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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Lead Tetraethyl as Initiator for Polymerization Reactions[1]

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Polymerizations of acrylonitrile have been accomplished with lead tetraethyl and lead tetraethyl–titanium tetrachloride catalysts. The latter catalyst was found to be effective in certain cases where the former was not. The presence of light, especially ultraviolet light, was found to be not only very beneficial but a necessity in reactions at low temperatures (around room temperature). The polymers produced had inherent viscosities in the range 0.9–5.0, but possessed none of the highly crystalline properties of olefin polymers prepared using the normal Ziegler catalysts.

Polymerizations using Ziegler catalysts have so far been restricted to α-olefins. Monomers containing functional groups (*e.g.*, vinyl chloride, acrylonitrile, etc.) appear to react with the usual catalysts, such as an aluminum trialkyl–titanium tetrachloride mixture, and destroy them. In an effort to find different catalysts which these monomers would not attack, it was thought that the heavier, less reactive metal alkyls might be of more use. Because of its ready availability, lead tetraethyl was among those metal alkyls studied.

A recent patent application[2] describes the use of a lead tetraethyl–titanium tetrachloride catalyst in the polymerization of olefins to yield highly crystalline polymers. These reactions usually were carried out under pressure with reaction temperatures of 90–180°.

The monomers selected for the present work were vinyl acetate, vinyl chloride, acrylonitrile and methyl methacrylate. A catalyst of lead tetraethyl and titanium tetrachloride was prepared in dry heptane and the reaction temperatures ranged from 0–60°. The best results were obtained with acrylonitrile and methyl methacrylate and, due to their similarity of reaction, a thorough investigation was undertaken with acrylonitrile. Typical results with this monomer are listed in Table I. A few reactions were run in duplicate and it was found that yields could be checked to ±0.5% and viscosities fell in the same general range.

TABLE I

POLYMERIZATION OF ACRYLONITRILE USING LEAD TETRAETHYL-TITANIUM TETRACHLORIDE AS CATALYST

Lead tetraethyl, % (based on monomer)	Titanium tetrachloride/lead tetraethyl (molar ratio)	Temp., °C.	Time, hr.	Conversion, %	Inherent viscosity in dimethylformamide, 25°
3.6	0.78	25	72	8.8	2.4
3.6	.78	50	48	23	4.5
3.6	.78	60	72	17	2.4
3.6	1.56	60	72	13	2.4
3.6	3.90	60	72	5.1	0.9
7.2	0.36	60	72	4.8	1.8
18.0	0.16	60	72	3.7	2.0

These results indicated that a large excess of either catalyst component was undesirable as both the conversion and inherent viscosity were lowered. While reaction would go at room temperature, heating at 50° seemed to give the best results. Increasing the temperature did increase the conversion, but lowered the viscosity of the product. Control reactions were run using lead tetraethyl alone and titanium tetrachloride alone as catalysts at 50° for 48 hours. No polymer was obtained from the titanium tetrachloride reaction but an 8% conversion was obtained using lead tetraethyl. This polymer had an inherent viscosity of 5.0.

X-Ray diffraction pictures of the polyacrylonitrile samples prepared from lead tetraethyl alone and from lead tetraethyl–titanium tetrachloride showed that neither polymer had highly crystalline properties. Further work involving changes in catalyst ratios and changes of solvent failed to produce any better results. Prolonged reaction times would raise the conversion but not sufficiently to be of great use.

Attention was then shifted to experiments involving the use of lead tetraethyl alone as catalyst. Numerous examples of free radical polymerizations involving lead tetraethyl as a catalyst can be found in the literature. However, they usually involve reaction temperatures in the range 200–400°, and often the polymerizations are run under high pressure. Young and Douglas[3] used lead tetraethyl as a catalyst in the polymerization of vinyl acetate and vinyl chloride in acetone solution. These reactions were run in an autoclave at 80–100°. No mention of the use of acrylonitrile was made.

Polymerizations of acrylonitrile using a lead tetraethyl catalyst went smoothly, although high conversions were not obtained. In an effort to increase the conversions, the use of ultraviolet light on the reactions was tested and found to be of great benefit. Higher conversions were obtained although smaller inherent viscosities indicated that lower molecular weight polymers were obtained.

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[2] Montecatini, Societa Generale per l'Industria Mineraria e Chimica, Australian Patent Application 26-356-16995, March 23, 1956.

[3] C. O. Young and S. D. Douglas, U. S. Patent 1,775,882, September 16, 1930.

Ultraviolet light alone would polymerize acrylonitrile to low conversion, but a 24-hour induction period was necessary for reaction to begin. Reactions using lead tetraethyl alone as catalyst were carried out in complete darkness and the discovery was made that for the lower temperature regions, the presence of light of some kind was a necessity for polymerization to occur. Typical results are listed in Table II.

TABLE II

THE EFFECT OF LIGHT ON POLYMERIZATIONS OF ACRYLONITRILE

Lead tetraethyl, % (based on monomer)	Titanium tetrachloride/lead tetraethyl (molar ratio)	Temp., °C.	Time, hr.	Light conditions	Conversion, %	Inherent visc. in dimethylformamide, 25°
3.6	0	50	48	Room light	8.0	5.0
3.6	0	50	168	Room light	13	4.5
0.36	0	50	168	Room light	0.3	4.1
7.2	0	50	72	Room light	25	4.3
3.6	0	60	72	Room light	35	4.2
3.6	0	30	336	Room light	0	..
3.6	0.78	25	168	Dark	0.8	1.7
18.0	.78	25	72	Dark	0.3	0.9
18.0	.78	25	72	Room light	16	3.3
18.0	0	25	72	Dark	0	..
18.0	0	25	72	Room light	3.4	2.4
0	0	25	72	U.v. light	11	3.8
3.6	0	25	24	U.v. light	56	1.8
3.6	0.78	25	72	U.v. light	60	1.7

The polymerizations listed in Table I had all been carried out under normal conditions of room lighting. Some of these were repeated in the dark and under ultraviolet light, and the same catalytic effect of light as with lead tetraethyl alone was noted. A 60% conversion could be obtained at room temperature from acrylonitrile using a lead tetraethyl–titanium tetrachloride catalyst after 72 hours reaction under ultraviolet light. Typical reactions of this kind are listed in Table II. The data in Table II could be reproduced easily as long as care was taken to keep traces of moisture and oxygen from the reactions.

Young and Douglas[3] mention the fact that actinic light can be used as an accelerating influence on lead tetraethyl-catalyzed polymerizations, but they apparently did not use it in their cited examples. The above results indicate that at least in the lower temperature regions (around room temperature), light of some kind is not only useful but necessary to make lead tetraethyl active as a polymerization initiator.

The presence of ultraviolet light was shown to be necessary in polymerizations of other vinyl monomers (vinyl acetate, vinyl chloride, methyl methacrylate) at room temperature when a lead tetraethyl catalyst was used. Polymerization of vinyl chloride and methyl methacrylate could be carried out with a lead tetraethyl–titanium tetrachloride catalyst at room temperature in the presence of ultraviolet light. However, the reactions with monomers other than acrylonitrile and methyl methacrylate did not proceed in very good conversion and varying experimental conditions did not make marked improvements.

These results on the initiation of polymerization by lead tetraethyl under the influence of light are consistent with the observations of Riccoboni[4] that lead tetraethyl showed continuous ultraviolet absorption which he attributed to its dissociation into radicals. He found that up to 450 mμ, log ϵ increases fairly uniformly with decrease in λ. Roberti, Pipparelli and Semmola[5] also report that sunlight causes degradation of lead tetraethyl. The present work indicates that lead tetraethyl is decomposed under the influence of light to produce radicals capable of initiating polymerization even at room temperature. The role of the titanium tetrachloride in these reactions is somewhat uncertain since the high crystallinity expected from Ziegler type catalysts is not obtained.

Experimental

Materials. Heptane.—Phillips Petroleum Co., pure grade heptane was refluxed over silica gel for eight hours, then over sodium for eight hours and carefully fractionated.

Titanium Tetrachloride.—Crude titanium tetrachloride was purified by the method of Clabough, *et al.*,[6] and stored in a dry-box containing a moisture-free nitrogen atmosphere. All reactions involving this compound were carried out in this dry-box.

Lead Tetraethyl.—Commercially available material was used without further purification.

Monomers such as acrylonitrile were dried and redistilled before use.

Polymerization Technique.—All polymerizations listed in Tables I and II were carried out on 10-g. samples of acrylonitrile dissolved in 80 ml. of heptane solvent. The following is a typical reaction. In a 4-ounce bottle equipped with a self-sealing rubber gasket was placed 80 ml. of heptane and the bottle was flushed with nitrogen. Appropriate amounts of lead tetraethyl and titanium tetrachloride were added and the resulting precipitate was allowed to stand overnight (about 16 hours). Then 10 g. of acrylonitrile was added and the bottle was again flushed with nitrogen and sealed. The reaction mixture was allowed to stand with no shaking in a bath at the desired temperature. At the end of the reaction time, the bottle was opened and the contents poured into methanol to decompose the catalyst and coagulate the polymer. The polymer produced (usually a colorless, powdery material) was washed with methanol and dried under vacuum. To reprecipitate the polymer, the crude solid was dissolved in dimethylformamide and the solution poured into methanol. The precipitate was filtered and dried. When no titanium tetrachloride was used, there was no necessity to allow the catalyst to stand overnight.

Ultraviolet Light.—The ultraviolet light used in these reactions was obtained from a Blak-Ray no. 15 long wave ultraviolet bulb manufactured by Ultra Violet Products, Inc., South Pasadena, Calif. At first, quartz reaction vessels were used but these were found to be no more effective than ordinary Pyrex glass bottles. Thus most reactions were run in normal 4-ounce glass bottles. The ultraviolet bulb always was placed at a distance of one foot from from the reaction vessel.

Viscosity measurements were run on about 0.25 g. of polyacrylonitrile per 100 ml. of dimethylformamide solution. Due to difficulties encountered in getting the polymer samples into solution, most of the samples were not exactly 0.25 g., but in the range 0.2–0.3 g. All measurements were made at 25°.

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(4) L. Riccoboni, *Gazz. chim. ital.*, **71**, 686 (1941).

(5) G. Roberti, E. Pipparelli and E. Semmola, *Ricerca Sci.*, **9** (II), 689 (1938); *C. A.*, **33**, 9610 (1939).

(6) W. S. Clabough, R. T. Leslie and R. Gilchrist, *J. Research Natl. Bur. Standards*, **55**, 261 (1955)