troleum ether produced bright yellow needles of α-chloro-β-nitrostyrene, m.p. 54–55°, yield 34%.

Anal. Calcd. for $C_8H_6ClNO_2$: C, 52.33; H, 3.29; N, 7.63. Found: C, 52.80; H, 3.52; N, 7.45.

Upon treatment with aniline in ethanol, α-anilino-β-nitrostyrene, m.p. 125–127°, was obtained. The oily isomer was not further characterized except that it formed this aminonitroölefin also.

Acknowledgment.—We are deeply grateful to Dr. Keith S. McCallum for measurement and interpretation of the infrared spectra and to Dr. J. F. Brown, Jr., of the General Electric Research Laboratory for helpful communications on this problem.

HUNTSVILLE, ALABAMA

[Contribution from the Research Laboratories, Eastman Kodak Co.]

Crystallizable Polystyrene. I. Polymerization of Styrene with Alfin Catalysts[1]

By Jack L. R. Williams, John VanDenBerghe, Kenneth R. Dunham and William J. Dulmage

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Alfin catalysts polymerize styrene to give an amorphous polymer which can be heated in a suitable crystallizing medium to produce crystalline polystyrene. Suitable polymerization media are pentane, hexane, cyclohexane, benzene and triethylamine. Efficient crystallization media are hydrocarbon solvents boiling above 90° and diethyl ether. Detailed procedures for the preparation and characterization of Alfin catalysts are given. Methods for the preparation of highly crystalline polystyrene are described.

The preparation of crystallizable polystyrene using Alfin catalysts was reported briefly in a previous communication.[2] Further information and experimental details are given in the present paper.

Polymerization of Styrene with Alfin Catalysts.—Morton[3] has shown that the intrinsic viscosity of Alfin-catalyzed polystyrene increases with higher ratios of sodium isopropoxide to allylsodium. Our work has confirmed this, but we have found that the ultimate degree of crystallinity is independent of the catalyst ratio. Typical examples are listed in Table I.

Table I

Polymerization of Styrene by Various Alfin Catalysts[a]

Catalyst ratio *i*-PrONa/allyl Na	Basicity, meq./ml.	Polystyrene viscosity [η]	Max. cryst.
90/10	1.10	2.27	Medium
80/20	0.86	1.58	Medium
73/27	.94	1.29	Medium
50/50	.90	1.05	Medium
20/80	.50	0.79	Medium

[a] Charge: 30 ml. of styrene, 200 ml. of hexane and 30 ml. of catalyst in a 380-ml. pressure bottle. Polymerizations were run at room temperature.

With each catalyst, a certain minimum amount was required to produce high yields of polymer. Above this minimum, larger amounts of styrene could be added to the catalyst without decreasing the percentage yield of polymer based on styrene. This effect is shown in Table II for a catalyst having a sodium isopropoxide to allylsodium ratio of 73 to 27 and a basicity of 0.85 meq. per milliliter.

As expected, the rate of polymerization, using Alfin catalysts, was dependent upon the temperature. With 30 ml. of styrene and 30 ml. of catalyst (sodium isopropoxide/allylsodium = 73/27; basicity 0.94 meq./ml.) in 200 ml. of hexane, the results shown in Table III were obtained at 0 and at 60°. X-Ray comparison of the polymers indicated that a larger percentage of the polymer made at the lower temperature was crystallizable.

Although polymerizations were generally run in hexane, interesting results were obtained with other media, as shown in Table IV.

Table II

Effect of Catalyst Concentration

Catalyst, ml.	Hexane, ml.	Styrene, ml.	Time, min.	Temp., °C.[a]	Yield, %	Crystallinity
10	200	30	160	24	0	.....
15	200	30	180	25	16	Medium
20	200	30	120	29.1	80	Medium
25	200	30	85	30.6	83	Medium
30	200	30	60	32.4	87	Medium
30	200	50[b]	52	41.9	91	Medium
30	200	50	40	38.2	95	Medium

[a] The temperature was recorded by means of a metal-stem dial thermometer taped to the side of the polymerization bottle. The bottles were shaken in air at room temperature and the polymerization was stopped immediately after the temperature had passed a maximum. [b] The styrene was added in 20-ml. increments during the course of the polymerization.

Table III

Effect of Temperature on the Rate of Polymerization

Polymerization Time, min.	Temp., °C.	Yield, %	Crystallinity
60	0	2.6	High
120	0	5.9	High
480	0	40	High
1140	0	77	High
2	60	37	Medium
5	60	72	Medium
10	60	92	Medium

Natta[4] suggested that a heterogeneous catalyst was necessary to produce isotactic polymers. This theory holds true, for on long standing the solid phase of an Alfin catalyst settles out to some extent, leaving a small upper layer of clear solvent. A 30-ml. portion of the clear hexane layer from an Alfin catalyst failed to initiate the polymerization

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(1) Communication No. 1844 from the Kodak Research Laboratories.

(2) J. L. R. Williams, J. VanDenBerghe, W. J. Dulmage and K. R. Dunham, This Journal, **78**, 1260 (1956).

(3) A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950).

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TABLE IV

EFFECT OF SOLVENT MEDIA ON THE POLYMERIZATION OF STYRENE

Catalyst,[a] ml.	Styrene, ml.	Medium Type	Medium Amount, ml.	Polymerization Time, min.	Polymerization Temp., °C.	Yield, %	Cryst.
30	30	Hexane	200	36	35.4[b]	81	Medium
30	30	Hexane	200	180	0	28	High
30	60	Hexane	200	180	0	58	High
45	50	Hexane/ether	396/4	135	−20	30	High
60	60	Hexane/ether	392/8	180	0	73	Very low
10[c]	30	Diethyl ether	200	5	41.4[b]	100	Nil
10	30	Diethyl ether	200	30	0	99	Nil
10	30	Diethyl ether	200	60	0	100	Nil
30	30	Diethyl ether	200	60	0	99	Nil
30	30	Dioxane	200	12	38+[b]	100	Nil
30	30	Dimethoxyethane	200	45	35.4[b]	99	Nil
15	15	Pyridine	100	130	31.7[b]	92	Nil
30	30	Triethylamine	200	1140	21.7[b]	19	Medium
30	30	Benzene	200	180	25	84	Medium
15	15	Cyclohexane	100	108	35.6[b]	40	Medium

[a] Sodium isopropoxide/allylsodium = 73/27; basicity 0.85 meq./ml. [b] Maximum temperature recorded by a dial thermometer taped to the side of the polymerization bottle. The bottle was shaken in air at room temperature. [c] Contained a trace of *o*-dinitrobenzene.

of styrene. After this same catalyst was shaken to resuspend the solid phase, 30 ml. of the dispersion produced a 94% yield of moderately crystallizable polymer.

In Table IV it is shown that when diethyl ether was used as the polymerization medium the rate of polymerization was increased and smaller amounts of catalyst initiated the reaction. In order to demonstrate that the active catalyst phase was insoluble in ether, the supernatant hexane layer was decanted from a well-settled Alfin catalyst. The residue was dispersed in diethyl ether and the solids were allowed to settle. The clear ether layer failed to polymerize styrene. When the residue was redispersed in hexane, it catalyzed the formation of a small amount of non-crystallizable polystyrene.

When the catalyst was left in ether for several days prior to use, it was totally inactivated.

Inactivation of the Alfin catalyst also occurred when the hexane was completely evaporated under reduced pressure in a stream of oxygen-free, dry nitrogen. The dry catalyst residue failed to initiate the polymerization of styrene vapor over a 24-hr. period. Redispersion of the dry catalyst in hexane failed to restore its activity.

The data listed in Table IV show that polystyrene samples prepared in pyridine or ether media were non-crystallizable. The addition of diethyl ether to the hexane polymerization medium reduced the crystallinity of the polymer in proportion to the amount added. The use of ether alone increased the rate of polymerization and the amount of heat evolved and gave amorphous polymer.

Other polymerization media which gave crystallizable polystyrene were pentane, benzene, cyclohexane and triethylamine. Benzene and cyclohexane, which were solvents for the polymer itself, apparently did not interact with active, heterogeneous catalyst surface.

There is, then, a definite relationship between the polymerization medium and the manner in which the catalyst functions. With certain media, such as diethyl ether, which gave only amorphous polymers, the results may be interpreted in several ways. An actual solubilization of the catalyst would give rise to homogeneous rather than heterogeneous polymerization. The increased rate of polymerization in diethyl ether could be regarded as evidence for the formation of many soluble catalyst ions uniformly dispersed throughout the medium. However, the inactivity of the clear ether layer of an Alfin catalyst, dispersed in ether and then allowed to settle, disproves this theory.

It might also be postulated that diethyl ether acts as a promoter for the catalyst and that heat generated at the catalyst surface by the increased rate of polymerization might be sufficient to cause racemization at the locus of polymerization. Since the use of diethyl ether at low temperatures with efficient heat transfer failed to yield isotactic polystyrene and since even the addition of 2% of ether to a hexane medium was sufficient to reduce the crystallinity of the polymer from a high to a very low value, this conclusion seems to be unwarranted.

A logical theory, which fits present experimental evidence, is that highly active, unstable ether-complexed regions are formed in the catalyst. These regions permit random orientation of the incoming monomer units and thus induce amorphous polymerization. The increased activity of the ether-complexed regions also promotes more rapid and consequently more highly exothermic polymerization. The instability of the ether-complexed catalyst is due to gradual reaction between the catalyst and the ether solvent.

Another possible explanation is that ether reacts with the heterogeneous catalyst, continually eroding it to provide highly reactive fresh surfaces which promote rapid, non-specific adsorption of the monomer units. In time, the catalyst is entirely destroyed by reaction with the ether.

It is evident that the Alfin-catalyst surface is a delicate composition which readily loses its specific activity by the addition of minute traces of moisture or oxygen or by the action of complexing or eroding solvents.

Crystallization of Alfin-catalyzed Polystyrene.—A number of aliphatic liquids function well as crystallizing media if the temperature is above a lower limit and if the polystyrene is not entirely soluble. With pentane, crystallization occurs at elevated pressures at temperatures above the boiling point. Within a given class of solvents, the higher-boiling media have greater solvent action, particularly for low molecular weight polystyrene. When partial solution occurs, an insoluble crystalline fraction and a soluble, non-crystalline but potentially crystallizable fraction are obtained, the soluble fraction generally containing a lower percentage of isotactic material than the insoluble residue. With heptane, octane and diethyl ether, the solvents normally used for crystallization, no solution occurred, the polymer being recovered without loss of weight. The thermal breakdown of the polymer which was sometimes encountered during crystallization with higher-boiling solvents could best be prevented by using heptane or diethyl ether at their boiling points. The results obtained with various crystallizing media are summarized in Table V.

Table V

Crystallization of Alfin-catalyzed Polystyrene in Various Media

Medium	Temp., °C.	Time, hr.	Intrinsic viscosity		Cryst.
			Before	After	
Pentane	B.p.	168	2.27	1.84	Nil
Pentane	65[a]	72	2.27	2.42	Medium
Pentane	90[a]	48	2.27	2.30	Medium
Hexane	25	48	2.27	2.21	Nil
Hexane	25	144	2.27	2.34	Very low
Hexane	B.p.	2	2.27	..	Very low
Hexane	B.p.	72	2.27	2.35	Low
Heptane	B.p.	2	2.27	2.35	Low
Heptane	B.p.	24	2.27	1.92	Medium
Octane	25	168	2.13	1.79	Very low
Octane	B.p.	156	2.13	1.25	Medium
Isoöctane	B.p.	48	2.27	1.98	Medium
Decane	B.p.	72	2.27	..	Medium
Hexene-1	B.p.	144	2.27	2.30	Medium
Diethyl ether	B.p.	30	2.27	..	Medium
Diisopropyl ether	B.p.	30	2.27	..	Medium
Methanol	B.p.	72	2.27	2.43	Nil
1-Butanol	B.p.	72	2.27	1.84	Low
1-Heptanol	B.p.	72	2.27	..	Soluble
1-Heptanol	95	24	2.27	..	Medium
1-Octanol	95	24	2.27	..	Medium
Cyclohexanol	B.p.	48	2.27	1.46	Very low[b]
Ethylene glycol	B.p.	144	2.27	..	Very low
2-Methoxyethanol	B.p.	144	2.27	2.36	Medium
Water	B.p.	72	2.27	..	Nil
Water[c]	B.p.	336	2.12	..	Nil
Air	100	168	2.27	2.18	Nil

[a] Heated in sealed pressure bottle. [b] Polymer was soluble in hot cyclohexanol. Crystallization apparently occurred while the solvent was still warm but after some of the polystyrene had precipitated. [c] Containing 0.5% of Duponol ME.

The rate of crystallization of polystyrene depends not only upon the crystallization medium and the temperature but also upon the percentage of isotactic material present. The greater the percentage of isotactic material, the faster will be the rate of crystallization.

In Table VI are compared the rates of crystallization, in diethyl ether, heptane and octane, of polystyrene having an intrinsic viscosity of 2.25.

Table VI

Crystallization of Polystyrene in Boiling Ether, Heptane and Octane

Time in boiling medium, hr.	Intrinsic viscosity after treatment in			Crystallinity after treatment in		
	Ether	Heptane	Octane	Ether	Heptane	Octane
0.5	2.27	2.20	2.10	Medium$^-$	Low$^+$	Medium$^-$
1	2.23	2.26	2.10	Medium$^-$	Medium	Medium$^-$
2	2.26	2.20	1.88	Medium	Medium	Medium$^-$
24	2.26	1.87	1.89	Medium$^+$	Medium	Medium$^-$

Determination of Crystallinity.—The degrees of crystallinity which are presented in the tables are qualitative estimates as observed from the X-ray diffraction photographs of the specimens. The specimens were approximately 0.5 mm. thick and were photographed with nickel-filtered CuKα radiation on flat plate films. The sample-to-film distance was 4 cm. and the exposure time was 1 hr. Figures 1a, b and c exhibit the low, medium and high degrees of crystallinity.

Experimental

Experimental details for the preparation of sodium dispersions and Alfin catalysts and for the ionic polymerization of styrene are scattered throughout the existing literature. For this reason, and because the exact manner of preparation of heterogeneous catalysts seems to have a pronounced effect upon their activity, detailed procedures are given here.

Preparation of Alfin Catalysts. A. Preparation of Sodium Dispersion.—In a dry, 2-l., three-necked creased flask equipped with a nitrogen inlet to maintain a nitrogen blanket above the surface of the reactants, an air condenser, a metal-stem dial thermometer extending to the bottom of the flask and a high-speed stirrer with a special "cruciform" impeller (Labline Stir-O-Vac), inserted to within one-half an inch of the bottom of the flask, were placed 500 g. of mixed xylenes (Eastman Kodak Technical Grade, dried over sodium) and 5 g. (1%) of oleic acid. The mixture was stirred at low speed until uniform, after which 500 g. of clean sodium (cut under xylene) was added. The flask was heated by means of a Glas-Col heating mantle until the temperature of the mixture reached 105°. The heat was shut off and the stirrer was started at low voltage to disperse the sodium. The stirrer speed was gradually increased by raising the voltage until a setting of 90 volts was reached (maximum rated speed of stirrer 20,000 r.p.m.). The mechanical heat input of the stirrer was sufficient to maintain the temperature of the mixture, but external heat should be added if necessary to keep the temperature at 105°. After 45 minutes at a setting of 90 volts, the stirrer was stopped and the light-gray dispersion was allowed to cool to room temperature. It was then siphoned by means of nitrogen pressure into large pressure bottles which had been flushed with nitrogen, and the bottles were capped with Neoprene-lined, self-sealing caps equipped with holes to accommodate 16-gauge syringe needles. The entire operation was performed in a nitrogen-filled dry-box.

B. Standardization of Sodium Dispersion.—The strength of the sodium dispersion was checked by direct titration. The dispersion was too thick to be measured accurately with a syringe or pipet, but the following procedure was found to work satisfactorily: The bottle containing the dispersion was shaken to obtain a uniform sample and about 5–6 ml. was withdrawn through the rubber-lined cap into a 10-ml. syringe. The dispersion was jetted carefully into a 5-ml. graduated cylinder until the level was exactly at the 5-ml. mark, care being taken not to get any dispersion on the walls of the cylinder above the 5-ml. mark. The dispersion sample was decomposed with 50 ml. of methanol in a nitrogen atmosphere. An equal volume of water was then added to the sample, and it was titrated with 0.5 *N* HCl to the phenolphthalein end-point.

Comparable results were obtained when the dispersion was decomposed with 2-methoxyethanol and the evolved hydrogen was measured.

C. Preparation of Amylsodium.—In a 2-l., three-necked flask equipped with a nitrogen inlet, a silver-plated copper-coil condenser, a metal-stem dial thermometer extending to the bottom of the flask, a dropping funnel and a high-speed stirrer was placed 800 ml. of hexane which had been dried over sodium and 92 g. (2 g. atoms) of 50% sodium dispersion. The stirrer was started at low speed and the flask was cooled by immersion in a bath of chilled 2-methoxyethanol which could be raised or lowered by means of a Lab-Jack. The bath was cooled by means of a copper coil through which methanol at −65° was circulated. The silvered-coil condenser was connected to this same circulating system. When the temperature inside the flask had dropped to 10°, the first few drops of 106.6 g. (122 ml., 1 mole) of freshly distilled amyl chloride were added from the dropping funnel. When the reaction had started, as evidenced by liberation of heat and darkening of the reaction mixture, the temperature of the reaction mixture was lowered to −20°. The stirrer speed was increased by raising the voltage to a setting of 85–90 volts, and the remainder of the amyl chloride was added dropwise at −20° over a period of 1.5 hr. Stirring was continued for 45 minutes after all of the amyl chloride had been added, while the temperature was allowed to rise to 0°. The amylsodium was black or deep, bluish-black in color and was almost pasty in consistency. Dry amylsodium is pyrophoric and must therefore be handled in an inert atmosphere.

D. Titration of Amylsodium.—The yield of amylsodium was determined by differential titration—the first titration to determine the total alkalinity (equation 1) and the second to determine alkalinity not due to amylsodium (equation 2). The difference between these titrations gave a measure of the actual amount of amylsodium.

$$\begin{array}{c} C_5H_{11}Na \\ + \\ \lbrack Na \rbrack \end{array} \xrightarrow{CH_3OH} \begin{array}{c} C_5H_{12} + CH_3ONa \\ + \\ \lbrack H_2 + CH_3ONa \rbrack \end{array} \xrightarrow{H_2O} \begin{array}{c} C_5H_{12} + CH_3OH + NaOH \\ + \\ \lbrack H_2 + CH_3OH + NaOH \rbrack \end{array} \qquad (1)$$

$$\begin{array}{c} C_5H_{11}Na \\ + \\ \lbrack Na \rbrack \end{array} \xrightarrow{C_6H_5CH_2Cl} \begin{array}{c} C_6H_5CH_2C_5H_{11} + NaCl \\ + \\ \lbrack Na \rbrack \end{array} \qquad (2a)$$

$$\begin{array}{c} C_6H_5C_6H_{13} + NaCl \\ + \\ \lbrack Na \rbrack \end{array} \xrightarrow{CH_3OH} \begin{array}{c} C_6H_5C_6H_{13} + NaCl \\ + \\ \lbrack H_2 + CH_3ONa \rbrack \end{array} \xrightarrow{H_2O} \begin{array}{c} C_6H_5C_6H_{13} + NaCl \\ + \\ \lbrack H_2 + CH_2OH + NaOH \rbrack \end{array} \qquad (2b)$$

The amylsodium dispersion was stirred or, if bottled, shaken to obtain uniform samples. Aliquots could be measured out either as described for the sodium dispersion or by very carefully pulling a sample into a syringe and reading the amount directly. With the latter method, a clean syringe was used for each sample, since the opaque amylsodium coating on the walls of the syringe made accurate measurement of further samples impossible. A 16-gauge hypodermic needle was used, since smaller-bore needles were plugged frequently by the thick dispersion.

A 2-ml. sample of amylsodium was measured out and decomposed with 50 ml. of methanol; 20 ml. of distilled water was added (equation 1), and the sample was titrated to the phenolphthalein end-point with 0.1 *N* HCl.

A 5-ml. sample of amylsodium dispersion was placed in 15 ml. of benzyl chloride (equation 2a); 15 ml. of methanol and 30 ml. of distilled water were added (equation 2b) and the sample was titrated with 0.1 *N* HCl to the phenolphthalein end-point.

Sample titration:

A 2-ml. sample in methanol required 20.15 ml. of 0.1 *N* HCl (equation 1); a 5-ml. sample in benzyl chloride required 4.30 ml. of 0.1 *N* HCl (equation 2).

Total alkalinity	$\frac{20.15 \times 0.1}{2}$	= 1.008 meq./ml.
Alkalinity other than amylsodium (residual free sodium)	$\frac{4.30 \times 0.1}{5}$	= 0.086 meq./ml.
Amylsodium		= 0.922 meq./ml.
Concentration of amylsodium	$\frac{0.922}{1.008}$	= 91.5% of the total alkalinity
Yield of amylsodium	0.922 meq./ml. × 1020 ml. (total volume of dispersion) = 940 meq. = 0.940 mole = 94%	

Since two equivalents of sodium are necessary to produce one equivalent of amylsodium, the yield of amylsodium may be checked as

$$\frac{0.922 \text{ meq. AmNa}}{0.922 + \dfrac{0.086 \text{ meq. free Na}}{2\text{Na/AmNa}}} = \frac{0.922}{0.965} = 95\%$$

E. Preparation of Alfin Catalyst.—The apparatus was the same as that used for the preparation of amylsodium (section C). In practice, it was frequently convenient to use the same flask; the total amount of amylsodium was calculated by titrating aliquots as described in section D, and the milliequivalents per milliliter were multiplied by the volume of the contents of the flask.

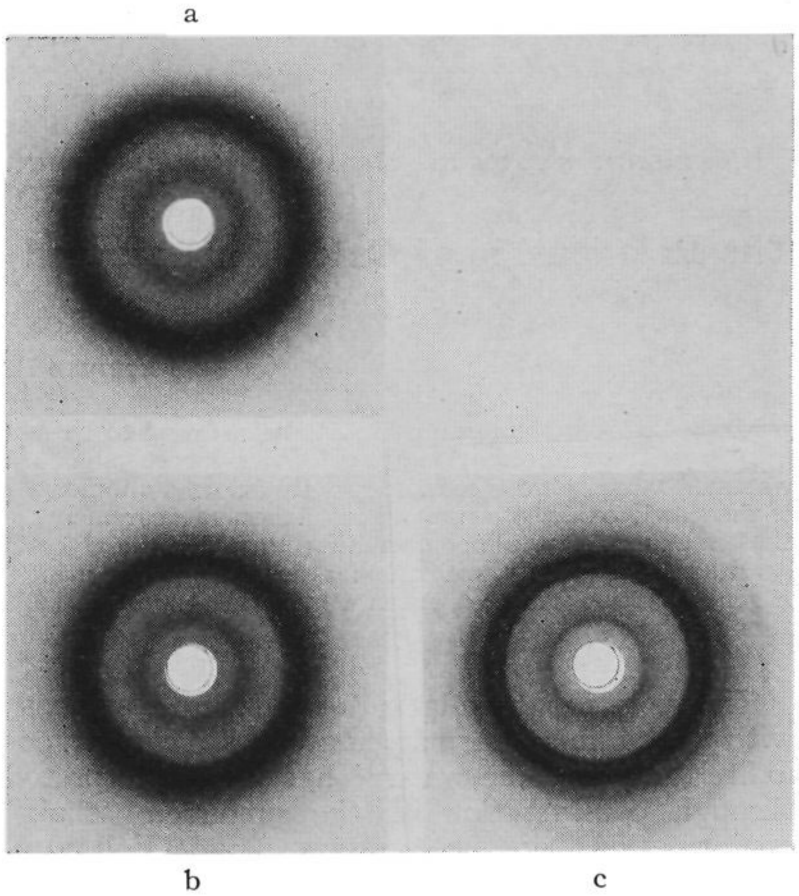

Fig. 1.—X-Ray diffraction photographs of partially isotactic polystyrene, crystallized by heating 14 hours in heptane at 90°. CuKα radiation: a, low crystallinity; b, medium crystallinity; c, high crystallinity.

Nine hundred and seventy-five milliliters of a dispersion containing 0.90 mole of amylsodium was stirred with a high-speed stirrer (setting 70 volts) at 0°, while 27.0 g. (34.5 ml., 0.45 mole) of dry isopropyl alcohol was added dropwise from the dropping funnel over a period of 1 hr. Stirring was continued for 30 minutes, after which the dropping funnel was replaced by a gas inlet tube extending to the bottom of the flask and dry propylene gas was bubbled in for 4 hr. The propylene was passed through a 3-ft. column packed with sodium hydroxide pellets to remove any traces of moisture. The temperature of the dispersion was allowed to rise from 0 to 25° during the time of addition, and methanol at −65° was pumped through the coils of the condenser to hold the propylene in the system. The rate of input of the propylene was reduced after the first hour so that the cold liquid propylene from the condenser would not cool the reaction mixture excessively. The color of the final product was dark green-gray. The Alfin catalyst was siphoned by means of nitrogen pressure into a large pressure bottle which had been flushed with nitrogen and the bottle was capped with a Neoprene-lined self-sealing cap. This catalyst consisted of a 1:1 molar ratio of sodium isopropoxide to allylsodium.

Alfin catalysts of different compositions were prepared in a similar manner by varying the amount of isopropyl alcohol added to the amylsodium initially and then passing in propylene to convert the remaining amylsodium to allylsodium.

F. **Titration of Alfin Catalyst.**—The physical state of the Alfin catalyst was such that it was relatively easy to measure out aliquots directly into a hypodermic syringe, using a 20-gauge needle. The bottle was shaken to give a uniform dispersion, and several 1-ml. samples were removed and each was decomposed in 25 ml. of methanol. An equal volume of distilled water was added to each sample, and it was titrated with 0.1 *N* HCl to the phenolphthalein end-point. The strength of the Alfin catalyst, measured as total alkalinity, was 0.8 to 0.9 meq. per milliliter. The conversion of amylsodium to Alfin catalyst was quantitative.

Polymerizations.—All solvents used were dried over sodium wire. In a dry pressure bottle which had been flushed with dry nitrogen was placed 200 ml. of dry hexane. After the bottle was capped with a self-sealing cap, a dial thermometer was clamped to the side of the bottle with adhesive tape in such a manner that good thermal contact with the bottle below the liquid level was ensured. The desired amount of styrene was then injected through the cap. The catalyst was injected into the bottle, which was then shaken using a wrist-action shaker. The temperature was read at 5-minute intervals, and the polymerization was allowed to proceed until a maximum value had been passed. The average reaction time was about 45 minutes. Controlled temperature runs were carried out in water-baths using a tumbling device for agitation. For the −20° runs, the wrist-action shaker was placed in a freezer. When runs were carried out below room temperature, the reactants were precooled before the catalyst was added. After the polymerizations had been completed, the materials were placed in methanol and leached for several hours to decompose the catalyst, the precipitated polystyrene was dissolved in benzene and the solution filtered free of sodium chloride. The clear solution was then washed with dilute acetic acid, followed by several washes with distilled water. The polymer was precipitated in methanol, filtered and dried.

Crystallization of Polymers.—The dried polymer samples were placed directly in the crystallizing medium and refluxed or held at the desired temperature for the required period of time.

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ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND NUTRITION, GRADUATE SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF PITTSBURGH]

The Relationship of Oxidation Rate and Molecular Conformation of Sugar Anomers[1]

BY RONALD BENTLEY

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Methyl α-D-arabinopyranoside has been found to be more rapidly oxidized by chlorine in aqueous solution than the β-anomer. The conformationally related L-fucose (solid α-anomer and equilibrium solution) was oxidized with bromine water; β-L-fucose was the more rapidly oxidized anomer. The equilibrium solution of L-fucose was found to contain 31.6% of the slowly oxidized α-anomer from these measurements. These observations support the theory that without exception, those anomers of stable conformation in which the glycosidic substituent is in an equatorial position are the more readily oxidized. Frequently, such anomers are the β-forms, using the nomenclature of Hudson's rule, but arabinose is an exception. A generalization has been drawn correlating conformation, optical rotation, configuration at C_1 and relative reactivity for anomeric pairs.

The more rapid oxidation of β- than α-D-glucose with potassium permanganate,[2] sodium hypoiodite[3] and bromine water[4,5] has been interpreted through consideration of the preferred "chair" conformations of the pyranose ring.[6] Following Reeves,[7] these conformations (Fig. 1) will be referred to as C 1 and 1 C, as shown. By analogy with the cyclohexane system,[8] reactions involving an equatorial (*e*) anomeric hydroxyl group would be expected to be more rapid than the same reaction with the sterically hindered, axial (*a*) anomeric group—provided that the reaction mechanism was a direct attack on the anomeric substituent. In the oxidation of pyranoses with buffered bromine solutions (*p*H 5.4, 0°), free bromine is the oxidant, and the initial product is the δ-lactone, formed without breaking the pyranose ring.[9] Gluconic acid is subsequently formed by hydrolysis. A similar oxidation is that of the methyl pyranosides to the same products with chlorine.[10] Among the pentoses and hexoses so far studied in the bromine oxidation, the β-anomers are more rapidly oxidized than the α[4,5,9]: the former compounds are all found to have the anomeric OH group in the equatorial position. The only exception among these compounds is L-arabinose, where the α-anomer is the more rapidly oxidized. Since the hydroxyl groups on C_1 and C_2 of β-L-arabinose, the ordinary solid form, are in a *cis* relationship and since L-arabinose has the C 1 conformation, it follows that the anomeric OH group of this compound is axial. The more rapid oxidation of the α-anomer would therefore be expected from the considerations just outlined.

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