(20.64 g.) was collected in several fractions (b.p. 80–103° (1.5 mm.), n^{25}_{D} 1.6418–1.6462). This corresponds to a 75% yield of crude XVII; however, the product was shown to contain the dimethyl sulfide of dithiocatechol. The principal product (13.6 g., b.p. 80–88° (1.5 mm.), n^{25}_{D} 1.6462) was used without further purification. A purer sample of XVII was obtained in the following way.

An ethereal solution (30 ml.) of the crude product (4.55 g.) was extracted with four 10-ml. portions of 10% sodium hydroxide and three 10-ml. portions of water. The dried ether layer was evaporated, affording a pale yellow oil (1.74 g.) which crystallized to a white solid (m.p. 24–27°). The reported[23] melting point of the dimethyldithiocatechol is *ca.* 25°. The basic extract was acidified (sulfuric acid), and the oil that separated was extracted (ether), dried ($MgSO_4$) and distilled. The distillate (b.p. 85–87° (1.6 mm.), 2.2 g., n^{25}_{D} 1.6470) showed absorption in the infrared at 2510 and 1317 cm.$^{-1}$ (characteristic of SH[17b] and $S–CH_3$,[17c] respectively).

Anal. Calcd. for $C_7H_8S_2$: C, 53.80; H, 5.16. Found: C, 53.22; H, 5.26.

Bis-(2-methylthiophenyl)-disulfide.—A mixture of XVII (0.774 g.), sodium hydroxide (97%, 0.35 g., 8.5 mmoles) and water (10 ml.) was heated on a steam-bath. The basic aqueous layer was decanted from the colorless, insoluble oil (m.p. 28–29°, presumably dimethyldithiocatechol), and iodine (0.23 g., 0.91 mmole) was added in small portions. The mixture was heated on a steam-bath for 1.5 hr. and was then cooled. The yellow solid (197 mg., m.p. 77–85°) that separated was recrystallized from petroleum ether, and the solid (108 mg., m.p. 82–85°), thus obtained, was chromatographed on Merck alumina (13 g., petroleum ether (3)–ether (1) as eluent). The product (53 mg.) melted at 85.5–86°.

Anal. Calcd. for $C_{14}H_{14}S_4$: C, 54.15; H, 4.55. Found: C, 54.14; H, 4.52.

2. **1-(*n*-Butylthio)-2-methylthiobenzene (XIII).**—A solution of impure XVII (5.0 g.) in ethanol (15 ml.) was added (20 min.) to a solution of potassium hydroxide (2.12 g., 0.032 mole) in ethanol (95%, 25 ml.), and the resulting mixture (nitrogen atmosphere) was stirred for 45 minutes. Butyl bromide (4.38 g., 0.032 mole) in ethanol (10 ml.) was added dropwise (10 min.), and the resulting mixture was stirred for 1.5 hr. at 25° and then for 1 hr. at the reflux temperature. The resulting mixture was filtered, concentrated, diluted with water and extracted with ether, and the resulting ether extract was extracted with 5% sodium hydroxide and washed with water. The resulting ether solution was dried and the concentrate (5.90 g.) was distilled (Piros–Glover column). The principal fraction (b.p. 147–149° (3.8 mm.), n^{25}_{D} 1.5949–1.5967) weighed 4.09 g. (60%).

Anal. Calcd. for $C_{11}H_{16}S_2$: C, 62.21; H, 7.60; S, 30.19. Found: C, 62.30; H, 7.61; S, 30.62.

The infrared spectrum was almost identical to a sample of XIII prepared from I. The preparation of derivatives of XIII has been described above.

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[23] J. Pollak, *Monatsh. Chem.*, **34**, 1681 (1913).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Polymerization of *l*-Propylene Oxide[1]

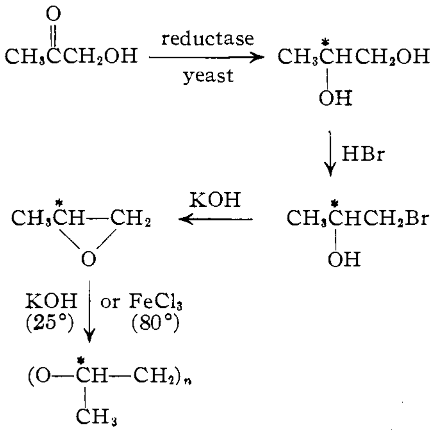
BY CHARLES C. PRICE AND MASEH OSGAN

RECEIVED MARCH 1, 1956

The polymerization of *l*-propylene oxide by potassium hydroxide gives low molecular weight, optically-active polymer, m.p. 55.5–56.5°, in sharp contrast to the liquid polymer formed from *dl*-propylene oxide under the same conditions. With ferric chloride catalysis, both *l*- and *dl*-propylene oxide give polymeric material which can be separated into amorphous intermediate molecular weight and crystalline (m.p. 70°) high molecular weight fractions. In this case there is no detectable difference, except for optical activity, between the products from optically-active and racemic monomer. This supports the view that catalysts can be highly selective in orienting the configuration of asymmetric centers along the polymer chain, and that such "isotactic" polymers have identical configurations of the asymmetric centers along the chain.

The list of polymers which have asymmetric centers along the chain and which have been prepared in amorphous and crystalline modifications includes polyvinyl ethers,[2] polypropylene and polystyrene[3] and polypropylene oxide.[4] The suggestion has been made that these differ due to the configuration of the asymmetric centers.[2,3] The term "isotactic" has been proposed for such polymers in which each successive asymmetric center has the same configuration.[3]

The purpose of the present investigation was to study the polymerization of *l*-propylene oxide,[5] since, of those monomers listed above, this is unique in having the asymmetric atom prior to polymerization. Should the polymerization proceed with either complete retention or complete inversion at the asymmetric center, the polymer would have not only all of the asymmetric centers of any one polymer molecule of the same configuration, but all the centers of all the polymer molecules would have the same configuration. It should, in short, be an optically active polymer.



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[1] Presented at the Delaware Valley A.C.S. Meeting, 16 February 1956 and the 129th National Meeting, Am. Chem. Soc., Dallas, Texas, April 1956; see also C. C. Price, M. Osgan, R. E. Hughes and C. Shambelan, THIS JOURNAL, **78**, 690 (1956).

[2] C. E. Schildknecht, *et al.*, *Ind. Eng. Chem.*, **40**, 2104 (1948); C. E. Schildknecht, S. T. Gross and A. O. Zoss, *ibid.*, **41**, 1998 (1949).

[3] G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); G. Natta and P. Corradini, *Makr. Chem.*, **16**, 77 (1955); C. W. Bunn and E. R. Howells, *J. Polymer Sci.*, **18**, 307 (1955).

[4] (a) H. Staudinger, "Hochmolekulare Organische Verbindungen," Springer, Berlin, 1932, p. 295; (b) U. S. Pat. 2,706,181 (April 12, 1955), M. E. Pruitt and J. M. Baggett (to the Dow Chemical Co.); U. S. Pat. 2,706,182 (April 12, 1955), M. E. Pruitt, J. M. Baggett, R. J. Bloomfield and J. H. Templeton (to the Dow Chemical Co.), *cf. C. A.*, **49**, 2395 (1955).

[5] P. A. Levene and A. Walti, *J. Biol. Chem.*, **68**, 415 (1926).

The monomer required was prepared by the procedure of Levene[5] and was polymerized by potassium hydroxide[6] and by ferric chloride.[4]

Experimental[7]

Materials.—The acetone, benzene and chloroform were "J. T. Baker Analyzed," reagent grade. They were filtered and used without purification. Baker A.R. grade potassium hydroxide (pellet), Baker and Adamson (technical, sublimed) ferric chloride and Mallinckrodt anhydrous ether (A.R.) were used as such.

The other reagents were prepared or purified as follows.

Carbon tetrachloride was freshly distilled over phosphorus pentoxide and redistilled over anhydrous potassium carbonate prior to usage.

Petroleum ether (high-boiling) was dried by refluxing over calcium hydride and fractionated, the fraction boiling from 65 to 80° being used.

Propylene Oxide (*racemic*).—Carbide and Carbon propylene oxide was refluxed for 2 hours over pellet potassium hydroxide and fractionated through a $^2/_3 \times$ 20-in. helices-packed column. The first and the last portions (approx. 15% each) were discarded and the middle fraction, b.p. 34.5–35°, was taken (70%).

(+)*l*-**Propylene Oxide.**—Levene's[5] synthesis was employed. One hundred g. of acetol, prepared[8] from α-chloroacetone and ethyl formate in methanolic potassium hydroxide, was reduced microbiologically by the reductase of yeast (Fleishman's brand of baker's yeast) to *l*-propylene glycol[9]; yield 60.7 g. (59%), b.p. 95–96° (15 mm.), $n^{25}\text{D}$ 1.4290, $d^{26}{}_{20}$ 1.027, $[\alpha]^{26}\text{D}$ −15.9° (dm., pure glycol). The propylene glycol was then converted to *l*-propylene bromohydrin with dry hydrogen bromide[10] at 0°; yield 65%, b.p. 59–60° (25 mm.), $n^{25}\text{D}$ 1.4770, $d^{26}{}_{20}$ 1.574, $[\alpha]^{25}\text{D}$ −3.6° (dm., pure bromohydrin) (lit. $[\alpha]\text{D}$ for *l*-propylene glycol,[8] −15°, $[\alpha]\text{D}$ for *l*-propylene bromohydrin,[10] −2.87°).

The (−)*l*-propylene bromohydrin was then cyclized to (+)*l*-**propylene oxide** with concentrated aqueous potassium hydroxide. The purified *l*-propylene oxide, obtained by refluxing the crude distillate of the cyclization over solid potassium hydroxide and triple distillation over potassium hydroxide pellets, weighed 20 g., b.p. 34.5–35°, $[\alpha]^{21}\text{D}$ +15° (40% in ether).

Solid Potassium Hydroxide Catalyst.[6]—Pellets of potassium hydroxide (containing 85% potassium hydroxide and 15% water) were ground as fine as possible in a mortar in a nitrogen dry box. The iron content of the potassium hydroxide used in these experiments was not more than 0.0003% according to the producer's analysis report on the label. However, in one of the experiments 20% by weight of potassium fluoride dihydrate was added to the potassium hydroxide powder as an iron(3) deactivator and the mixture was homogenized in an Osterizer in dry benzene. This also gave the same polymeric product upon polymerization of propylene oxide as the potassium hydroxide powder without addition of iron deactivator.

Preparation of "Ferric Chloride–Propylene Oxide Complex" Catalysts.[4b] 1.—To a mixture of 1 g. of ferric chloride and 18 ml. of ethyl ether under a slight nitrogen pressure, 6 ml. of propylene oxide was added dropwise with stirring and cooling in an ice–salt-bath. At the beginning the mixture became cloudy and a dark brown oil separated at the middle of the operation. When all the propylene oxide was added, the reaction mixture was allowed to come to room temperature (28–35°) and the mixture was stirred further for 10 minutes at this temperature. At this late stage of operation, in some experiments, a refluxing of the ether occurred, due to an exothermic reaction. The brown oil was almost dissolved at the end and addition of more propylene oxide did not cause any heat evolution. The volatile parts were then distilled at 25° or below and 25 mm. and the residue was left for one hour in a high vacuum system at room temperature. The catalyst obtained by this procedure was a reddish brown sticky paste, which was stored under nitrogen at −15°

2.—A pasty ferric chloride–propylene oxide complex catalyst was prepared, as above, from 3 g. of ferric chloride, 10 ml. of ether and 7 ml. of propylene oxide. This was dissolved in 40 ml. of acetone and 150 ml. of petroleum ether was added. A thick, heavy oil, insoluble in petroleum ether, separated (6 g.) which was redissolved in 30 ml. of acetone and filtered from the insoluble particles through a sintered glass funnel. The filtrate was evaporated *in vacuo* at room temperature, the residue being left overnight to dry in a high vacuum system. The catalyst obtained by this procedure was a dark brown powder with a metallic shine; it showed no evidence of crystallinity on X-ray examination.

The catalyst prepared according to procedure (1) was almost entirely soluble in a mixture of 33% or more of propylene oxide with diethyl ether, benzene or carbon tetrachloride, for catalyst concentrations greater than 2% based on the weight of propylene oxide. Below these limits, either the catalyst separated out as a brown powder immediately or the initial clear mixtures prepared at room temperature clouded within 10 minutes to 2 hours and the catalyst precipitated. At −78°, even for 10 hours, they remained in solution. Heating accelerated the precipitation.

The catalyst obtained according to procedure (2) was only partially soluble in the same propylene oxide–solvent mixtures.

In the following polymerization experiments, a freshly prepared catalyst (1) was used.

General Technique of Polymerization.—For kinetic studies, a single batch of propylene oxide–catalyst–solvent mixture of known concentration was prepared at first, then divided into approximately equal amounts in Pyrex tubes. The tubes were flushed with nitrogen and sealed. The sealed tubes were then placed in a constant temperature bath at 80 ± 0.5°. The tubes were removed from the bath at the appropriate times and quenched in a Dry Ice–acetone bath to stop polymerization. The tubes were then opened and the unreacted monomer and the solvent evaporated under vacuum at room temperature. The polymeric residue was then dried in a high vacuum system at room temperature for 15 hours. When necessary, the catalyst was removed by dissolving the residue in benzene and washing the benzene solution with aqueous hydrochloric acid solution. A typical experiment was conducted as follows.

About 48 ml. (33.7 g.) of ether and 20 ml. (17.2 g.) of propylene oxide were added to a 400-mg. sample of ferric chloride–propylene oxide complex catalyst. After a thorough mixing, the homogeneous reddish brown solution was cooled in ice-water and 8-g. portions of this mixture were charged into 18 × 180-mm. Pyrex tubes. The tubes were immediately chilled in Dry Ice–acetone and sealed after being flushed with nitrogen. After partial polymerization the tubes were quenched at −78° and then allowed to come to room temperature. A sufficient amount of benzene (50–200 ml.) was added, the amount of benzene being increased with increased polymerization time, in order to obtain a workable solution. The catalyst was then removed by washing with 10% aqueous hydrochloric acid (40–100 ml.). The colorless benzene solution of the polymer was washed subsequently with water (50 ml. twice), dilute aqueous sodium bicarbonate solution (50 ml.), and distilled water (100 ml. four times). The filtered benzene solution was then evaporated *in vacuo* at room temperature and the residue was left for 15 hours in a high vacuum system at room temperature. Longer drying times did not change the weight of the residue.

When fractionation was carried out to separate the crystalline polymer fraction, the crude polymer was dissolved in hot acetone to make an approximately 1–2% solution, cooled to about −30°, and the precipitated polymer was filtered under suction. The operation was repeated, and the crystalline fraction was dried by freeze-drying technique with benzene. White solid polymers of m.p. 69.5–70° were obtained. These materials showed a sharp X-ray diffraction pattern, the details of which will be reported elsewhere.

In all experiments, a qualitative test (precipitation from acetone at −30°) showed that some crystalline polymer was

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(6) C. C. Price and L. E. St. Pierre, Abstracts 126th Meeting, Am. Chem. Soc., Minneapolis, Minn., 12 Sept. 1955; THIS JOURNAL, **78**, 3432 (1956).

(7) All melting points and boiling points uncorrected. Optical rotations were determined in a tube of 1 dm. and with approximately 1 g./100 ml. solutions except where indicated otherwise.

(8) P. A. Levene and A. Walti, "Organic Syntheses," Coll. Vol. II, Reinhold Publ. Corp., New York, N. Y., 1943, p. 5.

(9) P. A. Levene and A. Walti, ref. 8, 1943, p. 545.

(10) P. A. Levene and A. Walti, *J. Biol. Chem.*, **68**, 418 (1926).

formed, even during the early stages of polymerization (4% conversion).

Viscosities were determined in benzene in an Ostwald viscometer[11] (0.5-mm. capillary bore, flow time for pure benzene 100–102 sec. at 25°) with 0.6–0.8 g./100 ml. solution at 25 ± 0.01°.

TABLE I

POLYMERIZATION OF PROPYLENE OXIDE IN ETHER ($[PO]_0$ = 0.335 g./g.) WITH 2.2% OF CATALYST (1) AT 80°

Time (hr.)	Conv., %	$(\ln \eta_{rel})/c$	Time (hr.)	Conv., %	$(\ln \eta_{rel})/c$
4	4.45	0.67	17	20.05	1.30
5	5.38	...	20	24.22	...
8	11.16	0.68	48	32.79	1.52
$10^1/_2$	11.42	0.69	50	40.55	...
15	12.53	...	75	50.84	...

TABLE II

PER CENT. OF CRYSTALLINE POLYMER AND INHERENT VISCOSITIES AT APPROXIMATELY *Equal* CONVERSIONS BY *Different* CATALYST CONCENTRATIONS, IN ETHER SOLUTION, $[PO]_0$ = 0.398 g./g.

Time, (hr.)	Conv., %	Cat., %	$(\ln \eta_{rel})/c$[a]	Cryst., %	$(\ln \eta_{rel})/c$[b]	$(\ln \eta_{rel})/c$[c]
17	9.23	1.31	2.84	25	4.05[d]	0.85
8	8.15	4.28	0.56	8	2.32	0.21
3	6.87	8.08	0.25	7.26	0.95	0.11

[a] Crude polymer. [b] Cryst. polymer fraction. [c] Amorph. polymer fraction. [d] $[\eta] = 3.5$.

TABLE III

THE RATE OF POLYMER FORMATION AT DIFFERENT INITIAL PROPYLENE OXIDE CONCENTRATIONS, IN ETHER AT 80°

$[PO]_0 = 0.265$; $[Cat] = 2.9\%$		$[PO]_0 = 0.493$; $[Cat] = 2.6\%$	
Time (hr.)	$[PO]_0/[PO]$	Time (hr.)	$[PO]_0/[PO]$
1	1.02	1	1.05
3	1.04	3	1.03
5	1.08	5	1.07
8	1.11	8	1.10
12	1.12	12	1.18
16	1.14	16	1.16
20	1.17	20	1.18
		50	1.39

TABLE IV

THE RATE OF POLYMER FORMATION AT DIFFERENT CATALYST CONCENTRATIONS, IN CARBON TETRACHLORIDE AT 80°

$[PO]_0 = 0.404$; $[Cat] = 1.56\%$		$[PO]_0 = 0.397$; $[Cat] = 5.04\%$		$[PO]_0 = 0.380$; $[Cat] = 10.5\%$	
Time (hr.)	$[PO]_0/[PO]$	Time (hr.)	$[PO]_0/[PO]$	Time (hr.)	$[PO]_0/[PO]$
1	1.04	1	1.04	1	1.086
2	1.05	1.5	1.05	1.5	1.233
2.5	1.07	2	1.058	2	1.212
3	1.06	2.5	1.068	2.5	1.251
3.5	1.07	3	1.087	3	1.308
4	1.08	4	1.110	4	1.525
5	1.11	5	1.139	5	1.763
6	1.11	6	1.166	6	1.892
8	1.13	8	1.254	8	2.686
10	1.15	10	1.366	10	3.850

Polymerization of *l*-Propylene Oxide with Solid Potassium Hydroxide Catalyst.—*l*-Propylene oxide (2.5 g.) and 0.5 g. of powdered potassium hydroxide were mixed in a Pyrex tube under nitrogen and sealed. The mixture was shaken for 50 hours at room temperature. The mixture was solidified to a wax at the end. It was dissolved in 250 ml. of benzene, washed with water, dilute aqueous sulfuric acid, aqueous sodium bicarbonate solution and finally with distilled water until neutral. After filtration of the benzene solution, the benzene was frozen and evaporated *in vacuo* and the residue was left for 12 hours in a high vacuum system (freeze-drying technique); 2.2 g. of a white, crystalline polymer was obtained. It melted sharply at 55.5–56.5°.

Anal. Calcd. for C_3H_6O: C, 62.04; H, 10.41. Found: C, 62.19; H, 10.34.

A sample of *dl*-propylene oxide (2.5 g.) was polymerized under exactly the same conditions. A liquid polymer was obtained (2.15 g.).

TABLE V

COMPARATIVE DATA FOR POLYMERS FROM POTASSIUM HYDROXIDE CATALYZED POLYMERIZATION OF *l*- AND *dl*-PROPYLENE OXIDE AT ROOM TEMPERATURE

	From *l*-	From *dl*-
Polymer $[\alpha]^{20}D$	$-16 \pm 5°$ (in C_6H_6)	...
(c 1%)	$+25 \pm 5°$ (in $CHCl_3$)	...
M.p., °C.	55.5–56.5	liquid[a]
$(\ln \eta_{rel})/c$	0.13	0.12
Yield, %	88	86

[a] Solidifies to a glass at −78°.

Polymerization of *l*-Propylene Oxide with Ferric Chloride–Propylene Oxide Complex Catalyst at 80° in Ether.—*l*-Propylene oxide (10 ml., 8.5 g.) was polymerized with 1% ferric chloride–propylene oxide catalyst (prepared with *dl*-propylene oxide according to procedure (1)) in 1:1 ether solution at 80° for 265 hours; 4.5 g. (52%) of a white snappy rubbery polymer was obtained. By fractionation of the crude polymer, 2.4 g. of amorphous and 2.1 g. of crystalline fractions were obtained.

dl-Propylene oxide was polymerized under the same conditions.

TABLE VI

COMPARATIVE DATA FOR POLYMERS FROM FERRIC CHLORIDE (1%) CATALYZED POLYMERIZATION OF *l*- AND *dl*-PROPYLENE OXIDE IN ETHER AT 80°

	From *l*-	From *dl*-
Polymer $[\alpha]^{20}D$ unfractd.	$+17 \pm 5°$ ($CHCl_3$)	...
$[\alpha]^{20}D$ cryst.	$+25 \pm 5°$ ($CHCl_3$)	...
	$-20 \pm 5°$ (C_6H_6)	...
$[\alpha]^{20}D$ amorph.	$+3 \pm 5°$ ($CHCl_3$)	...
	$-6 \pm 5°$ (C_6H_6)[a]	...
Softening point (cryst.), °C.	72–74	72–74
Freezing point (cryst.), °C.	75–72	75–72
Wt. cryst. fraction, g.	2.1	2.5
$(\ln \eta_{rel})/c$, cryst. fraction	3.11	3.12
$(\ln \eta_{rel})/c$, amorphous	1.37	1.18
$(\ln \eta_{rel})/c$, crude polym.	3.08	2.28
Total yield, g.	4.5	7.8

[a] (c = 2.6%).

In another parallel experiment, 1% by weight of the solid catalyst (2), 10 ml. (8.5 g.) of propylene oxide and an equal volume of dry ether were heated together at 80° for nine days. The mixture gradually increased in viscosity and at the end the solid catalyst was dispersed throughout the highly-viscous reaction mixture. Fractionation from acetone produced 2.5 g. of crystalline polymer and 5.2 g. of amorphous polymer, very similar to the results using the oily catalyst (1).

In order to determine whether the big difference in viscosity between the crystalline and amorphous polymers of Table VI was due to molecular weight and not an artifact resulting from association, viscosity measurements on a sample of crystalline polymer were run at two higher temperatures; $(\ln \eta_{rel})/c$ = 3.43 (25°), 3.35 (42.2°), 3.29 (53.6°). The very small change in inherent viscosity sug-

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(11) *Cf.* M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

gests little change in degree of association or of conformation of the polymer chain in solution.

The possibility that inversion of optical rotation of solutions of the polymer in benzene and in chloroform might arise from a sharp transition in conformation of the polymer chain[12] was considered. Experiment showed that optical rotation was, however, a linear function of the solvent composition for five different chloroform–benzene mixtures.

The identity of melting point of active and racemic crystalline polymer (Table VI) suggests that the racemate is a solid solution of *d*- and *l*-polymer molecules. This was confirmed by the melting point of a mixture of *l*- and *dl*-polymer. When heated very slowly (1°/5 min.) the melting point of active, *racemic* and the 1:1 mix was 69.5–70°. The 1:1 mix was prepared by dissolving equal portions of polymer in benzene and then vacuum freeze-drying the solution.

In order to establish whether the formation of *racemic* amorphous polymer from *l*-oxide resulted from racemization during or prior to polymerization, the following experiment was performed. A solution of *l*-propylene oxide in dry ether was made by mixing equal volumes (8 ml.) of each reagent. A part of this solution was polymerized for 44 hours with 1% ferric chloride–propylene oxide catalyst, then the unreacted monomer–solvent mixture was distilled off, by means of a stream of dry nitrogen, into a cold trap immersed in Dry Ice–acetone.

The rotation of the solution before polymerization and the rotation of recovered monomer–solvent mixture was determined in a 1-dm. tube. The specific rotation was then evaluated by calculation, the concentration of propylene oxide being determined by the procedure of Swern.[13] The retention of activity by the monomer indicated that racemization must occur during the propagation step.

	$\alpha^{21}\text{D}$	*l*-PO %	$[\alpha]^{21}\text{D}$	Conv., %
Before polymerization	6.05°	41	14.75	0
After polymerization	5.9°	39	15.1	4.8

Polymerization of *dl*-Propylene Oxide with Ferric Chloride–*l*-Propylene Oxide Complex Catalyst.—Ferric chloride (50 mg.) was suspended in 3 ml. of ether, the mixture was cooled to −78° and, under nitrogen, 1 ml. of *l*-propylene oxide was added. The mixture was then allowed to come to room temperature slowly under agitation. After being left for 15 minutes at room temperature, during which time a brown oil first separated and then redissolved, the volatile parts were removed by evaporation at room temperature under vacuum and the residue was left in a high vacuum system for 3 hours at 25°. To this, 12 ml. (10 g.) of *dl*-propylene oxide and 12 ml. of ether were added. The system was flushed with nitrogen and sealed. After 55 hours at 80°, the mixture was quenched at −78° and the crystalline fraction was worked up in the way described above; yield 110 mg., m.p. 71–74°. A 1.2% solution in chloroform was checked for optical rotation. Within experimental error, no optical activity could be detected.

Discussion

The formation of crystalline, low molecular weight, optically-active polymer from *l*-propylene oxide by potassium hydroxide polymerization, in contrast to the liquid polymer of the same molecular weight produced from *racemic* monomer under the same conditions, is dramatic evidence for the remarkable difference in physical properties which result from identical configuration of the asymmetric centers of this polymer.[14] The observations thus lend strong support to the suggestions[2,3] that earlier observations of amorphous and crystalline samples of several polymers with asymmetric centers may arise from such configurational differences.

We ascribe the considerable difference in melting point between the crystalline polymers from potassium hydroxide and ferric chloride catalyzed polymerizations, 5.5–56.5° and 70°, respectively, not to any configurational difference but to the large difference in the molecular weight for polymer prepared by the two procedures. The low melting polymer from potassium hydroxide catalysis has a molecular weight of approximately 2000–3000, while the high melting polymer from iron catalysis undoubtedly has a molecular weight greater by at least a factor of a hundredfold.

Support for the view that these polymers differ only in molecular weight comes from their X-ray diffraction patterns, their infrared spectra and their optical rotation. Powder X-ray patterns for all the samples of crystalline polymer, active and *racemic*, were identical and indicated an extremely high degree of crystalline order.[15] The infrared curves for all samples of crystalline polymer were indistinguishable; the major features of the spectra are summarized in Table VII. As can be seen from Tables V and VI, the high and low melting active polymer products had the same optical rotations, within the rather wide range of experimental

TABLE VII

MAJOR INFRARED ABSORPTION BANDS OF CRYSTALLINE POLYPROPYLENE OXIDE

Wave no., cm.$^{-1}$ ± 2	% Absorption, ± 5%: Cryst. PPO[a] m.p. 55.5–56.5°	Cryst. PPO[b] m.p. 70–75°	PPO[c] in soln.
3420	9	..	..
3300	..	..	5
3000	23	30	60
2870	26	36	64
1615	4	..	4
1575	..	..	8
1482	17	25	..
1450	18	27	36
1378	37	48	66
1345	11	19	35
1330	10	21	..
1300	23	30	33
1255	10	10	23
1240	19	25	..
1138	61	64	..
1100	57	68	93
1038	20	36	..
1012	13	23	23
932	34	50	..
918	22	37	28
868	6	11	15
833	13	21	12

[a] KBr disc. [b] As film of 0.01 cm. thickness. [c] CCl_4 solution of cryst. PPO (m.p. 70–75°), 0.265-cm. cell, *c* = 3% (approximately corresponds to absolute concn. of cryst. film), position of peaks identical with amorphous polymers.[6]

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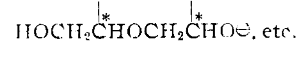
(12) P. M. Doty, Abstracts, 129th Meeting, Am. Chem. Soc., Dallas, Texas, April 10, 1956.

(13) D. Swern, T. W. Findley, G. N. Billen and J. T. Scanlan, *Anal. Chem.*, **19**, 414 (1947).

(14) We believe that this polymerization involves a potassium alcoholate type intermediate and proceeds so as to retain the original configuration of the asymmetric center

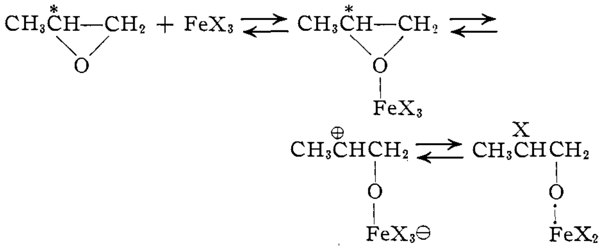


(15) We are indebted to Robert E. Hughes and Charles Shambelan for these observations. They will publish a detailed analysis of the X-ray data elsewhere. The strong spacings correspond to 4.25 and 5.20 Å.

error imposed by the need to run the measurements in dilute solution.

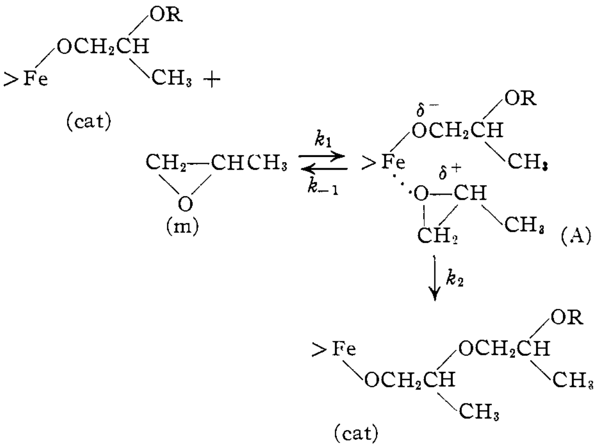
The fact that ferric chloride catalysis of either *l*- or *dl*-propylene oxide gave mixtures of amorphous and crystalline polymer, virtually indistinguishable except for optical activity, raises some interesting questions concerning the mechanism of this "isotactic" polymerization. The fact that *l*-propylene oxide with potassium hydroxide gave an excellent yield of polymer which was almost entirely crystalline, whereas with ferric chloride it gave polymer only partially crystalline, indicates that the potassium hydroxide polymerization proceeds with a high degree of retention of asymmetry, whereas the ferric chloride catalysis can involve considerable racemization of the asymmetric centers.

The formation of any crystalline polymer at all from racemic monomer must be due to asymmetric catalytic sites, presumably *d*- and *l*-propylene oxide–ferric chloride complexes, which have the feature of exhibiting highly preferential reactivity for propylene oxide of one particular configuration. It is our opinion that the catalyst sites effective in producing the crystalline polymer are heterogeneous, asymmetric centers, while the catalyst producing the amorphous polymer is in solution. The fact that the catalyst complex formed from ferric chloride and *l*-propylene oxide gave optically inactive crystalline polymer can be advanced as further support for the racemizing influence of ferric chloride. The fact that ferric chloride is a Lewis acid would make the following type of racemization appear reasonable. So far, however, we have been unable to isolate any propylene chlorohydrin from the ferric chloride–propylene oxide catalyst.



Since the polymerization with this iron catalyst was (or soon became) heterogeneous, the interpretation of the kinetic data in Tables I–IV is difficult. The data in Tables I and III indicate that the rate was essentially independent of the propylene oxide concentration over a considerable range. The data in Tables II and IV indicate approximately direct dependence of the rate on initial catalyst concentration. The dependence of polymer molecular weight on catalyst concentration and conversion (Tables I and II) is in accord with a stepwise buildup of polymer molecules, at least during the early course of the polymerization.

From the data in hand, we wish to propose the following scheme for the polymerization.[16] The exclusive opening of the ring at the secondary carbon may be due to the SNi type process, in contrast to the usual SN1 or SN2 reactions of propylene oxide.



The rate expression for polymerization by this scheme[15] is

$$-d(m)/dt = k_1k_2(\text{cat})(m)/(k_{-1} + k_1(m))$$

If $k_1(m) >> k_{-1}$, then the rate of polymerization will be independent of monomer concentration and dependent only on the catalyst sites available. If the iron alcoholate bond is stable, there will be very little tendency for termination of growth as long as monomer is available. As a monomer molecule coördinates with the iron atom (k_1) the cationic character of the secondary carbon of the oxide ring and the anionic character of the alcoholate oxygen will each increase, promoting the migration of the latter to the former as the propagation step in the polymerization (k_2). Carbonium ion character at the secondary asymmetric carbon of each successive *l*-propylene oxide monomer would account for the racemization necessary to obtain the amorphous polymer produced from this monomer.

We believe that the formation of crystalline polymer from either *l*- or *dl*-monomer takes place at the surface of heterogeneous catalyst sites. If the iron atom involved in the process is at a surface (or highly coördinated), the space available around the iron atom for accommodation of the incoming epoxide is limited, perhaps, we believe, so limited that the configuration of the adjacent asymmetric center in the alcoholate will determine the configuration of the epoxide which can coördinate.

What we propose then is that the reaction proceeds through an "internal" displacement in the complex (A), either in solution to give *racemic* amorphous polymer molecule, or at a surface site to give optically-active, crystalline polymer molecules.[17] Some support for this view may be derived from the difference in molecular weight between the two fractions (see Table VI). The catalyst centers in solution, in addition to having less rigid steric requirements for the coördination step, would also be more susceptible to displacement of the growing alcoholate group, leading to chain termination and lower molecular weight material, as is observed for the amorphous polymer.

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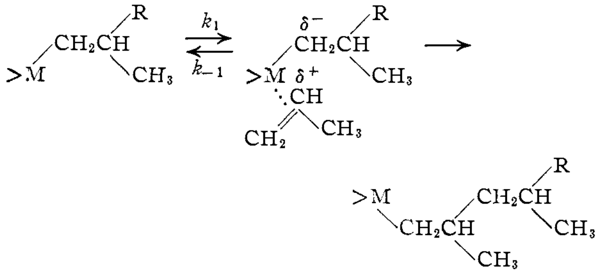
[16] This scheme is kinetically similar to that for the polymerization of propylene with aluminum bromide catalysis proposed by C. M. Fontana and G. A. Kidder, THIS JOURNAL, **70**, 3745 (1948).

[17] An alternative possibility would be that the crystalline and amorphous materials are formed by entirely different mechanisms, the former by ring opening at the primary carbon, the latter by ring opening at the secondary carbon.

By analogy, one may suggest that the new contribution to olefin polymerization which makes possible "isotactic" polymers of propylene and styrene,[3] is similar utilization of the type of mechanism proposed by Fontana,[15] but at a heterogeneous surface site (or other sterically-restricted center) where the steric requirements are so rigid as to orient the new asymmetric center to the same configuration as its predecessor.[18,19]



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[18] J. C. Bailar, Jr., H. B. Jonassen and A. D. Gott (THIS JOURNAL, **74**, 3132 (1952)), report the partial resolution of a racemate depending on the difference in ease of coördination of enantiomorphs with asymmetric inorganic complexes.

[19] The nomenclature and classification of the course of a polymerization proceeding *via* the mechanism we propose is worthy of some consideration. Viewed from the growing polymer chain, the process would appear to be base-catalyzed or anionic. Viewed from the monomer molecule, a key step is the coordination with a Lewis acid center, suggesting acid-catalyzed or cationic character. Actually, the process as suggested would be coöperative; we suggest it be called "coördinate propagation."

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Preparation of *p*-Vinylphenyl Thioacetate,[1] its Polymers, Copolymers and Hydrolysis Products. Water-soluble Copolymers Containing Sulfhydryl Groups[2]

BY C. G. OVERBERGER AND ALEXANDER LEBOVITS

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The preparation of *p*-vinylphenyl thioacetate is described. This monomer was polymerized and copolymerized with methyl methacrylate by free radical catalysis. After hydrolysis, polymers soluble in base were obtained which were precipitated by acids and oxidizing agents. This oxidation could be reversed by thioglycolate ion or cysteine in strong alkaline solution. In addition it was found that the hydrolyzed copolymer could reactivate urease which had been inactivated by iodine oxidation at a similar rate as that determined with thioglycolic acid.

A number of polymers having oxidation–reduction properties have been reported recently in the literature.[3,4] The object of this investigation was the preparation of soluble polymers having oxidation–reduction properties. Such polymers would be expected to be soluble in organic solvents as well as aqueous base and their solubility would decrease on oxidation or acidification. In the former case the decrease in solubility is due to cross-linking of the thiol groups of two polymer chains forming disulfide bridges. If it is remembered that it takes only two thiol groups on a polymer chain to be oxidized—provided that the disulfide link is intermolecular—to form a cross-link, it would be expected that a small degree of oxidation will render the polymer insoluble. It has been reported that polyvinyl mercaptan is insoluble and infusible,[5] and such insolubility has actually been observed by us and by Gregor, *et al.*,[6] who prepared this polymer in a different way. On the other hand the possibility exists that oxidation will lead to some intramolecular disulfide formation which will not decrease the solubility appreciably.

The poly-*p*-thiolstyrene was precipitated from its basic solution on acidification. Introduction of carboxyl groups by copolymerization has been observed to counteract this effect, and thus polymer solutions could be obtained at a suitable *p*H for use in a study of their effect on radiation and reactivation of deactivated urease.

One of the difficulties in preparing monomeric *p*-thiolstyrene was the very likely addition of the sulfhydryl group across a styrene double bond,[7] which would interfere with the synthesis and normal polymerization. To circumvent this difficulty the thiol group was protected by acetylation prior to introduction of the double bond, and liberated by hydrolysis after polymerization.

p-Vinylphenyl thioacetate (I) was prepared by the following scheme. *p*-Aminoacetophenone (II) was diazotized and allowed to react with potassium ethyl xanthate. The intermediate xanthate ester III was not isolated but reduced directly with sodium borohydride in alcohol solution followed by saponification to give *p*-thiol-α-methylbenzyl alcohol (IV) in 66% yield. Although III has been reported previously[8] as an intermediate for *p*-thiolacetophenone (V), the preparation of III and IV is given here in detail, since minor deviation from the procedure has resulted in low yields or in total failure to obtain IV. IV was converted to the

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[1] This is the 12th in a series of articles concerned with the synthesis of monomers and their polymerization; for the previous paper in this series, see C. G. Overberger and L. C. Palmer, THIS JOURNAL, **78**, 666 (1956). For a preliminary report of this work, see C. G. Overberger and A. Lebovits, *ibid.*, **77**, 3675 (1955).

[2] This paper comprises a portion of a thesis presented by Alexander Lebovits in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] H. G. Cassidy, M. Ezrin and I. H. Updegraff, THIS JOURNAL, **75**, 1615 (1953).

[4] G. Manecke, *Z. Elektrochem.*, **58**, 369 (1954).

[5] M. M. Brubaker, U. S. Patent 2,378,536 (June 19, 1945).

[6] H. P. Gregor, D. Dolar and G. K. Hoeschele, THIS JOURNAL, **77**, 3675 (1955).

[7] F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928); T. Posner, *Ber.*, **38**, 646 (1905).

[8] G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939).