl_2/NEt_3/AlEt_2Cl$	Petrol	592 635 660
$CoCl_2/NEt_3/AlEt_2Cl$[1]	Benzene	595 632 660
$CoCl_2/AlEt_2Cl$	Benzene	590

[1] Excess NET_3.

As the polymerization proceeds there is an increase in the concentration of metal-carbon bonds estimated by H^3 concentration after termination by CH_3OH^3. The concentrations of metal-carbon bonds are very much greater than found in the high cis polymerizations. The highest concentration observed was 8×10^{-3} mole/liter, but more usually with liquid polymer forming reactions was in the region of 10^{-3} mole/liter and for the trans polymer producing reaction was 10^{-4} mole/liter (Table XI). These concentrations reflect the relatively low molecular weights of the polymers produced by the donor-modified catalysts. The concentration of metal-carbon bonds increases with time to a maximum and subsequently falls at high conversions. The polymer-metal bonds will include those which are growing and are presumably attached to cobalt and "dead" polymer molecules formed by transfer to diethylaluminum chloride. The fall in concentration towards the end of the reaction (above 70% conversion) suggests that a termination or decomposition reaction is also occurring. From the maximum number of metal-carbon bonds produced in the cobalt chloride system no more than about 1–20% of the cobalt atoms can be involved in the polymerization, whereas with soluble cobalt salts considerably more of the cobalt is active. The molecular weights of the trans polymers calculated from the metal-polymer bond concentration and the intrinsic viscosities of the polymers correlate fairly well. (Typically $[\eta] = 1.43$, M_n (calc.) = 87,000 compared with $M_\eta = 140,000$). Data for the liquid polymers

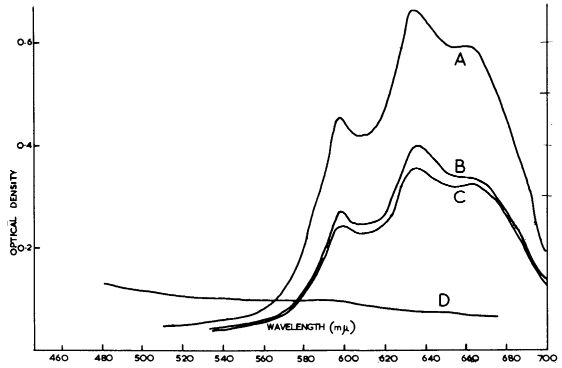

Figure 11. Absorption spectra in benzene; ratios of Al/Co/NEt$_3$; A—10/1/7.7; B—10/1/23; C—0/1/7.7; D—10/1/1.4; (CoCl$_2$: 2 grams/liter; dilution A and C: × 10; B: × 20)

show some evidence for the presence of polymer molecules which do not contain polymer-metal bonds, e.g. ($[\eta] = 0.15$ gave M_n (calc.) = 37,000 compared with $M_\eta = 10{,}000$).

In the discussion so far the effect of the donor in modifying the catalytic complex and thence the polymerization has been considered. A further possibility is that the donor changes the structure of the organometal compound itself. Thus Zambelli (*25*, *33*) and Caunt (*4*) have suggested that ethylaluminum dichloride reacts with a donor to give diethylaluminum chloride and the donor complex of aluminum chloride, and it is possible that similar changes occur with $AlEt_2Cl$ resulting in the formation of triethylaluminum. The complex of $AlEt_3$ and NEt_3 added to cobalt chloride gave a small yield of polymer of 65% trans, 10% cis, and 25% 1:2 structure, whereas the $AlCl_3NEt_3$ complex was ineffective. A mixture of NEt_3 complexes of $AlCl_3$ and $AlEt_3$ in the ratio of 1:2 gave a very small yield of polymer, whereas premixing the $AlCl_3$ and $AlEt_3$ in the same proportions followed by the donor gave a normal polymerization to high trans polymer. The results, although not entirely conclusive, suggest that $AlEt_2Cl$ does not disproportionate to give $AlEt_3$ and $AlCl_3$; complexes of these with cobalt salts need not be considered as participating in the polymerization.

The experimental work reported here with two very different catalyst systems shows that generalizations about the influence of electron donors cannot be made easily. Changes in polymerization rate are generally observed, and the reactions may be inhibited at sufficiently high donor concentrations or with strong donors. Changes in polymer structure may also occur. A common feature of the systems studied is the competition for the donor between the organometal and transition metal compounds. In the systems studied no change in the basic mechanism of polymerization resulted from the presence of donors.

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6

Polymerization of Higher Aldehydes

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Convenient and generally applicable methods for preparing amorphous and crystalline isotactic polyaldehydes have been developed in the last few years. Stabilization of polyaldehydes has been improved by end-capping and capping and adding antioxidants and other stabilizers. The higher stability permitted these polymers to be characterized more adequately. Solubilities, solution viscosities, end groups, melting points, and gel points of polyaldehydes were determined. Other important advances were made in the copolymerization of aldehydes, and in the understanding of some of the factors influencing the stereoregularity of aldehyde polymerization.

In the last few years, particularly since the commercialization of polyformaldehyde, polymers of higher aldehydes (*50, 51, 52*) have become quite popular. This has become noticeable in a sharp increase in the number of patents and papers from different laboratories.

A brief historical background of the polymerization of higher aldehydes is given in Table I. After the initial discovery of the first polyaldehydes, (poly-*n*-butyraldehyde, polyisobutyraldehyde, polyheptaldehyde) by Bridgeman and Conant (*6, 9, 10*), most of the work in subsequent years was devoted to polyacetaldehyde, first prepared by Letort and Travers in 1936 (*27, 48*). In the years thereafter the polymerization of acetaldehyde was studied in more detail in an attempt to clarify uncertainties in polymerization conditions, improve the polymer yield, and understand the mechanism of polyacetaldehyde formation (*29*). Polymer characterization and polymer degradation were also investigated (*12, 55*).

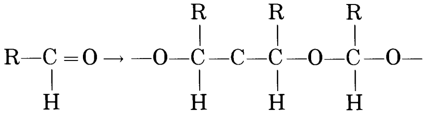
By 1951 (*29*) it had been concluded that polyacetaldehyde is an amorphous polyacetal of very high molecular weight. The polymerization of acetaldehyde is initiated by free radicals assisted by the crystallization of the monomer (crystallization polymerization).

Table I. Polymerization

Author	*Initiator*
Conant	None
Letort, Travers	None
Letort school	None or Peroxides
Vogl	Cationic
Furukawa	γ-Alumina
Cons. für Elektroch.	BF_3
Kargin, Chachaty	
	Crystalline,
Vogl	Anionic
Furukawa	Aluminum org. comp.
Natta	Aluminum org. comp.

Letort found later that the crystallization polymerization of acetaldehyde is favorably influenced by acids (*28*)

We started our investigation in 1957 and worked out initially reliable methods for preparing amorphous atactic polyacetaldehyde (*16*). Soon thereafter we discovered crystalline isotactic polyaldehydes (*49, 51*). Detailed studies of polymerization conditions, polymer structures, and stabilization of the polymers followed.



$$\underset{\displaystyle H}{R{-}\overset{|}{\underset{|}{C}}}{=}O \rightarrow {-}O{-}\underset{\displaystyle H}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}{-}C{-}\underset{\displaystyle H}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}{-}O{-}\underset{\displaystyle H}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}{-}O{-} \qquad R = \text{alkyl}$$

Subsequently, and independently from us, Furukawa (*17, 18, 19, 21*) and Natta (*34, 36*) also succeeded in preparing amorphous and crystalline polyaldehydes.

This review discusses mainly our own work and points only briefly to major contributions from other laboratories. Amorphous elastomeric polyacetaldehyde will be discussed first.

With cationic initiators, acetaldehyde polymerizes in high yields to a very high molecular weight, atactic elastomer. The best results were obtained with BF_3 in ether-pentane mixtures or ethylene at –60° to –120° C. In fact, when BF_3 is used as the initiator for the acetaldehyde polymerization and in ethylene as the solvent at temperatures of –110° to –120° C., acetaldehyde does not need to be specially purified for preparing reasonably good polyacetaldehyde. Acetaldehyde taken directly from Eastman bottles and used for polymerizations gives polyacetaldehyde with an η of about 2. Other Lewis and Brönsted acids also produced the amorphous elastomer (*50, 51, 52*) as indicated in Table II. A pK of <2 appears to be necessary for organic acids to be effective as initiators. A number of other compounds such as AlF_3 would probably be

of Higher Aldehydes

Polymerization Technique	*Aldehyde*	*Year*
High pressure	C_2–C_7	1930
Crystallization Polymerization	Acetaldehyde	1936
Crystallization Polymerization	Acetaldehyde	1942–1954
Solution and Bulk	Acetaldehyde	1958
Bulk	Acetaldehyde	1959
Solution	Acetaldehyde Copolymerization	1959
x-rays, γ-rays	Acetaldehyde	1960
Isotactic Polyaldehydes		
	Higher aldehydes	1958
	Higher aldehydes	1959
	Higher aldehydes	1959

initiators for the acetaldehyde polymerization; their inactivity seems to be caused by their insolubility in the reaction mixture.

In order to obtain high polymers rather than the trimer paraldehyde, the acetaldehyde polymerization must be carried out at low temperatures, and a proper balance of initiator activity and choice of solvent must be maintained. With a reasonably active initiator, increasing the polymerization temperature or the polarity of the solvent favors trimerization over polymerization.

Table II. Polymerization of Acetaldehyde

Solvent: Ether Temperature: −65° C.

Initiator	*Concentration in Weight % Monomer*	*Solvent: Monomer*	*Results*
H_3PO_4, HCl		2:1	Polymer
CF_3COOH			> 75%
AsF_3, $AsCl_3$	0.1–0.5		
$AlCl_3$, SbF_3, etc.			
H_2SO_4, P_2O_5			
BF_3, $FeCl_3$, $SnCl_4$	0.05–0.2	2:1	Paraldehyde
PCl_3			

No Polymerization: Carboxylic Acids to pK <2 $BeCl_2$, AlF_3, etc.

The polyacetaldehyde thus prepared has the same properties and structure as Letort's polyacetaldehyde which was obtained by "crystallization polymerization." This indicates that "crystallization polymerization," the only previously known method of acetaldehyde polymerization, is only a special case of acid-initiated or cationic acetaldehyde polymerization. We feel that Letort's proposal (*29*) that the peroxide-induced acetaldehyde polymerization (crystallization polymerization) as a radical polymerization can now be reinterpreted in the following way: The initiating species, which is prepared by reacting acetaldehyde with a controlled amount of oxygen, is obtained via a free radical reaction. The actual polymerization of acetaldehyde proceeds, however, by a cationic mechanism. (The "crystallization polymerization" of acetaldehyde is inhibited when the glass vessels are washed with soap or alkali solutions and enhanced when treated with strong acids.) Recently, Walling has reinvestigated the high pressure aldehyde polymerization and found no evidence for a free radical nature of the aldehyde polymerization (*53*).

In addition to well-recognized cationic initiators for the solution polymerization of acetaldehyde (*50, 51, 52*) more specialized systems for preparing elastomeric polyacetaldehyde have been uncovered. They include the polymerization of acetaldehyde by condensing the monomer onto γ-alumina (*17, 18, 19, 21*) from the vapor phase or polymerization with acid-treated oxide supports (*43, 54*), the use of phosphines (*20*) as initiator and polymerization by x-rays (*41*) and γ-rays (*8*).

The most widely used initiator systems for acetaldehyde polymerization contain aluminum alkyls and zinc alkyls modified with water, alcohols, and amines (*14, 15, 24, 25, 37, 39, 42, 44, 47*).

Elastomeric polyacetaldehyde is amorphous and "atactic." High resolution NMR studies were carried out in order to determine the actual tacticity of the polymer (*4, 5, 23*). Polyacetaldehyde consists mainly of heterotactic sequences; isotactic sequences are also present in the polymer. The ratio of heterotactic to isotactic varies, but it is usually between 2–3:1. A detailed description of the tacticity determination by high resolution NMR will be given in a subsequent paper by Goodman and Brandrup (*23*).

Other polyaldehydes, such as poly-*n*-butyraldehyde, can also be obtained as amorphous polymer with cationic initiators, although an increase in the bulkiness of the side chain facilitates the formation of stereoregular polymers or at least increases the regularity of the polymer.

Polyacetaldehyde has fairly low thermal and oxidative stability as compared with other polymers (*12, 55*). This was one of the main reasons for the lack of interest in this polymer. The stability of polyacetals depends in general upon the purity of the polymer, the kinds of impurities in the polymer, and the nature of the end groups. All these points are essential for effectively stabilizing polyacetaldehyde.

The thermal stability of elastomeric polyacetaldehyde could be improved by end-capping the hydroxyl end groups with acetic anhydride in order to prevent chain unzipping. Further stabilization was obtained by adding polyamide as a thermal stabilizer and an aromatic amine antioxidant.

The above samples had a $k_{111^\circ \text{C.}}$ of 0.01%/min. and a $k_{138^\circ \text{C.}}$ of 0.1%/min. when the degradation rate of stabilized polyacetaldehyde samples was measured isothermally in a nitrogen atmosphere at 11° C. and 138° C.

Table III. Mechanical Properties of Elastomeric Polyacetaldehyde

Temperature, ° C.	*Tensile Strength, p.s.i.g.*	*Ultimate Elongation, %*
23	25–27	580
–10	170	15
–40	990	11

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Stablized polyacetaldehyde was compression molded at 105° C. and 5,000–10,000 p.s.i.g. into about 100-mil films, and some mechanical properties were measured. The tensile strength and ultimate elongation of polyacetaldehyde is typical for an uncured elastomer, and recovery was good even at high elongations. The samples were measured at different temperatures as seen in Table III. The drop in elongation and increase in tensile strength suggest a transition point around −10° C.

Internal friction measurements have also been carried out on amorphous polyacetaldehyde and showed a main amorphous transition at −18° C. Poly-*n*-butyraldehyde had a transition at room temperature (Figure 1).

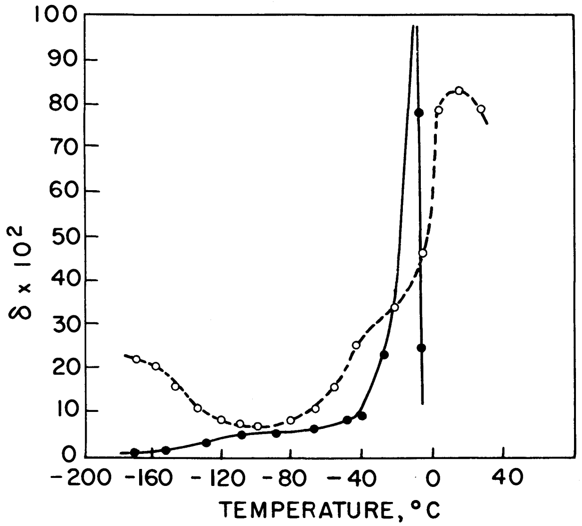

Figure 1. Internal friction of polybutyraldehyde (broken curve) and polyacetaldehyde (solid curve)

Aldehydes like olefins were expected to be capable of undergoing stereoregular polymerization. Crystalline polymers of acetaldehyde and higher aldehydes, later proven to be isotactic (*35*), have been prepared at low temperatures with both anionic and cationic initiators. It is much easier to prepare crystalline polyaldehydes with anionic initiators. Alkali metals, alkali metal alkoxides, Grignard reagents, butyllithium, and Ziegler-type initiators gave high yields of isotactic polymers.

Table IV gives an example of our own work on the polymerization of a number of higher aldehydes. Potassium triphenylmethoxide—a soluble initiator—polymerized a number of higher aldehydes to crystalline isotactic polyaldehydes. Table V lists a number of alkali alkoxides and other related compounds used as initiators for the *n*-butyraldehyde polymerization. Neither the type of the alkoxide nor the cation is of any great importance for the polymerization rate, the polymer yield, and stereoregularity of the resulting polyaldehyde as long as the initiator is adequately soluble in the reaction mixture.

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Table IV. Polymerization of Aldehydes to Crystalline Isotactic Polymers[e]

Aldehyde	*Yield*
Acetaldehyde	+++[a, d]
Propionaldehyde	+++
n-Butyraldehyde	+++
Isobutyraldehyde	+++
n-Valeraldehyde	+++
n-Heptaldehyde	+++
n-Octaldehyde	++[b]
Chloral	+++
3-H-Perfluoropropionaldehyde	+++
Phenylacetaldehyde	+++
3-Methoxy-propionaldehyde	+++
Cyclohexaldehyde	+[c]

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[a] +++ = > 75% yield
[b] + = 20–25% yield
[c] + = traces
[d] 72% total; 45% crystalline
[e] Initial reaction temperature, −75° C., initiator, potassium triphenylmethoxide; solvent, propylene; solvent: monomer ratio, 4:1

Table V. Alkali Metal Initiators Used in This Work

Anion	*Lithium*	*Sodium*	*Potassium*	*Cesium*
Methoxide	x(0)	x(0)	–	–
Ethoxide	x	–	–	–
Isopropoxide	x	x	–	–
n-Butoxide	x	–	–	–
sec-Butoxide	x	x	x	–
tert-Butoxide	x	x	x	–
Cyclohexoxide	–	x	x	–
Benzoxide	–	x	x	–
Diphenylmethoxide	–	x	x	–
Triphenylmethoxide	x	x	x	x
Phenoxide	–	x(0)	–	–
Benzophenone Ketyl	–	x	x	–
DMF	–	x	x	–
Acetylacetonate	–	–	x	–
Butyl	x	–	–	–
Alkalimetal	x	x	x	x

—Journal of Polymer Science

x = Used as initiator, polymerization occurred.
x(0) = Used as initiator, no polymerization.
– = Was not prepared.

Good yields of polyaldehydes are favored in solvents of low dielectric constant. For this reason, aliphatic hydrocarbons are the "best" solvents. However, polymerizations were also carried out effectively in aromatic hydrocarbons and monoethers. An increase in the dielectric constant of the reaction medium (Figure 2) causes a marked decrease in polymer yield. This seems to indicate that the polymer-monomer equilibrium is shifted toward the monomer. In the case of dielectric constants substantially higher than 10 (acetonitrile), no polymerization is observed. This may either mean that the cation is highly

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complexed and is not capable of bringing new monomer to the growing chains or that the ion pair of the growing polymer end is incapable of growth because of dissociation.

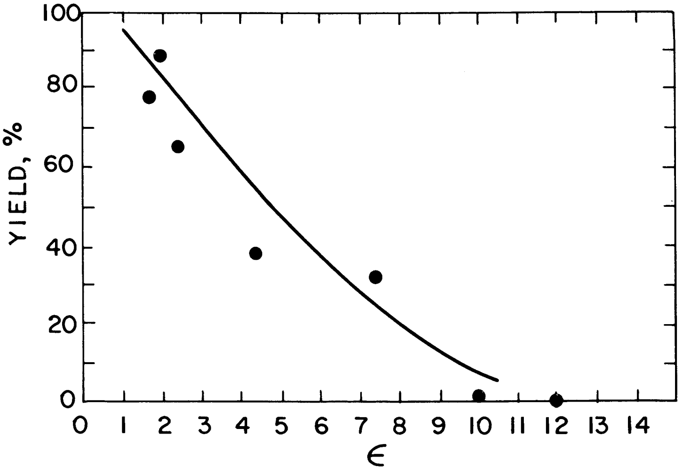

Figure 2. Influence of the dielectric constant ε of various solvents upon the polymerization of n-butyraldehyde. Initial reaction temperature, −75° C.; time, one-half hour; initiator, potassium triphenylmethoxide (0.13 mole %); solvent, n-butyraldehyde (ratio, 4:1)

Polymerization of aldehydes can be accomplished only at low temperatures. The influence of temperature on aldehyde polymerization initiated by potassium triphenylmethoxide is shown in Figure 3 with *n*-butyraldehyde as the example. At −78° C. the polymerization goes to high conversions (95%); the conversion decreases substantially with increasing temperature. No polymerization is observed above −15° C.

Rate of aldehyde polymerization was studied at −75° C. Figure 3 shows that polymerization commences rapidly and is two-thirds complete in 5 minutes; in 10 minutes equilibrium is reached at around 95–97% conversion.

Typical cationic initiators such as BF_3·etherate and $SnBr_4$ also gave isotactic polymers as a relatively small portion of the total polymer in addition to "atactic" polymer of varying stereoregularity.

Aluminum organic compounds play a very important role in aldehyde polymerizations. Furukawa and other Japanese workers have investigated extensively aluminum organic compounds as initiators. Polyaldehydes of a wide range of stereoregularity from completely amorphous to almost 100% isotactic polymers, have been obtained. Aldehyde polymerizations initiated with aluminum alkyls gave essentially atactic polyaldehydes. Substituting alkyl groups in triethylaluminum by reaction with alcohols or amines modifies the initiators to give polymers of higher stereoregularity (*20*). Increasing stereoregularity of the polyaldehydes was particularly noticed when the alcohols were very bulky, as for example borneol as compared to methanol (*20*).

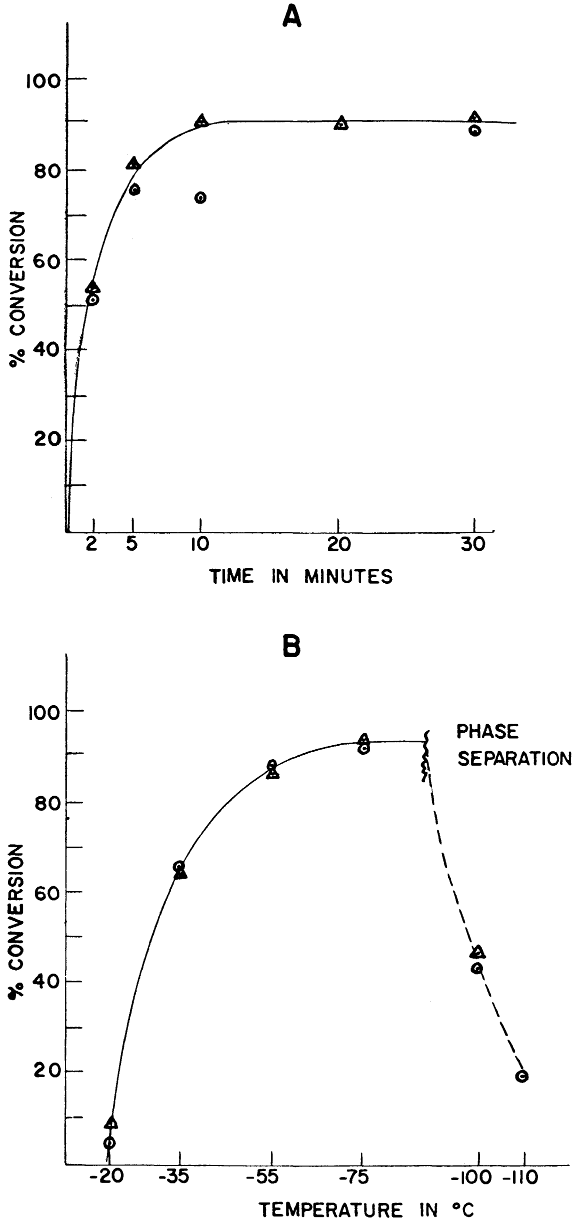

Figure 3. Conversion in n-butyraldehyde polymerizations; potassium triphenylmethoxide (0.2 mole %) as initiator in 25% pentane solutions; Δ = by gas chromatography, O = isolated and weighed. A = time dependence of conversion at −75° C. B = temperature dependence of conversion after 10 minutes reaction time

The same initiator and the same reaction conditions do not always form the same degree of regularity in all aldehyde polymers. Bulky side groups, such as in the case of *n*-heptaldehyde or isobutyraldehyde, favor the formation of polymers of higher crystallinity and presumably higher stereoregularity.

Natta and co-workers (*35*) have shown by careful x-ray investigation that crystalline polyaldehydes are isotactic polymers crystallizing in a four-fold helix with an identity period of 4.8 A. (Figure 4).

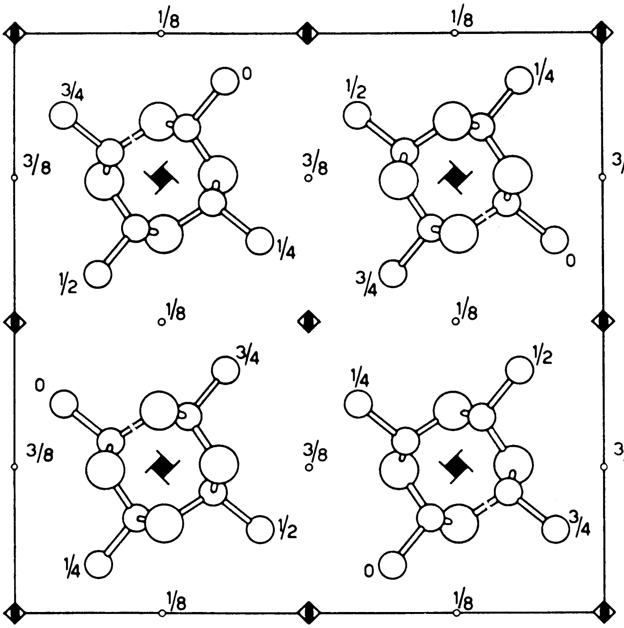

Figure 4. Model of isotactic polyacetaldehyde. Projection on (001). (From J. Furukawa and T. Saegusa, "Polymerization of Aldehydes and Oxides," Interscience Publishing Co.).

Like atactic higher polyaldehydes, the isotactic polyaldehydes are also unstable even at room temperature. However, end-capping rendered them stable to higher temperatures and permitted extensive purification and characterization of the polymers (*50, 51, 52*).

Most isotactic polyaldehydes are insoluble at room temperatures but are soluble at elevated temperatures in some solvents. We have studied the gel point, which is a measure of polymer solubility. A number of polyaldehydes were investigated in tetrahydronaphthalene; polyformaldehyde has the highest gel point observed—namely, about 200° C. For the series of unbranched polyaldehydes the gel point decreases with the increasing length of the aliphatic side chain (Table VI) and parallels the melting points of the polymer.

Aromatic hydrocarbons with aliphatic side chains of a certain chain length are solvents for poly-*n*-butyraldehyde at elevated temperatures as are partially

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or completely hydrogenated cyclic hydrocarbons and higher boiling halogenated olefins (Table VII).

Table VI. Gel Points of Isotactic Aldehyde Polymers in Tetralin: 5% Solids

Polymer	*Gel Point, ° C.*
Formaldehyde	200
Propionaldehyde	85[a]
n-Butyraldehyde	130
Isobutyraldehyde	185
n-Valeraldehyde	85
n-Heptaldehyde	30
n-Octaldehyde	<20
n-Butyraldehyde/Isobutyraldehyde	150

—Journal of Polymer Science

[a] This sample was of distinctly lower crystallinity.

Table VII. Solvents for Acetate End-Capped Poly-*n*-Butyraldehyde

Solvent	*Solution Temperature, ° C.*	*Gel Point, ° C.*
Norbornene	b.p.	m.p.
p-Diethylbenzene	105	55
tert-Butylbenzene	140	70
Tetrachloroethylene	b.p.	70
Decahydronaphthalene	165	80
Dihydrocyclopentadiene	140	80
Trichloroethylene	b.p.	80
p-Cymene	170	100
Dibenzyl	150	120
p-Xylene	b.p.	130
Tetrahydronaphthalene	160	130
Naphthalene	b.p.	150

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The solution temperature indicates the temperature at which the polymer had completely dissolved (2% solids). Gel point in this table is the temperature at which the first noticeable cloudiness is observed.

Solution viscosities were determined at elevated temperatures on purified polyaldehyde samples, and inherent viscosities as high as 0.85 have been obtained. Isotactic poly-*n*-butyraldehyde solutions in purified tetrahydronaphthalene are stable in the viscometer at 140° C. for at least 2 hours.

The inherent viscosity values have been compared with end group determinations of the acetate end groups of completely acetylated poly-*n*-butyraldehyde. For this purpose, the intensity of the carbonyl band of the acetate end groups (5.72 μ) was determined by infrared and was related to an internal standard giving what we call the end group ratio $(I_{5.72\,\mu}(/I_{4.75\,\mu})$. The end group ratio was plotted against the inherent viscosity to give a comparison of the end group "molecular weight" with the inherent viscosity (Figure 5). The

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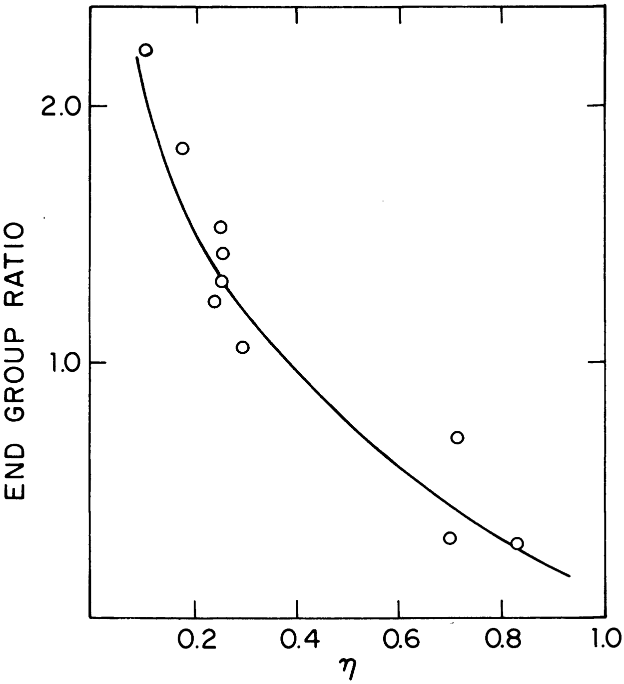

Figure 5. Solution viscosity vs. end group relationship for poly-n-butyraldehyde. The inherent viscosity was measured in 0.5% tetrahydronaphthalene at 140° C. Cold pressed wafers (0.2mm.) of completely acetate, end-capped, and refined poly-n-butyraldehyde samples were used for the infrared determinations

end group ratio of a polyaldehyde sample is easily determined, and tedious purification procedures to prepare a polyaldehyde sample that is stable to the conditions of a solution viscosity determination can be avoided.

Isotactic polyaldehydes melt (with some decomposition) at a somewhat higher temperature than the corresponding olefin polymers (Table VIII) (*7*), particularly in the higher members of the homologous series. Like isotactic polyolefins, branched isotacting polyaldehydes melt substantially higher than the corresponding unbranched polymers.

Optically active polyaldehydes possessing optically active side chains, such as poly-(R)(+)-citronellal, poly-(R)(+)-6-methoxy-4-methylhexanal, and poly-(S)(+)-2-methylbutanal, have been prepared by Goodman (*1*, 22). The optical activity of the polymers was enhanced as compared with their model compounds. It was concluded that the enhancements of the optical activity arose from a conformational rigidity around the asymmetric center in the side chain of the polymer. From degradation studies of the polymers it was concluded that the optical activity of the monomer was unchanged, and no racemization had occurred during polymerization and degradation.

The cyclopolymerization of 1,6-dienes has its counterpart in dialdehyde polymerization as shown by Overberger *et al.* (*40*), Aso and Aito (*2*, *3*, *33*), and

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Table VIII. Melting Points of Crystalline Isotactic Polyaldehydes

Temperature = ° C.

Monomer	*Polyaldehyde* *X = 0*	*Polyolefin* *X = CH₂*
$CH_3CH = X$	165[b]	165
$CH_3CH_2CH = X$	185[a]	125
$CH_3(CH_2)_2CH = X$	225[a]	75
$CH_3(CH_2)_3CH = X$	155 (85°)	None
$CH_3(CH_2)_5CH = X$	150 (75°)	None
$CH_3(CH_2)_6CH = X$	35	None
$(CH_3)_2CH \cdot CH = X$	> 260 (dec)	310
$HCH = X$[c]	178	137

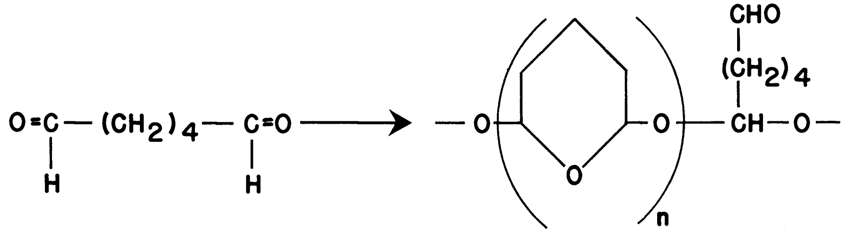
—Journal of Polymer Science

[a] With some decomposition

[b] Uncapped sample

[c] Added for comparison

others. Glutaraldehyde and 3-substituted glutaraldehydes (*3, 31*) polymerized to polyacetals containing mainly tetrahydropyrane rings and only a small amount of a polymer with pendent aldehyde groups.



Copolymers of higher polyaldehydes have only recently been investigated more intensively. Copolymerization of acetaldehyde with formaldehyde gave an elastic copolymer when *iso*-Bu_3Al was used as the initiator (*30*). A number of higher aldehydes could be incorporated into polyacetaldehyde by copolymerization, using BF_3 as initiator (*11*), to give amorphous copolymers. Crystalline, probably isotactic copolymers have been reported. Comonomers used were acetaldehyde, propionaldehyde, *n*-butyraldehyde and isobutyraldehyde (*46, 50, 51, 52*). All these copolymers appear to be random copolymers. Block copolymerizations have been carried out using living olefin and vinyl polymers as initiators and continuing the polymerization with an aldehyde as the second monomer (*13, 38, 45*). Copolymerization of higher aldehydes with ketenes to give polyesters has also been described (*32*).

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7

Symmetry and Repetition Theory in Classifying Stereoregular Polymers

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A general and precise description of stereoisomerism in polymers is suggested on the basis of the repetition theory which describes the distinct patterns along a line that can be obtained from a three-dimensional motif. The probability models for describing the stero-sequence length in various possible cases of interest in stereoregular polymers are discussed. It is shown that for describing the stereosequence structure, the simplest probability model must involve a Markov chain with four probability parameters.

In considering the structural regularity of polymers, it is important to distinguish between two types of isomerism that may be possible for the repeating unit in the polymer chain: geometrical isomerism and stereoisomerism. Geometrical isomerism arises from the possibility of two or more distinct geometrical arrangements of the repeating chemical unit. The high cis or high trans polydienes, even though commonly referred to as stereoregular polymers, refer to this type of geometrical regularity of the repeating monomer units.

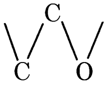
Stereoisomerism, on the other hand, arises primarily because of the two or more distinct ways in which adjacent repeat units containing asymmetric groups can be superimposed. The stereoregular isotactic and syndiotactic polymers are examples of this type of isomeric structures. The repeating structural unit in some polymers may exhibit both stereo and geometric types of isomerism.

Classifying Stereoisomerism in Polymers on the Basis of Repetition of a Three-Dimensional Motif

The well known rule for classifying stereoregular polymers states that in isotactically regular polymers the substituent groups on the asymmetric carbons of the repeating units are oriented similarly either above or below

In Elastomer Stereospecific Polymerization; Johnson, B., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

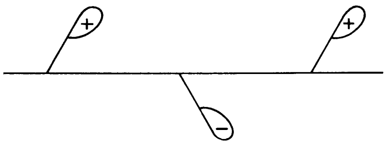
the plane of the extended zig-zag chain of the polymer; in syndiotactically regular polymers the substituent groups on adjacent repeat units are alternately above and below the plane of the extended zig-zag chain of the polymer. This simple rule for classifying the stereoregular polymers is applicable to the extended polymer chains of substituted olefins like propylene, styrene, etc. This rule, if applied for example to the stereoregular polymers from propylene oxide, will lead to an erroneous conclusion. In isotactic polypropylene oxide, as will be clear from the discussion in this paper, the methyl groups attached to the asymmetric repeating units are alternately above and below the plane of



zig-zag chain.

A stereoregular polymer chain in its fully extended form can be considered as having the symmetry associated with a line group (*3*). A precise and general basis for classifying the stereoregular polymers can therefore be developed by considering the abstract problem: What are the distinct patterns that can be generated by repeating a three-dimensional motif along a line (*3*)? This consideration not only provides a general and precise method for classifying stereoregular polymers but also emphasizes the symmetry between adjacent monomer repeat units. Further, it suggests a convenient notation for the theory (*1*) used to characterize stereosequence length in polymers.

All the patterns that can be generated by repeating a three-dimensional motif along a line fall into two, and only two, classes. One general class of such patterns is shown in Figure 1. The + and − signs in Figures 1 and 2 represent the projection of the motif above and below the plane of the paper. The characteristic feature of this class of patterns is that it can be generated by rotation of the motif through a specified angle (here 180°) and translation by a repeat distance. No additional symmetry operations are needed. Adjacent motifs in such patterns may be designated as being related by Proper Rotation.



Equivalent Figures

Figure 1. Repetition of a three-dimensional motif by Proper Rotation and translation

The second class of patterns that can be obtained by repeating a three-dimensional motif along a line is shown in Figure 2. The patterns of this class are generated by: (a) rotating the motif through a certain angle; (b) reflecting it in a plane and then translating by a repeat distance. They cannot be generated without using a mirror plane. In the schematic pattern shown in Figure 2 the angle of rotation is 0°. We shall designate the adjacent motifs in such patterns as being related by Improper Rotation.

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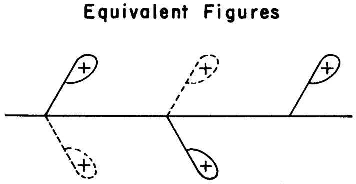
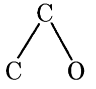
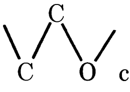


Figure 2. Pattern of a three-dimensional motif by repetition along a line by Improper Rotation and translation; angle of rotation = 0.

In the abstract sense the asymmetric monomer repeat unit may be considered a three-dimensional motif, and the polymer chain may, in this sense, be considered as the repetition of this motif along a line. The relations of symmetry between adjacent three-dimensional motifs in the two general patterns that can be generated by repetition along a line provide a general and precise basis for classifying stereoregular polymers. This basis is that the adjacent monomer units are in isotactic placement if these can be superimposed by Proper Rotation, and they are in syndiotactic placement if superposition can only be made by Improper Rotation. The stereoregular polymers contain sequences of monomer repeat units in isotactic or syndiotactic placements.

Stereoregular Structures of Polypropylene Oxide

The enumeration and geometry of the possible stereoregular structures of polypropylene oxide illustrate the value of the above concepts of symmetry. Propylene oxide monomer has a truly asymmetric carbon, and the repeat unit in the polypropylene oxide chain can be either of the two optical isomeric forms. Further, in the skeletal repeat unit , either of the two carbons can be asymmetric centers. These considerations and the symmetry relations between adjacent repeat units in stereoregular polymers show: (1) there are four nonsuperimposable planar structures of isotactic polypropylene oxide if the direction along the polymer chain is fixed; (2) the methyl groups in the isotactic planar structure are alternately above and below the plane of the  chain. The four planar isotactic structures of polypropylene oxide may be designated for convenience as *d* (up), *d* (down), *l* (up) and *l* (down) isotactic structure (*12*). The *d* (up) and *d* (down) structures are superimposable by turning the polymer chain end-over-end; so are the *l* (up) and *l* (down) structures. In crystallization of isotactic polypropylene oxide obtained from polymerization of racemic monomer, all the four chain structures may be able to fit together in the crystal without a serious packing difficulty because the oxygen and methylene groups are isoelectronic and are of similar size (*12*).

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Stereosequence Distribution in Stereoregular Polymers

There is increasing evidence that, except for special cases, the majority of stereoregular polymers does not consist of either purely isotactic or purely syndiotactic placements of the monomer unit in the chain. Sequences of one stereoisomer interspersed with sequences of random placements represent perhaps more closely the general situation in stereoregular polymers. In the case of polypropylene oxide (*1*), the stereosequence length greatly depends on the catalyst used in the polymerization. In order to characterize the stereostructure, (i.e., distribution of stereosequence lengths) of the polymer chains, it is necessary first to select a probability model which will satisfactorily describe the various possible cases of interest in stereoregular polymers. For this purpose we adopt the following notation, first suggested by Gornick (7), for describing the symmetry superposition relation between adjacent monomer repeat units in the chain: When two adjacent monomer repeat units are in isotactic placement, we shall say they are related by a +; when they are in syndiotactic placement, we shall represent these as related by a –. In terms of this notation, a string of + represents a polymer chain which is completely isotactic, while a string of – represents a chain consisting of only syndiotactic placements.

Several probability models have been suggested for characterizing stereosequence length and relating it to the polymerization (*4, 7, 9, 10, 11*). However,

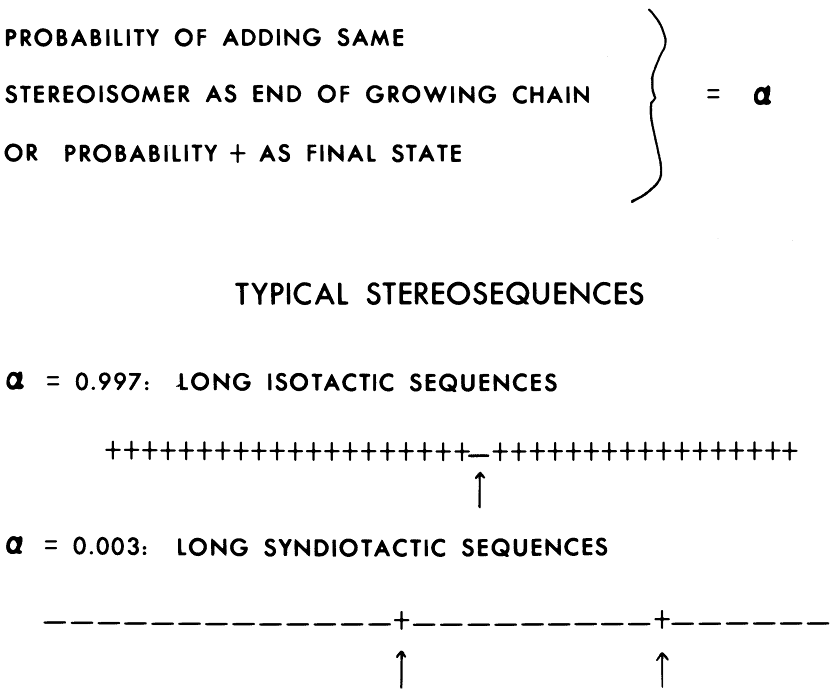

Figure 3. Chain stereostructures described by one-parameter model

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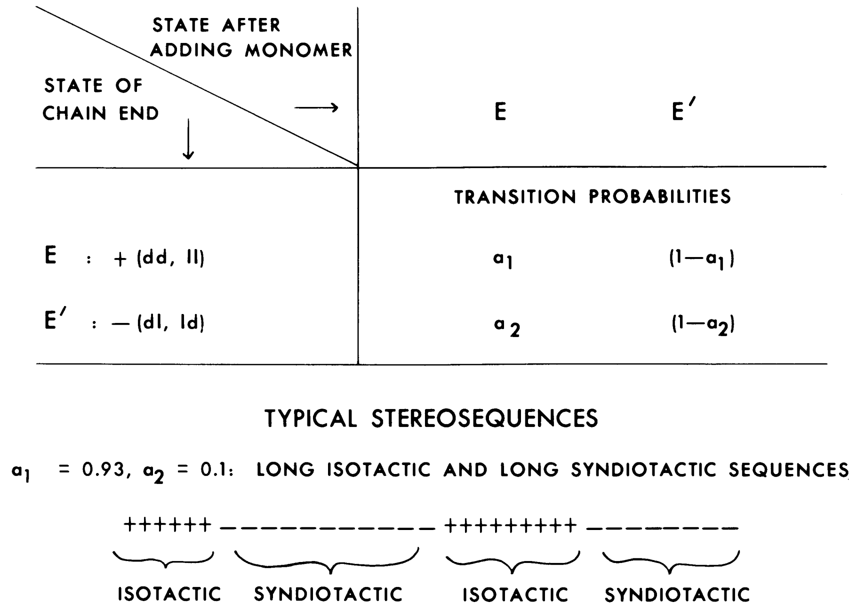

Figure 4. Chain stereostructures described by two-parameter model

the limitations of the various probability models in describing the stereostructure of the polymer chain with sufficient generality have not been fully appreciated.

The simplest probability model is the one-parameter model as used by Coleman (*4*) and Newman (*10*) based on the preferred probability α, such that after adding a monomer to the growing chain, the chain end is in + state. The typical stereostructures that can be described by this model are shown in Figure 3.

If the value of this probability parameter is $\alpha \simeq 1$, an essentially isotactic structure is obtained. If, on the other hand $\alpha \simeq 0$, almost all the monomer units in the chain are in syndiotactic placements. If the polymer is capable of crystallization and the crystallization takes place under equilibrium conditions, then the limitation of this model is that a small melting point depression implies also a high degree of percent crystallinity. Although there are a number of systems, for example stereoregular methyl methacrylate (*2*, *8*), in which this is true and this model is valid, this is not the case for polymers of propylene oxide from different catalysts that we discuss in another chapter (*1*).

A two-parameter model represents the case where the probability of the final state of the growing chain depends upon the configuration of the last two units after a monomer unit is added. The probability parameters and some of the typical structures that can be described by this model are given in Figure 4. In this model α_1 is the probability that a growing chain end in the + state will continue to be in + state, after a monomer unit is added; α_2 is the probability that a growing chain end in the − state will result in the +

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state after a monomer unit is added. As shown in Figure 4, for typical values of the parameters α_1 and α_2 this model is suitable for describing chains containing blocks of isotactic and syndiotactic placements such as those in some samples of polymethyl methacrylate (*2, 6, 8*). From this two-parameter model it follows that a polymer chain can have long nonisotactic sequences only by having long syndiotactic sequences. Thus, the chain structures in which long stereosequences are interspersed by long atactic sequences cannot be described by this model. For some crystalline fractions of polypropylene oxide (*1*) with a relatively high melting point and yet a low degree of crystallinity, this model would imply that a polymer with predominantly syndiotactic structure crystallizes in isotactic structure. This model is therefore not sufficiently general to represent the stereostructures of polymers.

The simplest statistical model which is sufficiently general to represent the sequence distribution in propylene oxide polymers and other polymers of similar structure is one in which the configuration of the last three monomer units in the chain determine the configuration of the next unit coming onto the chain. The configuration of the triad of three successive units may take on eight possible arrangements as given in Table I. However, since the stereoregularity of a chain is really defined in terms of the relative rather than the absolute configuration, the number of configurations of the triad of three successive units which are of interest in considering stereosequence structure reduces to four. There are thus four states of a triad which are of interest in considering stereosequence structures. The addition of the next unit may be thought of as leading to a new triad, consisting of the last two units plus the unit added. Each state of the system can thus be thought of as passing on to a new state of the system with a given transition probability. Since there are four original states of the system, we have the transition probabilities (Figure 5) that each of the states given at the left pass into one of the states given at the right. Thus, this statistical model involves a Markov chain (*5*) with four parameters.

Table I. Configuration Triads of Three Successive Units

E_1		E_2	
DDD LLL	+ +	DDL LLD	+ −
E_3		E_4	
DLL LDD	− +	DLD LDL	− −

+ = Isotactic Placement: (DD, or LL)
− = Syndiotactic Placement: (DL, or LD)

Stereostructures for some typical values of the four probability parameters α_1, α_2, α_3, and α_4 are given in Figure 6 to show that by properly choosing values of the transitional probabilities, the stereostructure of the chains can be represented with sufficient generality.

This model is used to develop a theory which permits us to characterize the average sequence length of the isotactic and uncrystallizable units in propylene oxide polymers made with different catalysts (*1*).

FOUR PARAMETER MODEL

STATE OF CHAIN END ↓ \ STATE AFTER ADDING MONOMER →	E_1	E_2	E_3	E_4
	← TRANSITION PROBABILITIES			→
E_1 : ++ (ddd, lll)	a_1	$(1-a_1)$	0	0
E_2 : +— (ddl, lld)	0	0	a_2	$(1-a_2)$
E_3 : —+ (dll, ldd)	a_3	$(1-a_3)$	0	0
E_4 : —— (dld, ldl)	0	0	a_4	$(1-a_4)$

Figure 5. Matrix of transition probabilities in four-parameter model

$a_1 = a_2 = 0.95$

$a_3 = a_4 = 0.05$

$a_1 = 0.95$

$a_2 = a_3 = a_4 = 0.5$

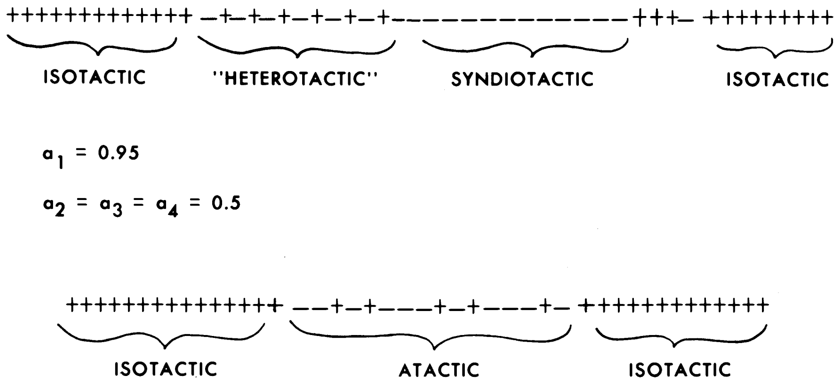

Figure 6. Stereoregular structures of polymer chains described by the four-parameter model

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8

Characterizing Stereosequence Length of Propylene Oxide Polymers from Different Catalysts

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A general theory for characterizing the stereosequence length in stereoregular polymers by using the polymer melting point and degree of crystallinity is presented. The method is applied to determine the isotactic stereosequence lengths of polypropylene oxide polymers prepared from the following catalyst systems: (1) ferric chloride; (2) diethyl zinc and water; (3) diethyl zinc-water and isopropylamine. The stereosequence length of isotactic units in polypropylene oxide from ferric chloride catalyst is considerably longer than those in polypropylene oxide from the diethyl zinc-water and diethyl zinc–water-isopropylamine catalyst systems. The stereosequence lengths of isotactic units in polypropylene oxide fractions from diethyl zinc-water and diethyl zinc–water-isopropylamine are approximately equal, but the lengths of atactic sequences differ appreciably.

A number of catalyst systems have been described (*4, 10, 14, 16, 17, 19, 21*) which result in stereoregular polypropylene oxide. Propylene oxide polymers prepared with different catalysts differ not only with respect to the weight percent of the stereoregular fraction, but also with respect to the distribution of the stereosequence lengths in their crystalline fractions. Characterizing the sterosequence length in the propylene oxide polymers made with different catalysts is important because it is very likely that the elastomeric copolymers made with different catalysts have the same relative differences in the stereosequence lengths of propylene oxide units as do the homopolymers. Characterizing the

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stereosequence length in copolymers of propylene oxide is not possible at the present time.

This paper describes the theory which permits us to characterize adequately the stereosequence length in stereoregular polymers from the equilibrium percent crystallinity at room temperature and from the melting points of the polymers. Results based on this theory are given on the characterization of the isotactic stereosequence length in the "crystalline" fractions of polypropylene oxide polymers made from the following catalyst systems: (a) ferric chloride (*17, 19*); (b) diethyl zinc-water (*10*); (c) diethyl zinc-water-isopropylamine; (d) diethyl zinc-water-cyclohexylamine (*14*).

The stereoregularity—i.e., distribution of the stereosequence length in these polymers—has a marked effect on the crystallization rates and the morphology of the crystalline aggregates. These differences, in turn, influence the dynamic mechanical properties and the temperature dependence of the dynamic mechanical properties. In order to interpret any differences in the dynamic mechanical properties of polymers and copolymers of propylene oxide made with different catalysts, it was interesting to study the differences in the stereosequence length in the propylene oxide polymers made with a few representative catalysts.

Results and Discussion

Outline of Theory to Characterize Stereosequence Length. In a previous paper (*1*) it was shown that the most general model for describing the stereoregular structure of a polymer molecule involves a Markov chain (*18*) in which the steric configuration of an oncoming group is determined by the configuration of the three previous monomer units. The sequence distribution of such a model would be characterized by four independent parameters corresponding to the various possible transition probabilities, α_{ij}, that a given triad, E_i, be followed by a triad E_j.

Although several techniques have been used to characterize stereosequence distribution, we suggest that the percent crystallinity and temperature of melting measurements are more generally applicable than any other technique presently available. Bovey and co-workers (7) showed how NMR measurements can be used to determine the triad distribution in polymers such as polymethyl methacrylate in which there is sufficient difference between the NMR spectra corresponding to syndiotactic, isotactic, and heterotactic triads to allow quantitative measurements to be made. This type of measurement unfortunately is restricted to few systems and would lead to a unique description of the stereostructure of the chain only when a model involving one or two probability parameters is applicable (*See* Appendix I).

On the other hand, the temperature of melting and crystallinity measurement can describe only those stereosequences that crystallize. In propylene oxide polymers which we have studied, for example, isotactic sequences are the only ones that crystallize. Therefore, in these polymers we can determine only the stereosequence length of isotactic units and the average length of the uncrystallizable units. The syndiotactic and atactic sequences in the uncrystallizable blocks are not distinguishable from the crystallinity and melting temperature measurements.

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Two quantities—P_1, the concentration of the isotactic triad and α_1, the probability that an isotactic triad be followed by another isotactic triad—are sufficient to describe the sequence length of the isotactic units. The concentration of the various triad states can be expressed in terms of the various transition probabilities of the four-parameter model discussed previously (*1*). It can be shown that in the expressions for the probabilities of the various triads, the four transition probability parameters occur in such a combination that the concentration of the various triad states like P_1, etc. depend on only two independent parameters (Appendix I).

The two parameters P_1 and α_1 or their equivalents needed to determine the average sequence length of the isotactic crystallizable units can be determined from the melting temperature and the percent crystallinity of the polymer. The probability, $P^+(\xi)$, that a given sequence of +'s is exactly of length ξ is:

$$P^+(\xi) = P_1\alpha_1^{(\xi - 2)}\,(1 - \alpha_1)^2 \tag{1}$$

In this equation P_1 is the probability that any triad taken at random be in the configuration + +; α_1 is the probability that a triad in the configuration + + be followed by a second triad in the configuration + +.

The probability that any given monomer unit be a member of a sequence of exactly $(\xi - 1)$ units all in a + configuration is given by:

$$F(\xi_+) = (\xi - 1)\,P^+(\xi - 1) \tag{2}$$

Equations 1 and 2 completely describe the distribution of all sequences of isotactic units of length greater than 3 in terms of just two parameters, P_1 and α_1. In order to determine these quantities from crystallization data, we have used Flory's theory for the crystallization of copolymers (*9*). Flory's theory is based on the assumption that there is an equilibrium between a sequence of crystallizable monomer units in the amorphous phase and a crystallite of given length. Although this theory may be somewhat naive in terms of the present-day concepts of polymer crystallization, its success in predicting the melting point of copolymers must mean that the resulting equations are essentially correct provided the sequences of crystallizable units are relatively short. In homopolymers or systems involving very long sequences of monomer units, it is quite possible that chain folding might occur and that the thermodynamic conditions in the chain selection process would need modification. In the case of polypropylene oxide, we believe that we are not in serious error in assuming the applicability of the Flory approach.

Flory considers two distribution functions needed to characterize the system. The first is the "initial" distribution, the distribution of crystallizable sequences in the uncrystallized polymer. For stereoregular polymers, as discussed above, this is described by Equation 2. The second distribution function, which is a function of temperature, is the equilibrium distribution which follows from the condition that all sequences of length greater than ξ be in equilibrium with crystallites of each length ξ. Crystallization can occur only at values of ξ for which the initial distribution exceeds the equilibrium distribution. The extent of crystallization depends on the difference between the initial and equilibrium distributions. At any temperature there will exist a critical chain length, ξ_c, below which crystallization cannot occur. For the four parameter model discussed in the previous paper, ξ_c is related as shown in Appendix II, to P_1 and α_1 by the equation:

$$\xi_c = \frac{2 \ln \frac{\theta}{\theta_M} - \ln \frac{P_1}{\alpha_1^2} D}{\theta - \theta_M} \tag{3}$$

Here θ is a reduced temperature given by:

$$\theta = \frac{\Delta H_u}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \tag{4}$$

ΔH_u is the heat associated with the melting of one mole of monomer units, T_0 is the melting temperature of the pure isotactic polymer; θ_M is the value of θ when $T = T_M$ and T_M is the melting temperature of partially isotactic polymer; D is a function of the surface free energy per unit surface associated with the end surfaces of the crystallite.

The weight fraction of crystalline material at equilibrium with the melt at any temperature, as shown in Appendix II, is given by:

$$X = \frac{P_1}{\alpha_1^2} e^{-\xi_c'} \left[1 - A^2 + \xi_c'(1 - A) \right] \tag{5}$$

where $\xi_c' = \theta_M \cdot \xi_c$; and $A = \dfrac{\theta_M}{\theta}$

The parameter α_1 is simply related to the melting point by:

$$-\ln \alpha_1 = \frac{\Delta H_u}{R} \left(\frac{1}{T_M} - \frac{1}{T_0} \right) \tag{6}$$

Equations 3, 5, and 6 show that from the melting point of the polymer and its comparison with that of a polymer which has infinitely long isotactic sequences, we can determine α_1, and from the percent crystallinity at a given temperature we can calculate ξ_c and hence, P_1.

Characterizing the Stereosequence Length of Propylene Oxide Polymers. The samples used in this study were the crystalline fractions of propylene oxide polymers made with various catalysts. Two methods were used to separate the fraction showing crystalline order (as judged from x-ray diffraction patterns) from the amorphous fraction:

(a) Cooling an acetone solution of the polymer at room temperature to −20° C. and maintaining this temperature overnight. The crystalline fraction was centrifuged at −20° C. from the solution in which the amorphous fraction remained dissolved.

(b) Polypropylene oxide was dissolved in isopropyl alcohol at +55° C. and then cooled to 25° C. The crystalline fraction was separated by centrifugation. Both methods gave essentially equivalent separation of the crystalline fraction from the fraction of the material which was either amorphous or had quite a low degree of crystallinity.

The percent crystallinity as a function of temperature was determined from the dilatometrically measured changes in specific volume with temperature. Density of the fractions at 25° C. was measured by the density gradient tube method (*2*). The density of the crystalline material (1.102 grams/cc.) was calculated from the unit cell dimensions (*23*), and the density of the amorphous material (1.003 grams/cc.) was calculated from the temperature *vs.* specific volume curve at temperatures greater than the melting point. Plots of specific volume *vs.* temperature for the four samples used in this study (Figure 1) were obtained from dilatometric measurements. For these dilatometric measurements the samples were sealed in glass dilatometers with mercury as the confining liquid. The samples in the dilatometers were melted at about 35°–50° C. above the estimated melting point and held at this temperature for about 4 hours. The dilatometers were then allowed to cool slowly overnight to

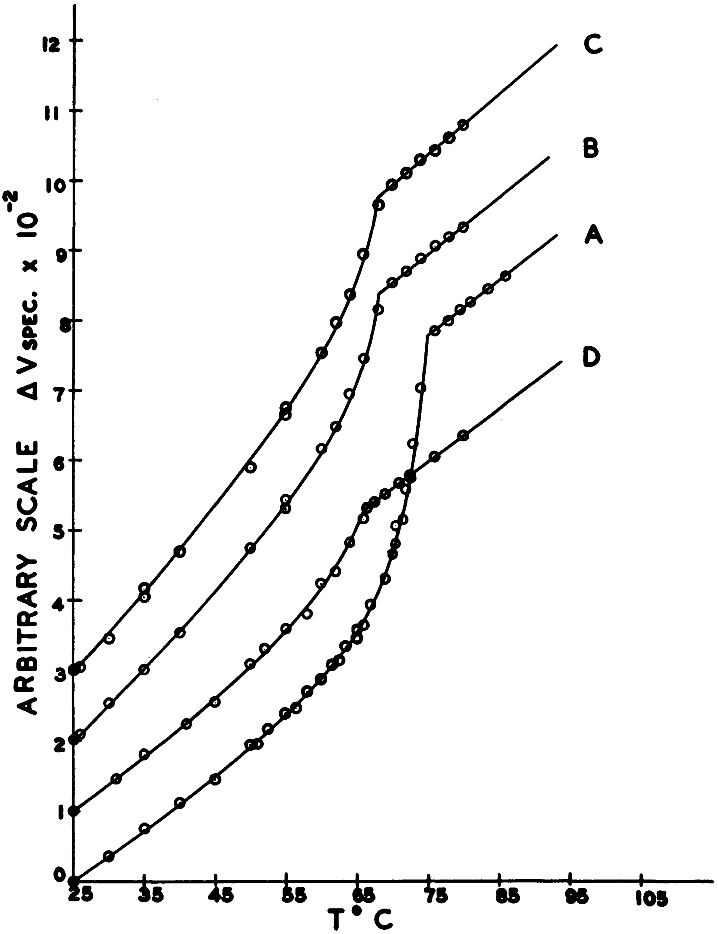

Figure 1. Specific volume change vs. temperature for crystalline fractions of propylene oxide polymers from different catalysts

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Table I. Temperature of Melting and Percent Crystallinity of Crystalline Fractions of Propylene Oxide Polymers from Different Catalysts

Sample	*Catalyst*	*Separation Method*	*Percent Crystallinity*	*Melting Temp, ° C.*
A1	$FeCl_3$	Acetone, R.T.	56	75.8
A	$FeCl_3$	Acetone, –20° C.	49	75
B	$Zn(C_2H_5)_2$-H_2O Cyclohexylamine	Acetone, –20° C.	34	68
C	$Zn(C_2H_5)_2$-H_2O Isopropylamine	Acetone, –20° C.	34	68
D	$Zn(C_2H_5)_2$-H_2O	Isopropyl alcohol, 25° C.	15	66

room temperature. The change in specific volume with temperature was then measured by raising the temperature in steps of about 0.5° C. and holding at each temperature for about one-half hour. In the melting temperature region, 2–3 hours were allowed at each temperature and in some cases overnight. The melting point was taken as the temperature at which the volume-temperature curve became linear. We believe that in samples of comparatively low crystallinity and stereoregular sequence length, the melting points so determined are very nearly the equilibrium melting points. Table I gives the melting temperatures, crystallinity at room temperature, and the catalyst used in preparing these polymers.

The difference in the range of temperature over which melting occurs in these polymers, as seen in Figure 1, is a consequence of the differences in the distribution of crystallite sizes in these polymers. The thermodynamic theory outlined in the foregoing is the theoretical tool which allows us to relate the distribution of crystallite sizes to the distribution of stereosequence length. Table II gives the pertinent parameters as well as the average lengths of the isotactic sequences and non-crystallizable sequences in these polymers. In our calculations we have used value of 75.8° C. for T_0, the melting point of the most crystalline fraction of polypropylene oxide from ferric chloride catalyst, and a value of 2000 cal./mole for ΔH_u, the heat of fusion per mole of monomer unit. It should be noted that even though samples C and D, propylene oxide polymers from $Zn(C_2H_5)_2$-water-isopropylamine and $Zn(C_2H_5)_2$-water respectively, have almost the same melting point and average length of isotactic sequences, there is a considerable difference in the percent crystallinity and the average length of uncrystallizable sequences. This is reflected in the difference in the value of P_1. (The value of 75.8° C. for T_0 is undoubtedly somewhat low. However, this choice should not cause serious error in the value of the parameters α and P_1. Calculations of T_0 from the percent crystallinity, assuming a one parameter model, gave a value of 79° C. This necessarily will

Table II. Stereosequence Length in Propylene Oxide Polymers

Catalyst	*Transition Probability α_1 (++)→(++)*	*Relative Probability of (++) States: P_1*	*Av. Length Isotactic Sequence*	*Av. Length Uncrystallizable Sequence*
$FeCl_3$	0.992	0.710	122	122
$Zn(C_2H_5)_2$-H_2O Isopropylamine	0.93	0.447	14	28
$Zn(C_2H_5)_2$-H_2O	0.92	0.196	12.5	70

be too high and may be regarded as upper bound for T_0. Another value for T_0 in the range of 75.8°–79° C. will not seriously effect the relative values of the parameters for the polymers which are of interest in the present studies.)

Temperature Dependence of Percent Crystallinity. Efficiency of Crystallization and "Car Parking" Correction. In order to use Equation 5 to predict the melting behavior—i.e., the temperature dependence of percent crystallinity—and in order to characterize polymers of a high degree of crystallinity from crystallinity data at temperatures well below the melting point, an additional correction factor is needed. The percent crystallinity of a polymer will usually be less than that predicted by Equation 5. There are several factors which limit the efficiency with which a potentially crystallizable chain is used in crystallization: (a) Under many conditions, if not most, the crystallization process is controlled by kinetic, rather than thermodynamic considerations (*11*); (b) A polymer chain which passes through more than one crystallite will be under strain in the region between crystallites (*22*); (c) There is a limit to the efficiency with which a crystallizable sequence can be used in crystallization. This important limitation on the efficiency of utilizing crystallizable sequences is best expressed by reference to Figure 2. Under the usual conditions of crystallization, an upper bound is expected for the size of crystallites which can be formed at any temperature. If crystallites are randomly placed along crystallizable sequences, there may be sequences left between these crystallites too small to allow further crystallization. This problem has been treated by Gornick and Jackson (*13*). As shown in Figure 2, the problem is analogous to that of parking cars at random along an unmarked curb. If the space between the cars is smaller than the car length, this space is wasted for further

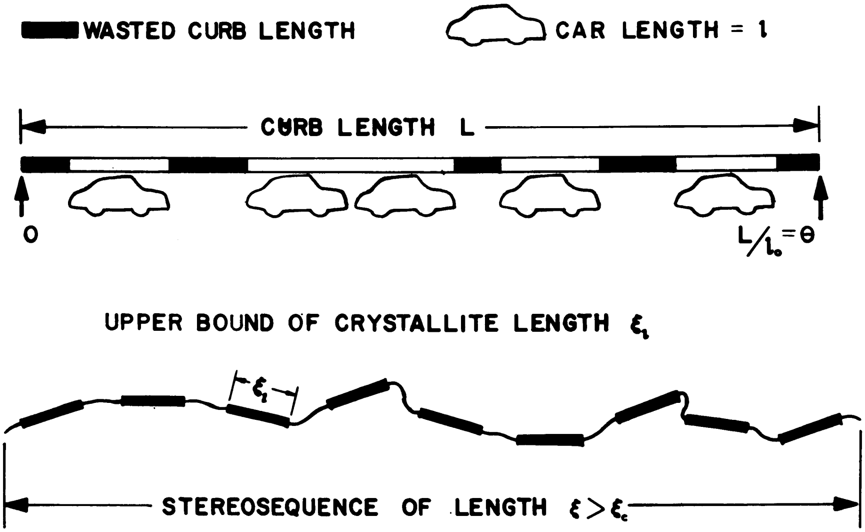

Figure 2. Schematic representation of "car parking" effect and upper bound of crystallite length

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parking. The mathematical problem of parking cars at random along an unmarked curb has been considered by other investigators (*20*). It can be shown that for long curbs the efficiency term corresponding to this process approaches 0.7, while for short curbs it approaches the reciprocal of the curb length. If the curb length is variable, that is, if our sequence distribution is that predicted by the four-parameter statistical model, an average value of the efficiency factor can be found. In Figure 3 we have compared the experimentally determined crystallinity as a function of temperature with that obtained using the four parameter model and that obtained with the four parameter model including the efficiency correction. The excellent agreement between theory and experiment indicates that this correction for the factors that limit efficiency of crystallization is at least qualitatively correct. It should be emphasized that this correction is mainly applicable when the crystallizable sequence is not much longer than the crystallite. It is quite possible that very long sequences will crystallize by a chain folding mechanism. In this case the efficiency of crystallization is also limited so that our efficiency factor may still not be very much in error.

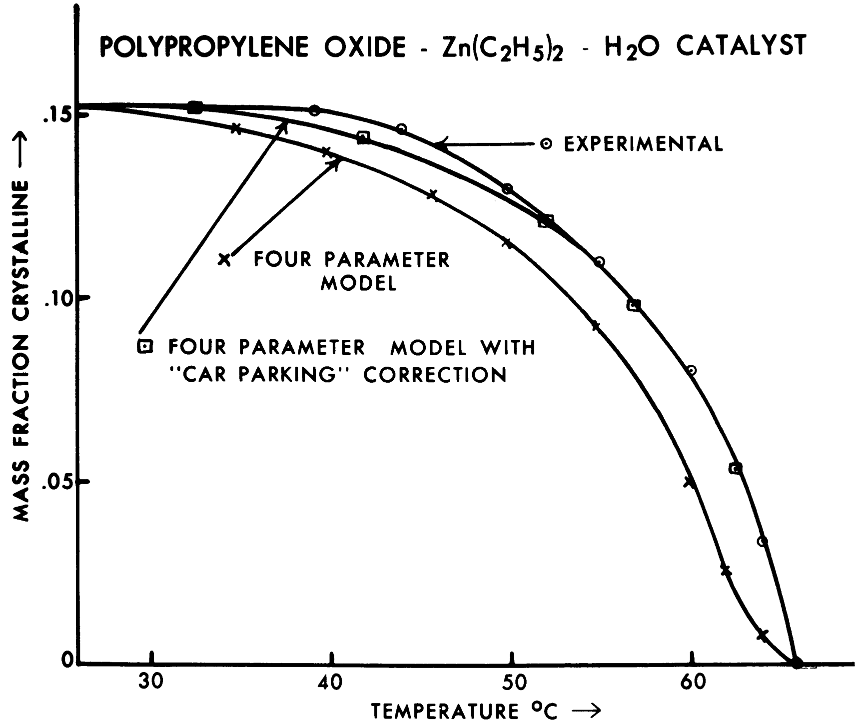

Figure 3. Experimental and theoretical plots of the crystalline mass fraction vs. temperature for a stereoregular polypropylene oxide fraction; X—four-parameter model; ⊡—four-parameter model with "car parking" correction.

Effect of Stereosequence Length On Crystallization Kinetics and Morphology. The length of crystallizable stereosequences and of uncrystallizable sequences

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have marked effect on the texture and morphology of the spherulitic structure and on the isothermal crystallization kinetics of the propylene oxide polymers of different steric regularity.

Figure 4 shows photomicrographs of (a) a polypropylene oxide with long average stereosequence length (Sample A), and (b) a polypropylene oxide with a short stereosequence length (Sample C).

The spherulite formed from the sample with the longer stereosequence has a denser structure with a greater frequency of fibrillar branching than does the other spherulite from the sample with shorter stereosequence. This is in accord with the mechanism of spherulitic crystallization recently proposed by Keith and Padden (*15*).

The stereosequence length also has a marked effect on the isothermal crystallization kinetics of the propylene oxide polymers. These studies and analysis of results on crystallization kinetics will be described in detail in another communication. Here we summarize briefly the main conclusions of the effect of stereosequence length on the isothermal crystallization rates.

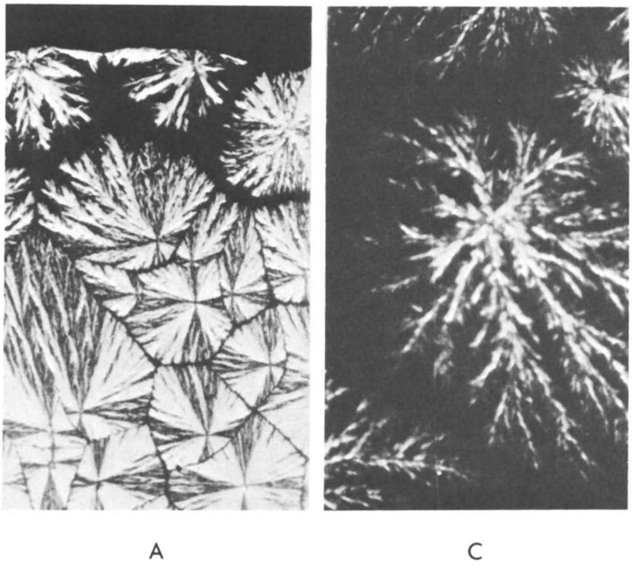

Figure 4. Effect of stereoregularity on texture of propylene oxide polymers at same degree of supercooling $\Delta T = 30°$ C. Sample A with long stereosequence length; sample C with short stereosequence length.

The isotherms obtained in dilatometric measurements of the crystallization rate could be fitted with an Avrami (*3*) type equation only by assuming the existence of a secondary crystallization process much slower than the rate of spherulitic growth observed microscopically, and by taking into account the experimentally determined form of the nucleation rate. The nucleation rate was found to be a first-order process. Assuming that the secondary crystalliza-

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tion was also a first-order process, an excellent fit was found between the crystallization data and the theoretical plot.

The crystallization kinetic results for propylene oxide polymers of different steric regularity are summarized in Table III.

Table III. Effect of Stereoregularity on Crystallization Kinetics of Propylene Oxide Polymers

Catalyst	*Cryst. Temp., °C.*	*ΔT, °C.*	*Primary Crystallization*		*Spherulitic Growth Rate G (cm./min.)*	*Secondary Crystallization*	
			τ_M *min.*	τ_c *min.*		*A*	τ_s/τ_c
$FeCl_3$	45	30	3.5	12.6	8.2	0.26	1.7
	50	25	15	40.2	4.5	0.26	1.7
	55	20	130	170	0.82	0.26	1.7
$Zn(C_2H_5)_2$-H_2O Isopropylamine	38	30	10	19	6.0	0.26	7.6
	43	25	22	40	2.5	0.26	7.6
	48	20	70	92	0.90	0.26	7.6

The primary crystallization process is characterized by three parameters. These are the rate of radial growth of the spherulite, G, the time constant for nucleation, τ_n, and the time constant for the primary crystallization process, τ_c, which is determined from the Avrami equation. All three parameters seem to depend on the stereoregularity of the polymer, but the nucleation rate seems to depend most strongly.

A more important effect of stereoregularity is found by considering the secondary crystallization process. The secondary crystallization process is characterized by two parameters. These are: A, the fraction of the crystallizable material involved in the secondary crystallization process, and τ_s, the time constant for the secondary process. The noteworthy result is that the ratio (τ_s/τ_c) is almost independent of temperature but very sensitive to the stereoregularity of the polymer. The secondary crystallization process is slower for polymers having short stereosequence lengths than for those having longer stereosequence lengths, even though the primary crystallization process is only slightly affected by stereoregularity.

Appendix

I. Relations Between Probability (P_i) of Triad States and Transition Probability Parameters (α_1). The four possible states of three successive monomer units in the polymer chain were defined previously (*1*) as: $E_1 = + +$; $E_2 = + -$; $E_3 = - +$ and $E_4 = - -$; where the + and − define the relative configuration of two adjacent monomer units in the polymer chain. In accordance with the nomenclature of Bovey (*7*), we call the sequence (+ +) isotactic, (+ −), or (− +) heterotactic, and (− −) syndiotactic. The transition probabilities between various states were defined for the four-parameter model (*1*).

Here we derive the relations between the probability of any triad of monomers in a given state in terms of the transition probabilities, and show that the four transition probability parameters occur in such a combination that the concentration of the various triad states depends only on two independent parameters.

The four equations relating the various transition probabilities and the probabilities P_i of any triad being in the state i are:

$$\alpha_1 P_1 + \alpha_3 P_3 = P_1 \tag{I-1}$$

$$(1 - \alpha_1) P_1 + (1 - \alpha_3) P_3 = P_2$$

$$\alpha_2 P_2 + \alpha_4 P_4 = P_3$$

$$(1 - \alpha_2) P_2 + (1 - \alpha_4) P_4 = P_4$$

By adding the last two (or first two) equations, we see that $P_2 = P_3$. From the first and last equations,

$$P_1 = \frac{\alpha_3}{1 - \alpha_1} P_3$$

$$P_4 = \frac{1 - \alpha_2}{\alpha_4} P_2 = \frac{1 - \alpha_2}{\alpha_4} P_3 = \left(\frac{1 - \alpha_2}{\alpha_4}\right)\left(\frac{1 - \alpha_1}{\alpha_3}\right) P_1 \tag{I-2}$$

Defining two parameters u, and v as:

$$u = \frac{1 - \alpha_1}{\alpha_3} \quad \text{and} \quad v = \frac{1 - \alpha_2}{\alpha_4},$$

one gets $P_2 = P_3 = u\, P_1$; and $P_4 = uv\, P_1$. (I-3)
Also, since $\sum P_i = 1$, we obtain

$$P_1 = \frac{1}{1 + 2u + uv} \tag{I-4}$$

The above equations show that although the model contains four independent parameters, the frequency of occurrence of triads are determined by only two independent parameters, u and v. From this it also follows that the condition that the triads have the distribution found by Bovey (*5*, *6*) for methyl methacrylate—i.e., $P_2^2 = P_1 P_4$, is equivalent to $u = v$ and not the more restricted condition $u = v = 1$ which arises from the Bernoulli triad model of Coleman and Fox (*8*).

II. Theory For Determing Parameters In Probability Model For Stereosequence Structure of Polymer Chains From Percent Crystallinity and Melting Temperature. Flory's thermodynamic treatment of the crystallization and fusion of copolymers (*9*) forms the basis for determining the parameters in probability models for stereosequence structure from the percent crystallinity and melting temperature of stereoregular polymers. In the following we give the derivations of Equations 3, 5, and 6 used for evaluating the average length of isotactic sequences. The analysis developed here is similar to that of Gornick (*12*). In order to clarify the theoretical treatment, we summarize also in the following, the important steps and assumptions in Flory's theory (*9*).

At equilibrium between melt and crystallites, the chemical potential of the melt must be equal to the chemical potential of each crystallite. That is, the free energy change on melting one monomer unit should be equal to the product

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of the temperature and the entropy change which occurs on the melting of one unit. As a first approximation, only the entropy of mixing needs to be considered. It follows then, that the probability of finding sequences of length ξ or greater in a melt in equilibrium with a crystallite of length ξ is:

$$P_{\xi} = e^{-\Delta F_{\xi}/RT} \tag{II-1}$$

Here ΔF_{ξ} is the free energy change on melting a sequence of ξ monomer units from a crystallite of length ξ; and

$$\Delta F_{\xi} = \xi \Delta F_u - 2\sigma_e \tag{II-2}$$

Here ΔF_u is the standard free energy change per repeat unit on melting, and σ_e is the surface free energy change per chain at the ends of the crystallite. It can be shown that the surface free energy associated with lateral surfaces may be ignored in the present case.

Also,

$$\begin{aligned} \Delta F_u &= \Delta H_u - T\Delta S_u \\ &= \Delta H_u \left(1 - \frac{T}{T_0}\right) \end{aligned} \tag{II-3}$$

where $T_0 = (\Delta H_u / \Delta S_u$ is the melting point of the pure homopolymer.

Substitution into the equation for P_{ξ} gives:

$$\begin{aligned} P_{\xi} &= \exp\left[-\Delta F_{\xi}/RT\right] = \exp\left[-\frac{\xi \Delta H_u}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{2\sigma_e}{RT}\right] \\ &= \frac{1}{D} e^{-\xi\theta} \end{aligned} \tag{II-4}$$

where $D = e^{-2\sigma_e/RT}$, and $\theta = (\Delta H_u/R)[1/T - 1/T_0]$. The quantity θ can be considered as a reduced temperature scale. We assume, as did Flory, that D has the value of e^{-1}.

To relate the above probability to the composition of the melt, let us consider the following: Let ω_j be the weight fraction of crystallizable monomer units in sequences containing exactly j units. The probability $P_{\xi j}$ that a given unit be in a sequence of exactly j units and be followed by at least $\xi - 1$ crystallizable units is the product of ω_j and the number of possible positions in the sequence of j units which are followed by at least $\xi - 1$ crystallizable units: $(j - \xi + 1/j)$.

If P_{ξ} is the concentration of units of length ξ which can be incorporated into the crystallite,

$$P_{\xi} = \sum_{j=\xi}^{\infty} P_{\xi,j} = \sum_{j=\xi}^{\infty} \frac{j - \xi + 1}{j} \cdot \omega_j \tag{II-5}$$

If crystallites of length ξ, $\xi + 1$, and $\xi + 2$ exist then for three successive values of ξ we may write the recursion formula:

$$P_{\xi} - 2P_{\xi+1} + P_{\xi+2} = \frac{\omega_{\xi}}{\xi} \qquad \text{(II-6)}$$

or,

$$\frac{\omega_{\xi}}{\xi} = \frac{1}{D}\left[e^{-\xi\theta} - 2e^{-(\xi+1)\theta} + e^{-(\xi+2)\theta}\right]$$

Then,

$$\omega_{\xi} = \frac{\xi}{D} e^{-\xi\theta}\left[1 - e^{-\theta}\right]^{2} \qquad \text{(II-7)}$$

This equation defines the distribution of sequence lengths in the melt which will be in equilibrium with the crystallites of size ξ.

The initial distribution ω^0_{ξ} on the other hand, is the distribution of sequences in the uncrystallized amorphous polymer. This initial distribution, ω^0_{ξ}, of course, is determined in the case of stereoregular polymers by the particular statistics and probability parameters applicable to the system.

Crystallization will take place to such an extent as to reduce the initial distribution ω^0_{ξ} to the equilibrium distribution ω_{ξ}, and it can only occur at such lengths for which the initial distribution exceeds the equilibrium distribution. There thus exists at each temperature a critical chain length, ξ_c, the shortest sequence length that can crystallize at this particular temperature.

To demonstrate the procedures to be used to obtain probability parameters from crystallization data, let us consider the distribution which occurs if we have a single parameter model. Under these conditions the equilibrium distribution is,

$$\omega^0_{\xi} = \xi\alpha^{\xi}(1 - \alpha)^2 \qquad \text{(II-8)}$$

where $\alpha = \alpha_1$ and $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4$.

The extent of crystallization at any sequence length is then $\omega^0_{\xi} - \omega_{\xi}$, the difference between the initial and equilibrium distributions. The critical chain length is then given by the condition:

$$\omega^0_{\xi} = \omega_{\xi} \qquad \text{(II-9)}$$

Therefore,

$$\xi_c\alpha^{\xi_c}(1 - \alpha)^2 = \frac{\xi_c}{D} e^{-\xi_c\theta}(1 - e^{-\theta})^2$$

or,

$$e^{(\theta + \ln\alpha)\xi_c} = \frac{1}{D}\left[\frac{1 - e^{-\theta}}{1 - \alpha}\right]^2 \qquad \text{(II-10)}$$

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On solving this equation for ξ_c,

$$\xi_c = \frac{\ln\left[\frac{1}{D}\cdot\frac{1-e^{-\theta}}{1-\alpha}\right]^2}{\theta + \ln\alpha} \qquad \text{(II-11)}$$

If there is no upper bound to the crystallite size, the melting point will be the temperature at which $\xi_c \longrightarrow \infty$, or, $\theta = -\ln\alpha$.
Therefore,

$$\left[\frac{1}{T_M} - \frac{1}{T_0}\right]\cdot\frac{\Delta H_u}{R} = -\ln\alpha \qquad \text{(II-12)}$$

As we shall see, this equation also defines the melting point for a statistical model containing four parameters where we let $\alpha = \alpha_1$.

For the one-parameter model, crystalline weight fraction, X, at any temperature is given by:

$$X = \sum_{\xi_c}^{\infty} (\omega_\xi^0 - \omega_\xi)$$

$$= \sum_{\xi_c}^{\infty}\left[\xi\,\alpha^{\xi}(1-\alpha)^2 - \frac{\xi}{D}e^{-\xi\theta}(1-e^{-\theta})^2\right]$$

$$= (1-\alpha)^2\sum_{\xi_c}^{\infty}\xi\alpha^{\xi} - \frac{(1-e^{-\theta})^2}{D}\sum_{\xi_c}^{\infty}\xi(e^{-\theta})^{\xi} \qquad \text{(II-13)}$$

Evaluating the series gives:

$$X = \alpha^{\xi_c+1}\left[1 + \frac{\xi_c(1-\alpha)}{\alpha}\right] - \frac{1}{D}e^{-(\xi_c+1)^{\theta}}\left[1 + \xi_c\frac{(1-e^{-\theta})}{e^{-\theta}}\right] \qquad \text{(II-14)}$$

For purposes of calculation, this can be further simplified to give:

$$X = \alpha^{\xi_c}\left\{\alpha + \xi_c(1-\alpha) - \frac{1}{D}\frac{e^{-\xi_c^{\theta}}}{\alpha^{\xi_c}}\left[e^{-\theta} + \xi_c(1-e^{-\theta})\right]\right\} \qquad \text{(II-15)}$$

Using the Equation (II-10) for ξ_c, we obtain

$$X = \alpha^{\xi_c}\left\{\alpha + \xi_c(1-\alpha) - \frac{1}{D}\left(\frac{1-\alpha}{1-e^{-\theta}}\right)^2 D[e^{-\theta} + \xi_c(1-e^{-\theta})]\right\}$$

$$= \alpha^{\xi_c}(1-\alpha)^2\left[\frac{\alpha}{(1-\alpha)^2} - \frac{e^{-\theta}}{(1-e^{-\theta})^2} + \xi_c\left(\frac{1}{1-\alpha} - \frac{1}{1-e^{-\theta}}\right)\right] \qquad \text{(II-16)}$$

Recognizing that $\alpha = e^{-\theta_M}$

$$X = (1 - e^{-\theta_M})^2 e^{-\xi_c \cdot \theta_M} \left[\frac{e^{-\theta_M}}{(1 - e^{-\theta_M})^2} - \frac{e^{-\theta}}{(1 - e^{-\theta})^2} + \xi_c \left(\frac{1}{1 - e^{-\theta_M}} - \frac{1}{1 - e^{-\theta}} \right) \right] \qquad \text{(II-17)}$$

Since both θ_M and θ are in general much less than unity, $e^{-\theta_M} \sim 1 - \theta_M$ and $e^{-\theta} \sim 1 - \theta$.

Then,

$$\xi_c \approx \frac{2 \ln \dfrac{\theta}{\theta_M} - \ln D}{\theta - \theta_M} \qquad \text{(II-18)}$$

$$\approx \frac{R}{\Delta H_u} \cdot \frac{\ln \left(\dfrac{T_0 - T}{T_0 - T_M} \right) \dfrac{T_M}{T} - \ln D}{\dfrac{1}{T} - \dfrac{1}{T_M}}$$

where T_0 is the melting point of pure isotactic polymer and T_M the melting point of the polymer being studied.

The expression for X can be simplified in a similar manner,

$$X \approx \theta^2{}_M e^{-\xi_c \theta_M} \left[\frac{e^{-\theta_M}}{(1 - e^{-\theta_M})^2} - \frac{e^{-\theta}}{(1 - e^{-\theta})} + \xi_c \left(\frac{1}{1 - e^{-\theta_M}} - \frac{1}{1 - e^{-\theta}} \right) \right]$$

$$= \theta^2{}_M \cdot e^{-\xi_c \cdot \theta_M} \left[\frac{1 - \theta_M}{\theta^2{}_M} - \frac{1 - \theta}{\theta^2} + \xi_c \left(\frac{1}{\theta_M} - \frac{1}{\theta} \right) \right]$$

$$\approx e^{-\xi_c \theta_M} \left[1 - \left(\frac{\theta_M}{\theta} \right)^2 + \xi_c \theta_M \left(1 - \frac{\theta_M}{\theta} \right) \right] \qquad \text{(II-19)}$$

If we let $\xi_c \cdot \theta_M = \xi_c'$,

and

$$\frac{\theta_M}{\theta} = A = \frac{T_0 - T_M}{T_0 - T} \left(\frac{T}{T_M} \right)$$

$$X = e^{-\xi_c'} [1 - A^2 + \xi_c' (1 - A)] \qquad \text{(II-20)}$$

Equations II-12, II-19, and II-20 form the basis for calculating the percent crystallinity as a function of temperature for the one-parameter model. Calculations of crystalline weight fraction based on the above equations gave values at each temperature which were considerably higher than those found experimentally.

The critical chain length ξ_c for the four-parameter model can be found in a similar manner to that used above. In this case, as discussed earlier (Equation 1), the probability $P^+(\xi)$ that a given sequence of +'s is exactly of length ξ is given by:

$$P^+(\xi) = P_1 \alpha_1{}^{(\xi - 2)} (1 - \alpha_1)^2$$

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Therefore, in this case, $\omega_\xi^0 = \xi \, P^+(\xi)$, and

$$\frac{\xi_c}{D}\,(1-e^{-\theta})^2 e^{-\xi_c\theta} = P_1\xi_c \cdot \alpha_1^{\xi-2}\,(1-\alpha_1)^2 \tag{II-21}$$

or,

$$e^{-\xi_c(\theta+\ln\alpha_1)} = \frac{DP_1}{\alpha_1^2}\left(\frac{1-\alpha_1}{1-e^{-\theta}}\right)^2$$

or,

$$\xi_c = -\frac{1}{(\theta+\ln\alpha_1)}\ln\frac{DP_1}{\alpha_1^2}\left(\frac{1-\alpha_1}{1-e^{-\theta}}\right)^2$$

Again, in this case the melting point occurs when $\theta = -\ln\alpha_1$ provided there is no upper limit to crystallite size.

The degree of crystallinity is calculated in the same manner as for the one-parameter model.

$$X = \sum_{\xi_c}^{\infty}(\omega_\xi^0 - \omega_\xi)$$

$$= \sum_{\xi_c}^{\infty}\left[\frac{P_1\,\xi\alpha_1^{\xi}(1-\alpha)^2}{\alpha_1^2} - \frac{\xi}{D}\,(1-e^{-\theta})^2 e^{-\xi\theta}\right] \tag{II-22}$$

Except for numerical coefficients, the summations involved in (II-22) are of the same form as in Equation (II-13). Thus we obtain:

$$X = P_1\left(\frac{1-\alpha_1}{\alpha_1}\right)^2\sum_{\xi_c}^{\infty}\xi\alpha_1^{\xi} - \frac{(1-e^{-\theta})^2}{D}\sum_{\xi_c}^{\infty}\xi e^{-\xi\theta}$$

$$= \frac{P_1}{\alpha_1^2}\alpha_1^{\xi_c+1}\left[1+\xi_c\left(\frac{1-\alpha_1}{\alpha_1}\right)\right] - \frac{1}{D}\,e^{-(\xi_c+1)\theta}\left[1+\frac{\xi_c(1-e^{-\theta})}{e^{-\theta}}\right]$$

$$= \alpha_1^{\xi_c}\left\{\frac{P_1}{\alpha_1} + \frac{P_1(1-\alpha_1)\,\xi_c}{\alpha_1^2} - \frac{1}{D}\,\frac{e^{-\theta\xi_c}}{\alpha^{\xi_c}}\left[e^{-\theta}+\xi_c(1-e^{-\theta})\right]\right\}$$

$$= \alpha_1^{\xi_c}\left\{\frac{P_1}{\alpha_1} + \frac{P_1(1-\alpha_1)\,\xi_c}{\alpha_1^2} - \frac{1}{D}e^{-(\theta+\ln\alpha_1)\xi_c}\left[e^{-\theta}+\xi_c(1-e^{-\theta})\right]\right\} \tag{II-23}$$

Again using the definition of ξ_c, we obtain:

$$X = \alpha_1^{\xi_c}\left\{\frac{P_1}{\alpha_1} + \frac{P_1(1-\alpha_1)\,\xi_c}{\alpha_1^2} - \frac{1}{D}\cdot\frac{P_1(1-\alpha_1)^2\cdot D}{\alpha_1^2(1-e^{-\theta})^2}\left[e^{-\theta}+\xi_c(1-e^{-\theta})\right]\right\}$$

$$= \alpha^{\xi_c}(1-\alpha)^2\cdot\frac{P_1}{\alpha_1^2}\left[\frac{\alpha_1}{(1-\alpha_1)^2} - \frac{e^{-\theta}}{(1-e^{-\theta})^2} + \xi_c\left(\frac{1}{1-\alpha_1} - \frac{1}{1-e^{-\theta}}\right)\right] \tag{II-24}$$

This equation is almost identical with the result obtained previously (Equation II-16), except it is modified by the inclusion of the factor (P_1/α_1^2).

In effect, this is merely a factor which reduces the precent crystallinity and forms the second parameter of our theory.

By analogy with the Equations II-18 and II-19,

$$\xi_c \approx \frac{2 \ln \dfrac{\theta}{\theta_M} - \ln \dfrac{DP_1}{\alpha_1}}{\theta - \theta_M} \qquad \text{(II-25)}$$

and

$$X = \frac{P_1}{\alpha_1^2} e^{-\xi'} \left[1 - A^2 + \xi_c' (1 - A)\right] \qquad \text{(II-26)}$$

where $\xi_c' = \theta_M \xi_c$ and $A = \theta_M/\theta$.

The net effect of the factor P_1/α_1^2 is, of course, to modify the percent crystallinity at every temperature. Calculation shows that this model gives a much better fit of the crystallinity *vs.* temperature curve, but there are still significant deviations which can best be taken care of by considerations of crystallization efficiency and the "car parking" correction.

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An Initial Survey of the Polymerization Kinetics of 4-Methylpentene-1

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An initial survey of the polymerization kinetics of 4-methylpentene-1 using the catalyst system α-titanium trichloride-diethylaluminum chloride was made in an essentially bulk system. The overall polymerization rate was first-order with respect to the monomer concentration and also to the titanium trichloride component of the catalyst system. At constant concentration of trichloride, the observed rate was approximately independent of the aluminum alkyl. In the temperature range 30°–60° C., the activation energy for the overall process was 15 kcal./mole. A retardation period which decreased with increasing temperature was observed throughout the experimental work. The polymer viscosity (RSV) decreased with increasing temperature and with increasing titanium trichloride, indicating a chain transfer reaction occurring with this compound. No change in viscosity was observed as the aluminum alkyl concentration was varied by a factor of 10.

The recent literature contains several excellent studies of the physical properties of poly-4-methylpentene-1, yet little has been published on the details of the kinetics of polymerization via Ziegler-Natta catalyst systems. A number of papers discuss in detail the solid and solution properties of poly-4-methylpentene-1 (*7*, *9*, *10*, *11*). Various complex catalysts have been used to prepare polymer samples for study. Natta (*13*) described the preparation of a highly crystalline polymer using α-$TiCl_3$ and $Al(C_2H_5)_3$. Campbell (*4*) described the preparation of polymer using a catalyst derived from $TiCl_4$ and $LiAl\ (C_{10}H_{21})_4$. Others have used α- or γ-$TiCl_3$ with $Al(C_2H_5)_2Cl$ (*7*, *9*). Descriptions of the

In Elastomer Stereospecific Polymerization; Johnson, B., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

polymerization have been limited to such details as the effect of catalyst composition upon polymer yields and characteristics. For example, Watt (*15*), using the catalyst systems $TiCl_4$ and $Al(C_2H_5)_3$ or $Al(i\text{-}C_4H_9)_3$, determined the effect of catalyst composition upon activity and stereospecificity. In only one instance (*2*) has any kinetic data been reported for the particular system reported here.

This paper presents some of our initial results from a kinetic study of 4-methylpentene-1 polymerization using the catalyst system α-$TiCl_3$ $Al(C_2H_5)_2Cl$. The discussion will be limited to some aspects of the bulk system in the temperature range 30°–60° C.

Experimental

Materials. The 4-methylpentene-1, supplied by the California Chemical Co., was distilled, deaerated, dried, and stored over calcium hydride in a nitrogen atmosphere. A typical analysis of the monomer by gas chromatography showed 97.7% α-isomer, 2.2% β-isomer, and 0.1% higher boiling fractions. The α-$TiCl_3$, AA grade, was obtained from the Stauffer Chemical Co. The $Al(C_2H_5)_2Cl$, obtained from the Ethyl Corp., was used as a dilute solution in *n*-heptane (0.2 gram/ml.). Phillips (pure grade) *n*-heptane was dried over calcium hydride and deaerated before using.

Catalyst Preparation. Previous results obtained in our laboratories showed that the catalyst system used in this study yields polymer of high crystallinity and low percentages of heptane solubility. We have found that preforming and aging the catalyst components further increases the crystallinity and improves reproducibility of kinetic data.

The catalyst components were added to a reaction flask in the following order: α-$TiCl_3$, *n*-heptane (10 ml.), and $Al(C_2H_5)_2Cl$ solution. The mixture was then stirred for 15 minutes at room temperature and preheated to reaction temperature for about 5 minutes before introducing the monomer.

Polymerization. The polymerization reactions were carried out in borosilicate glass aerosol compatibility tubes of 12-oz. capacity (Fischer and Porter Co.). These were fitted with the necessary valves and connections to provide a blanket of inert gas while the reagents were added. The solid catalyst component was added to the reaction flask in a dry box; all other ingredients were added via syringe. The monomer was allowed to equilibrate at reaction temperature for at least one-half hour before being added to the preheated and aged catalyst slurry. Vigorous stirring was maintained by a magnetic stirring bar assembly throughout the course of reaction to assure uniform composition. The polymerization was followed to a maximum of 20% conversion; at higher conversions stirring becomes ineffective.

The course of the reaction was followed gravimetrically by taking samples of the mixture at convenient time intervals. In order to take aliquots, the reaction vessel was provided with a stainless steel dip tube which extended to the bottom of the vessel. Aliquots were forced through the dip tube by nitrogen pressure into a tared sampling tube where the reaction was instantaneously quenched with a known quantity of methanol. The sampling tube and contents were weighed, and the weight of the aliquot was determined by difference.

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The quenched reaction mixture was then carefully transferred to a large beaker and diluted with more methanol to precipitate any polymer remaining in solution. The precipitated polymer was filtered, washed several times with methanol, and dried to constant weight at 60° C. in a vacuum oven. The percent conversion was calculated from the weight of the original reaction mixture, the weight of the aliquot taken, and the weight of the isolated polymer.

Viscosities. The reduced solution viscosities (RSV) of the polymers (0.1 gram per 100 ml. of solution) were measured at 135° C. in decalin using modified Ubbelohde viscometers.

Treatment of Data

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Assume as a model for a Ziegler-Natta system the diffusion of monomer to a site of catalytic activity—presumably one of a number of sites on a solid particle—where it is inserted into a growing polymer chain. For the bulk polymerization of a monomer such as 4-methylpentene-1 where polymer is insoluble in monomer, the solid catalyst particle becomes the center of an expanding sphere of precipitated polymer chain(s) growing from the inside. On this molecular level, the rate of chain growth will be directly proportional to the monomer activity at the individual sites. At equilibrium the monomer activity at each site encapsulated in precipitated polymer will equal that of the surrounding bulk monomer, [Mo]. Under nonequilibrium conditions, where the rate of diffusion of monomer from the bulk monomer thru the precipitated polymer to the polymerization site becomes comparable to the rate of polymerization at that site, the localized activity will be lower, and the rate of polymerization will be correspondingly lower.

Depressed rates have been observed in Ziegler-Natta systems with monomers other than 4-methylpentene-1. Bier (*1*) suggested that the slowly decreasing rates of propylene polymerization under polymer precipitating conditions with the catalyst system α-$TiCl_3$–$Al(C_2H_5)_2Cl$ are caused by diffusion control. In another case Burnett and Tait (*3*) found depressed rates of styrene polymerization under polymer-precipitating conditions with the catalyst system α-$TiCl_3$–$Al(C_2H_5)_3$. At styrene concentrations less than $3.5M$ in heptane (isotactic polystyrene precipitates in this region of monomer concentration) a plot of polymerization rate *vs.* styrene concentration falls below the extrapolated linear plot by a factor of 2.

On a macroscopic level the polymerization kinetics will follow the usual relationship where equilibrium, as described above, exists (Equation 1).

$$\frac{d[P]}{dt} = k_p\,[C^*]\,[Mo] = k\,[Mo] \qquad (1)$$

where

P = moles of monomer units converted to polymer
C^* = moles of active polymer at time t
k_p = rate constant for propagation

Under nonequilibrium conditions, [Mo] will be a lower, generally unknown value varying from site to site. Treatment of data reflecting diffusion control will result in low values for the rate constants if one assumes the monomer activity to be [Mo] rather than its true lower value.

For treatment of the polymerization data for bulk 4-methylpentene-1, the integrated form of Equation 1 was used.

$$[\mathrm{P}] = k\,[\mathrm{Mo}]\,t \qquad (2)$$

Since $\frac{[\mathrm{P}]}{[\mathrm{Mo}]}$ = fractional conversion x, Equation 2 may be rewritten as:

$$\frac{\frac{[\mathrm{P}]}{[\mathrm{Mo}]}}{t} = \frac{x}{t} = k\ \mathrm{sec.}^{-1} \qquad (3)$$

Results and Discussion

In Figure 1 conversion *vs.* time at varying levels of $TiCl_3$ is plotted according to Equation 3. After an initial retarded period the plot is linear to at least 20% conversion. The slope after the period of retardation was taken as the rate of polymerization, k. In polymerizations carried to over 20% conversion we have found that the rate, k, begins to fall off slowly, owing to either

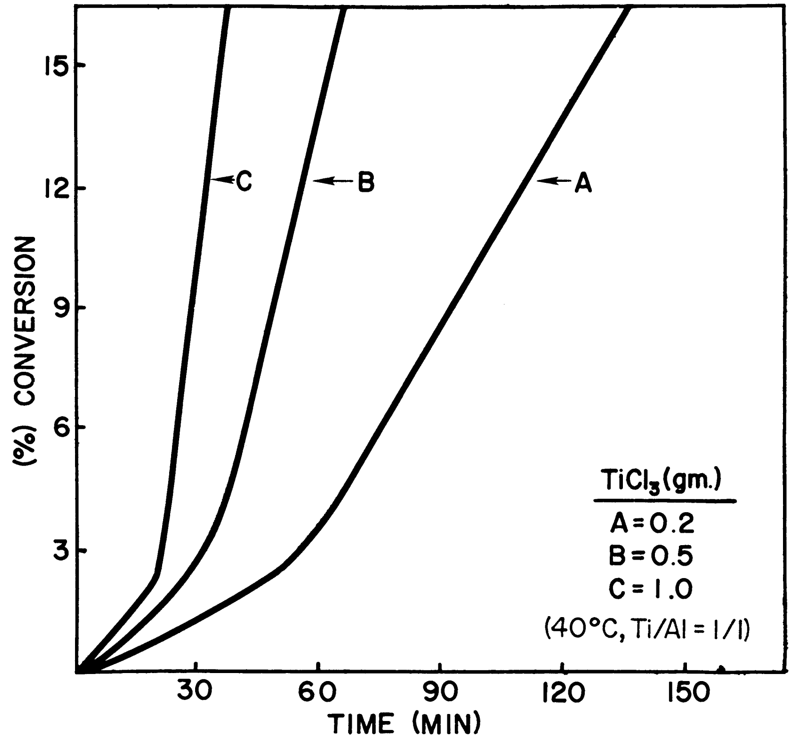

Figure 1. Effect of $TiCl_3$ on monomer conversion

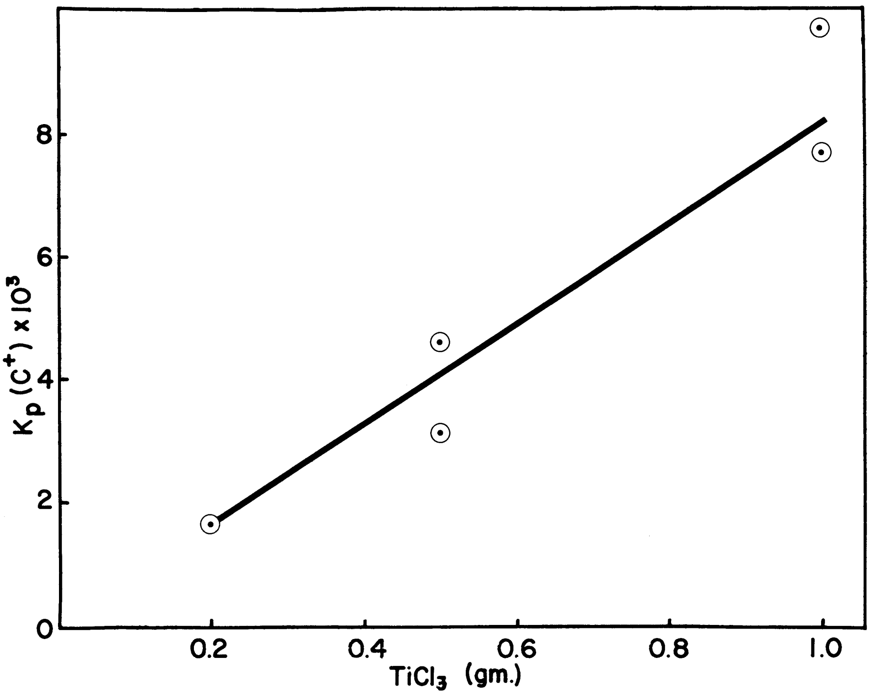

Figure 2. Rate vs. $TiCl_3$

inactivation of catalytic sites or the onset of diffusion control of the rate, or both.

A plot of rate (taken from Figure 1) *vs.* weight of $TiCl_3$ in Figure 2 is linear, indicating the usual situation in Ziegler-Natta systems that the number of active sites is proportional to the $TiCl_3$ present.

Figure 3 shows the conversion-time relationship for varying aluminum to titanium ratios. It can be seen that the rate decreases nonuniformly with increasing aluminum-titanium ratio. The small change in rate resulting from a 10-fold change in aluminum-titanium ratio indicates a low order of dependence of the rate upon the $Al(C_2H_5)_2Cl$ concentration. This low order of rate dependence upon the alkyl aluminum concentration suggests that the main course of the process is insensitive to excess alkyl, but that some side effects exist.

Conversion *vs.* time at 30°, 40°, 50°, and 60° C. is shown in Figure 4. An Arrhenius plot of the polymerization rate *vs.* temperature in Figure 5 indicates an activation energy of about 15 kcal.

The retardation period for each rate curve was taken as the intersection of the extrapolated linear portion of the curve with the time axis. Increased temperature shortens the retardation period as shown in Figure 4. The plot in Figure 6 of retardation times, taken from Figure 4, *vs.* temperature suggests that the retarded period may be made immeasurably short by polymerizing at higher temperatures. The cause of the retardation period is unknown;

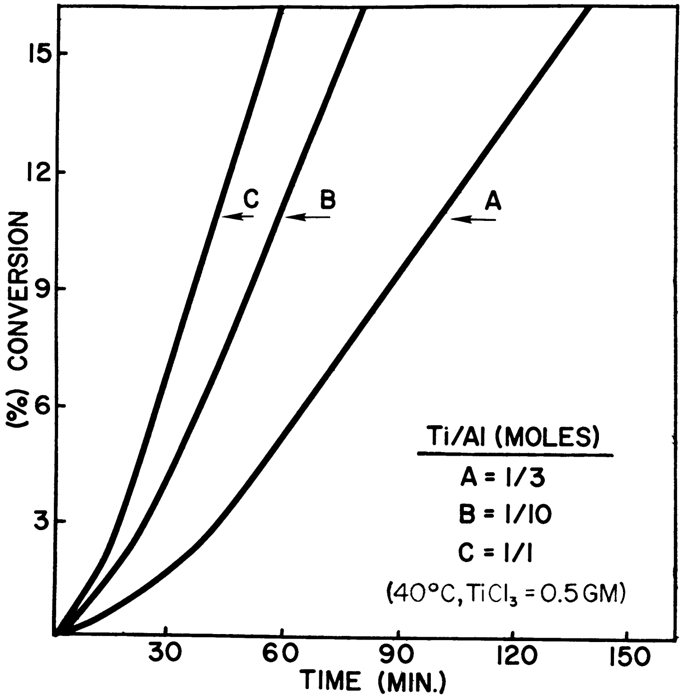

Figure 3. Effect of $Al(C_2H_5)_2Cl$ on monomer conversion

suggested causes are (1) the low level of 4-methylpentene-2 contaminant, (2) a slow initiation process, or (3) a change in the catalyst brought about by adding monomer to the preformed catalyst. We have done some further work with the internal olefin in an effort to determine if this isomer causes the slow initial period. Known mixtures of the two isomers containing 0.05, 0.1, and 0.5 mole fraction 4-methylpentene-2 were prepared. In duplicate experiments, the mixture with 4-methylpentene-2 of 0.1 mole fraction gave longer retardation periods and lower overall rates of polymerization than the monomer containing 2% of the isomer. The monomer mixture with 0.5 mole fraction of 4-methylpentene-2 did not polymerize. One experiment using 0.05 of the β-isomer gave an anamolous rate of polymerization. It was slightly faster than our usual rates with standard 4-methylpentene-1.

Burnett (*2*), using a dilatometric method to study the polymerization in heptane, reported a first-order dependence of the reaction rate on the monomer and the α-$TiCl_3$ concentration, but little or no dependence on the aluminum alkyl. A "settling" period was observed which could not be correlated with the various components of the reaction system. An activation energy, measured after the settling period, was found to be 7.7 kcal./mole.

The variation of the reduced solution viscosity of the polymer with percent conversion for two typical experiments is shown in Figure 7. Within experimental error the polymer solution viscosities are independent of the conversion in the temperature range studied. This same relation was found by Vesely (*14*) for the system propylene, α-$TiCl_3$-$Al(C_2H_5)_3$ at 50° C. In some instances gradual increases in the viscosity with conversion were noted. The relative constancy of the solution viscosities suggests either (1) the absence of long living chain ends in this systems, or (2) the presence of long living chain ends which may be encapsulated and sterically deactivated by polymer.

Table I shows the effect of the catalyst components and temperature on the reduced solution viscosity. The viscosities at 1, 5, 10, and 15% conversion are given in each case.

In Table I*A*, at a constant Ti/Al ratio of 1/1, as the weight of $TiCl_3$ is increased, a decrease in polymer molecular weight (inferred from viscosity data) is evident. Thus a transfer process dependent upon the $TiCl_3$ is indicated. This has been observed previously with propylene at various temperatures in the α-$TiCl_3$-$Al(C_2H_5)_3$ system (*8*, *12*) and also with the catalyst system employed here (*5*).

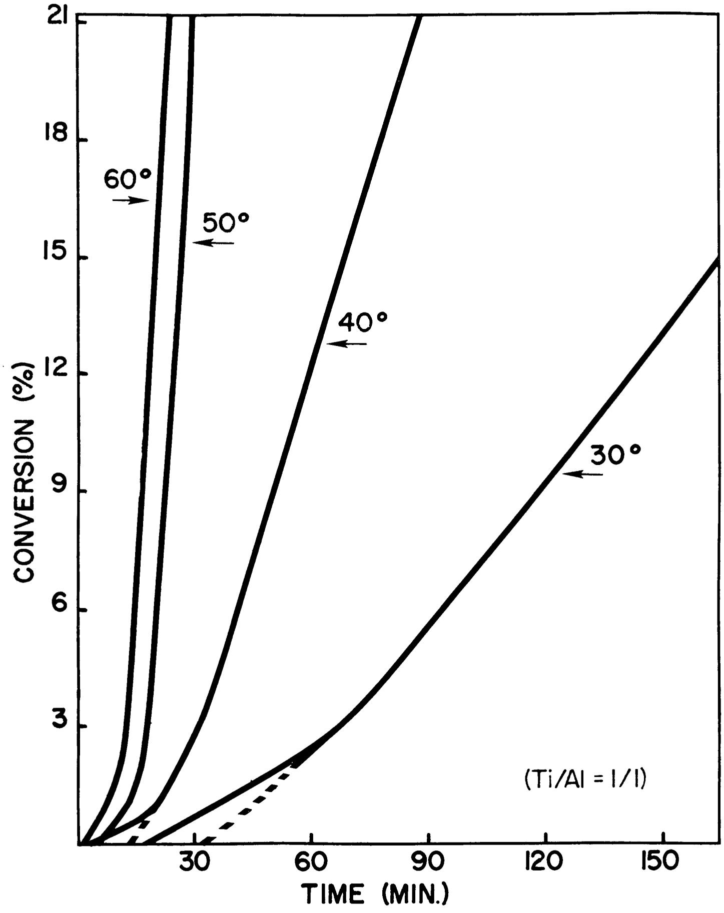

Figure 4. Effect of temperature on monomer conversion

In Elastomer Stereospecific Polymerization; Johnson, B., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

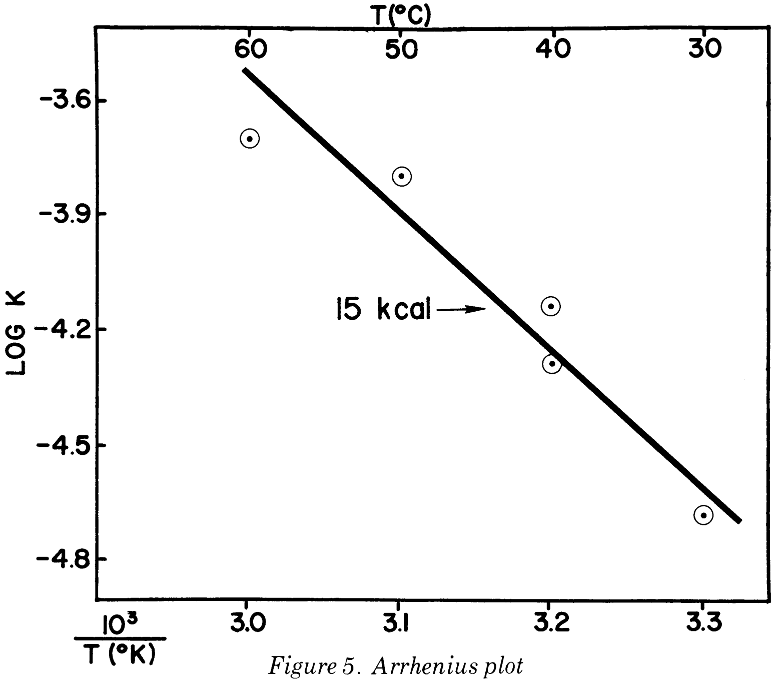

Figure 5. Arrhenius plot

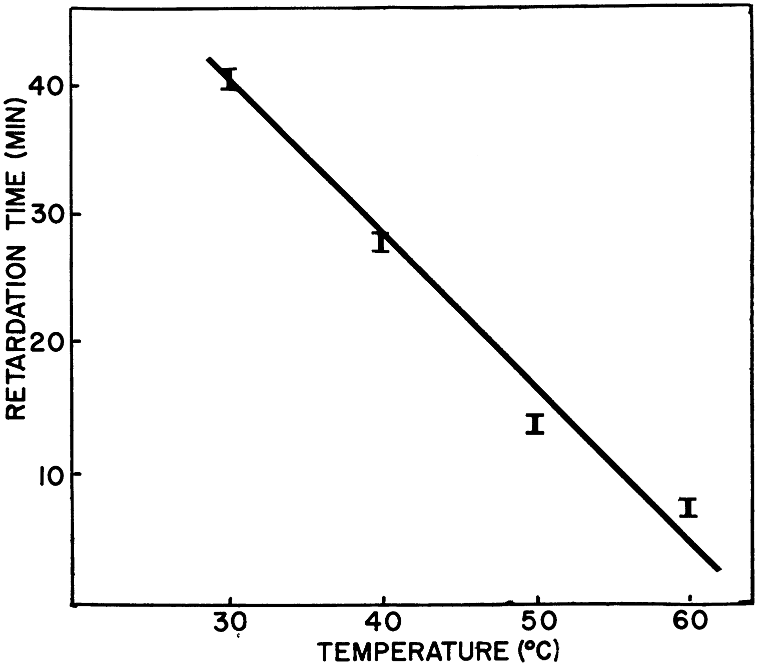

Figure 6. Temperature vs. retardation time

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Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

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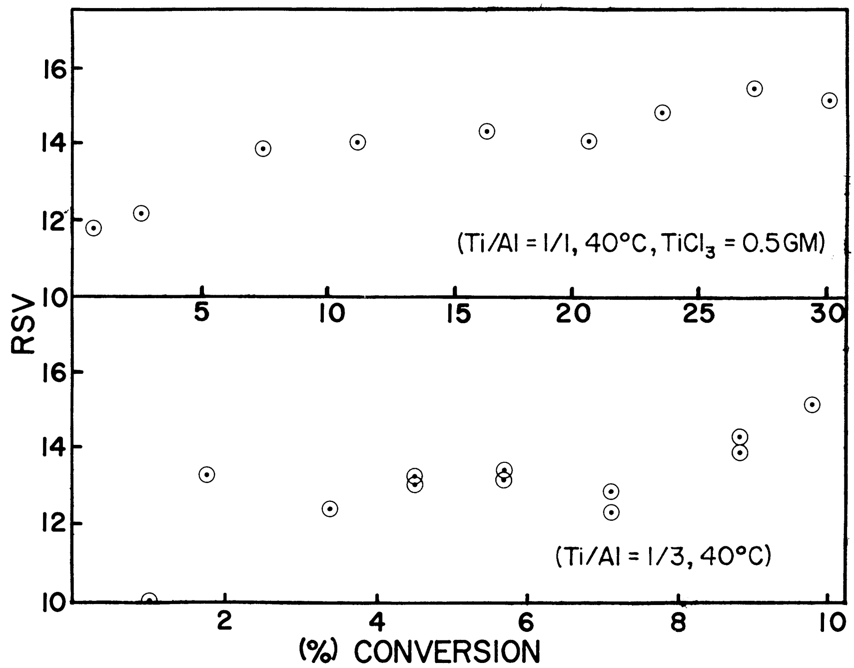

Figure 7. RSV vs. percent conversion

Table I. Variation of Reduced Solution Viscosity with $TiCl_3$, Ti/Al, and Temperature

	RSV			
	1%	*5%*	*10%*	*15%*
A. $TiCl_3$ Grams				
0.2	18.0	15.0	11.0	15.7
0.5	11.8	13.0	14.0	14.4
0.5	10.3	12.8	14.4	14.3
1.0	9.8	10.7	12.2	12.8
1.0	10.0	10.0	11.3	11.7
B. Ti/Al (Moles)				
1/1	10.3	12.3	14.4	14.3
1/1	11.8	13.0	14.0	14.4
1/3	10.1	13.2	15.2	. . .
1/10	10.0	13.8	14.0	. . .
C. Temp. (° C.)				
30	12.8	13.2	14.0	. . .
40	11.8	13.0	14.0	14.4
40	10.3	12.8	14.4	14.3
50	7.5	10.1	9.9	11.1
60	8.0	9.9	11.6	. . .

Table I*B* shows that a 10-fold increase in the concentration of the aluminum alkyl has no significant effect on the reduced solution viscosities, thus indicating the absence of a chain transfer process with the aluminum alkyl.

In Elastomer Stereospecific Polymerization; Johnson, B., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

This is at variance with some previous findings (*5, 6*) showing chain transfer with aluminum alkyls in propylene polymerizations. However, it is in good agreement with Watt's (*15*) data on 4-methylpentene-1 polymerization using a similar catalyst system; the molecular weight (reduced specific viscosity of the heptane insoluble polymer) showed no change with increasing concentration of the aluminum alkyl.

The dependence of the molecular weight on temperature is given in Table I*C*. The viscosity data show a tendency to decrease with increasing temperatures, and although the effect is not large, it is further indication of a chain transfer process occurring in this system.

The usual termination and chain transfer reactions may be postulated in this system as in other Ziegler-Natta systems. We feel that termination by unimolecular disproportionation observed in systems at higher temperatures does not occur in our system owing to the moderate temperatures involved. Concerning the bimolecular chain transfer reactions often postulated in other systems we feel those involving α-$TiCl_3$ and monomer are dominant; transfer with solvent (*n*-heptane) is unlikely owing to the low concentration, and transfer with alkyl was not observed experimentally. No absorption in the infrared spectra owing to vinylidene end groups arising from a monomer transfer could be detected; however, this was not unexpected because of the high molecular weight of the polymer.

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10

Transition Metal Catalyst Systems for Polymerizing Propylene

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The composition of the Ziegler-Natta catalyst influences its activity in polymerizing propylene and forming crystalline or amorphous polymer. With $TiCl_4$ or VCl_4 as a catalyst base material, effective polymerization is achieved when these compounds are reduced in a separate reaction 80° C. or 170° C. by $AlEt_3$ at an Al/Ti or Al/V ratio of about 1/3 with formation of β-$TiCl_3$, γ-$TiCl_3$ or VCl_3, followed by activation with an alkylaluminum compound. The activity so obtained is unmatched by corresponding catalysts which have been reduced and activated in one step. Crystallinity of polypropylene is influenced not only by the type of transition metal compound but also to a large extent by the type of alkylaluminum activator.

Many combinations of a transition metal compound, and an alkylmetal compound are able to induce the polymerization of α-olefins. It is generally agreed that transition metal compounds are active only when reduced to a lower valence, but it is still a matter of some dispute as to which valence.

The function of the alkylmetal compound, normally an aluminum compound, may be twofold. First, it reduces the transition metal compound, if necessary, to a compound of lower valence; second, it activates this compound of lower valence to be a polymerization catalyst. The nature of this activation and the mechanism of the polymerization have been the subject of much speculation (*5, 8, 11, 12, 16, 19, 21, 25, 32*).

Thus, in the often used $TiCl_4$-based catalysts diluted $TiCl_4$ is first reduced by reacting with, for instance, $AlEt_3$ to a solid brown, black, or sometimes purple reaction product which is subsequently activated with the same or sometimes another alkylaluminum compound. Cooper and Rose (*10*) showed that the composition of the reaction product formed in the reducing step may

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vary widely depending on the reaction conditions and on the type of alkylaluminum compound used. Al(alkyl)$_3$ in particular is likely to reduce $TiCl_4$ to compounds of titanium of valence lower than 3, whereas Al(alkyl)$_2$Cl usually does not reduce $TiCl_4$ further than $TiCl_3$ (*3, 10, 18, 22*).

The importance of a controlled reduction of $TiCl_4$ for preparing a catalyst of optimum activity has often been overlooked although, in fact, activity may vary widely if the reduction conditions are changed.

In the light of existing knowledge on the reduction of $TiCl_4$, we systematically varied the compositon of the $TiCl_3$-containing precipitate produced in the reducing reaction and the activation of this precipitate in order to find the composition of an optimum catalyst. The knowledge gained with these $TiCl_4$-based catalysts was also used to compound catalysts from VCl_4 and $VOCl_3$ as base materials.

The polymerization rate of propylene and the amorphous polymer content of the polymer produced were used as criteria for the effectiveness of a catalyst combination. In this connection it seemed worthwhile to try to produce a polypropylene of either very low or very high amorphous content, the former being of interest as a plastic and the latter possibly as a material with elastic properties. The molecular weight of the polymer was an additional factor to be considered.

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Experimental Procedure

Polymerization was effected batch-wise in 600 ml. solvent at atmospheric pressure in a 1000-ml. three-necked flask provided with a stirrer and connected to a buret for catalyst and solvent supply. Isooctane (2,2,4-trimethylpentane) was used as the main polymerization solvent. About 7% of *n*-decane was present in this solvent if the catalyst had been reduced at 170° C.

In most experiments the catalyst was prepared by a two-step mixing procedure. In a first step a reduced transition metal compound was produced: a 0.1*M* solution of an alkylaluminum compound reacted with a similar solution of a transition metal compound at a predetermined Al/transition metal molar ratio for 2 hours at 80° C. in isooctane or for 1 hour at 170° C. in *n*-decane. To avoid local overreduction of the transition metal compound as much as possible, the solution of the alkylaluminum compound was added to the solution of the transition metal compound thus ensuring the presence of an excess of the latter during the mixing stage.

The reduced transition metal compound so prepared, for instance $TiCl_3$, was diluted and activated by adding an alkylaluminum compound without a preceding washing or filtration treatment. After 5 minutes of aging at reaction temperature, polymerization was started by introducing gaseous propylene into the diluted catalyst slurry. In all polymerizations, concentration of the transition metal compound was 5 mmole/liter.

All solutions were handled under a blanket of nitrogen to avoid the influence of oxygen. Much care was taken to purify the propylene, the nitrogen, and the solvents. For oxygen removal, nitrogen and propylene were passed over heated copper at a temperature of 250° C. and 150° C., respectively. These gases and the solvent were dried by passing them through columns

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filled with Linde Molecular Sieves No. 4. The final water and oxygen content of the gases and solvents was less then 5 p.p.m. The purity of the alkylaluminum compounds was checked by analysis. This showed, for instance, that the $AlEt_3$ used contained at least 92.9% ethyl groups, not more than 2.7% hydride groups, and 1.8% butyl groups.

Polymerization was terminated by adding a small amount of an ethanol-HCl-H_2O mixture and some antioxidant. After washing, the solvent was usually removed from the polymer slurry by steam stripping. Sometimes, when the polymer was highly amorphous, it was precipitated with a threefold volume of ethanol instead. The polymer was vacuum dried at 60° C.

The rate of polymerization is expressed as yield per liter per hour—i.e., as an average value since the actual rate of polymerization depends on time, as a rule decreasing gradually; the time of polymerization was standardized to 1 or 2 hours in order to facilitate comparisons.

For characterizing the polymer with respect to crystallinity, the hexane soluble polymer content was determined by extracting with boiling *n*-hexane for 1½–4 hours (depending on soluble polymer content). The soluble fraction thus obtained is predominantly amorphous, and the residue is crystalline. Except for crystallinity, the solubility also depends to some extent on molecular weight since low molecular weight material dissolves more easily than high molecular weight polymer of the same degree of crystallinity.

The limiting viscosity number (*LVN*) of the polymers—i.e., the intrinsic viscosity at zero concentration and shear rate, was determined from the inherent viscosity measured at 0.05 to 0.2 grams/100 ml. concentration in decalin at 135° C. with a Schulken-Sparks viscometer.

Catalyst Systems Based on Various $TiCl_3$-Containing Precipitates

Polymerization Activity. In a few preliminary experiments listed in Table I, the catalysts prepared in separate reduction and activation steps were compared with catalysts prepared by mixing in one step under various conditions—viz., at ultimate dilution or under the normal conditions of the reducing step. Catalysts prepared by such one-step procedures proved to have a diminished—often strongly diminished—activity compared with two-step catalysts of about the same overall composition.

Table I further lists some polymerizations in which $TiCl_3$ was prepared at 80° C. or 170° C. by reduction with various alkylmetal compounds in stoichiometric alkyl/Ti ratios. The highest rate of polymerization is observed when $TiCl_4$ is reduced with $AlEt_3$. $Al(n\text{-propyl})_3$ yields a slightly less active catalyst. The butyllithium-reduced precipitate has a still lower activity, whereas $AlEt_2Cl$- and $AlEtCl_2$-reduced precipitates lag even further behind. This order is roughly independent of whether reduction took place at 80° C. or 170° C.

Figures 1–3 give results of more extended series of polymerizations with various $TiCl_3$-containing precipitates activated with either $AlEt_3$ or $AlEt_2Cl$. These precipitates were obtained by reacting $AlEt_3$ with $TiCl_4$ at molar ratios varying between 0.2 and 1.0 and a reaction temperature of either 80° C. or 170° C. It appears that in all three types of catalysts considered, independently of preparation temperature, the catalyst is most active when the precipitate

Table I. Polymerization of Propylene with Catalysts Based on $TiCl_4$ and Activated with $AlEt_3$[1]

Catalyst Components mmole/liter ultimate conc.					
Components in Reducing Step	*Reducing Conditions*	*Activating Compound*	*Av. Rate, grams/liter/hr.*	*LVN*	*Hexane Soluble Polymer, %*
	Comparison one step-two step				
5 $TiCl_4$ + 5 $AlEt_3$	2 hr. 80° C.		3.5	2.2	59
5 $TiCl_4$ + 2 $AlEt_3$	2 hr. 80° C.	3 $AlEt_3$	26	2.7	56
5 $TiCl_4$ + 7 $AlEt_3$	2 hr. 80° C.		3.9	2.5	53
5 $TiCl_4$ + 2 $AlEt_3$	2 hr. 80° C.	5 $AlEt_3$	22	2.1	51
5 $TiCl_4$		15 $AlEt_3$	11	2.3	27
5 $TiCl_4$ + 2 $AlEt_3$	2 hr. 80° C.	15 $AlEt_3$	36	4.8	27
5 $TiCl_4$		25 $AlEt_3$	7.5	2.8	47
5 $TiCl_4$ + 25 $AlEt_3$	5 min. 20° C.		0.5	1.7	
5 $TiCl_4$ + 25 $AlEt_3$	2 hr. 80° C.		0		
5 $TiCl_4$ + 1.67 $AlEt_3$	2 hr. 80° C.	25 $AlEt_3$	24	4.3	20
	Stoichiometric reduction at 80° C.				
5 $TiCl_4$ + 5 Li Bu	½ hr. 80° C.	15 $AlEt_3$	13	2.9	39
5 $TiCl_4$ + 2.5 $AlEt_2Cl$	2 hr. 80° C.	15 $AlEt_3$	6.3	2.1	40
5 $TiCl_4$ + 5 $AlEt_2Cl$	2 hr. 80° C.	15 $AlEt_3$	11.4	2.4	39
5 $TiCl_4$ + 1.67 $AlEt_3$	2 hr. 80° C.	15 $AlEt_3$	22	3.4	21
5 $TiCl_4$ + 2 $AlEt_3$	2 hr. 80° C.	15 $AlEt_3$	36	4.8	27
	Stoichiometric reduction at 170° C.				
5 $TiCl_4$ + 5 Li Bu	1 hr. 170° C.	15 $AlEt_3$	19	2.1	49
5 $TiCl_4$ + 2.5 $AlEt_2Cl$	1 hr. 170° C.	15 $AlEt_3$	7.2	3.4	25
5 $TiCl_4$ + 5 $AlEtCl_2$	1 hr. 170° C.	15 $AlEt_3$	5.8	2.9	27
5 $TiCl_4$ + 1.67 $AlEt_3$	1 hr. 170° C.	15 $AlEt_3$	34	5.0	15
5 $TiCl_4$ + 2.5 $AlEt_3$	1 hr. 170° C.	15 $AlEt_3$	40	5.7	16
5 $TiCl_4$ + 1.67 $Al(n\text{-}Pr)_3$	1 hr. 170° C.	15 $AlEt_3$	26	4.9	18

[1] Conditions of polymerization: 2 hours at 60° C., 1 atm.; $TiCl_4$ concentration in first step reduction reaction: about 70 mmole per liter.

is prepared at an $AlEt_3/TiCl_4$ molar ratio of 0.3–0.4 which corresponds to about equimolar amounts of ethyl and $TiCl_4$. This optimum activity is particularly sensitive to the Al/Ti ratio for the $AlEt_2Cl$-activated catalyst systems (*1, 33*).

Those precipitates that give the highest rate of polymerization moreover induce—according to Figures 1–3—formation of polypropylene of the lowest hexane soluble polymer content—i.e., of relatively high crystallinity. The *LVN* of the polymer is also optimum when these most active catalysts are used.

Another rule that manifests itself is that polypropylene, produced with $TiCl_3$-containing precipitate reduced at 170° C., normally has a lower hexane soluble polymer content than polypropylene prepared with corresponding catalysts based on $TiCl_3$ reduced at 80° C.

Composition of the Precipitates. Arlman, de Jong (*3*), and many others (*1, 6, 15, 20, 33*) have showed that $TiCl_4$ is quantitatively reduced by $AlEt_3$ to $TiCl_3$ under the conditions used to prepare the catalyst for our polymerization studies—i.e., at 80° C. or 170° C. if the $AlEt_3/TiCl_4$ molar ratio is about ⅓.

The reaction to be expected is:

$$3\ \mathrm{TiCl_4} + \mathrm{Al(C_2H_5)_3} \rightarrow 3\ \mathrm{TiCl_3} + \mathrm{AlCl_3} + 3\ \mathrm{C_2H_5^{\cdot}} \quad (1)$$

However, at 80° C. according to analysis of the reaction products, the main conversion may, according to Arlman and de Jong (*3*), approach Reaction 2.

$$5\ \mathrm{TiCl_4} + 2\ \mathrm{Al(C_2H_5)_3} \rightarrow 5\ \mathrm{TiCl_3} + \mathrm{Al_2C_2H_5Cl_5}\ 5\ \mathrm{C_2H_5^{\cdot}} \quad (2)$$

Part of the ethyl radicals formed may also be able to reduce $TiCl_4$ to $TiCl_3$ under formation of ethyl chloride.

The precipitate prepared at 80° C. at about the stoichiometric $AlEt_3/TiCl_4$ ratio of ⅓ has a reddish-brown color, and, according to x-ray analysis, consists of β-$TiCl_3$, whereas the product prepared at 170° C. at the same Al/Ti ratio has a purple color and the structure of γ-$TiCl_3$ (*4, 24, 26*). Analysis further showed that the $TiCl_3$ thus formed contains an appreciable amount of aluminum compounds, and if prepared at 80° C., also some ethyl groups. These aluminum compounds, which apparently consist mainly of $AlCl_3$, and possibly of some Al_2EtCl_5, are taken up in the crystal lattice of the $TiCl_3$ since they could not be removed by washing and hardly show up in the x-ray diagram (*4, 24*). About one out of every six titanium atoms is replaced by aluminum in the 80° C. solid reaction product (*4*), whereas in the 170° C. product, this

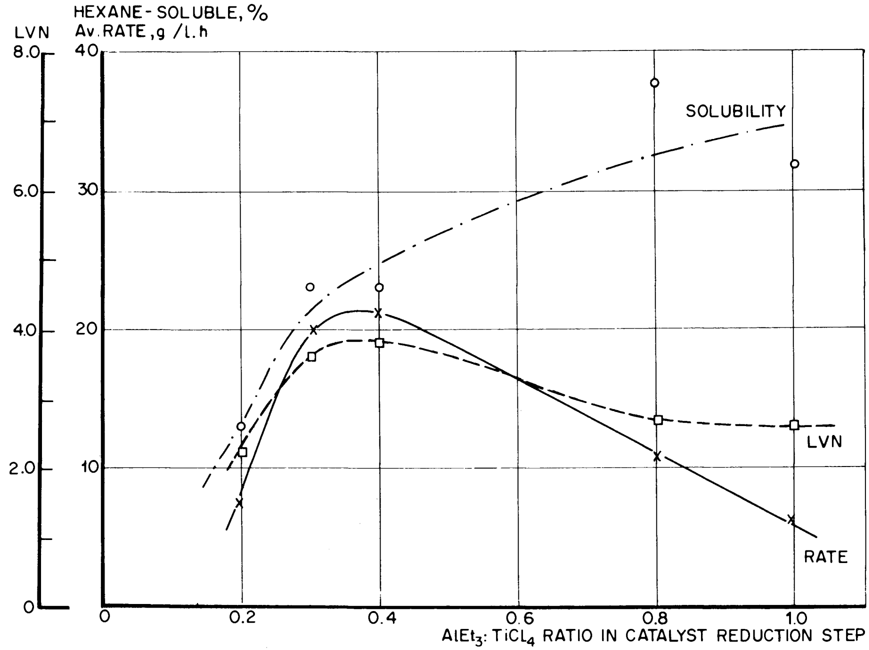

Figure 1. Influence of the $AlEt_3$: $TiCl_4$ ratio in the 80° C. reducing reaction on polymerization at 60° C. after activating 5 mmole/liter of the Ti compound with 24 mmole/liter $AlEt_3$

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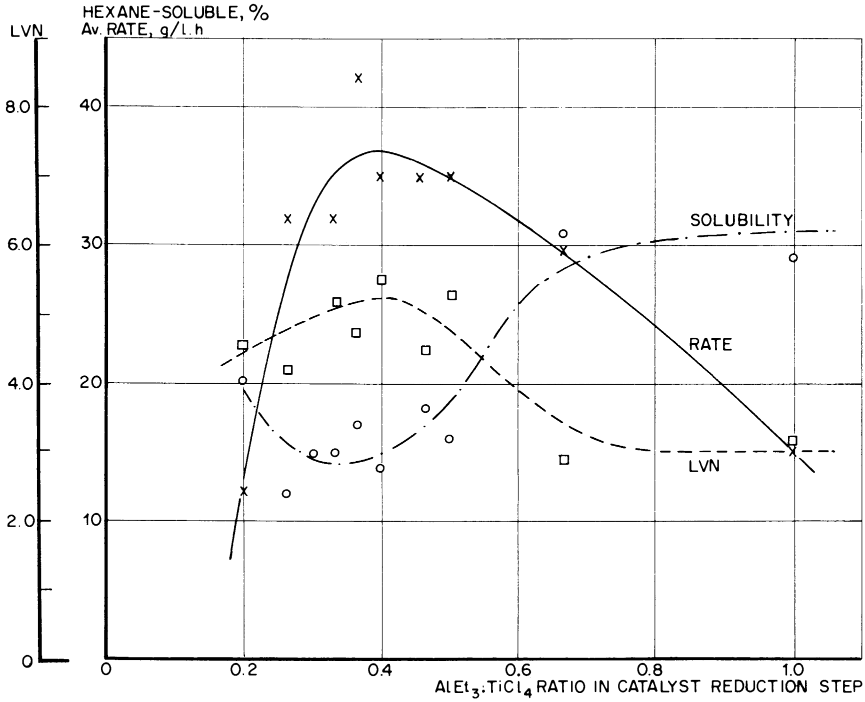

Figure 2. Influence of the AlEt₃: TiCl₄ ratio in the 170° C. reducing reaction on polymerization at 60° C. after activating 5 mmole/liter of the Ti compound with 15 mmole/liter AlEt₃

replacement may be as much as one out of every three titanium atoms (*4, 20, 26*).

When more than the stoichiometric amount of $AlEt_3$ is used to reduce $TiCl_4$, in particular at Al/Ti ratios higher than 0.45, the reaction product is not brown or purple and crystalline anymore but black and amorphous (*4*). Under such conditions $TiCl_4$ is overreduced with formation of miscellaneous titanium compounds of valence <3 containing $TiCl_2$ and possibly also some alkyltitanium chloride (*10, 18*).

A similar black precipitate is formed when butyllithium reacts with $TiCl_4$ in a stoichiometric Li/Ti ratio of 1. Butyllithium might seem to be an ideal reducing agent because one would expect a straight-forward simple reaction:

$$TiCl_4 + LiC_4H_9 \rightarrow TiCl_3 + LiCl + C_4H_9^{\cdot} \quad (3)$$

In fact, the black color of the precipitate indicates that because of its vigorous reducing capacity, butyllithium, even when added dropwise at room temperature in dilute solution (100 mmole/liter) to the $TiCl_4$ solution, forms overreduced Ti compounds (*14*), leaving part of the $TiCl_4$ unreacted. The C_4H_9 radical may also have contributed towards the reduction.

It is important to note that although an excess of $AlEt_3$ reduces $TiCl_4$ to a black titanium compound, β-$TiCl_3$ is slow in reacting with $AlEt_3$ while purple γ-$TiCl_3$ stays purple and is considerably stable (*27*).

The polymerization results as given in Table I and Figures 1–3 can now be interpreted by assuming that an optimum polymerization activity is connected with the presence of β-$TiCl_3$ or γ-$TiCl_3$ and the absence of $TiCl_4$ or overreduced titanium compounds. The fact that this optimum activity is not always found with precipitates prepared at exactly the theoretical $AlEt_3/TiCl_4$ molar ratio of 0.33, but rather at ratios between 0.35 and 0.40, may be caused by side reactions. It is also likely that traces of unavoidable impurities in these small scale polymerizations inactivate a small part of the $AlEt_3$ used.

Remarkably the $AlCl_3$ formed according to the Reaction 1 and incorporated in the $TiCl_3$ crystal lattice does not interfere noticeably with the crystallinity of the polymer formed (*4*, *6*, *26*). Presence of $AlCl_3$ in $TiCl_3$ might even accelerate the rate of polymerization. Such an effect might be expected from loosening of the $TiCl_3$ crystal structure or formation of lattice faults similar to the well known effects of reducing $TiCl_3$ particle size by grinding. Also the cationic character and its reactivity with $AlEt_2Cl$ might be taken into account for interpreting a possible favorable effect of $AlCl_3$ on the polymerization activity of $TiCl_3$, although $AlCl_3$ in a γ-$TiCl_3$ lattice is insoluble and is not converted into soluble compounds by adding $AlEt_2Cl$ or even $AlEt_3$ (*3*).

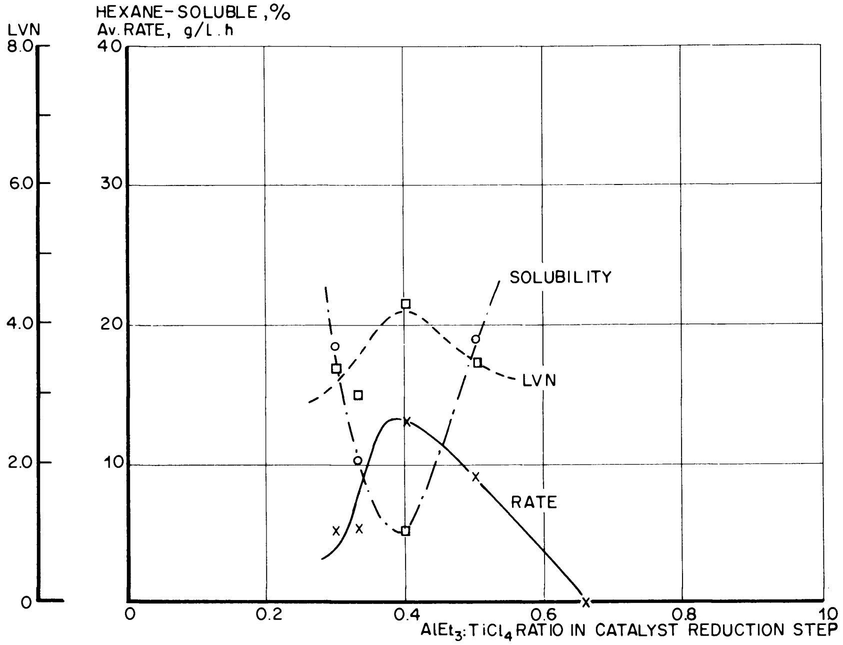

Figure 3. Influence of the $AlEt_3$: $TiCl_4$ ratio in the 170° C. reducing reaction on polymerization at 60° C. after activating 5 mmole/liter of the Ti compound with 15 mmole/liter $AlEt_2Cl$

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β-$TiCl_3$ Catalyst Systems

Influence of Activator. With a β-$TiCl_3$ precipitate of optimum activity, prepared by reaction at 80° C. of $TiCl_4$ with $AlEt_3$ at an Al/Ti ratio of 0.35–0.40, a further study was made of the effect of amount and type of activator on the polymerization of propylene. As stated above, it should be realized that this precipitate contains at least $\frac{1}{6}$ mole $AlCl_3$ per mole $TiCl_3$ and moreover a few alkyl groups.

Table II lists the results of a number of polymerizations performed with such catalysts at 60° C. It appears that $AlEt_2OEt$, particularly if a small amount of $AlEt_3$ is added, is a very good activator giving a high rate of polymerization and leading to formation of a polypropylene that is exceptionally strongly amorphous, up to 66% being soluble in boiling hexane (2). High rates of polymerization are also obtained on activation with $AlEt_3$. Products of a relatively low hexane soluble content are obtained, although at a rather low rate on activating with $AlEt_2Cl$ or $Al(n\text{-}Pr)_2Cl$.

Table II. Polymerization of Propylene with β- or γ-$TiCl_3$ Catalyst Activated with Various Alkylaluminum Compounds[1]

Catalyst Components, mmole/liter	*Av. Rate, grams/liter/hr.*	*LVN*	*Hexane Soluble Polymer, %*
β-$TiCl_3$-based catalysts			
5 β-$TiCl_3$ + 2.5 $AlEt_3$	17	3.4	49
5 β-$TiCl_3$ + 5 $AlEt_3$	22	2.1	51
5 β-$TiCl_3$ + 15 $AlEt_3$	36	4.8	27
5 β-$TiCl_3$ + 5 $AlEt_2Cl$	3.3	3.5	15
5 β-$TiCl_3$ + 15 $AlEt_2Cl$	6.2	2.9	21
5 β-$TiCl_3$ + 15 $Al(n\text{-}Pr)_2Cl$	7.2	3.0	14
5 β-$TiCl_3$ + 5 $AlEt_2OEt$	38	2.3	66
5 β-$TiCl_3$ + 15 $AlEt_2OEt$	39	2.7	50
5 β-$TiCl_3$ + 5 $AlEt_2OEt$ + 1$AlEt_3$	52	2.3	66
γ-$TiCl_3$-based catalysts			
5 γ-$TiCl_3$ + 2.5 $AlEt_3$	31	3.7	30
5 γ-$TiCl_3$ + 5 $AlEt_3$	30	4.7	24
5 γ-$TiCl_3$ + 15 $AlEt_3$	40	5.7	16
5 γ-$TiCl_3$ + 15 $Al(n\text{-}Pr)_3$	33	4.3	25
5 γ-$TiCl_3$ + 15 $AlEt_2Cl$	13	3.4	4
5 γ-$TiCl_3$ + 25 $AlEt_2Cl$	13	3.7	5
5 γ-$TiCl_3$ + 15 $Al(n\text{-}Pr)_2Cl$	10	3.4	4
5 γ-$TiCl_3$ + 15 $AlEtOEtCl$	20	3.5	20
5 γ-$TiCl_3$ + 5 $AlEt_2OEt$	27	2.7	53
5 γ-$TiCl_3$ + 15 $AlEt_2OEt$	20	3.1	50
5 γ-$TiCl_3$ + 5 $AlEt_2OEt$ + 1$AlEt_3$	37	2.4	50
5 γ-$TiCl_3$ + 15 $AlEtCl_2$	<0.2		

[1] Preparation of β-$TiCl_3$ and γ-$TiCl_3$: 5 mmole of $TiCl_4$ + 2 mmole of $AlEt_3$, 2 hours at 80° C. or 170° C., respectively, at a $TiCl_4$ conc. of 70 mmole per liter. Conditions of polymerization: 2 hours at 60° C., 1 atm.

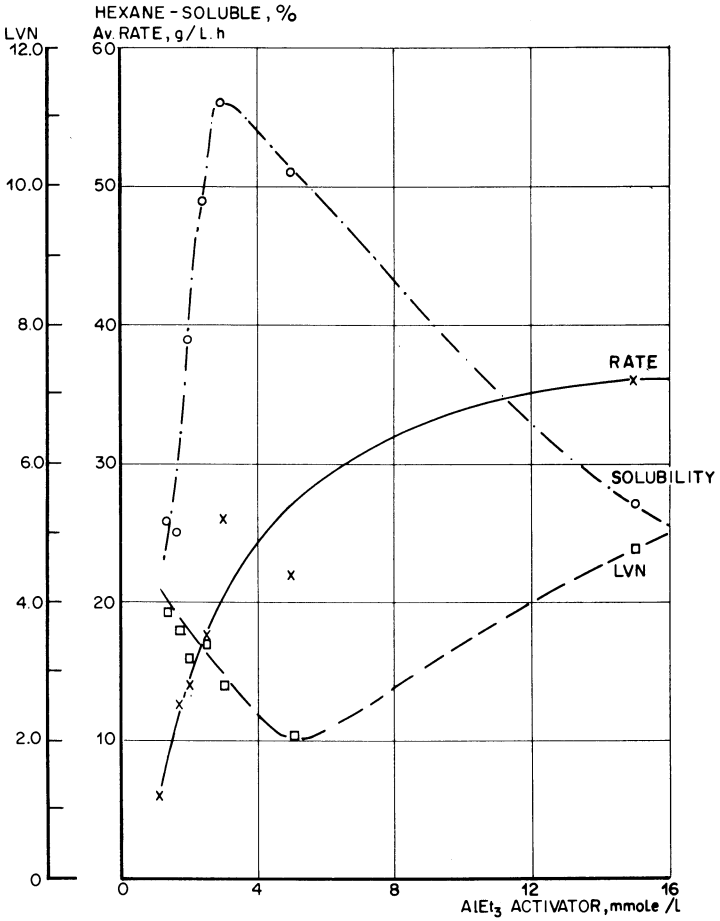

Figure 4. Polymerization of propylene at 60° C. as affected by amount of $AlEt_3$ used to activate 5 mmole/liter β-$TiCl_3$

Figure 4 shows that the rate of polymerization increases sharply with increasing concentration of $AlEt_3$ in the lower ranges, to level off for the higher $AlEt_3$ concentrations. Soluble polymer content reaches a maximum of about 55% with a catalyst having an $AlEt_3/TiCl_3$ ratio of 0.8. The *LVN* passes a minimum near this ratio which again points to a correlation between solubility and *LVN*.

Influence of Temperature on Polymerization. Figures 5 and 6 show, for β-$TiCl_3$ catalyst systems activated with $AlEt_3$ and $AlEt_2OEt$ + $AlEt_3$, to what extent the polymerization of propylene at atmospheric pressure is affected by temperature. The rate of polymerization is highest near 60° C. The drop in rate above that temperature is caused mainly by the decrease in concentration of propylene dissolved in isooctane when the boiling point of the latter (99° C.) is approached; it may also be caused partly by thermal deactivation of the

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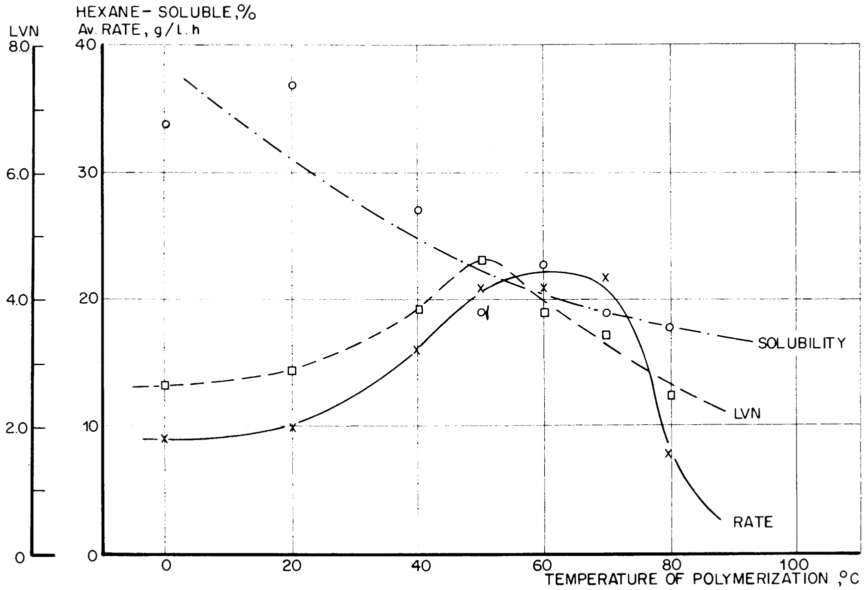

Figure 5. Influence of temperature on polymerization with catalyst consisting of 5 mmole/liter β-$TiCl_3$ and 24 mmole/liter $AlEt_3$

catalyst, presumably by a continuing reduction of β-$TiCl_3$ to catalytically less active compounds.

The hexane soluble polymer content of polymer prepared with the $AlEt_3$-activated catalysts decreases if polymerization takes place at higher temperatures. On the other hand, with the $AlEt_2OEt$-activated catalysts the hexane soluble fraction is greatest in the polymer prepared at 60° C. The decrease in *LVN* with rising temperature above 60° C. points to an increasing rate of termination or chain transfer and a decreasing rate of propagation connected with lower propylene concentration.

γ-$TiCl_3$ Catalyst Systems

Influence of Activator. A γ-$TiCl_3$ precipitate of optimum activity was prepared in a way similar to that described above by reaction at 170° C. of $TiCl_4$ with $AlEt_3$ at an al/Ti ratio of 0.40. Such γ-$TiCl_3$ may contain up to ⅓ mole $AlCl_3$ per mole $TiCl_3$. The data on a few typical polymerizations concerning the effect of amount and type of activator given in Table II show that catalysts based on this γ-$TiCl_3$ in various respects produce similar results as β-$TiCl_3$-based catalysts although there are a few important differences.

High rates of polymerization are again observed on activation with $AlEt_2OEt$ or $AlEt_3$. Polymer with highest amorphous content is produced with an $AlEt_2OEt$ activation, whereas $AlEt_2Cl$-activated γ-$TiCl_3$ produce polymer of strikingly high crystallinity (*1, 33*). Remarkably, AlEtOEtCl can act as an activator while most other alkylaluminum compounds that contain only one alkyl group per aluminum atom, such as $AlEtCl_2$, are virtually inactive.

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Figure 7 shows the effect on polymerization of the amount of $AlEt_3$ used for activating γ-$TiCl_3$ in more detail. Similar to what was observed for the β-$TiCl_3$-based catalyst (Figure 4), it appears that with more $AlEt_3$ the rate of polymerization increases at first rather strongly and levels off at high $AlEt_3$ concentration. Hexane soluble polymer content is maximum and *LVN* minimum with a catalyst consisting of $AlEt_3$ γ-$TiCl_3$ in a 1/5 ratio.

As a rule, polymerization is faster with catalysts based on γ-$TiCl_3$ than with those based on β-$TiCl_3$ except for some of the $AlEt_2OEt$-activated systems. Polymer produced with a γ-$TiCl_3$ catalyst usually has a slightly higher *LVN*

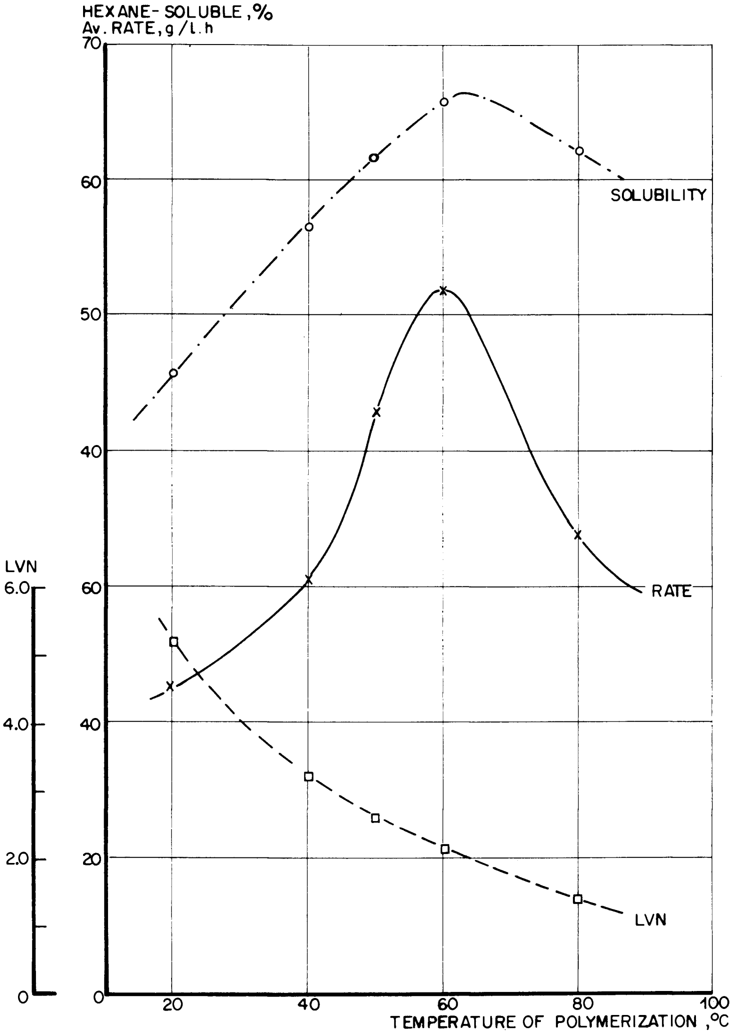

Figure 6. Influence of temperature on polymerization with catalyst consisting of 5 mmole/liter β-$TiCl_3$, 5 mmole/liter $AlEt_2OEt$ and 1 mmole/liter $AlEt_3$

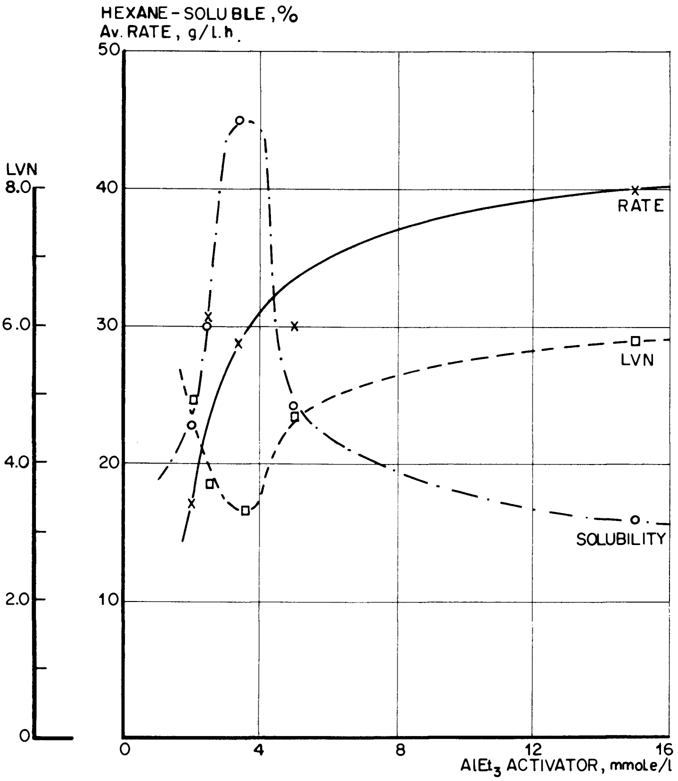

Figure 7. Polymerization of propylene at 60° C. as affected by amount of $AlEt_3$ used to activate 5 mmole/liter γ-$TiCl_3$.

and a significantly lower hexane soluble polymer content than the β-$TiCl_3$-produced polymer. Although the hexane soluble polymer content is not independent of *LVN*, it can nevertheless be concluded that for preparing a polymer of high crystallinity, a γ-$TiCl_3$-based catalyst is to be preferred to a β-$TiCl_3$-based catalyst.

Influence of Temperature on Polymerization. The effect of temperature on the polymerization with various γ-$TiCl_3$-based catalysts is shown in Figures 8, 9, and 10. In some respects, this effect is similar to that shown in Figures 5 and 6 for β-$TiCl_3$-based catalysts. The rate of these polymerizations at atmospheric pressure is again highest at 60° C., presumably for the same reasons as given above for the β-$TiCl_3$ catalyst.

With $AlEt_3$ or $AlEt_2Cl$ activation, hexane soluble polymer content of the polypropylene produced is lowest near the same temperature of 60° C., but with $AlEt_2OEt$ activation it reaches a high value at 60° C. The *LVN* tends to decrease with rising temperature.

Activation with Mixed Alkylaluminum Compounds. A few examples of specific effects observed if mixtures of different alkylaluminum compounds are used for activating $TiCl_3$ are mentioned in Table II, according to which some

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$AlEt_3$ added to $AlEt_2OEt$ increases the rate of polymerization considerably. Figure 11 shows the large effect of adding some $AlEt_3$ or $AlEtCl_2$ to $AlEt_2Cl$ in activating γ-$TiCl_3$. Adding $AlEtCl_2$ reduces the rate of polymerization to a very low value, whereas adding about 25% $AlEt_3$ to $AlEt_2Cl$ increases the rate to a value far exceeding that observed for the separate aluminum components. Adding either $AlEtCl_2$ or $AlEt_3$ to $AlEt_2Cl$ causes a decrease in *LVN* and an increase of the hexane soluble content, the latter particularly with $AlEt_3$.

Figures 12 and 13 show how ethyl-, chlorine-, and ethoxy-group content of the mixture of alkylaluminum compounds used for activating γ-$TiCl_3$ influences the polymerization of propylene. The various contents of these groups were obtained by mixing calculated amounts of $AlEt_3$, $AlEt_2Cl$, $AlEt_2OEt$, $AlEtOEtCl$, $AlEtCl_2$, and ethanol. The graphs show curves for equal rates of polymerization and for equal hexane soluble polymer content.

According to Figure 12 very high polymerization rates are found in a region covering alkylaluminum compounds in which about 25–30% of the ethyl groups of $AlEt_3$ are replaced by chlorine and/or ethoxy groups. Replacing more ethyl groups reduces the rate of polymerization again. A remarkable point is that replacing more ethyl groups by mixed ethoxy-chlorine groups

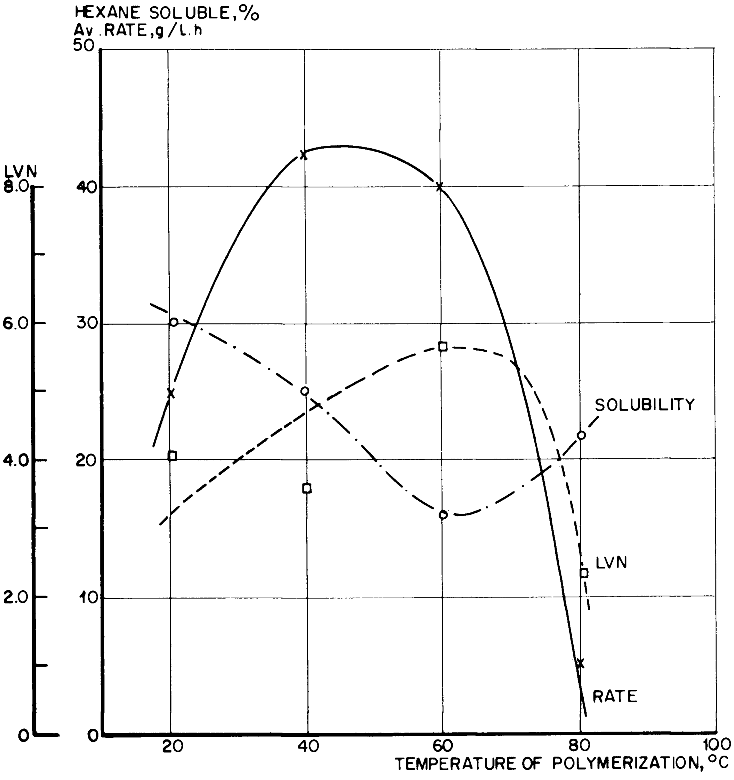

Figure 8. Influence of temperature on polymerization with catalyst consisting of 5 mmole/liter γ-$TiCl_3$ and 15 mmole/liter $AlEt_3$

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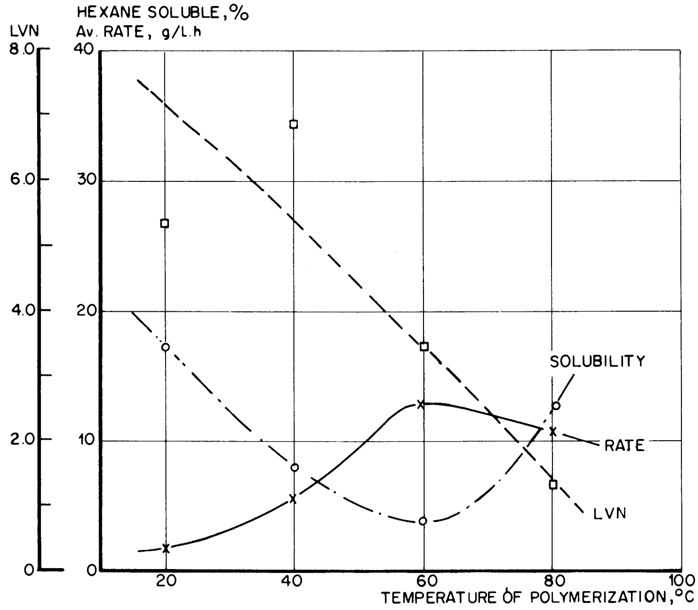

Figure 9. Influence of temperature on polymerization with catalyst consisting of 5 mmole/liter γ-$TiCl_3$ and 15 mmole/liter $AlEt_2Cl$

reduces the rate far less than replacement by either chlorine or ethoxy groups. For instance, a catalyst activated with AlEtOEtCl produces polypropylene at a considerably higher rate than one activated with $AlEt_2Cl$ even though the latter compound contains twice as much ethyl.

To a certain extent hexane soluble polymer content, shown in Figure 13, runs parallel with rate—i.e., amorphous polymer content is highest in the catalyst composition region of highest rate of polymerization. An important exception is found with aluminum compounds containing about one chlorine, two to one ethyl and zero to one ethoxy groups per aluminum atom. Catalysts activated with compounds of this class produce polymer of low amorphous content at a fair rate. Such compounds are prepared, for example, by adding some $AlEt_2OEt$, AlEtOEtCl, or ethanol to $AlEt_2Cl$.

LVN values of the polymers considered in Figures 12 and 13 were between 2.4 and 5.7, most in the region from 3 to 4. Lowest *LVN* values were found for polymers of highest amorphous content produced with a catalyst containing ethoxy groups. On the other hand, adding some $AlEt_2OEt$ or ethanol to $AlEt_2Cl$ increased the *LVN* from 3.4 to as high as 5.

VCl_4-Based Catalysts

Table III lists results of polymerizations with various VCl_4-based catalysts. In most of these polymerizations VCl_4 was first reduced in a separate reaction at 80° C. or 170° C. with $AlEt_3$ or $AlEt_2Cl$ in slight excess of the stoichiometric molar ratios: $AlEt_3/VCl_4 = 1/3$ or $AlEt_2Cl/VCl_4 = 1/2$. Under these conditions VCl_3 was expected to be formed similarly to $TiCl_3$ from $TiCl_4$.

It appears that a one-step VCl_4-$AlEt_3$ catalyst as well as the corresponding two-step catalyst of similar composition based on a reduction product of VCl_4 prepared at 80° C., are virtually inactive for polymerization. Carrick *et al.* (*7, 9*) have indicated that with an excess of metal alkyl compounds VCl_4 is easily reduced to vanadium compounds of valence lower than 3. This may be true also for VCl_3 prepared at 80° C. in the separate reduction step of catalyst formation. The low stability towards further reduction of such VCl_3 may be connected with the fact that it is not crystalline but amorphous (*28*). Apparently, vanadium compounds of valence lower than 3 thus obtained are not at all active for polymerization. Activation with $AlEt_2Cl$ or, in particular with $AlEt_2OEt$ of the VCl_3 precipitate prepared at 80° C., leads to a catalyst of

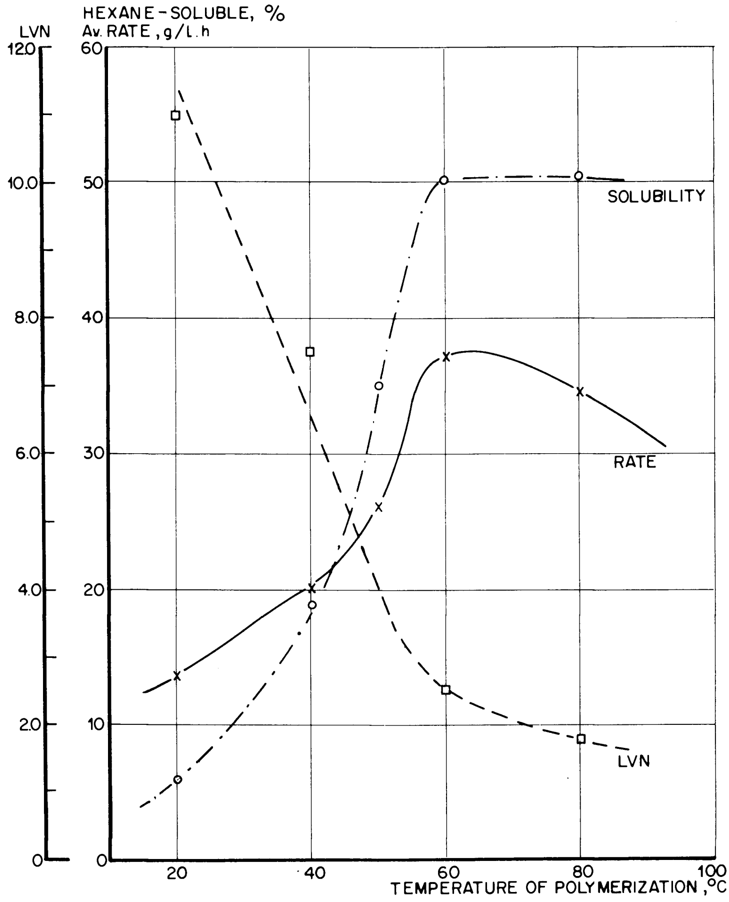

Figure 10. Influence of temperature on polymerization with catalyst consisting of 5 mmole/liter γ-$TiCl_3$, 5 mmole/liter $AlEt_2OEt$, and 1 mmole/liter $AlEt_3$

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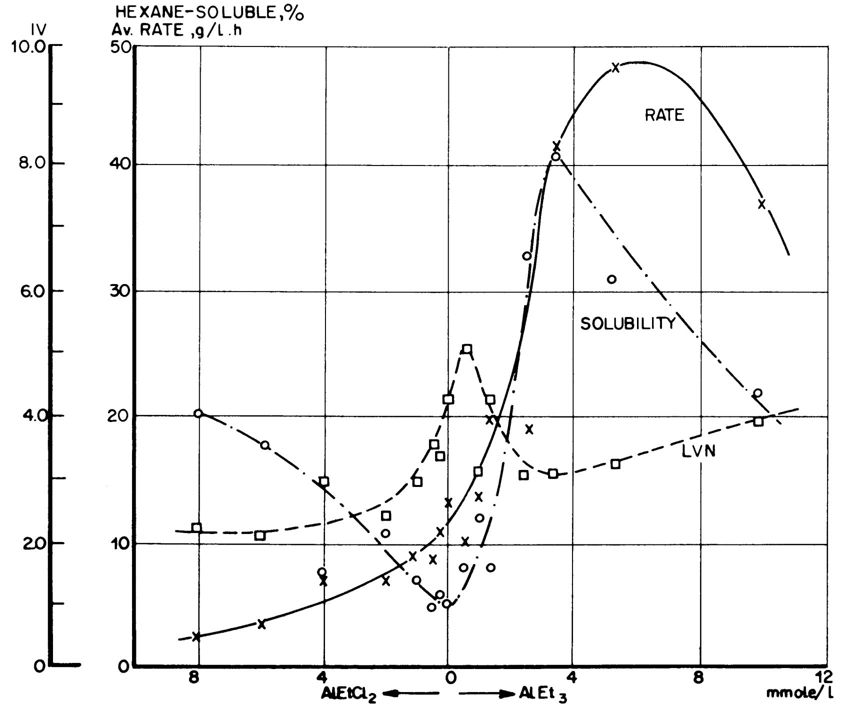

Figure 10. Influence of temperature on polymerization with catalyst of 5 mmole/liter γ-$TiCl_3$, 5 mmole/liter $AlEt_2OEt$, and 1 mmole/liter $AlEt_3$

considerable activity. This indicates that these aluminum compounds react less vigorously with VCl_3 under formation of inactive vanadium compounds than $AlEt_3$ does.

Like the analogous $TiCl_3$ product, VCl_3 prepared in a special reduction step at 170° C. with $AlEt_3$ appears to be much more stable and displays a considerably higher polymerization activity than a VCl_3 precipitate prepared at 80° C. The contrast is particularly obvious on activation with $AlEt_3$.

A VCl_3 precipitate of even higher activity is obtained on reducing VCl_4 with $AlEt_2Cl$ at 170° C; in this respect the vanadium compounds differ from the titanium compounds shown in Table I. Presumably the vigorous reduction of VCl_4 with the very vigorous agent $AlEt_3$ causes some formation of VCl_2 besides unreacted VCl_4. The more gentle $AlEt_2Cl$ may not run to overreduction, although again at higher $VCl_4/AlEt_2Cl$ ratios, for instance at a ratio $1/1$, a precipitate of low catalytic activity is formed, presumably again overreduced vanadium compound. The evidence indicates that the main polymerization activity is connected with VCl_3 and not with compounds of lower valence.

Of the alkylaluminum activators tested $AlEt_2OEt$ induces the highest rate of polymerization. A very important feature of VCl_4-based catalysts is that they produce highly amorphous polypropylene with a hexane soluble polymer content of up to 72%.

$VOCl_3$-Based Catalysts

In forming catalysts from $VOCl_3$, a separate reduction step does not offer any advantage as far as rate is concerned (Table IV). It is likely that mild conditions suffice to reduce $VOCl_3$ and an intermediate reduced compound such as $VOCl_2$ to less active compounds of lower valence (*9*). An indication that this assumption is correct, is that the highest average rate of polymerization is found at 20° C. instead of at 60° C. as for $TiCl_3$. Also the rate of polymerization at 60° C. strongly decreases with time. Moreover, a mild activating agent like $AlEt_2Cl$ induces a much faster polymerization than the vigorous $AlEt_3$, which may not only activate but also rapidly overreduce the vanadium compound.

Polypropylene produced with $VOCl_3$-based catalysts usually have a strikingly high hexane soluble polymer content—i.e., they are of low crystallinity. This conclusion is in substantial agreement with the results of Pasquon *et al.* (*29, 30, 31*) concerning the polymerization of propylene with $VOCl_3$-Al(hexyl)$_3$ catalysts.

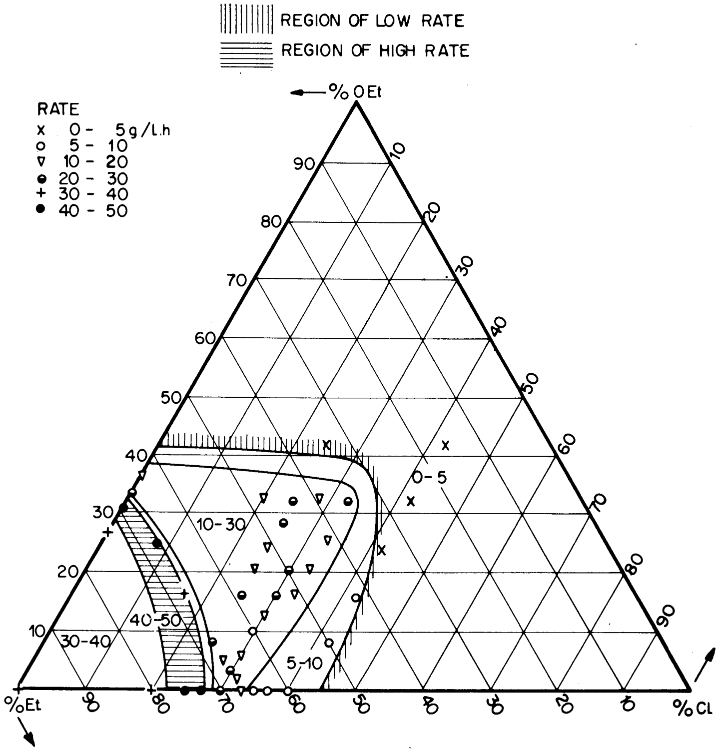

Figure 12. Rate of polymerization of propylene at 60° C. as influenced by the ethyl, ethoxy, and chlorine content of the Al compound used as activator for γ-$TiCl_3$. Catalyst: 5 mmole/liter γ-$TiCl_3$ and 15–20 mmole/liter alkylaluminum compound. Polymerization conditions: 2 hours at 60° C. at 1 atm.

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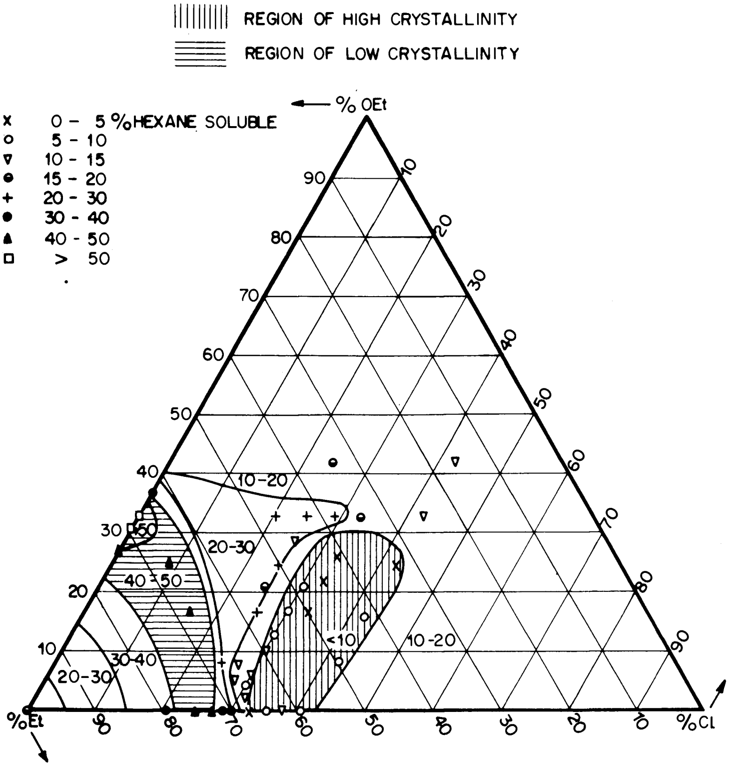

Figure 13. The hexane solubility of polypropylene produced at 60° C. as influenced by the ethyl, ethoxy, and chlorine content of the Al compound used as activator for the γ-$TiCl_3$-based catalyst

Table III. Polymerization of Propylene Activated with Various

Catalyst components mmole/liter ultimate conc.

Components in Reducing Step	*Reducing Conditions*	*Activating Compound*
5 VCl_4		15 $AlEt_3$
5 VCl_4 + 2 $AlEt_3$	1 hr. 80° C.	15 $AlEt_3$
5 VCl_4 + 2 $AlEt_3$	1 hr. 80° C.	15 $AlEt_2Cl$
5 VCl_4 + 2 $AlEt_3$	1 hr. 80° C.	15 $AlEt_2OEt$
5 VCl_4 + 2 $AlEt_3$	1 hr. 170° C.	15 $AlEt_3$
5 VCl_4 + 2 $AlEt_3$	1 hr. 170° C.	15 $AlEt_3$
5 VCl_4 + 2 $AlEt_3$	1 hr. 170° C.	15 $AlEt_2Cl$
5 VCl_4 + 2 $AlEt_3$	1 hr. 170° C.	15 $AlEt_2OEt$
5 VCl_4 + 2.7 $AlEt_2Cl$	1 hr. 170° C.	5 $AlEt_3$
5 VCl_4 + 2.7 $AlEt_2Cl$	1 hr. 170° C.	15 $AlEt_2Cl$
5 VCl_4 + 2.7 $AlEt_2Cl$	1 hr. 170° C.	15 $AlEt_{1\frac{1}{2}}Cl_{1\frac{1}{2}}$
5 VCl_4 + 2.7 $AlEt_2Cl$	1 hr. 170° C.	15 $AlEtOEtCl$
5 VCl_4 + 2.7 $AlEt_2Cl$	1 hr. 170° C.	15 $AlEtCl_2$
5 VCl_4 + 2.7 $AlEt_2Cl$	1 hr. 170° C.	15 $AlEt_2OEt$

[1] VCl_4 concentration in reduction step: about 70 mmole per liter.

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Discussion

The most striking result of these studies is that catalysts based on a one-step reaction of $TiCl_4$ or VCl_4 with an alkylaluminum compound are bound to give less than optimum rate of polymerization. Apparently several of the titanium or vanadium and alkylaluminum compounds formed in this reaction do not contribute to polymerization. The one-step catalyst mixtures are obviously unsuitable for kinetic studies because of their uncontrollable composition and often because of instability.

A procedure in which the catalyst is prepared in two steps, one involving reduction and the other activation, has several advantages. Specific, reduced transition metal compounds, such as β-$TiCl_3$, γ-$TiCl_3$, or VCl_3 can be prepared which not only may be more stable towards overreduction but also are more specific catalytically than the undefined transition metal precipitates obtained in single-step procedures. Another advantage is that in the two-step procedure, the alkylaluminum compound used in the activating step may be different from the compound in the reducing step, thus offering a wider choice of compounds for each step.

All $TiCl_4$- or VCl_4-based catalyst systems studied showed highest polymerization activity if these compounds were reduced to the trivalent state. Reduction to a lower valence is always accompanied by a decrease in rate of polymerization, which indicates that the main catalytic activity of these catalyst systems is directly connected with the trivalent compounds.

Crystallinity of the polypropylene formed is strongly influenced by the type of transition metal compound and to a less extent by type of alkylaluminum compound of the catalyst. Catalysts based on γ-$TiCl_3$, β-$TiCl_3$, and VCl_3 and activated for instance with $AlEt_2Cl$ produce in typical cases, polymers of 4, 21, and 72% hexane soluble polymer content, respectively. This is a strong indication that the type of transition metal compound not only

with VCl_4-Based Catalysts Reduced and Alkylaluminum Compounds[1]

Polymeriz. Conditions	*Av. Rate, grams/liter/hr.*	*LVN*	*Hexane Soluble Polymer, %*
2 hr. 60° C.	0		
2 hr. 60° C.	0.2	5.9	
2 hr. 60° C.	7.8	3.7	60
2 hr. 60° C.	27	6.9	32
2 hr. 60° C.	25	5.7	50
2 hr. 60° C.	16	4.0	45
2 hr. 60° C.	15	3.7	61
2 hr. 60° C.	32	6.5	44
1 hr. 60° C.	21	5.6	65
1 hr. 60° C.	34	3.1	72
1 hr. 60° C.	17	1.9	33
1 hr. 60° C.	20	3.5	24
1 hr. 60° C.	5	0.9	13
1 hr. 60° C.	61	5.2	54

Table IV. Polymerization of Propylene Activated with Various

Catalyst Components mmole/liter ultimate conc.		
Components in Reducing Step	*Reducing Conditions*	*Activating Compound*
5 $VOCl_3$ + 2.7 $AlEt_2Cl$	1 hr. 170° C.	15 $AlEt_2Cl$
5 $VOCl_3$ + 2.7 $AlEt_2Cl$	1 hr. 170° C.	5 $AlEt_2OEt$ + 1 $AlEt_3$
5 $VOCl_3$		3 $AlEt_3$
5 $VOCl_3$		3 $AlEt_3$
5 $VOCl_3$		3 $AlEt_3$
5 $VOCl_3$		15 $AlEt_3$
5 $VOCl_3$		15 $AlEt_3$
5 $VOCl_3$		15 $AlEt_2Cl$
5 $VOCl_3$		15 $AlEt_2Cl$
5 $VOCl_3$		15 $AlEt_{1\frac{1}{2}}Cl_{1\frac{1}{2}}$
5 $VOCl_3$		15 $AlEtCl_2$

controls the rate of polymerization (*8*, *13*, *17*, *21*) but also the structure (*11*, *12*). Obviously those catalysts that produce highly amorphous polypropylene are more suitable for preparing amorphous, rubberlike copolymers of various α-olefins (*23*).

The type of alkylaluminum compound used as a catalyst activator has a far from negligible influence on the polymer structure. Activators like $AlEt_2Cl$, $AlEt_3$, and $AlEt_2OEt$ in combination, for instance, with γ-$TiCl_3$ produce polymers of 4, 16, and 50% hexane soluble polymer content, respectively. The effect of $AlEt_3$ in this respect may be obscured by the fact that it is capable of overreducing $TiCl_3$. This is obvious in particular with β-$TiCl_3$ but may also be the case at the active polymerization sites of γ-$TiCl_3$. $AlEt_2OEt$ may form a complex that, although accelerating the rate of polymerization, influences the steric purity of the polymer strongly. Possibly this compound might exchange alkoxy groups for chlorine with the $TiCl_3$ molecules thus destroying the lattice structure of $TiCl_3$ and the stereo regulating effect on polymerization connected with this crystal lattice.

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with $VOCl_3$-Based Catalysts, Reduced and Alkylaluminum Compounds

Polymeriz. Conditions	*Av. Rate, grams/ liter/hr.*	*LVN*	*Hexane Soluble Polymer, %*
1 hr. 60° C.	4.7	4.7	23
1 hr. 60° C.	5.5	6.9	18
1 hr. 0° C.	4	1.5	68
1 hr. 20° C.	12	2.6	71
1 hr. 60° C.	6.3	4.2	81
1 hr. 20° C.	7.0	3.8	31
1 hr. 60° C.	3.0	3.4	27
1 hr. 20° C.	21	2.1	51
1 hr. 60° C.	11	4.5	60
1 hr. 60° C.	4.2	3.5	56
1 hr. 60° C.	3.7	0.9	79

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Transition Metal Catalyst Systems for Polymerizing Butadiene and Isoprene

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Reducing $TiCl_4$ at 80° C. by $AlEt_3$ at an Al/Ti ratio of about 1/3, leading to formation of $AlCl_3$ containing β-$TiCl_3$, followed by activation with some $AlEt_3$, $AlEt_2Cl$, or $AlEt_2OEt$ is an effective way to study the influence of catalyst composition on the polymerization of dienes to polymers of high cis-1,4 content. Catalysts consisting of β-$TiCl_3$ and $AlEtCl_2$ polymerize butadiene to a crystalline trans-1,4 polymer, whereas isoprene in benzene is polymerized to cyclized rubber. Crystalline *trans*-1,4-polybutadiene and polyisoprene are formed with catalysts containing coprecipitated blends of β- or γ-$TiCl_3$ and VCl_3. Molecular weight of *cis*-polybutadiene prepared with cobalt catalyst systems can be regulated effectively by using specific blends of $AlEtCl_2$ and $AlEt_2Cl$ as activators. Polyisoprene prepared with such cobalt systems contains 19–36% of 3,4-structure.

Zieglers' discovery in 1954 that certain transition metal compounds combined with special alkylmetal compounds can induce the polymerization of ethylene has been extended rapidly to the polymerization of other monomers, among which are butadiene and isoprene. Some of these catalyst combinations have been found capable of inducing the formation of stereoregular polydienes. An interesting aspect of this type of polymerization is its mechanism (*10, 14, 16, 18, 39*).

To establish conditions that lead to the formation of stereoregular cis or trans polymers from butadiene and isoprene, a series of combinations of a transition metal compound with and alkylaluminum compound were tested for catalytic effect. In this connection considerable attention was given to those catalyst systems that had been found attractive for the stereospecific polymeri-

In Elastomer Stereospecific Polymerization; Johnson, B., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

zation of propylene (*5*). In this investigation iodine-containing catalysts, such as those based on TiI_4, which are known (*43*) to be active in forming polybutadiene of up to 95% cis-content have been left out of consideration.

Experimental Procedure

Polymerization. Polymerizations were effected batchwise at atmospheric pressure in 500-ml. three-necked flasks containing 150 or 300 ml. solvent with catalyst. The reactor was provided with a stirrer, gas inlet, gas outlet, and a buret for solvent, catalyst, and monomer supply.

Two methods of catalyst preparation were followed, viz., with or without a separate reducing step. When the catalyst was not separately reduced, its components were simply mixed in the desired ultimate concentrations. In the procedure involving a separate reducing step the diluted transition metal compound was first reduced with $AlEt_3$ to a specific compound of lower valence. The compound thus formed was activated by adding a certain amount of an alkylaluminum compound, which was not necessarily the same as the one used for the reduction. The solvent was either benzene or isooctane (2,2,4-trimethylpentane). In the experiments with catalyst prepared at 170° C. the resulting solution contained 7% by volume *n*-decane.

Polymerization was started either by introducing gaseous butadiene continuously into the catalyst-containing solvent at atmospheric pressure for 10–60 minutes or by gradually running an amount of isoprene corresponding to 10% of the solvent volume into the reactor flask in the first half-hour of a total polymerization period of 1–2 hours. After polymerization the polymer was precipitated by pouring its solution into a threefold volume of methanol or ethanol containing 1% of antioxidant. The rubber was dried at 56° C. in vacuo.

During this procedure much care was taken to exclude impurities such as oxygen and water. All ingredients were handled under a blanket of nitrogen. Solvents, monomers, and nitrogen were dried over Linde Molecular Sieves No. 4. Generally these feeds contained less than 5 p.p.m. water, as measured with a modified Karl Fischer equipment or a Beckman electrolytic hygrometer, and less than 5 p.p.m. of oxygen, as measured with a Hersch cell analyzer.

Evaluating the Polymer. The intrinsic viscosity (*IV*) of the polymer was determined at 25° C. with solutions in benzene or toluene containing 0.1 gram/liter polymer and calculated with the equation: $IV = (\ln \eta_{rel})/C$. In many cases some gel formation made *IV* determination for the whole polymer impracticable. Hoekstra viscosities of a number of polymers were measured at 100° C. with the Hoekstra (Wallace) plastometer (*42*). This instrument provides bulk viscosity data for rubbers on a scale 0 (low viscosity) to 100 (high viscosity).

The structure of the polymers was determined by conventional procedures from the infrared absorption of the solutions in CS_2 or $CS_2 + CCl_4$ (1:1) containing 10 grams rubber/liter (*11, 12, 15, 23, 44*). Bands at 11.0 μ, 10.36 μ, and 13.60 μ were used to determine 1,2, trans-1,4 and cis-1,4 content of polybutadiene, respectively. Bands at 11.25 μ, 2.46 μ, and 2.39 μ were used to determine 3,4 cis-1,4, and cis-1,4 + trans-1,4 content of polyisoprene, respectively. The bands of polyisoprene were calibrated by measurements with

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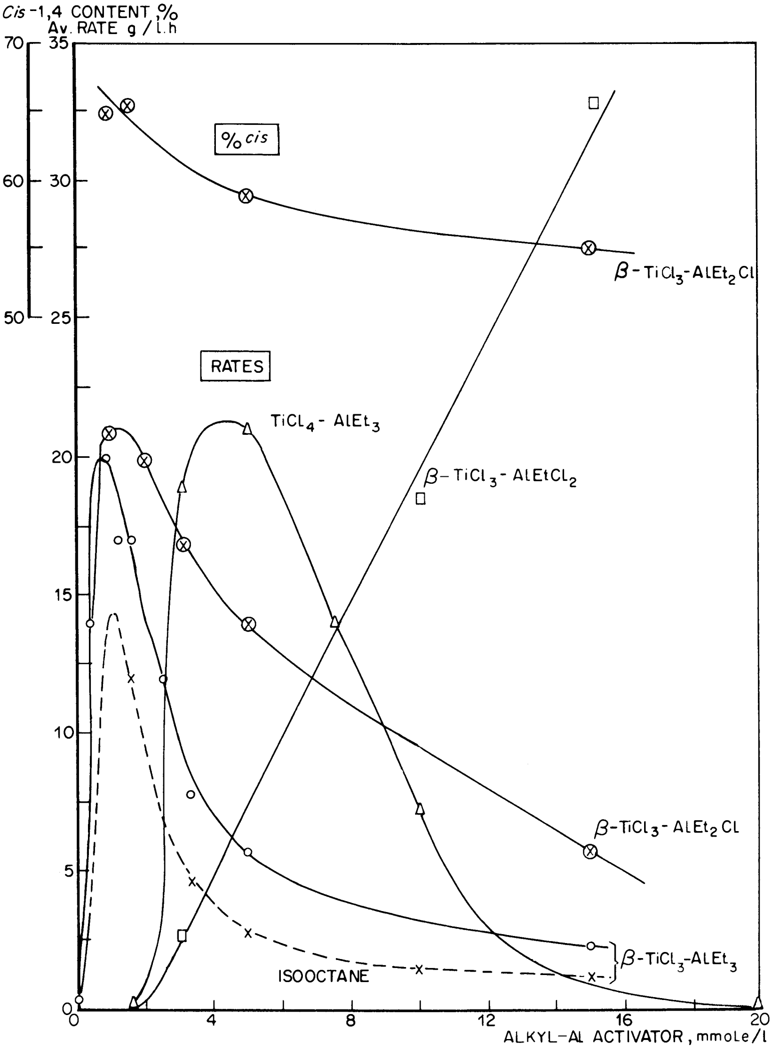

Figure 1. The rate of polymerization of butadiene at 60° C. (1 hour) with catalyst systems based on $TiCl_4$ or β-$TiCl_3$ (5 mmole/liter) activated with increasing amounts of various alkylaluminum activators; cis-1,4 content of polymer produced with β-$TiCl_3$–$AlEt_2Cl$ catalyst. Solvent: benzene, unless indicated.

deproteinized natural rubber and gutta-percha (*24*). The precision of these measurements was within 1%. Where necessary the polymer was somewhat milled down to ensure a good solubility.

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Catalysts Based on $TiCl_4$

Catalyst Preparation. Catalysts consisting of simple combinations of $TiCl_4$ and Al (alkyl)$_3$ have often been used to prepare polybutadiene (*20, 35*) or polyisoprene (*1, 21, 40, 41, 45*). It has been shown by Arlman *et al.* (*8, 9*) that on combining these components, $TiCl_4$ is reduced by part of the alkylaluminum compound to a brown solid compound of lower valence consisting mainly of β-$TiCl_3$, whereas Cooper and Rose (*13*) demonstrated that with an excess of alkylaluminum compound, reduction may proceed to compounds of titanium of valence 2 and even lower.

In polymerizing propylene there were many indications that the main catalytic activity of $TiCl_4$-based Ziegler catalysts is connected with this $TiCl_3$ (*5*). The continued reduction, for example, to blackish $TiCl_2$ leads to a catalyst of lowered activity. $TiCl_4$ as such is not an active catalyst component in polymerizing mono-olefins, although by virtue of its being a Friedel-Crafts type of compound, it may influence rate of polymerization, molecular weight, and structure of the polymer and even induce polymerization of diolefins. Furthermore, presence of $TiCl_4$ along with $AlEt_2Cl$ or $TiCl_3$ with $AlEt_3$ during polymerization has the considerable drawback of resulting in a change of catalyst activity with time since the components of the catalyst continue to react with each other. This also affects the structural homogeneity of the polymer.

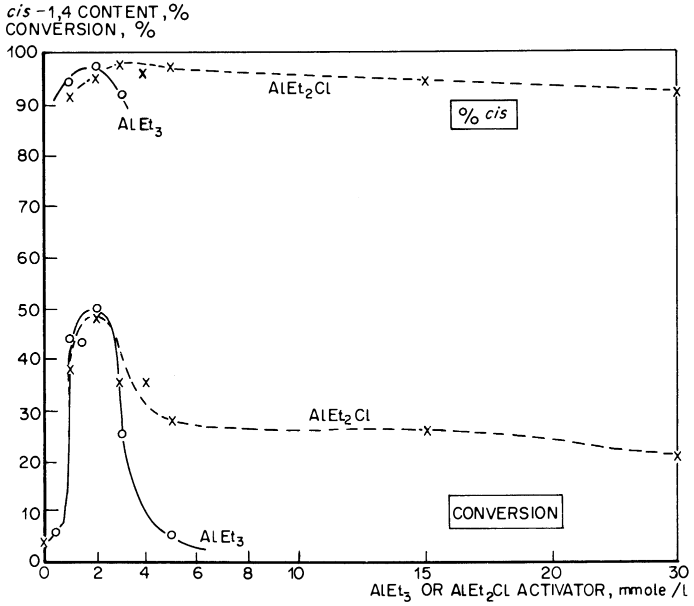

Figure 2. Conversion of isoprene after 2 hours at 60° C. in isooctane with catalyst systems based on β-$TiCl_3$ (5 mmole/liter) activated with increasing amounts of $AlEt_3$ or $AlEt_2Cl$; cis-1,4 content of polymer produced with these catalysts.

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Table I. Polymerization of Butadiene at 60° C. on Transition

Catalyst Components, mmole/liter	*Solvent*
$TiCl_3$-containing catalysts	
5 $TiCl_4$ + 5 $AlEt_3$	benzene
5 $TiCl_4$ + 5 $AlEt_3$	isooctane
5 β-$TiCl_3$ + 1 $AlEt_3$	benzene
5 β-$TiCl_3$ + 1 $AlEt_3$	isooctane
5 β-$TiCl_3$ + 1 $AlEt_3$	benzene
5 β-$TiCl_3$ + 1 $AlEt_2Cl$	benzene
5 β-$TiCl_3$ + 1 $AlEt_2Cl$	benzene
5 β-$TiCl_3$ + 15 $AlEt_2Cl$	benzene
5 β-$TiCl_3$ + 1 $AlEt_2OEt$	benzene
5 β-$TiCl_3$ + 5 AlEt OEtCl	benzene
5 β-$TiCl_3$ + 15 $AlEtCl_2$	benzene
5 γ-$TiCl_3$ + 10 $AlEt_3$	benzene
VCl_3-containing catalysts	
4 β-$TiCl_3$ + 1 VCl_3 (80° C.) + 15 $AlEt_3$	benzene
4 γ-$TiCl_4$ + 1 VCl_3 (170° C.) + 15 $AlEt_3$	benzene
4 γ-$TiCl_4$ + 1 VCl_3 (170° C.) + 15 $AlEt_2OEt$	benzene
4 γ-$TiCl_4$ + 1 VCl_3 (170° C.) + 15 $AlEt_2Cl$	benzene
2.5 γ-$TiCl_4$ + 2.5 VCl_3 (170° C.) + 15 $AlEt_3$	benzene
5 VCl_3 (80° C. prepared) + 15 $AlEt_3$	benzene
5 VCl_3 (170° C. prepared) + 15 $AlEt_3$	benzene
5 VCl_3 (80° C. prepared) + 15 $AlEt_2OEt$	benzene
Co-containing catalysts	
0.075 Co naphthenate + 10 $AlEtCl_2$	benzene
0.075 Co naphthenate + 10 $AlEtCl_2$	benzene
0.075 Co naphthenate + 10 $AlEtCl_2$	isooctane
0.075 Co naphthenate + 10 $AlEt_{1\frac{1}{2}}Cl_{1\frac{1}{2}}$	benzene
0.075 Co naphthenate + 10 $AlEt_2Cl$	benzene
0.1 $CoCl_2$ in ethanol + 10 $AlEt_{1\frac{1}{2}}Cl_{1\frac{1}{2}}$	benzene

[1] Partial monomer pressure: 1 atm.

These difficulties are largely avoided when $TiCl_4$ and Al $(alkyl)_3$ are used at the stoichiometric 1/1 ratio. Such a combination would react under moderate conditions of temperature and concentration as follows:

$$TiCl_4 + Al\ (alkyl)_3 \rightarrow TiCl_3 + Al\ (alkyl)_2Cl + alkyl^{\bullet}$$

In fact, this particular combination is highly effective in polymerizing isoprene to a high cis polymer (*1, 21, 40, 41*). In a more general sense, however, such a simple one-step procedure imposes a severe limitation when studying the

with Various Catalyst Combinations Based
Metal Compounds[1]

Polym. Cond.	*Av. Rate of Polym., grams/liter/hr.*	*IV*	*Structure, %*	
			cis	*trans*
1 hr. 60° C.	21	2.0	61	36
1 hr. 60° C.	13			
1 hr. 60° C.	20		59	35
1 hr. 60° C.	12			
1 hr. 20° C.	6.3		71	27
1 hr. 60° C.	21	2.6	65	33
1 hr. 20° C.	3.3		78	20
1 hr. 60° C.	5.7	0.95	55	41
1 hr. 60° C.	44	2.7	55	41
1 hr. 60° C.	31			
1 hr. 60° C.	33	0.43		>99
1 hr. 60° C.	2.7		8	92
5 min. 60° C.	68			>95
10 min. 60° C.	155	7.3		>95
10 min. 60° C.	130			>95
30 min. 60° C.	10			
10 min. 60° C.	110			>95
60 min. 60° C.	4.5			>95
60 min. 60° C.	2.7			>95
10 min. 60° C.	42			>90
30 min. 60° C.	230	gel		
15 min. 20° C.	760	gel		
30 min. 20° C.	37	gel		
10 min. 20° C.	250	1.8	>95	
30 min. 20° C.	23	0.5		
20 min. 20° C.	240	2.2		

effect of catalyst composition on the polymerization. In particular catalysts consisting of $TiCl_4$ and Al $(alkyl)_3$ at ratios much different from 1/1 run into the danger of overreducing $TiCl_4$ when excess Al $(alkyl)_3$ is used, or insufficient reduction when there is too little of it, both conditions being highly undesirable during the polymerization for the reasons mentioned above.

Considering that in composing a Ziegler catalyst two different reactions are usually involved—reducing the transition metal compound and activating the reduced compound—it is likely that optimal conditions for these two reactions are not necessarily the same. For instance, the amount and type of

Table II. Polymerization of Isoprene with on Transition

Catalyst Components, mmole/liter	*Solvent*
$TiCl_3$ containing catalysts	
5 β-$TiCl_3$ + 2 $AlEt_3$	isooctane
5 β-$TiCl_3$ + 2 $AlEt_3$	benzene
5 β-$TiCl_3$ + 3 $AlEt_2Cl$	isooctane
5 β-$TiCl_3$ + 2 $AlEt_2OEt$	benzene
5 β-$TiCl_3$ + 5 $AlEt_{1\frac{1}{2}}Cl_{1\frac{1}{2}}$	isooctane
5 γ-$TiCl_3$ + 2 $AlEt_3$	isooctane
5 γ-$TiCl_3$ + 15 $AlEt_3$	isooctane
VCl_3 containing catalysts	
4 γ-$TiCl_3$ + 1 VCl_3 + 5 $AlEt_3$	isooctane
4 γ-$TiCl_3$ + 1 VCl_3 15 $AlEt_3$	isooctane
2.5 γ-$TiCl_3$ + 2.5 VCl_3 + 15 $AlEt_3$	isooctane
2.5 γ-$TiCl_3$ + 2.5 VCl_3 + 15 $AlEt_2Cl$	isooctane
2.5 γ-$TiCl_3$ + 2.5 VCl_3 + 15 $AlEt_2OEt$	isooctane
5 VCl_3 + 15 $AlEt_3$	isooctane
Co containing catalysts	
0.1 Co naphthenate + 10 $AlEtCl_2$	benzene
0.1 Co naphthenate + 40 $AlEtCl_2$	benzene
0.1 Co naphthenate + 10 $AlEtCl_2$	isooctane
0.1 Co naphthenate + 10 $AlEt_{1\frac{1}{2}}Cl_{1\frac{1}{2}}$	isooctane
0.1 Co naphthenate + 10 $AlEt_2Cl$	isooctane
0.1 $CoCl_2$ in ethanol + $AlEtCl_2$ + 6 $AlEt_2Cl$	benzene

Monomer concentration in solvent: 9% vol.

alkylaluminum compound required for an optimal effect in each step may be different.

Saltman (*39*) has indicated a way out of this difficulty by preparing β-$TiCl_3$ from $TiCl_4$ in a separate reducing reaction with a stoichiometric amount of $AlEt_3$—i.e., at an $AlEt_3/TiCl_4$ ratio of 1.0 or 0.5 followed by removal of the $AlEt_2Cl$ or $AlEtCl_2$ formed by washing. The $TiCl_3$ precipitate is then activated with a fresh amount of alkylaluminum compound.

In the present investigation $TiCl_4$ was reduced with $AlEt_3$ at an Al/Ti molar ratio of 1/3, the following reaction being expected to occur:

$$3\ TiCl_4 + Al(C_2H_5)_3 \rightarrow 3\ TiCl_3 + AlCl_3 + 3\ C_2H_5^{\bullet}$$

In practice the required amount of a 0.1*M* solution of $AlEt_3$ was added to a similar $TiCl_4$ solution. A small (10–20%) excess of $AlEt_3$ over the ratio of 1/3 served to counteract any disturbing impurity and proved to be beneficial for obtaining reproducible results. Reduction was completed by heating for 1 hour at 80° C. during which a reddish-brown precipitate was formed consisting, according to x-ray analysis, of β-$TiCl_3$ (*9, 30*). Analysis showed that the $AlCl_3$ formed is largely taken up in the β-$TiCl_3$ lattice structure and cannot

Various Catalyst Combinations Based
Metal Compounds[1]

Polym. Cond.	*Conversion, %*	*IV*	*Structure*
2 hr. 60° C.	50		97% cis
2 hr. 60° C.	31	2.4	97% cis
2 hr. 60° C.	36		98% cis
2 hr. 60° C.	34	2.1	92% cis
2 hr. 60° C.	0		
2 hr. 60° C.	3		
2 hr. 60° C.	2		
1 hr. 60° C.	30	12	>95% trans
1 hr. 60° C.	30	4.8	>95% trans
1 hr. 60° C.	35	3.9	>95% trans
1 hr. 60° C.	3		
1 hr. 60° C.	12	5.0	>90% trans
1 hr. 60° C.	4		>95% trans
1 hr. 60° C.	30	0.22	cyclized
1 hr. 60° C.	41	0.04	cyclized
1 hr. 60° C.	100	gel	20% 3,4
1 hr. 60° C.	95	3.4	36% 3,4
1 hr. 60° C.	12	1.5	36% 3,4
1 hr. 60° C.	56	2.5	31% 3,4

be removed by washing. Some alkyl groups may also be present in the precipitate (*8, 9*). On heating the $AlEt_3$-$TiCl_4$ (1:3 molar) reaction mixture for 1 hour at 170° C. a purple precipitate, consisting mainly of γ-$TiCl_3$, is formed.

The β-$TiCl_3$ or γ-$TiCl_3$ precipitate thus prepared may contain, fixed in its crystal lattice, 1 $AlCl_3$ for every 3–6 $TiCl_3$ molecules. Without washing, it was further diluted and activated with the required amount and type of alkylaluminum compound to be used as a polymerization catalyst. It has been shown for γ-$TiCl_3$ that the $AlCl_3$ in the $TiCl_3$ lattice is not converted into soluble compounds on adding $AlEt_3$ or $AlEt_2Cl$ (*8*). This may also apply to $AlCl_3$ fixed in a β-$TiCl_3$ lattice.

These two-step prepared catalysts have been found (*5*) highly active for polymerizing propylene, often considerably more so than similar catalyst combinations mixed in one step. The two-step catalysts tend, moreover, to induce formation of polypropylene of increased stereospecific purity.

Polymerization. Figures 1 and 2 show how activating β-$TiCl_3$ with various amounts and types of alkylaluminum compounds affects polymerization of butadiene and isoprene (*2, 3*). Tables I and II give additional information on the polymerization with the best of these catalysts and with a few other catalyst systems.

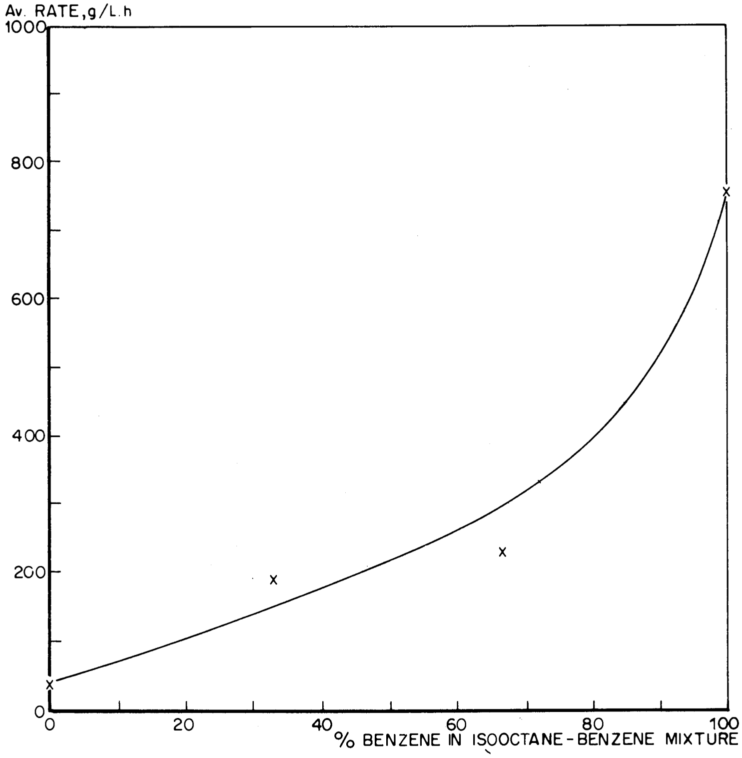

Figure 3. Influence of solvent composition on polymerization rate of butadiene at 20° C. (15–30 min.); catalyst: 0.075 mmole Co-naphthenate + 10 mmole $AlEtCl_2$ per liter.

First, it appears that the polymerization rate of butadiene is somewhat higher in benzene than in isooctane, whereas with isoprene it is the reverse. Furthermore, Table I shows that the polymerization rate of butadiene is much higher at 60° C. than at 20° C. when using $TiCl_4$-based catalysts.

The rate of polymerization further depends strongly on the amount of alkylaluminum compound used for activating β-$TiCl_3$. With $AlEt_3$ or $AlEt_2Cl$ a pronounced optimum in rate is observed, both for butadiene and isoprene, at an $AlEt_3/TiCl_3$ or $AlEt_2Cl/TiCl_3$ ratio of 1/5 to 2/5. Adding more $AlEt_3$ causes catalytic activity to drop sharply, whereas with $AlEt_2Cl$ the decrease is much more gradual. Since this drop in activity with more $AlEt_3$ is not observed in polymerizing propylene (*5*), it is unlikely that it results from reducing β-$TiCl_3$ to inactive compounds (although the change in color from brown to black might suggest this). Also a similar inactivating reduction effect is not to be expected from $AlEt_2Cl$. A reason for the decrease, indicated by Saltman (*39*), might be that at higher alkylaluminum concentration, the diolefins tend to polymerize to volatile oligomers rather than to rubberlike polymers. As an activator $AlEtCl_2$ differs from $AlEt_3$ or $AlEt_2Cl$ in that the rate of polymerization increases proportionally with its concentration as shown in Figure 1 for butadiene.

The polybutadiene prepared at 60° C. with $AlEt_3$- or $AlEt_2Cl$-activated β-$TiCl_3$ contains only 55–66% cis structure, depending on alkylaluminum concentration as shown in Figure 1. Lowering the temperature of polymerization to 20° C. increases the cis content to 78%. Polybutadiene of pure trans-1,4 structure, although of rather low molecular weight, is obtained with the β-$TiCl_3$-$AlEtCl_2$ catalyst systems, according to x-ray analysis (*4*). This may be partly the reason why with catalysts of low $AlEt_3/TiCl_4$ ratio, which in reaction may form $TiCl_3$ and $AlEtCl_2$, polybutadiene of predominant trans-1,4 structure is produced (*20, 35*) (although unreacted $TiCl_4$ may have a similar effect).

Polyisoprene prepared with β-$TiCl_3$ catalyst activated with $AlEt_3$ or, in particular, $AlEt_2Cl$ has a high structural purity. Optimum cis-contents of up

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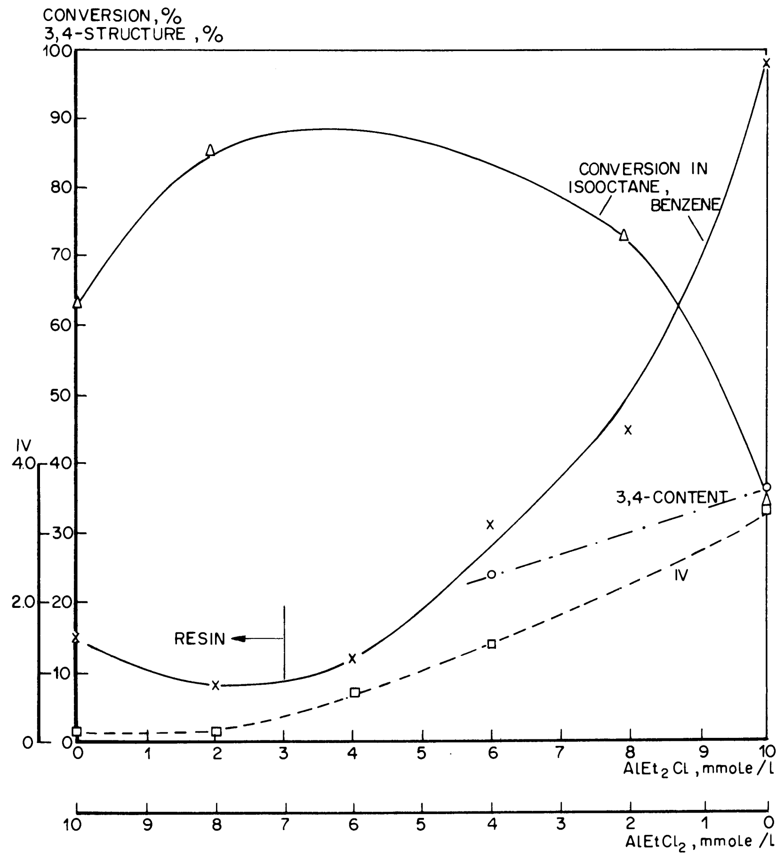

Figure 4. Influence of $AlEtCl_2/AlEt_2Cl$ ratio in activator on the polymerization of isoprene at 20° C. (1 hour); catalyst: 0.1 mmole Co-naphthenate per liter; IV and 3,4-content of product prepared in benzene.

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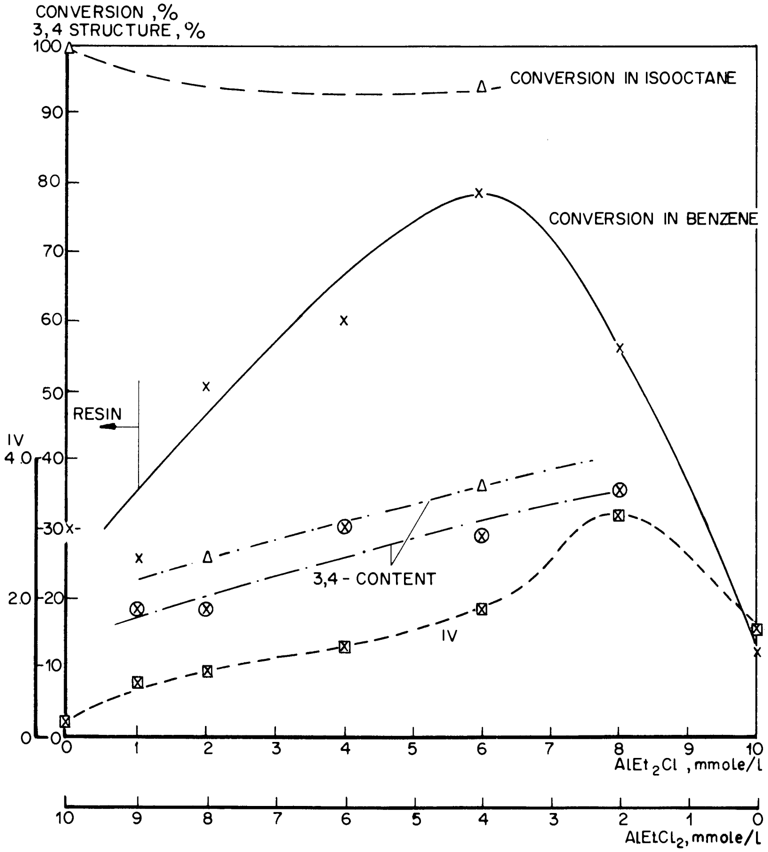

Figure 5. Influence of $AlEtCl_2/AlEt_2Cl$ ratio in activator on the polymerization of isoprene at 60° C. (1 hour); catalyst: 0.1 mmole Co-naphthenate per liter; (Δ) refers to isooctane solvent, the other points to benzene.

to 98% are obtained with catalysts of an Al/Ti ratio of 1/5 to 2/5—i.e., under conditions coinciding with those for optimum rates of polymerization. $AlEtCl_2$ polymerizes isoprene, even without β-$TiCl_3$, apparently by a cationic mechanism (*26*). The polymer formed has the typical resinous appearance of cyclized rubber.

For butadiene Figure 1 shows that the polymerization activity of an optimum one-step $TiCl_4$-$AlEt_3$ catalyst does not differ much from the two-step β-$TiCl_3$-$AlEt_3$ or -$AlEt_2Cl$ catalysts, although for optimum activity the latter catalysts require, in total, less alkylaluminum compound.

Catalysts based on γ-$TiCl_3$, prepared by reducing $TiCl_4$ with $AlEt_3$ at 170° C., have, according to Tables I and II, only a low activity for polymerizing butadiene or isoprene. The structure of the polymer formed with such a catalyst is largely trans-1,4 (*33*).

Catalysts Based on VCl_4

Tables I and II include some polymerizations with catalysts consisting of VCl_3 and an alkylaluminum activator. This VCl_3 was prepared in a similar way as β- or γ-$TiCl_3$ in the preceding polymerizations in a separate reduction of VCl_4 with $AlEt_3$ in a slight excess over the stoichiometric Al/V ratio of 1/3. The polymerization activity of this type of catalyst is relatively low and is highest with $AlEt_2OEt$ as an activator. Improving the dispersion of VCl_3—e.g., by precipitation on a support (*27*), is known to increase the rate of polymerization considerably.

A very effective method (*19*) for increasing the catalytic activity of VCl_3 is forming this compound in a coprecipitate with $TiCl_3$ by reduction at 80° C. or preferentially at 170° C. of blends of $TiCl_4$ and VCl_4 with $AlEt_3$, again at a transition metal/Al ratio of about 1/3. Tables I and II show that catalysts based on such VCl_3-$TiCl_3$ blends, when activated with $AlEt_3$ or $AlEt_2OEt$, not only polymerize the diolefins at a high rate but induce formation of crystalline polymers of trans-1,4 structure like VCl_3-based catalyst themselves do (*31, 32, 34*). $AlEt_2Cl$ is a less suitable activator in this case; it leads to formation of a polymer of much lower crystallinity at a relatively low rate. Presumably the function of $TiCl_3$ in the VCl_3-$TiCl_3$ blend is mainly to provide a large surface

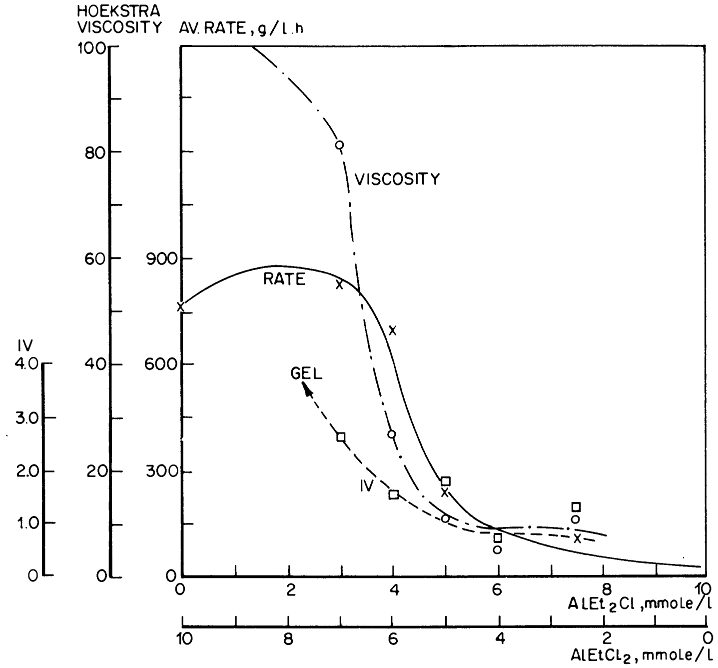

Figure 6. Influence of $AlEtCl_2/AlEt_2Cl$ ratio in activator on the polymerization of butadiene in benzene at 20° C. (10 min.); catalyst: 0.075 mmole Co-naphthenate per liter.

for VCl_3. An indication for this is that the blend prepared by reduction at 80° C., which contains β-$TiCl_3$, is also suitable for forming trans polymer (Table I), although β-$TiCl_3$ itself produces polymer of high cis content.

Catalysts Based on Cobalt Compounds

It is now well established that many cobalt compounds activated with an alkylaluminum halide may induce polymerization of butadiene to a polymer of over 96% cis-1,4 content *(17, 22, 25, 28, 29, 36, 37)*. To obtain a catalyst of high catalytic activity, it is desirable to use cobalt compounds that are soluble in the polymerization solvent such as cobalt naphthenate or a complex of $CoCl_2$ with $AlCl_3$ (*37*) or pyridine (*28*). An effective catalyst is also formed by dissolving $CoCl_2$ in ethanol (solubility, 54 grams in 100 ml.) and dispersing this solution in the polymerization solvent (*6*).

The results of polymerizing with catalysts consisting of cobalt naphthenate or ethanolic $CoCl_2$ and activated with mixtures of $AlEt_2Cl$ and $AlEtCl_2$ are given in Figures 3–8, whereas a few of the most typical results are included in Tables I and II. In these polymerizations the catalyst was compounded in one step since nothing could be gained by preparing it in separate reducing and activating steps.

According to Figure 3, with cobalt catalysts also, polymerization of butadiene is much more rapid in benzene than in isooctane, whereas, according to Figures 4 and 5 the opposite is true for isoprene. Polymerization of isoprene is, with a few exceptions, more rapid at 60° C. than at 20° C. At atmospheric pressure, butadiene polymerizes as rapidly at 20° C. as at 60° C., but here lowering of the actual butadiene concentration in the solvent as a result of the temperature increase should be taken into account. The rate of polymerization of butadiene decreases strongly according to Figure 6 and 7, when the $AlEt_2Cl/AlEtCl_2$ ratio exceeds one.

An important feature of the $AlEt_2Cl$-$AlEtCl_2$ activator combination is that it enables one to control the molecular weight of polybutadiene (*7, 25*). As shown in Figures 6 and 7 the *IV* of the polymer increases strongly with decreasing $AlEt_2Cl/AlEtCl_2$ ratio. With an activator containing more than 70% $AlEtCl_2$ the polymer formed is even slightly cross-linked. Similarly, by adjusting the $AlEt_2Cl/AlEtCl_2$ ratio, polybutadienes of any desired Hoekstra viscosity can be produced. A further control may be obtained by diluting the benzene solvent with an aliphatic solvent like hexane which reduces the molecular weight (*22*).

The influence of $AlEt_2Cl/AlEtCl_2$ ratio depends on the absolute concentration of both alkylaluminum components. Table III shows that with more $AlEtCl_2$ both the polymerization rate and the *IV* increases, whereas with more $AlEt_2Cl$ the rate and the *IV* decrease. The effect of $AlEtCl_2$ on *IV* may result partly from an independent cross-linking reaction under the influence of this Friedel-Crafts catalyst. The decrease caused by $AlEt_2Cl$ is usually not as large as the increase caused by $AlEtCl_2$ when the two concentrations are changed in the same proportion.

Polyisoprene differs strongly from polybutadiene in the dependence of its *IV* on the $AlEt_2Cl/AlEtCl_2$ ratio in the activator. High *IV* polyisoprene

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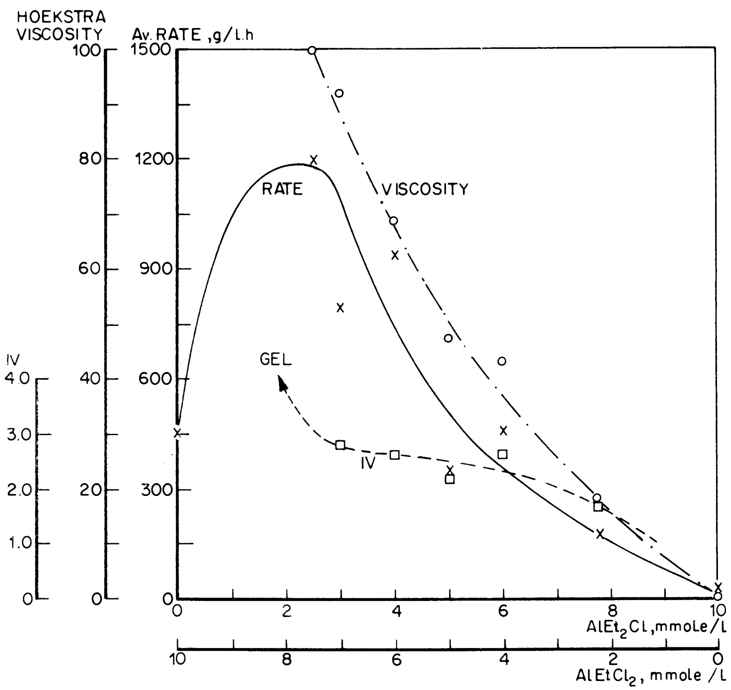

Figure 7. Influence of $AlEtCl_2/AlEt_2Cl$ ratio in activator on the polymerization of butadiene in benzene at 20° C. (10–30 min.); catalyst: 0.1 mmole of $CoCl_2$-ethanol per liter.

Table III. Influence of Varying $AlEtCl_2$ and $AlEt_2Cl$ Catalyst Concentration on the *IV* of Polybutadiene[1]

Catalyst Components mmole/liter					
$AlEtCl_2$	*$AlEt_2Cl$*	*Co naphthenate*	*Cl_2/Cl ratio in alkyl-Al*	*Av. Rate of Polymerization grams/liter/hr.*	*IV*
4	6	0.015	0.67	68	1.1
8	0	0.015	1.33	190	2.4
4	0	0.015	. . .	170	3.5
4	3	0.015	1.33	100	1.0
4	6	0.015	0.67	68	1.1
4	9	0.015	0.44	60	0.54
4	12	0.015	0.33	30	0.23

[1] Conditions of polymerization: 20 minutes at 25° C. in benzene

is formed when the $AlEt_2Cl/AlEtCl_2$ ratio is larger than 1. This polyisoprene has for about 19–36% a 3,4-structure. The content of 3,4-structure increases when less $AlEtCl_2$ is present in the activator as shown in Figure 4 and 5. With an activator containing more than 70% $AlEtCl_2$ the reaction product, when prepared in benzene, has a very low *IV* and may consist of resinous cyclized

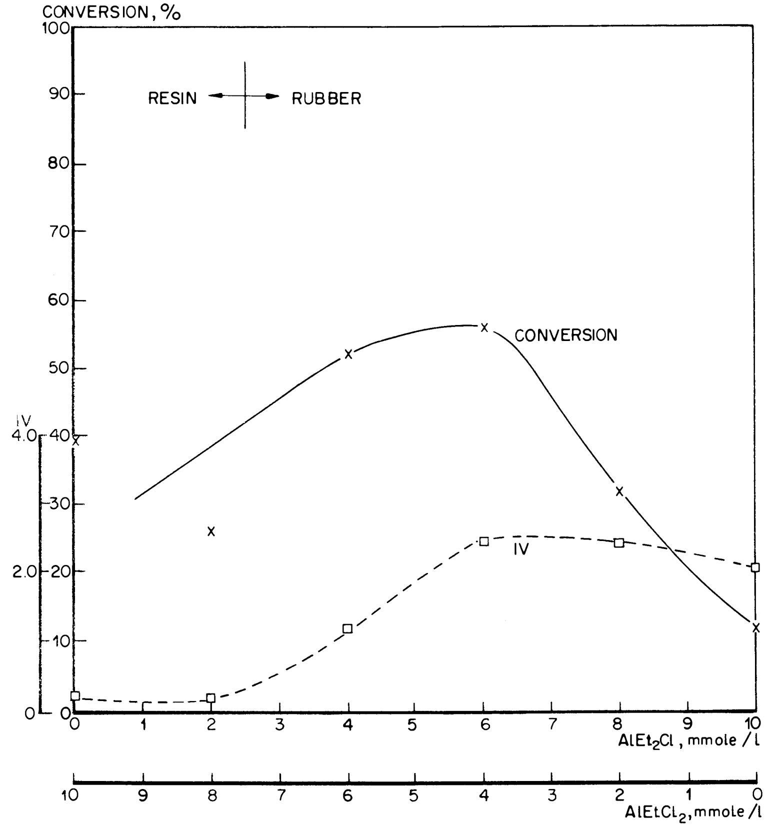

Figure 8. Influence of $AlEtCl_2/AlEt_2Cl$ ratio in activator on the polymerization of isoprene at 60° C. (1 hour); catalyst: 0.1 mmole of $CoCl_2$-ethanol per liter.

rubber. This cyclized rubber is doubtless formed in a secondary reaction under the influence of the Friedel-Crafts catalyst $AlEtCl_2$, which, as indicated in Table II, is capable, even in absence of transition metal compound, of polymerizing isoprene to cyclized rubber. Cyclization can largely be prevented by polymerizing in an aliphatic solvent like isooctane.

Results obtained with catalysts based either on ethanolic $CoCl_2$ or on Co-naphthenate do not differ much, as comparing Figure 6 with Figure 7 and Figure 5 with Figure 8 will show. Apparently the minute amount of ethanolic $CoCl_2$ does not disturb the polymerization activity.

Discussion

A remarkable difference between butadiene and isoprene is that with polymerization catalysts based on β-$TiCl_3$, VCl_3, or cobalt compounds the structure of polybutadiene is mixed *cis*-1,4-+ *trans* 1,4, high *trans*-1,4, and high *cis*-1,4, respectively, whereas with polyisoprene it is high *cis*-1,4, high *trans*-1,4, and mixed 1,4 + 3,4, respectively. Apparently the type of transition metal compound of the polymerization catalyst controls the structure of the polymers formed from diolefins, and moreover this controlling influence is highly specific for a certain monomer structure.

The type of alkylaluminum compound has only a secondary influence on structure in the polymerization of diolefins in contrast to its strong effect on the structure of polypropylene. An exception is $AlEtCl_2$, which, apparently in connection with its cationogenic character, with β-$TiCl_3$ induces polymerization to *trans*-1,4 polybutadiene and, even without transition metal compound, leads to formation of cyclized polyisoprene. Incidentally, this indicates that polybutadiene is much more stable towards cyclization than polyisoprene.

Another difference is that to obtain high rate of polymerization of butadiene an aromatic solvent is preferred to an aliphatic solvent, whereas with isoprene, aliphatic solvents are preferable except when polymerizing to cyclized polymer. Obviously these solvent effects depend on strength of monomer-solvent or rubber-solvent interaction, a good solvent being favorable for building up a high concentration of monomer and for dissolving the polymer formed. In cationogenic $AlEtCl_2$-catalyzed reactions the polarity of the solvent is, of course, also very important.

Reducing the transition metal compound in a separate reaction before activating it in a second step gives wider scope to the study of the effect of catalyst composition on the polymerization of dienes. For instance, separating the two steps—reduction of $TiCl_4$ to $TiCl_3$ and activation of the $TiCl_3$ thus formed—may eliminate some undesirable side reactions during catalyst formation, in particular overreduction of $TiCl_3$. Besides, in such a two-step procedure different types and amounts of alkylaluminum compounds best suited for the specific purpose can be used in each step.

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