

SYMPOSIUM ON FOREIGN DEVELOPMENTS IN PETROCHEMICALS  
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.  
AMERICAN CHEMICAL SOCIETY  
ATLANTIC CITY MEETING, SEPTEMBER 8-13, 1968

A NEW POLYMERIZATION PROCESS FOR THE PRODUCTION  
OF DIFFERENT PROPYLENE OXIDE RUBBERS

By

Maseh Osgan, Philippe Teyssie, and Jean-Pierre Wauquier  
Institut Francais du Petrole, 92=Rueil - Malmaison, France

INTRODUCTION

The objective of this paper is to present some recent developments in the polymerization of propylene oxide with a new class of catalysts.

Poly(propylene oxide) presents a chain of repeating propylene units, spaced with ether oxygen, -O-, linkages. These latter reduce the barrier to free rotation around the single bonds of the chain backbone, due to steric interaction of methyl groupings. The result is a high chain mobility down to very low temperatures provided the regularity of -HCCH<sub>3</sub>- units is kept sufficiently low, so that there is no appreciable extent of crystallization. This high chain mobility, together with an average chain length sufficiently high (average mol weight above 200,000) and adequate means to introduce interchain attachments (e.g. cross-linking) represents the basic requisite for a rubber. Therefore, the polymerization of propylene oxide may open the way of converting the propylene surplus to a useful rubber, provided the price of propylene oxide from propylene becomes sufficiently low, and in the meantime a rubber based on propylene oxide finds acceptance on the market.

Propylene oxide is known to polymerize by acidic and basic catalysts. However, a transfer reaction of the growing chain end with the monomer limits, its average mol weight to less than 10,000. Only with the advent of coordination type catalysts was it possible for Dow chemists to obtain first in 1955 mol weights exceeding 100,000 (1). These first catalysts, based on ferric compounds had two shortcomings. The product characteristics were less suitable to make a good rubber and the rate of polymerization was too slow for practical purposes. Subsequently through controlled hydrolysis of Group II and III metalalkyls, viz. dialkylzinc and trialkylaluminum, catalysts were discovered with much higher activity, giving a poly(propylene oxide) with improved product characteristics (2). Drawbacks of this latter system are the high cost of the catalysts, problems involved in their large scale preparation and the relatively high catalyst concentrations required for the polymerization process. Although there was no obvious ground to suppose that highly active catalysts can only be obtained from metalalkyls, work published between 1958 and 1966 was directed to such systems.

We shall report here a new class of catalysts (3) which can be prepared in a simple manner starting from inexpensive materials such as aluminum isopropoxide and zinc acetate. Then we shall give the general features of the propylene oxide polymerization with these catalysts and the characteristics of the poly(propylene oxide) obtained.

EXPERIMENTAL

Materials

Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (A. R. grade) was dehydrated by refluxing with acetic anhydride (99%) and subsequent washing with toluene. Aluminum isopropoxide, technical grade, was distilled, after stripping off the free isopropyl alcohol under vacuum.

Propylene oxide was first refluxed over potassium hydroxide pellets, distilled, then refluxed over calcium hydride and distilled under argon (containing less than 5 ppm water according to manufacturer's specification). For large scale polymer preparation, propylene oxide was used as such, after drying over molecular sieves (3A).

Solvents, n-heptane (Phillips, pure grade) toluene, etc., were dried over calcium hydride (laboratory) or molecular sieves (large scale) and distilled, except tetrahydronaphthalene, which was treated with concentrated sulfuric acid prior to drying.

Techniques

From catalyst preparation up to short-stopping of the polymerization, reagents were stored and handled under pure grade argon (or nitrogen). Transfer of materials was done by now

widely utilized syringe and hypodermic needle techniques through self-sealing serum stoppers (including dilatometry). Large volumes of solutions were siphoned through stainless steel capillaries (18 G through 15 G). In large scale polymerizations this technique was utilized only for transfer of catalyst solutions, the remaining being transferred quickly. For this latter operation a 20 liter stainless steel reactor with anchor-type stirrer was utilized. All other operations were done in standard laboratory all-glass apparatus with ground-glass joints.

Dilatometric studies were done in precision bore tubings of appropriate i. d., which permits about 25 cm height variation for contraction due to full conversion of monomer to polymer. They were calibrated with mercury, and volume of contraction versus conversion was verified by isolation of the polymer.

#### Analytical

Metals were determined by volumetry with EDTA, alcohols, ester, etc., by GLPC (Aerograph 200A) by use of an internal reference.

#### Catalyst Preparation

Into 111 g (0.6 mole) anhydrous zinc acetate covered with 100 ml tetrahydronaphthalene, 451 ml of a solution of aluminum isopropoxide (2.66 M/l, 1.2 moles) was added under stirring, at room temperature. It was then heated quickly to 175-176°C under vigorous stirring. The mixture became homogeneous in about 10 minutes, while the volatiles were allowed to distill through a Vigreux column. As soon as the reaction mixture became homogeneous, the temperature was allowed to rise to 199-202°C and it was kept at this temperature until the end of preparation (350 min.).

The solution was colorless at the early stages of the reaction, then it gradually became intense yellow. The heavy solvent was then removed under vacuum and the glassy yellow residue was taken in n-heptane.

#### Polymerization

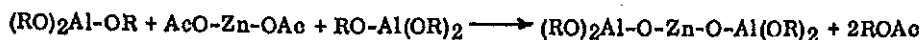
Polymerizations were done in the laboratory in sealed glass tubes previously purged with argon, placed in a slowly rotating tube-holder immersed in a constant temperature bath.

#### Induction Times

Induction times for oxygen uptake were determined in o-dichlorobenzene solution by a procedure similar to that of Dulong (4).

### CATALYST PREPARATION

The catalyst is prepared by a condensation reaction between an aluminum alcoholate and zinc acetate, with elimination of two moles of ester:



(R = iso-Pr, for example).

This condensation is best carried out in the presence of a solvent which facilitates the heat transfer and permits close temperature control. Aromatic or aliphatic hydrocarbons, such as tetrahydronaphthalene, decahydronaphthalene, or petroleum cuts of adequate boiling range were found most satisfactory.

The course of the condensation reaction is presented in Figure 1. It can be seen that the first acetate on zinc diacetate is much more reactive than the second acetate. Thus at 170-180°C the elimination of one mole ester per mole zinc acetate is practically complete within 10-20 minutes. At this stage the product is completely solubilized in the reaction medium. The ester is separated by distillation through a suitable column.

The elimination of the second acetate on zinc is much slower. In order to obtain an acceptable rate it is preferred to increase the temperature up to about 200°C. At this stage secondary reactions appear, producing, along the expected isopropyl acetate, some isopropyl alcohol and acetone. GLPC analysis of the gas stream indicates the presence of olefins, mainly of propylene and of hydrogen. Since aluminum alcoholates are known to catalyze hydride transfer, hydrogen is probably formed through dehydrogenation of isopropyl alcohol, this accounting also for the formation of acetone. It remains to explain the formation of isopropyl alcohol along with propylene. The literature on the decomposition of aluminum alcoholates is somewhat controversial (5). Our own experience indicates that aluminum isopropoxide alone does not decompose at 200°C. The fact that we observe this secondary reaction at the second stage, i. e. after the formation of at least one  $>Al-O-Zn$ -bond, and our interpretation of the results on the decomposition of zirconium alcoholates studied by Bradley and Faktor (6) seem to indicate that decomposition of

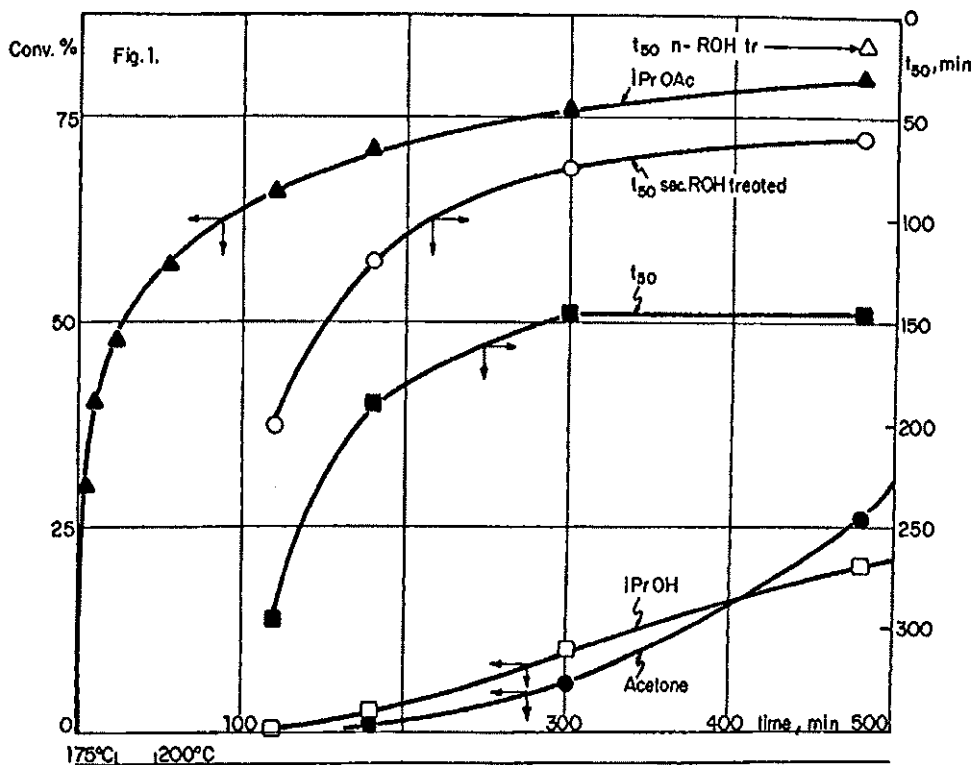


FIGURE 1. Elimination of isopropylacetate, isopropanol and acetone in the course of condensation of aluminum isopropoxide with zinc acetate; catalytic activities of the condensation product at various stages of the condensation (polymerization conditions: n-heptane; 60°C; PO 1.0 M/l; catalyst 0.050 at g/l (Al + Zn)).

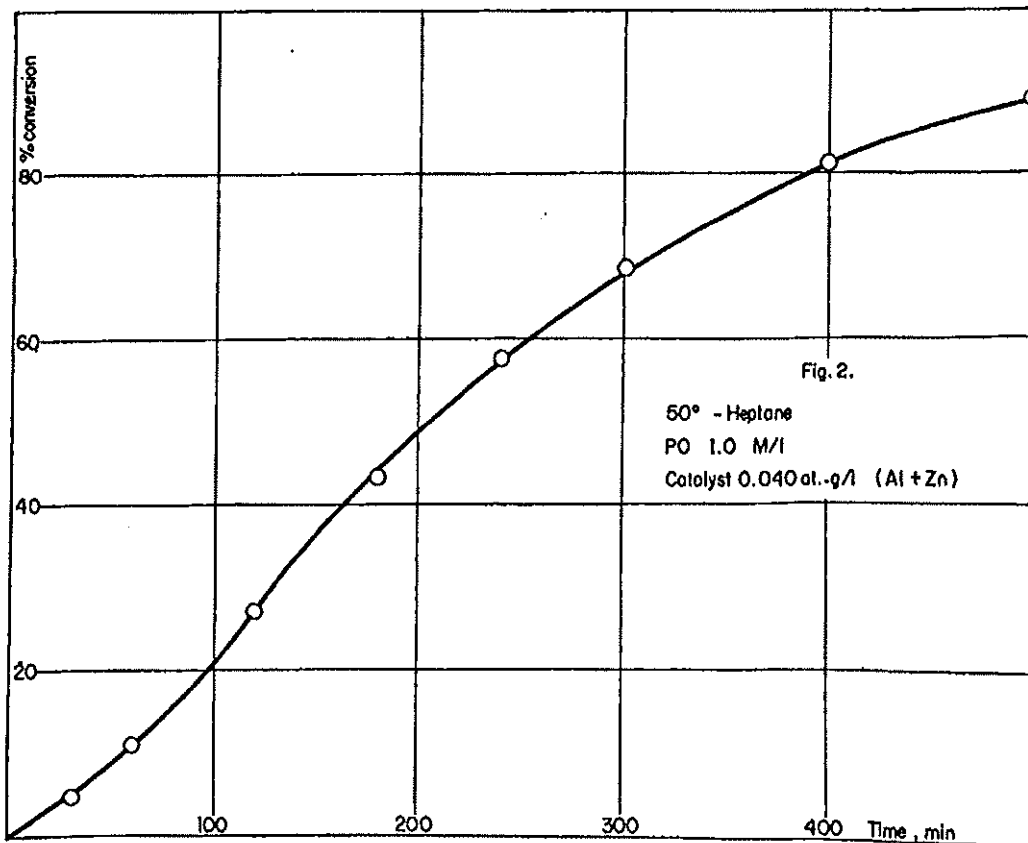
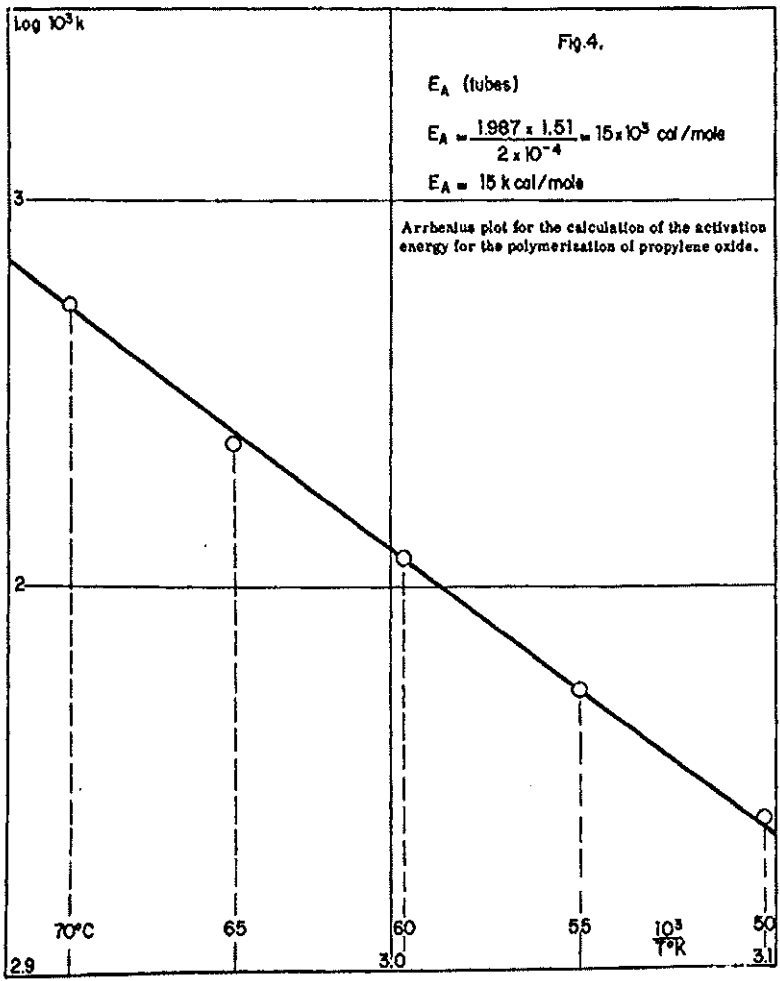
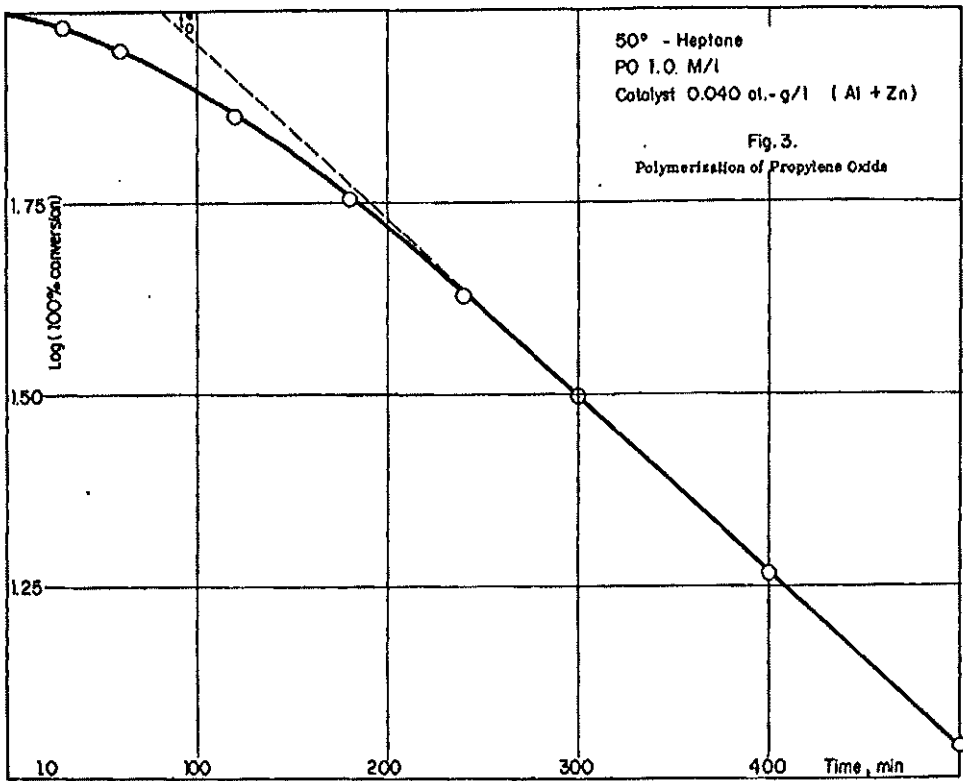


FIGURE 2. Polymerisation of propylene oxide.



metal-OR is catalyzed by metal-O-metal groupings. Such a catalysis would explain claims of decomposition of simple aluminum alcoholates at temperatures below 200°C, assuming that some adventitious water first produces some  $>Al-O-Al<$  species.

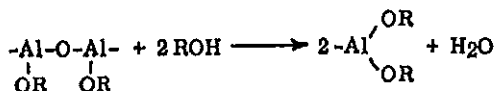
Determination of the isopropoxy groupings eliminated by formation of isopropyl acetate, isopropyl alcohol and acetone alone does not allow a good agreement with the OR/Al ratio found on the final product, unless we assume that 2 moles of OR are lost per mole of isopropyl alcohol (or acetone) produced. Such a stoichiometry indicates that the decomposition reaction is specifically:



In order to explain this stoichiometric specificity producing equimolar amounts of alcohol and corresponding olefin, it seems tempting to suggest that the decomposition is taking place through an intermediate containing the corresponding ether complexed on the Al-O-Al. This mechanism is similar to that proposed several years ago by Balaceanu and Jungers (7).

The result of the above-mentioned decomposition reaction is the formation of Al-O-Al groupings, in addition to the Al-O-Zn groupings through the main reaction. The activity of the condensation products as a polymerization catalyst for propylene oxide (Figure 1) seems to be dependent on the extent of ester elimination. On the other hand, if the condensation reaction is carried further, the secondary reaction takes over the ester elimination reaction, giving finally insoluble and catalytically less active products. Thus, in practice the reaction can be carried out only to the extent where there is about 80-90% of the ester eliminated, giving a product which analyzes for OR/Al = 1.2 to 1.3. Choosing the reaction temperature lower than 190°C, it is possible to obtain products with OR/Al = 1.9; the ester elimination is, however, somewhat lower under these conditions and the condensation product is less active.

We have found somewhat unexpectedly that Al-O-Zn bonds are extremely stable towards alcohols, while the Al-O-Al bonds, at least to some extent, are broken by this reagent according to the reaction:



Condensation products with OR/Al = 0.8 to 1.2 can be modified up to OR/Al = 1.7 by such a treatment. Further, depending on the nature of the alcohol and the reaction conditions, treatment with an alcohol may result in: 1) an increased or decreased catalytic activity, with only a change of polymerization rates; 2) a simultaneous change in the stereospecificity of the polymerization reaction; 3) a change in the kinetics of the polymerization, e.g. from first order versus the catalyst concentration to a higher order; 4) a change in composition of the soluble species, i.e. from Al/Zn = 2.0 to Al/Zn = 3.0.

It is obvious that for practical purposes, the above preparation, followed by an activation step if needed, can be carried out as a single-pot operation. The catalyst, which is highly soluble in aliphatic and aromatic solvents, can be obtained as a solution. This yellow solution is indefinitely stable provided it is protected against moisture.

Finally, it has to be mentioned that the above reaction was found to be quite general when applied to other metals. Active polymerization catalysts are obtained when the mid-metal is a divalent one, such as Mg, Cd, Cr (II), Mn (II), Fe (II), or Co (II).

## POLYMERIZATION OF PROPYLENE OXIDE

### Overall Kinetics

A preliminary kinetic study of the polymerization of propylene oxide was carried out with the aim of evaluating polymerization conditions and catalyst behavior. Unless specified, this was conducted at 50° for convenience.

A typical dilatometric plot (catalyst R = iso-Pr) is illustrated in Figure 2. At the early stages of polymerization, there is a steady increase of the rate, followed by a period, where it starts to drop off exponentially. It is better seen in Figure 3, on a semilogarithmic scale, that the later stage obeys a first order rate for propylene oxide. For initial PO concentrations in n-heptane, from 0.1 to 1.0 M/l, the first order rate constant,  $k_1$ , calculated from the later stages of the polymerization, remains constant. At 2.0 M/l initial PO concentration and above,  $k_1$  decreases with increasing PO concentration. We ascribe this steady decrease of  $k_1$  to an increase of bulk dielectric constant of the medium, since we observe the same trend on 1.0 M/l propylene oxide solutions, by varying the solvent of polymerization:

<u>Solvent</u>	<u>Dielectric Constant</u>	<u>Rel. <math>k_1</math></u>
n-Heptane	1.88	1.0
Toluene	2.32	0.75
o-Dichlorobenzene	9.81	0.38

The effect of catalyst concentration was studied in sealed tubes by isolation of the polymer at 40 to 70% conversion and calculation of  $t_{50}$ , time required for 50% conversion. For catalysts, where R = iso-Pr, sec-Bu,  $t_{50}$  was found inversely proportional with the concentration, hence first order in catalyst. For catalysts activated by treatment with a primary alcohol, e. g. n-BuOH, the apparent order was above unity; plots of  $\log c$  vs.  $\log t_{50}$  gave straight lines with slopes  $\approx 1.5$  in n-heptane and  $\approx 2$  in toluene.

The energy of activation for the overall polymerization rate in n-heptane (for catalyst R = iso-Pr) was found from the Arrhenius plot (Figure 4) equal to  $15 \pm 1$  kcal/mole.

#### Effect of Polymerization Variables on Mol Weight

Mol weights estimated from intrinsic viscosities did not show any significant change with conversions (from 40 to 90%) or with the temperature of polymerization, at least in the range 50 to 70°C; the intrinsic viscosities were usually between 6.5 and 8.5 dl/g (in toluene at 30°C). Effect of water: the presence of water affects strongly both the rate of polymerization and the mol weights. This is shown by the results, summarized in Table I, of two series of polymerizations carried out in the presence of added water.

Table I

#### Effect of the Presence of Water

<u>Exp. No.</u>	<u>H<sub>2</sub>O/Al</u>	<u>Conversion, %</u>	<u>(<math>\bar{m}</math>), dl/g</u>
a) Polymerization time 4 hours*			
1	0	71	5.2
2	0.05	49	4.0
3	0.25	17	3.0
4	0.5	11	1.7
b) Polymerization time 39 hours			
5	0.5	93	2.3
6	1.0	68	1.4
7	1.5	54	1.2
8	2.0	36	0.6

\* In n-heptane at 50°C with propylene oxide 1.0 M/l and catalyst (R = iso-Pr) 0.060 g atom/l.

Separate experiments by IR-spectroscopy revealed that small increments of water added to catalyst (e. g. water/Al = 0.05) liberate alcohol immediately. This means that water attacks firstly the OR groupings on Al. Consequently, the effect of water on the polymerization might be due in fact to the presence of alcohol; the same effect was observed indeed by addition of equivalent quantities of alcohol. On the other hand, if the alcohol liberated by addition of water is removed by a vacuum treatment (stripped-off), the original activity usually is restored. From Table I it can be seen that alcohol acts as a retardant and reduces the mol weights. Comparison of experiments 4 and 5 shows that low mol weight chains produced, due to the presence of alcohol, undergo a further slow growth.

#### Short-stopping of the Polymerization

Poly(propylene oxide) is known to be highly sensitive to oxidative degradation (4). Therefore, its utility is dependent on an adequate stabilization. Furthermore, when it is obtained by polymerization with metallic catalysts, the effect of such metallic residues on the stability of the polymer needs careful consideration. Finally, for large scale polymerizations, catalyst removal is often a cumbersome and costly operation. Hence, termination of the polymerization process

by an adequate short-stopping agent, which permits leaving the catalyst in the product, seemed of sufficient interest for a systematic study.

Previous results of the effect of water on the polymerization indicated that although reagents like water or alcohol will significantly reduce both the rate of polymerization and the mol weight of the polymer, they do not show a sharp effect of deactivation at relatively low ratios of reagent to catalyst. A sharp inhibitory effect seemed to depend on a specific interaction with zinc. Among such reagents, certain amines (and amides) were found most interesting. Thus, at a molar ratio of amine to zinc of 1 to 5 we have found a sharp catalyst deactivation. This finding, we believe, may have interesting implications regarding the nature of the active species, besides its practical utility discussed below.

Poly(propylene oxide), obtained by the catalysts described in this work, were found to exhibit an unexpected stability against oxidative degradation when they were short-stopped with certain amines. Autoxidation tests at 130°C, in *o*-dichlorobenzene solution, indicated significant induction periods for oxygen uptake, as shown in Table II.

Table II

Effect of Short-stopping Agent on Induction Time,  $t_i$ , for Oxygen-uptake at 130°C in *o*-Dichlorobenzene Solution (5%)

<u>Short-stopping Agent*</u>	<u><math>t_i</math>, hours</u>
Water	0.17
Isopropylamine	5.0
<i>n</i> -Butylamine	3.0
Diisobutylamine	3.2
Cyclohexylamine	3.5
Aniline	250
<i>N</i> -Methylaniline	350
Poly(propylene oxide), <u>catalyst removed</u>	0
+ aniline	0
+ <i>N</i> -Me-aniline	150

\* Amine/Zn (mole ratio) 1.0, Zn  $\approx$  0.025 g. atom %.

Apparently catalyst-amine combination has a definite antioxidant effect. The magnitude of this effect does not seem related to the shielding of the amine nitrogen, since there is little difference between *n*-butylamine and isopropylamine or di-isobutylamine. The antioxidant effect is, however, dramatically increased with aromatic amines. This stabilizing effect, of catalyst-amine combination on poly(propylene oxide), is supported by the results of additional aging experiments carried out on polymer films, in air-circulated oven (Geer) at 70°C. These are summarized in Table III.

Table III

Air-circulated Oven Aging of Poly(propylene oxide) Films (about 1 mm) at 70°C

<u>Short-stopping Agent (about 1.5%)</u>	<u>Intrinsic Viscosities, dl/g after Oven Aging, in Days</u>		
	<u>0</u>	<u>3</u>	<u>7</u>
Isopropylamine	9.5	7.9	7.0
Aniline	10.8	11.1	11.9
<i>N</i> -Methylaniline	8.5	8.7	8.3

In these tests there was practically no weight loss at the end of 7 days, except an initial loss of 1-2% probably due to residual solvent. Moderate weight losses, around 10%, were observed after 12 days for samples short-stopped with isopropylamine, and no weight loss could be detected over a 60-day period for those short-stopped with aniline.

## POLYMER CHARACTERISTICS

Catalysts described in this paper are distinguished essentially by their stereospecificity. Those obtained (and activated) with a secondary alcohol, such as isopropyl alcohol or sec-butyl alcohol give a nearly amorphous polymer, while those activated with a primary alcohol, e.g. n-butanol, give a moderately crystalline polymer. Polymer properties are summarized in Table IV.

Table IV

Properties of Poly(propylene oxide)  
Obtained with Catalysts of this Work

	Catalyst in which R =	
	<u>sec-alkyl</u>	<u>n-alkyl</u>
Glass transition temp. <sup>a</sup>	- 75°C	- 75°C
Melting point <sup>a</sup>	50°C	65°C
% Crystallinity <sup>b</sup>	5-7	20-25
$\bar{M}_c^c$	$2 \times 10^5$ to $10^6$	$5 \times 10^5$ to $2 \times 10^6$
$\bar{M}_w/\bar{M}_n$ (excl. oligomers)	both	1.3 to 1.5
% Oligomers ( $\bar{M}_n$ 800) <sup>d</sup>	both	5 to 20%

Techniques:

- a DTA
- b X-ray
- c Mechrolab 502 membrane osmometer
- d Extraction with heptane-methanol at room temperature or isooctane at 0°C

A distinguishing feature of our catalysts seems to be very narrow mol weight distribution of the polymers obtained, excluding the oligomeric fraction.

Poly(propylene oxides) obtained by sec-alkyl type catalysts, when peroxide-cured, or when their copolymers with allylglycidyl ether (3-7%) are vulcanized by an accelerated sulfur recipe, show good overall properties (8) for an elastomer: low temperature (brittleness), ozone resistance, and oven aging resistance were found excellent. The rebound was fair to good.

They rate poor, however, in solvent resistance for high octane solvents (e.g. fuel ASTM B: isooctane/toluene 7:3). Consequently, polymer modification, by introduction of a suitable comonomer seems indicated to increase solvent resistance.

### CONCLUSIONS

The catalysts of this work are essentially metal oxide alkoxides. In common with previously known hydrolyzed metal alkyl catalysts, they contain metal-oxygen-metal groupings. This supports the generally accepted view (2), that such groupings are necessary for catalytic activity. In contrast with the hydrolyzed metal alkyl catalysts, our catalysts, despite their high activity, do not contain metal to carbon bonds. Therefore, we may conclude that such metal to carbon bonds are not essential for catalytic activity.\*

Low cost of catalyst preparation, convenience of the polymerization process yielding a stable product and good overall properties of this latter as an elastomer are factors which should encourage its development to useful new rubbers. Incorporation of a comonomer in about 5 to 20% should allow manufacture of tailor-made rubbers for particular end-uses. Availability of catalysts giving essentially amorphous or up to 25% crystalline polymers yields both amorphous and crystallizable (self-reinforcing) types of rubbers. Such a development should find an impetus in the predicted decrease in the actual price of propylene oxide.

### ACKNOWLEDGMENTS

The authors would like to acknowledge contributions of Drs. J. Gaillard (large scale preparation and short-stopping), M. Mollard (oxidation stability), and J. P. Silly (dilatometry).

\* After this work was completed, two recent disclosures on highly active heterogeneous catalysts, i.e. bimetallic cyanide complexes (9) and zinc xanthates, etc. (10), substantially confirm our conclusions.



## LITERATURE CITED

- (1) Dow Chemical Co., U.S. 2,706,181-2 (April 12, 1955).
- (2) Vandenberg, E. J., *Polymer Sci.* 47, 149 (1960);  
Sakata, R., Tsuruta, T., Saegusa, T., and Furukawa, J., *Makromol. Chem.* 40, 64 (1960);  
For a recent review of. Gurgiolò, A. E., *Rev. Macromol. Chem.* 1, 76 (1966).
- (3) Osgan, M., and Teyssie, Ph., *J. Polymer Sci. B*, 5, 789 (1967).
- (4) Dulog, L., and Storck, G., *Makromol. Chem.* 91, 50 (1966).
- (5) Shulman, G. P., Trusty, M., and Vickers, J. H., *J. Org. Chem.* 28, 907 (1963).
- (6) Bradley, D. C., and Faktor, M., *J. Appl. Chem.*, 435 (1959).
- (7) Balaceanu, J. C., and Jungers, J. C., *Bull. Soc. Chim. Belge* 80, 476 (1960).
- (8) Gruber, E. E., Meyer, D. A., Swart, G. H., and Weinstock, K. V., *Ind. Eng. Chem., Prod. Res. Develop.* 3, 194 (1964);  
Allen, G., and Crossley, H. G., *Polymer (Lond.)* 5, 553 (1964).
- (9) General Tire and Rubber Co., US 3,278,457-9 (Oct. 11, 1966).
- (10) Lal, J., *J. Polymer Sci. B*, 5, 793 (1967).