*Polymerization of Allyl Chloride by Ziegler's Catalyst**

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(Received July 11, 1960)

In recent years many papers have been published on the stereospecific polymerization of α-olefins by Ziegler's catalyst. However it is well known that the catalyst, by itself, has little effect on the stereospecific polymerization of monomers containing any heteroatom, such as oxygen, nitrogen, sulfur or halogen, except only vinyl butyl ether, a stereospecific polymerization of which was found by Natta1).

An attempt was made on the polymerization by Ziegler's type catalysts with allyl chloride as a monomer containing heteroatom. Since allyl chloride was first polymerized by Staudinger2) to a syrupy low polymer, many investigations were done on the polymerization of this monomer, but no solid polymer has been obtained due to the "degradative chain transfer"3) in its radical polymerization.

By Ziegler's type catalysts allyl chloride

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* Presented at the 5th Meeting on High Polymer Chemistry, Kōbe, June, 1959.

1) G. Natta et al., *Angew. Chem.*, **71**, 205 (1959).

2) H. Staudinger and Th. Tleitmann, *Ann.*, **480**, 92 (1930).

3) P. D. Bartlett and R. Alschul, *J. Am. Chem. Soc.*, **67**, 812, 816 (1945). F. M. Lewis and F. R. Mayo, *J. Am. Chem. Soc.*, **76**, 457 (1954).

reacted rather rapidly at low temperatures with evolution of hydrogen chloride and gave a solid polymeric material. In the polymer produced the chlorine content was very much reduced for polyallyl chloride $[C_3H_5Cl]_n$ and indications of some unsaturation were observed. It was found that the polymerization took place only with catalysts having Al-Cl bond. Furthermore, the polymerization was accelerated by the presence of a small amount of benzene, which incorporated in the polymer.

On the basis of these results it was concluded that the polymerization of allyl chloride with Ziegler's type catalysts does not proceed by an anionic mechanism which is characteristic of these catalysts, but occurs with a some Friedel-Crafts type reaction caused by compounds such as Et_2AlCl, $EtAlCl_2$ or $AlCl_3$ formed in the reaction mixture. Also a cationic mechanism is likely to contribute simultaneously to the polymerization.

Similar results were obtained with the polymerization using allyl fluoride, allyl bromide, and 3, 3, 3-trichloropropene-1 as the monomer, respectivey.

Experimental

Materials. — *Allyl Chloride.* — Commercial allyl chloride was purified by distillation and a fraction of b. p. 44.0~45.0°C was used.

Allyl Bromide. — Synthesized according to Kamm and Marvel[4]. B. p. 70°C.

Allyl Iodide. — Prepared from allyl chloride and sodium iodide as described by Letsinger and Traynham[5]. B. p. 48°C/108 mmHg.

Allyl Fluoride.—Prepared from silver fluoride and allyl iodide[6], and collected in a trap cooled in a dry ice-acetone bath. An infrared absorption spectrum of the gaseous sample was shown in Fig. 2.

3, 3, 3-Trichloro-1-propene. (*Nippon Soda Co.*). — Distilled and a fraction of b. p. 50~53°C/80 mmHg was used.

n-Hexane. — Purified in the usual manner and stored over metallic sodium.

Triethylaluminum. — Supplied by Mitsui Chem. Ind. Co. and was used as a solution in *n*-heptane.

Titanium Tetrachloride.—Supplied by Osaka Titanium Co. and was used as a solution in *n*-heptane.

Apparatus. — A 50 ml. five-necked flask[7] fitted with a thermometer, a stirrer, a nitrogen gas inlet tube and two silicone rubber caps was used as the polymerization vessel. Catalyst components, monomer, and solvent were introduced into the vessel through rubber caps with a hypodermic syringe.

Preparation of Catalysts.—After the vessel was flushed by dry nitrogen, 20 ml. of *n*-hexane and 0.25 g. of titanium tetrachloride were introduced. With boiling the mixture gently, 0.15 g. of $AlEt_3$ was slowly added dropwise, and heating was continued for further 5 min. and cooled. After precipitating the solid catalyst complex the supernatant liquid was removed by a syringe under dry nitrogen. The catalyst was washed three times with 20 ml. of *n*-hexane, and then 20 ml. of *n*-hexane and 0.15 g. of $AlEt_3$ was added.

Other catalysts of Ziegler's type were prepared in the same manner but the wash procedure was omitted.

Polymerization. — The catalyst was cooled to the polymerization temperature in a dry ice-acetone bath and with stirring the monomer was slowly added dropwise. The reaction was exothermic and the heat evolved spontaneously at or after the addition of the monomer, when deep cooling was required to keep the temperature constant. After three to five hours the reaction was stopped by adding 10 ml. of methanol containing a small amount of hydrochloric acid and the polymer was precipitated by pouring the mixture into about 300 ml. of methanol. After standing overnight the polymer was collected and washed with methanol, and dried in vacuo. The polymer was reprecipitated from its benzene solution by methanol.

Allyl fluoride was polymerized as follows. The monomer gas was introduced by a gas inlet tube bubbling through the catalyst suspension and the unreacted monomer was recycled through a trap cooled in dry ice-acetone bath.

Double Bond Titration of Polymer. — A known amount of polymer (about 0.05 g.) was dissolved in 8 ml. of carbon tetrachloride in a 100 ml. glass stoppered flask and 2 ml. of 0.5 N bromate-bromide solution and 1.3 ml. of 10% sulfuric acid were added. After shaking the mixture vigorously for three minutes 2 ml. of 20% aqueous potassium iodide solution were added and again the mixture was shaken vigorously for a minute. The liberated iodine was titrated by 0.1 N sodium thiosulfate solution with starch as an indicator.

Reduction of Polymer with $LiAlH_4$.—A polymer of allyl chloride (0.25 g.) polymerized by $AlEt_3$-$TiCl_4$ catalyst and containing 20.81% by weight of chlorine was reacted with 0.4 g. of $LiAlH_4$ in 30 ml. tetrahydrofuran. The reaction was carried out under dry nitrogen in a sealed tube with shaking for 150 hr. at 60°C. After cooling, the reaction mixture was poured into methanol containing nitric acid to decompose excess $LiAlH_4$. The precipitated polymer was collected, washed with methanol and dried in vacuo. The chlorine content of the product was 7.50% (by wt.).

Results

The results were summarized in Tables I, II and III.

During the polymerization, especially in its initial stage, usually a sudden increase in temperature of the reaction mixture and a evolution of hydrogen chloride were observed, while the color of the catalyst turned to reddish brown gradually.

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[4] O. Kamm and C. S. Marvel, "Organic Syntheses", Coll. Vol. 1, (1956), p. 27.

[5] R. L. Letsinger and J. G. Traynham, *J. Am. Chem. Soc.*, **70**, 2818 (1948).

[6] M. H. Meslans, *Compt. rend.*, **111**, 882 (1890).

[7] S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, This Bulletin, **32**, 1094 (1959).

TABLE I. POLYMERIZATION OF ALLYL CHLORIDE WITH ZIEGLER'S CATALYST

Monomer: 5 ml. (4.70 g.), Catalyst: $AlEt_3$ 0.30 g. + $TiCl_4$ 0.25 g. ($AlEt_3/TiCl_4$=2 mol./mol.), Solvent: *n*-Hexane.

Polymerization			Polymer				
Temp. °C	Time hr.	Solvent ml.	Yield %	Cl-content*1 %	M. p. °C	η_{sp}/C*5 dl./g.	Double bond mol./C_3-unit
20	3	15	29.3	12.53*2	73～ 75	0.043	0.16
0	5	20	9.9	20.61	80～ 81	0.035	—
−10	5	20	9.1	19.55	85～ 86	0.040	—
−20	5	20	9.6	21.40*3	89～ 91	—	0.17
−30	5	45	7.1	18.26*4	105～108	0.081	0.13
−70	170	20	1.5	22.25	73～ 75	—	—

*1 Theoretical value for poly(allyl chloride) $[-CH_2-CH(CH_2Cl)-]_n$: 46.33%.

*2 C, 74.64%; H, 9.20%; corresponding to $C_3H_{4.4}Cl_{0.17}$.

*3 C, 69.30%; H, 8.71%; corresponding to $C_3H_{4.5}Cl_{0.32}$.

*4 C, 73.21%; H, 8.66%; corresponding to $C_3H_{4.3}Cl_{0.25}$.

*5 Benzene solution (C=0.5 g./dl.) at 30°C.

TABLE II. POLYMERIZATION OF ALLYLHALIDES WITH ZIEGLER'S CATALYST

Catalyst: $AlEt_3$ 0.30 g. + $TiCl_4$ 0.25 g. ($AlEt_3/TiCl_4$=2 mol./mol.)
Solvent: *n*-Hexane.

Monomer ml.		Polymerization		Solvent ml.	Polymer				
		Temp. °C	Time hr.		Yield g.	Halogen content, % Found	Theoretical	M. p. °C	η_{sp}/C(30°C) dl./g.
CH_2=CH-CH_2F	1.0*1	50	45	20	0.030	—	31.63	—	—
	3.2*1	25	7	25	0.050	3.2		97～ 98	—
	1.2*1	−20	2.5	25	0.030	1.5		75～ 77	—
CH_2=CH-CH_2Br	3.5	−20	5	20	0.255	30.00*2	66.05	85～ 87	0.025
CH_2=CH-CH_2I	3.0	−20	5	20	trace	—	75.55	—	—
CH_2=CH-CCl_3	2.0	20	5	20	0.180	35.28	73.14	135～140	—

*1 The quantities were shown as volumes at −80°C.

*2 C, 61.14%; H, 7.49%; corresponding to $C_3H_{4.4}Br_{0.22}$. Double bond 0.12 mol./C_3-unit.

The polymer obtained was a powder colored in faint yellow, having a melting point between 70～110°C and soluble in benzene, toluene, and tetrahydrofuran. Generally the chlorine content of the polymer was less than a half of the theoretical value (46.33%) for polyallyl chloride $[-CH_2-CH(CH_2Cl)-]_n$. The low viscosity of the polymer solution is indicative of the fairly low molecular weight of the polymer.

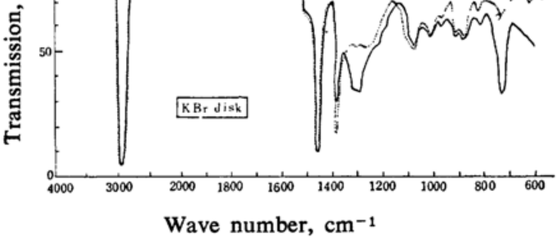


Fig. 1. Infrared absorption spectra of the polymer of allyl chloride (——) and its reduction product with $LiAlH_4$ (……).

Infrared spectra of a typical sample of the polymer and of its reduction product by lithium aluminum hydride were shown in Fig. 1. The absorption bands arising from C-Cl linkage appeared at 730 cm^{-1} and about 1300 cm^{-1}, and the intensities were decreased with the reduced polymer. At 1378 cm^{-1} and 1460 cm^{-1} are located the absorption bands due to the presence of methyl and methylene groups, respectively. The former increased its intensity relatively to the latter by the reduction of the polymer, indicating the presence of $-CH_2Cl$ groups in the polymer. The bands in a region between 800 cm^{-1} and 1000 cm^{-1} seems to be characteristic of various types of double bonds. In addition to this spectral data the double bond titration of the polymer showed about 0.15 mol. unsaturations per monomer unit in general (Tabel I).

These polymers were shown to be amorphous by their X-ray diffractions.

The chlorine content of the polymer was independent of the polymerization temperature in the range between 0°C and −70°C, while the conversion was strongly depressed at −70°C. The melting point of the polymer and its solution viscosity in benzene decreased slightly with raising the polymerization temperature (Table I).

The polymerizations of allyl fluoride, allyl bromide and 3, 3, 3-trichloro-1-propene by $AlEt_3$-$TiCl_4$ catalyst gave similar solid polymers as obtained from allyl chloride and their halogen contents were also much less than the theoretical values calculated for the monomeric units (Table II). The polymers of allyl fluoride and allyl bromide gave the similar infrared absorption spectra as that given by the polymer of allyl chloride, but the very weak band at 1070 cm^{-1} was considered to be of the C–F linkage in the former polymer (Fig 2). The band appeared to arise from the C–Br linkage was located at 569 cm^{-1} in the polymer of allyl bromide.

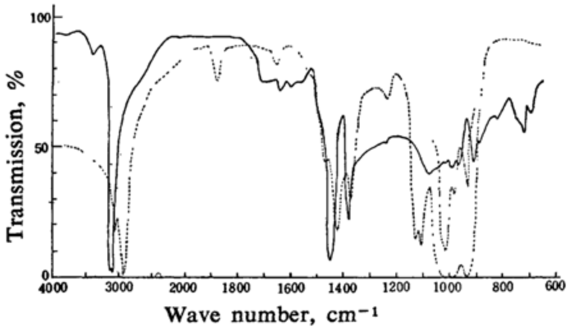


Fig. 2. Infrared absorption spectra of gaseous allyl fluoride (······) and its polymer (—— KBr disk).

Allyl iodide gave no polymer by $AlEt_3$-$TiCl_4$ catalyst under the same condition as in the polymerization of allyl chloride.

Various types of catalysts were examined for the polymerization of allyl chloride (Table III). Among the Ziegler's type catalysts used, all the compounds having Al–Cl linkage, either the linkage was original or formed from the catalyst components, were capable of polymerizing allyl chloride. However, the catalysts such as $AlEt_3$-$Ti(OBu)_4$, LiBu-$TiCl_4$ and $ZnEt_2$ (ether solution)-$TiCl_4$ gave no polymer under similar or even more drastic conditions. It should be noted, however, that the catalyst prepared from $AlEt_3 \cdot Et_2O$ and $TiCl_4$ hardly polymerized allyl chloride, although the catalyst might have possibly Al–Cl linkage in it.

Of the catalyst for cationic polymerization, what possessed Al–Cl linkage also functioned as catalyst for the polymerization of allyl chloride, while no polymer was obtained with $TiCl_4$ and $BF_3 \cdot Et_2O$. On the other hand, all the basic catalysts examined, such as LiBu, $ZnEt_2$(ether solution) and $AlEt_3$, had no catalytic activity for the polymerization.

It was found that an addition of benzene to the reaction mixture caused remarkable increase in the polymer yield (Table III) and also in the evolution of hydrogen chloride during the polymerization. An infrared absorption spectrum of the yielded polymer (Fig. 3) showed absorption bands due to skeletal vibrations of a benzene ring at 1605

TABLE III. POLYMERIZATION OF ALLYL CHLORIDE WITH VARIOUS CATALYSTS

Monomer: 3.5 ml., Solvent: *n*-Hexane 25 ml., Polymerization temperature: −20°C, Polymerization time: 5 hr.

Catalyst[*6]	Benzene g.	Polymer Yield %	Cl-content %	M. p. °C	η_{sp}/C[*5] dl./g.	Double bond (mol./C_3-unit)
$AlEt_3$-$TiCl_3$	0	5.0[*1]	14.79	94～ 95	0.050	—
$AlEt_3$-$VOCl_3$	0	6.4	18.71	86～ 89	0.043	—
$AlEt_3 \cdot Et_2O$-$TiCl_4$	0	0.8	—	—	—	—
Et_2AlCl-$TiCl_4$	0	10.8	19.20	83～ 85	0.050	—
Et_2AlCl-$TiCl_4$	1.0	31.6[*2]	16.77	116～118	0.093	0.08
Et_2AlCl	0	4.4	23.87	84～ 85	0.036	—
Et_2AlCl	1.3	29.6[*3]	15.05	99～102	0.072	0.06
$AlCl_3$	0	9.9	23.60	79～ 80	0.033	—
$AlCl_3$	1.0	44.7[*4]	17.66	—	—	—

[*1] Reaction time: 4 hr.

[*2], [*3], [*4] Benzene-insoluble fractions were 31.7, 11.5, and 16.8%, based on the total amounts of polymers, respectively. The following data described above were obtained on the soluble fractions.

[*5] Benzene solution (C=0.5 g./dl.) at 30°C.

[*6] The ratios of the two components were unity, except 0.2 of $AlEt_3/TiCl_3$.

cm^{-1} and 1498 cm^{-1}, indicating an existence of a benzene ring in the polymer chain. Furthermore, a part of this polymer was not soluble in any usual organic solvents and had no melting point even above 300°C, and was assumed to be a cross-linked polymer through benzene nuclei. The soluble fraction of this polymer had a higher melting point, a higher solution viscosity and a lower chlorine content, compared with the polymer formed under the same condition but without benzene.

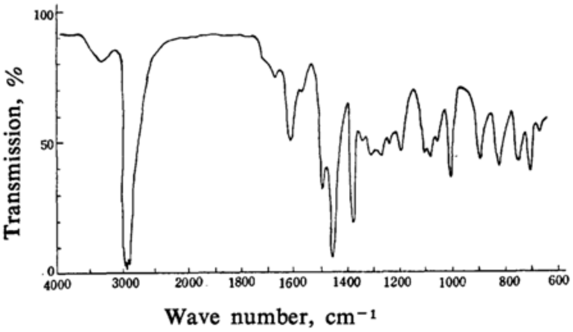
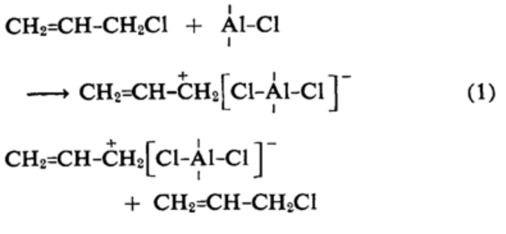


Fig. 3. Infrared absorption spectrum of the polymer of allyl chloride polymerized in the presence of benzene. KBr disk.

Discussion

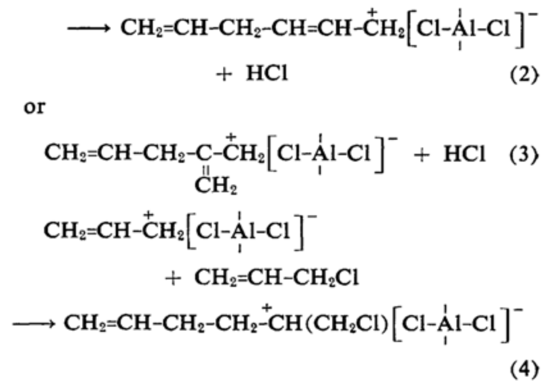
The results mentioned above reveals that the following features are involved in the polymerization of allyl chloride with Ziegler's type catalyst: a) An evolution of hydrogen chloride during the polymerization and a strongly reduced chlorine content of the resulting polymer. b) Only compounds containing Al-Cl bond such as Et_2AlCl, $EtAlCl_2$ and $AlCl_3$ function to polymerize allyl chloride. These compounds are powerful catalysts of Friedel-Crafts reaction. c) A marked increase in conversion with an addition of benzene to the system and an incorporation of benzene to the resulting polymer. d) An existence of double bonds in the polymer.

On the basis of these facts it is proposed that the Friedel-Crafts type reactions 1, 2 and 3 caused by a compound containing Al-Cl bond is essential in the polymerization of allyl chloride by Ziegler's type catalyst. It seems to be possible that a minor contribution of ordinary cationic processes 1 and 4 is involved and causes some complication in the reaction.



$$CH_2{=}CH{-}CH_2Cl + \overset{|}{\underset{|}{Al}}{-}Cl \longrightarrow CH_2{=}CH{-}\overset{+}{C}H_2\left[Cl{-}\overset{|}{\underset{|}{Al}}{-}Cl\right]^- \qquad (1)$$

$$CH_2{=}CH{-}\overset{+}{C}H_2\left[Cl{-}\overset{|}{\underset{|}{Al}}{-}Cl\right]^- + CH_2{=}CH{-}CH_2Cl$$



$$\longrightarrow CH_2{=}CH{-}CH_2{-}CH{=}CH{-}\overset{+}{C}H_2\left[Cl{-}\overset{|}{\underset{|}{Al}}{-}Cl\right]^- + HCl \qquad (2)$$

or

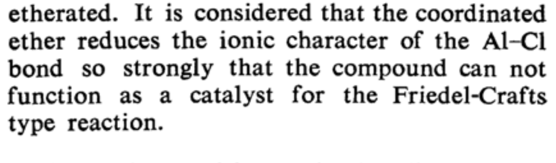
$$CH_2{=}CH{-}CH_2{-}\underset{\underset{CH_2}{\|}}{C}{-}\overset{+}{C}H_2\left[Cl{-}\overset{|}{\underset{|}{Al}}{-}Cl\right]^- + HCl \qquad (3)$$

$$CH_2{=}CH{-}\overset{+}{C}H_2\left[Cl{-}\overset{|}{\underset{|}{Al}}{-}Cl\right]^- + CH_2{=}CH{-}CH_2Cl \longrightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}\overset{+}{C}H(CH_2Cl)\left[Cl{-}\overset{|}{\underset{|}{Al}}{-}Cl\right]^- \qquad (4)$$

The reaction may proceed in such a manner as follows: a slow first stage of the reaction catalyzed by a small amount of original species having Al-Cl linkage, such as Et_2AlCl, $EtAlCl_2$ or $AlCl_3$, is followed by a faster reaction owing to a gradual accumulation of these catalyst compound generated by a reaction between $AlEt_3$ and hydrogen chloride liberated during the polymerization, and this finally leads to a violent rise of temperature of the reaction mixture.

The fact that the polymerization is strongly accelerated by adding a small amount of benzene to the system is a further evidence for the Friedel-Crafts type mechanism of the polymerization reaction. The benzene may undergo a variety of reaction, thus forming cross-linkages in some extent between polymer chains and giving a rather large amount of insoluble fraction of the polymer.

Methyl groups in the polymer may be produced by the reactions as following scheme.



$$\sim\underset{\underset{CH_2}{\|}}{C}\sim \xrightarrow{HCl} \sim\overset{Cl}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\sim$$

$$\sim\underset{\underset{CH_2Cl}{|}}{CH}\sim \xrightarrow{Et_3Al\ etc.} \sim\underset{\underset{CH_3}{|}}{CH}\sim \text{ or } \sim\underset{\underset{C_3H_7}{|}}{CH}\sim$$

In the case of $AlEt_3 \cdot Et_2O\text{-}TiCl_4$ catalyst, these components may also produce any compound such as Et_2AlCl, $EtAlCl_2$ or $AlCl_3$, but etherated. It is considered that the coordinated ether reduces the ionic character of the Al-Cl bond so strongly that the compound can not function as a catalyst for the Friedel-Crafts type reaction.

The authors wish to thank Mitsui Chem. Ind. Co. for the generous supply of triethylaluminum and Osaka Titanium Co. for titanium tetrachloride.

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