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The Low Temperature Polymerization of Propylene by Friedel-Crafts Catalysts[1]

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The polymerization of propylene at −78° by Friedel-Crafts reagents is accompanied by simultaneous inter- and intramolecular hydride transfers which give rise to ethyl and propyl groups on the polymer backbone. The resulting polymer structure is independent of the nature of the catalyst or co-catalyst used in the reaction. It is concluded that the rate-determining step in both monomer addition and hydride transfer steps is the formation of the carbonium ion from the undissociated polymer-catalyst complex.

The products obtained by the polymerization of α-olefins by Friedel-Crafts catalysts are often nonlinear polymers of complex structure. The carbonium ion, through which propagation proceeds, may enter into many side reactions, particularly at elevated temperatures. Seven such reactions have been listed by Meier and there are probably more.[2] Since the activation energies of these reactions differ from one another, their relative contributions to the total process change with temperature. In the case of isobutene, at −78° only linear propagation remains significant. However for propylene and most other alkenes, although simplification takes place, it is less striking, and at temperatures at which the reaction is quite slow, reactions other than linear propagation occur. To obtain a clearer picture of the mechanism of the cationic polymerization of α-olefins we have attempted to characterize, for propylene, the most important of these reactions from evidence based on the structures of the products and the way these structures depend on reaction variables.

Polymerization by the Al_2Br_6/HBr system. Infrared measurements, qualitative. We have taken as our starting point a well documented reaction, the polymerization of propylene by aluminum bromide–hydrogen bromide in butane at −78°. Fontana has studied the kinetics of this reaction in great detail but no over-all mechanism was proposed for the formation of the products, presumably as little was known about their composition.[3,4] It was recognized, however, that they were probably highly branched and that this branching arose from hydride transfers from polymer chains to carbonium ions.[5]

Fig. 1 shows the infrared spectrum of the highly viscous, liquid polymer prepared under these conditions. A molten, linear polypropylene is included for comparison. Two bands are particularly prominent in the cationic material and absent in the linear polymer. These are the bands at 769 cm.$^{-1}$ and 739 cm.$^{-1}$ We have assigned these bands to ethyl and propyl vibrations because:

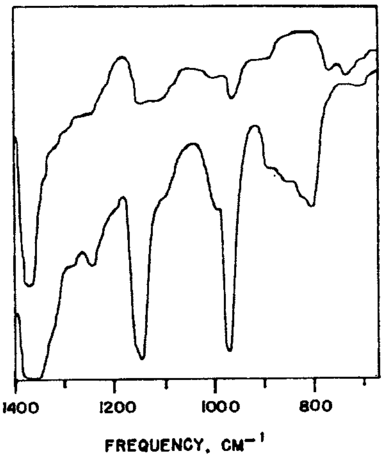

Fig. 1. Upper—Infrared spectrum of polypropylene prepared by cationic polymerization; Lower—Infrared spectrum of linear, molten polypropylene

(1) In low molecular weight hydrocarbons, bands at 770 cm.$^{-1}$ and 740 cm.$^{-1}$ have been assigned to these groups.[6]

(2) Polypentene-1 shows a band at 735 cm.$^{-1}$, polybutene-1 a band at 760 cm.$^{-1}$

(3) A range of polymers of known composition prepared by us having pendant ethyl, propyl, *n*-butyl, pentyl, and hexyl groups show that the band positions given in (2) are normal for propyl and ethyl groups in an "uncrowded" environment. The presence of adjacent groups causes the absorption of these groups to move to higher frequencies with a limit around 740 cm.$^{-1}$ and 770 cm.$^{-1}$ Polyhexene-1 has a butyl absorption at 725 cm.$^{-1}$ while polymers containing pentyl and higher groups absorb at even lower wave lengths.[7]

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[1] Presented at the St. Louis ACS Meeting, March 24, 1961.

[2] R. L. Meier, *J. Chem. Soc.*, 3656 (1950).

[3] C. M. Fontana, *Cationic Polymerization and Related Complexes*, ed. Plesch, Academic Press, New York, 1953.

[4] C. M. Fontana and G. A. Kidder, *J. Chem. Soc.*, **70**, 3745 (1948).

[5] C. M. Fontana, *J. Phys. Chem.*, **63**, 1167 (1959).

[6] S. Ställberg-Stenhagen, E. Stenhagen, N. Sheppard, G. B. B. M. Sutherland, and A. Walsh, *Nature*, **160**, 580 (1947).

[7] M. C. Harvey and A. D. Ketley, *J. App. Polymer Sci.*, in press.

TABLE I

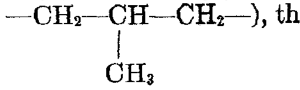
THE EFFECT OF THE REACTION CONDITIONS ON THE POLYMER STRUCTURE[a]

Run	Catalyst	Co-catalyst	Temp.	Solvent	Wt. % C_2H_5	Wt. % C_3H_7	Wt. % Isolated CH_3	Wt. % CH_3	% C_2H_5/ % C_3H_7
1B	Al_2Br_6	HBr	−78	Butane	10.1	5.7	—	24.7	1.8
1SA	Al_2Br_6	HBr	−160	Propane	5.9	4.7	0.4	24.1	1.2
2C	Al_2Br_6	HBr	−78	Methyl chloride	7.6	5.3	1.5	23.0	1.4
7J	Al_2Br_6	*d*-10-Camphor sulfonic acid	−78	Butane	9.4	4.7	0.3	26.6	2.0
14J	Al_2Br_6	1-Aminonaphthol sulfonic acid	−78	Butane	10.0	5.5	0.3	24.6	1.8
8J	Al_2Br_6	Nicotinic acid	−78	Butane	9.3	4.8	0.3	24.7	1.9
17J	Al_2Br_6	3-Dimethylamino-1,2-propanediol	−78	Butane	7.3	4.0	—	22.5	1.8
5R	$BF_3—(C_2H_5)_2O$	*i*-C_3H_7OH	−78	Butane	8.0	3.6	0.6	26.6	2.2

[a] Infrared calibrated with polymer standards.

The band at 915 cm.$^{-1}$ may be that which Natta has assigned to isopropyl in low molecular weight polypropylene.[8] The 1160 cm.$^{-1}$ band similarly may arise from the isopropyl skeletal vibration. However, there is no sign, at the highest resolution, of a 1370 cm.$^{-1}$, 1380 cm.$^{-1}$ doublet in the CH deformation band.

A diffuse band at 1160 cm.$^{-1}$ is probably due to nonconjugated unsaturation.

Infrared measurements. Quantitative. To obtain a quantitative picture of these products we have attempted to measure from the infrared the weight per cent content in the polymers of the following groups: *n*-propyl, ethyl, total methyl, and isolated methyl (methyl in  $—CH_2—\underset{CH_3}{\underset{|}{CH}}—CH_2—$), the latter being the form in which methyl occurs in the linear polymer.

To do this we measured the absorbance of concentrated solutions of low molecular weight, linear polypentene in carbon disulfide at 735 cm.$^{-1}$, polybutene in carbon disulfide at 760 cm.$^{-1}$ and polypropylene in carbon disulfide at 830 cm.$^{-1}$ (for isolated methyl). For total methyl the absorbance at 1379 cm.$^{-1}$ for a known solution of polypropylene in carbon tetrachloride was measured. In this way molar absorptivities of each group at these frequencies were obtained. Using these values it was then possible to calculate the weight per cent of propyl, ethyl, methyl and isolated methyl by measuring the corresponding absorbances of known solutions of the "cationic" polymers. Furthermore, knowing now the content of propyl, ethyl, and isolated methyl we could calculate the contribution which the methyls in these groups would make to the 1379 cm.$^{-1}$ band. When this contribution is subtracted the residual absorbance may be used to calculate "other" methyl, that is methyl not associated with the other groups measured.

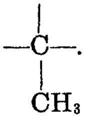
For the polymer prepared using Al_2Br_6/HBr at −78° we get:

Isolated methyl	Very low
Ethyl	10%
Propyl	5.7%
Total methyl	24.7%
"Other" methyl	17.3%

The value for total methyl seems incorrect since, if end groups (presumed to be isopropyl and unsaturation) are not *very* significant, total methyl should be about 35%, that is, unless methylene chains $(—CH_2—)_n$ are present. The infrared at 720 cm.$^{-1}$, characteristic of this structure, is quite transparent.

The reason for this becomes clear if, instead of polymers, we use hydrocarbons as our calibrating standards. Standardizing isolated methyl using 3-methylpentane, ethyl using 3-methylpentane, propyl using 2-methylpentane, and total methyl using both hexane and 3-methylpentane we now get:

Isolated methyl	Very low
Ethyl	16.3%
Propyl	6.2%
Total methyl	55.8%
"Other" methyl	42.6%

Using hydrocarbon standards, therefore, the methyl content calculated for the cationic polymer is too high unless there is a large contribution from  $—\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}—$. Since the 1379 cm.$^{-1}$ methyl band is not split, we know this is not the case.

The absorbances of all these groups depends therefore on their environment. We are presently studying this effect further using both polymeric and nonpolymeric materials of known composition. Meanwhile, in the absence of precise models for the "cationic" polymers it is not possible to measure an absolute value for the weight per cent of each group present.

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(8) G. Natta, *J. Polymer Sci.*, **34**, 531 (1959).

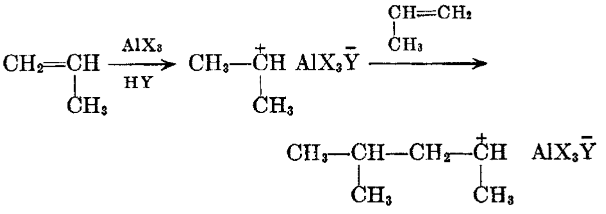
It is probably valid, however, to use the values given by either method to compare the composition of one "cationic" polymer *versus* another. Differences in the contents of each group can therefore be observed. In this way the effect of reaction conditions on the structure of the products can be found.

Effect of reaction conditions. Table I shows the weight per cent of each group in the products obtained under a wide range of reaction conditions. The values were obtained using linear polymers to calibrate the absorption bands.

Neither the ethyl nor the propyl content shows large variations. The isolated methyl absorption (830 cm.$^{-1}$) is exceedingly weak in every polymer. The ratio of wt. % ethyl/wt. % propyl is sensibly constant (column 10) with two exceptions—Run 2C and Run 15A.

DISCUSSION

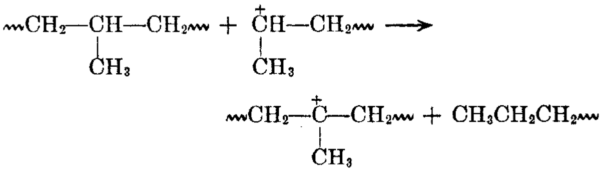
In the absence of side reactions, cationic polymerization of propylene would proceed through a secondary carbonium ion:



$$CH_2{=}\underset{CH_3}{CH} \xrightarrow[HY]{AlX_3} CH_3{-}\underset{CH_3}{\overset{+}{C}H}\ AlX_3\bar{Y} \xrightarrow{\underset{CH_3}{CH=CH_2}} CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}\underset{CH_3}{\overset{+}{C}H}\ AlX_3\bar{Y}$$

with the consequent formation of isolated methyl groups and isopropyl chain ends.

The n-propyl groups which we observe can arise from hydride transfer between the tertiary hydrogen on a polymer chain and the growing carbonium ion:



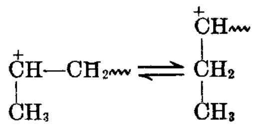
$$\sim CH_2{-}\underset{CH_3}{CH}{-}CH_2\sim + \underset{CH_3}{\overset{+}{C}H}{-}CH_2\sim \longrightarrow \sim CH_2{-}\underset{CH_3}{\overset{+}{C}}{-}CH_2\sim + CH_3CH_2CH_2\sim$$

The carbonium ion can, presumably, remove a hydride ion from its own chain or another. Either process gives rise to a new carbonium ion from which a branch may grow on the original chain. The ease with which this reaction may take place may be judged by Bartlett's observation that the analogous reaction in small molecule chemistry:

$$(CH_3)_3\overset{+}{C}\ Al\overset{-}{Cl_4} + C_2H_5(CH_3)_2CH \rightleftharpoons (CH_3)_3CH + C_2H_5(CH_3)_2\overset{+}{C}Al\overset{-}{Cl_4}$$
solvent

goes to completion at −20° in 0.001 sec.[9]

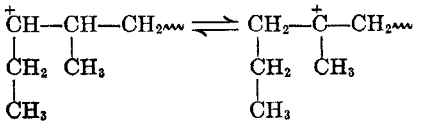
The presence of ethyl groups may be explained by rearrangement of the initially formed carbonium ion by an intramolecular hydride shift to another secondary carbonium ion of similar stability:



$$\underset{CH_3}{\overset{+}{C}H}{-}CH_2\sim \rightleftharpoons \begin{matrix}\overset{+}{C}H\sim\\ |\\ CH_2\\ |\\ CH_3\end{matrix}$$

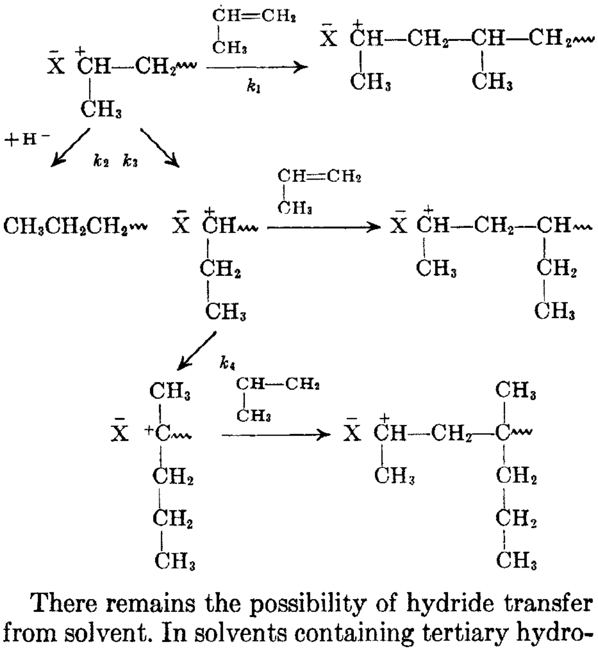
Good confirmation of these proposed reaction paths is provided by the infrared spectrum of the product obtained when butene-1 is polymerized at −80° by Al_2Br_6/HBr. The unrearranged polymer would have pendant ethyl groups. Intermolecular hydride transfers would yield n-butyl groups while the intramolecular hydride shift would give propyl groups. The spectrum of this material contains an extremely strong band at 736 cm.$^{-1}$ (propyl), one at 725 cm.$^{-1}$ (butyl), and a distinct but somewhat weaker band at 766 cm.$^{-1}$ (ethyl).

An alternative path by which propyl groups might be formed in the propylene case is a further intramolecular hydride shift:



$$\underset{\underset{CH_3}{CH_2}}{\overset{+}{C}H}{-}\underset{CH_3}{CH}{-}CH_2\sim \rightleftharpoons \underset{\underset{CH_3}{CH_2}}{CH_2}{-}\underset{CH_3}{\overset{+}{C}}{-}CH_2\sim$$

The total reaction scheme is therefore:



There remains the possibility of hydride transfer from solvent. In solvents containing tertiary hydrogen this certainly occurs. In isobutane, for example, only traces of polymer are formed, presumably due to the preponderance of this type of chain transfer, and the consequent formation of low molecular weight products. This observation is in accord with the proposed formation of n-propyl groups by intermolecular hydride transfer from polymer in butane. In solvents containing no tertiary hydrogens, hydride transfer with solvent will be much less

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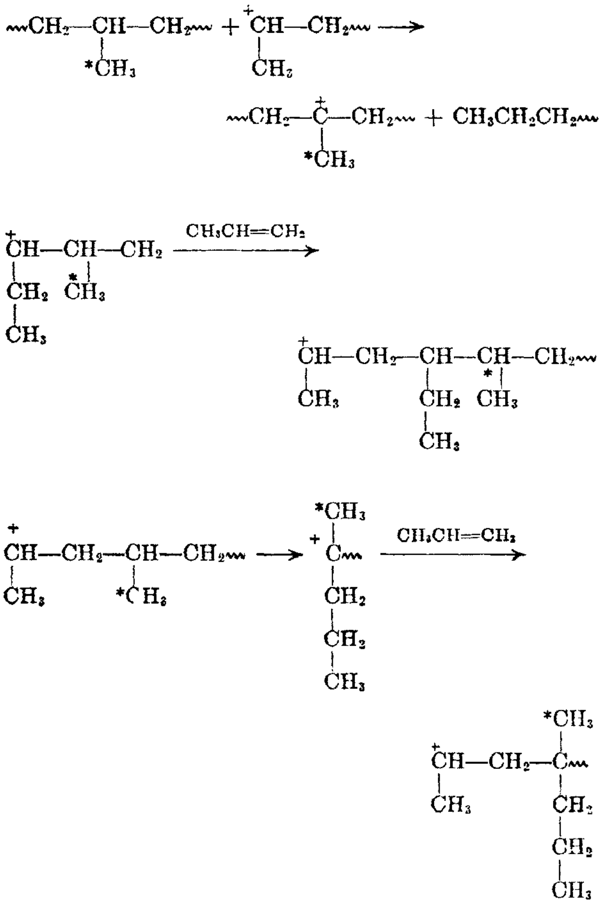
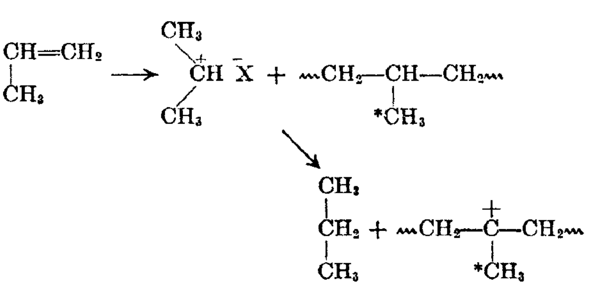
[9] P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1531 (1944).

important. No significant difference is found in the solution viscosities of polymers prepared in *n*-butane and methylchloride, which suggests that the solvent does not in these cases contribute largely to a process which destroys chain growth. However, this type of hydride transfer cannot be completely ruled out.

The formation of an ethyl or propyl group always results in the disappearance of isolated methyls other than the ones associated with the groups themselves. These methyls, which are the "other" methyls measured, are marked with an asterisk below:



For every one ethyl or propyl group formed, one "other" methyl should also be formed. Consequently, the weight-per cent methyl associated with ethyl and propyl groups should equal the weight-per cent "other" methyl. In fact, the weight-per cent "other" methyl is always much higher than this. Reactions must take place, therefore, which destroy isolated methyl groups, form "other" methyl groups and yet do not result in the formation of ethyl and propyl groups in the polymer. One possible reaction of this kind would be intermolecular hydride transfer to isopropyl carbonium ions:



The propane formed in this way would not be observed as an *n*-propyl group since it would be removed together with the butane solvent. To check this, reactions were run together with blanks to which no propylene was added. Analysis of the solvents by gas chromatography showed 2–3% propane in the runs and only 0.1% or less in the blanks. Attack of isopropyl carbonium ions on the polymer chain is therefore a reaction of considerable significance.

Referring again to Table I, the ratio of wt.-% ethyl/wt-% propyl is sensibly independent of the nature of the counter ion. This is true whether the co-catalyst alone is varied or both the catalyst and co-catalyst (Run 5-R). Most of the co-catalysts, it should be noted, were chosen to maximize any steric effects of the counter ion. It seems likely, therefore, that both the inter- and intramolecular hydride transfers occur *via* a relatively free carbonium ion rather than an intimate ion pair. This appears contrary to the situations observed with monomers such as styrene and isobutylene where transfer and termination steps are dependent on the nature of the catalyst.[10] The data do, however, support Mayo's interpretation of the kinetics of the cationic polymerization of propylene which involves the ionization of an undissociated catalyst polymer complex to the ion pair as a rate-determining step.[11] This ion pair may, or may not, add monomer before collapsing. It can also rearrange without affecting the kinetic picture.

Fontana[4] has proposed that monomer adds to the polymer-catalyst complex to give an unstable adduct which then rearranges to the relatively stable complex in the rate-determining step:

$$M_nC + M \longrightarrow M_nCM \xrightarrow{\text{slow}} M_{n+1}C$$

It is more difficult to see how this reaction scheme would give the same polymer structure independent of the nature of C.

Although change of counter-ion will not affect the ratio of products, both change in reaction temperature and the polarity of the solvent can affect the relative values of the rate constants k_2, k_3, and k_4. Runs 2-C and 1-SA show that this is so. Decreasing the temperature from −78° to −160° and increasing the dielectric constant of the

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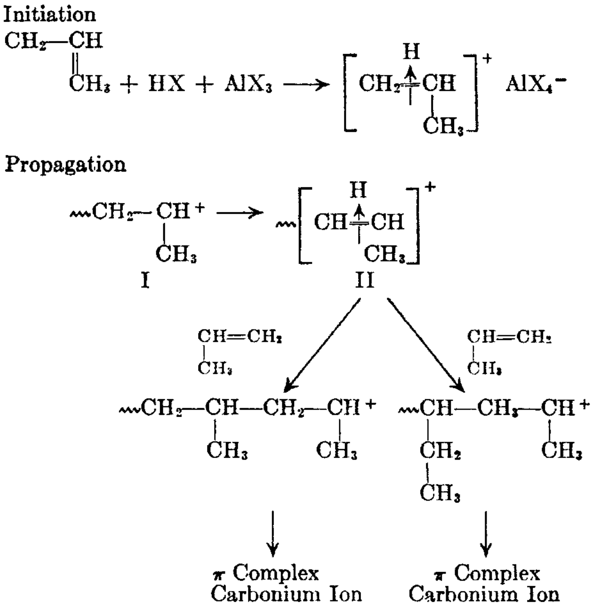
[10] P. H. Plesch, Society of Chemical Industry (U. K.) Plastics and Polymer Group Meeting, Nov. 22, 1960.

[11] F. Mayo and C. Walling, *J. Am. Chem. Soc.*, 71, 3845 (1949).

solvent from 1.5–12.5 significantly decreases the ethyl content relative to the propyl.

An alternative formulation of this reaction involved initiation and propagation *via* π complex intermediates rather than classical carbonium ions. Such intermediates have been proposed by Taft for the hydration of isobutylene.[12]



The initially formed carbonium ion I formed by monomer addition gives rise in each growth step to the π complex carbonium ion II. Addition of either a propylene molecule or a hydride ion could then take place at either carbon atom of the π complex without a "classical" carbonium ion rearrangement taking place. Propagation and rearrangement *via* this nonclassical intermediate could give the same kinetic results and product composition as those observed. It is difficult to see, however, how this reaction path could be distinguished from the classical scheme.

EXPERIMENTAL

Infrared spectra. All quantitative spectra were measured on a Perkin-Elmer 221 spectrophotometer.

Solutions of polymers prepared by cationic polymerization were prepared by weighing samples and adding 10 ml. of carbon disulfide or carbon tetrachloride. The mixtures were heated to dissolve the polymer, the bottles capped and reweighed on cooling. Solutions of linear polymers were prepared by extraction with carbon disulfide or carbon tetrachloride in a Soxhlet extractor. The solutions were then taken to dryness, the soluble polymer weighed and then taken up again in a known weight of solvent.

Gas chromatography. Solvents were analyzed for propane with a Perkin-Elmer 154 vapor chromatograph. A 6-ft. silver nitrate, diethylene glycol column together with a 12-ft. di-*n*-butyl maleate column was used at room temperature. A flow rate of 20 ml. min. was employed with helium as the carrier gas.

Materials. In all the work, Phillips research grade or Matheson C.P. grade butane and propylene were used. Aluminum halides were obtained from Fisher Chemical Co. Co-catalysts and complexing agents were A.R. Grade.

Polymerization at −78°. Except where otherwise stated, reactions were carried out at −78° in three necked, 500-ml. flasks fitted with stirrers and provision for flushing with nitrogen and adding reagents. The flask was immersed in a cooling bath and 200 ml. of liquid butane was added from a cylinder connected to a series of drying towers. 0.002 mole each of catalyst and co-catalyst weighed in a nitrogen-filled dry box were then added and stirring was commenced. When hydrogen bromide was used as co-catalyst, the flask containing the butane solution of the catalyst was connected to a gas transfer system. After evacuating, hydrogen bromide was introduced into the system and the amount dissolved in the butane calculated from the drop-in pressure. Thirty-five grams of liquid propylene condensed at −80° was blown into the flask with nitrogen to start the reaction. When reaction was complete, 100 ml. of heptane was added and the solution was shaken with water, dilute sodium hydroxide, and more water to remove both catalyst and co-catalyst. After drying, the solvent was evaporated. 50–75% yields of polymers, based on propylene, were obtained. Alternately, the reaction mixture was poured directly into 90% methanol-10% water and the precipitated polymer washed by decantation with methanol and "dried" in a vacuum oven. No difference was observed in the spectra of products isolated in these two ways. Polymerizations of butene-1 were carried out in the same way.

Polymerization at −160°. Reactions were carried out in double-walled vessels fitted with sealed stirrers. Provision was made for adding reagents and measuring internal temperatures. Propane solvent and propylene were cooled to −160° in liquid nitrogen and then added together with catalyst and co-catalyst to the reaction vessels. These were immersed in liquid nitrogen baths, the cooling efficiency of which could be controlled by varying the pressure in the jackets of the reaction vessels. The initial temperature of the reactants was thus maintained.

Effect of solvent. Typical procedures were used except that butane was replaced by methyl chloride, nitropropane and sulfur dioxide. No product was obtained using the last two solvents.

Effect of catalyst. Under the reaction conditions described, titanium tetrachloride and stannic chloride with water co-catalyst gave no products. Boron trifluoride, measured into the reaction vessel from a gas transfer system, gave a relatively nonviscous polymer of apparently lower molecular weight than that obtained using aluminum bromide.

Acknowledgment. We wish to thank Dr. F. X. Werber, D. F. Hoeg, and W. C. Overhults of the Washington Research Center for discussions and advice during the course of this work and Dr. R. W. McKinney, who carried out the gas chromatography.

CLARKSVILLE, MD.

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[12] J. B. Levy, R. W. Taft, and L. P. Hammett, *J. Am. Chem. Soc.*, 75, 1253 (1953).