The total distillate was dissolved in ether, the water separated, the ethereal layer dried, and the solvent evaporated. The crude octalin was distilled at atmospheric pressure, b.p. 189–193°, n_D^{25} 1.4890–1.4950, yield 110–130 g. (80–95%).

A mixture of three parts of octalin and one part of phosphorus pentoxide was heated at 140° for 3 hr. and processed in the usual manner.[3] The product was distilled at atmospheric pressure through an 18″ column packed with Podbielniak tantalum Heli-pak: fraction 1, b.p. 191–193°, n_D^{25} 1.4920–1.4940; fraction 2, b.p. 192–194°, n_D^{25} 1.4940–1.4970. Fraction 1 usually amounted to a 25% yield and fraction 2 to a 60% yield.

(*B*) *From tetralin.* In a three-necked, round-bottomed flask fitted with a glass stopper, a sealed all-glass stirrer and a reflux condenser closed with a calcium chloride tube were placed 500 ml. of ethylenediamine (distilled from sodium hydroxide pellets before use) and 66.1 g. (0.5 mole) of tetralin. Clean lithium wire (21 g., 3 moles) was cut into short pieces and a 5 g. portion was added to the reaction flask. Stirring was commenced and in about 20 min. the lithium began to dissolve and heat was evolved. When the bulk of the initial lithium had dissolved, the remainder of the lithium was added in portions of about 3 g. over a period of about 15 min. Near the end of the addition of lithium, the solution developed a blue color. Stirring was continued for an additional 30 min. during which time the blue coloration faded to a slate-gray color.

The reaction mixture was decomposed by the addition of 200 ml. of ethanol over a period of 20 min. and the solution then poured into 2 l. of ice water. The mixture was extracted with several portions of benzene, the benzene solutions washed with 5% sulfuric acid and water. The solvent was removed and the product distilled at atmospheric pressure through a 20″ column, b.p. 194–196°, n_D^{25} 1.4950–1.4970, yield 48 g. (71%).

9-Nitroso-10-chlorodecalin. A solution of 45 g. (0.33 mole) of mixed octalins, prepared above, and 75 g. (1 mole) of ethyl nitrite in 100 ml. of glacial acetic acid was allowed to react with 75 ml. of concentrated hydrochloric acid at −15° in the usual manner and after 2 hr. the blue crystalline solid was removed by filtration. The solid was recrystallized from acetone twice to yield 35–40 g. (50–60%), m.p. 91–92° (lit.[2] 92°).

The yield of this derivative when pure Δ^9-octalin was employed was 77%.

Δ^9-*Octalin.* In an all-glass apparatus were placed 30 g. (0.46 mole) of zinc dust and a solution of 35 g. (0.17 mole) of 9-nitroso-10-chlorodecalin in 300 ml. of dry ether and to the stirred mixture was added 6 ml. of concentrated hydrochloric acid over the period of 10 min. The stirring was continued for 12 hr., then an additional 30 g. portion of zinc dust and 6 ml. of hydrochloric acid was added. The mixture was allowed to stir for an additional 24 hr., the zinc dust removed by filtration and washed with ether. The combined filtrate and washing were washed with sodium bicarbonate and water and then dried. After removal of the solvent, the Δ^9-octalin was distilled at atmospheric pressure, b.p. 194–196°, n_D^{25} 1.4971, yield 13.8 g. (59%).

When 9.8 g. of the purified material was heated with 5 g. of phosphorus pentoxide under the usual conditions and the product distilled, the following fractions were obtained: (1) b.p. 193–194°, n_D^{25} 1.4910, yield 1.7 g.; (2) b.p. 194–195°, n_D^{25} 1.4930, yield 0.6 g.; (3) b.p. 195.0–195.5°, n_D^{25} 1.4960, yield 7.8 g.; (4) b.p. 195.5–196.0°, n_D^{25} 1.4965, yield 2.3 g.

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Crystallizable Polystyrene. III. A Comparison of Crystallinities of Polystyrenes Prepared Using Various Catalysts

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Received October 18, 1957

In preceding publications,[1–3] crystallizable polystyrene was prepared by the use of Alfin catalysts and alkali-metal derivatives of arylmethanes. It is the purpose of this paper to demonstrate the difference in crystallizability between polystyrenes made using Alfin-type catalysts and arylmethane–alkali-metal catalysts, and those prepared using a Ziegler-type polymerization system.

The isotactic polystyrenes, prepared using various catalysts, are listed in Table I in the order of increasing crystallizability. X-ray diffraction photographs of these polymers are presented in Fig. 1.

TABLE I

CRYSTALLINITY OF ISOTACTIC POLYSTYRENES

Catalyst	(η)	Yield, %	Figure Number
Alfin catalyst	2.98	77.0	1
Triphenylmethyl potassium	1.58	11.1	2
Modified Ziegler, Run 1 system	1.14	0.13	
Modified Ziegler, Run 2 system	4.42	72.0	3

The most striking difference between polystyrenes obtained from organo-alkali-metal catalysts and those obtained from a Ziegler-type catalyst, is the higher degree of crystallinity obtained in the latter case. The order of increasing crystallizability was found to be the following: Alfin, triphenylmethylpotassium, and Ziegler-catalyzed polystyrene. Although only very low yields were obtained at first, using the Ziegler system, it was discovered that, by modification of the Ziegler system, high yields of isotactic polystyrene were obtained. In attempts to repeat the method described in the Ziegler Australian Patent No. **14116**, it was expedient to substitute trimethylaluminum for triethylaluminum. It was also necessary to run the reactions under atmospheric pressure. By employing these two changes, the catalyst prepared according to the reaction sequences described by Ziegler gave

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[1] J. L. R. Williams, J. VanDenBerghe, W. J. Dulmage, and K. R. Dunham, *J. Am. Chem. Soc.*, **78**, 1260 (1956).

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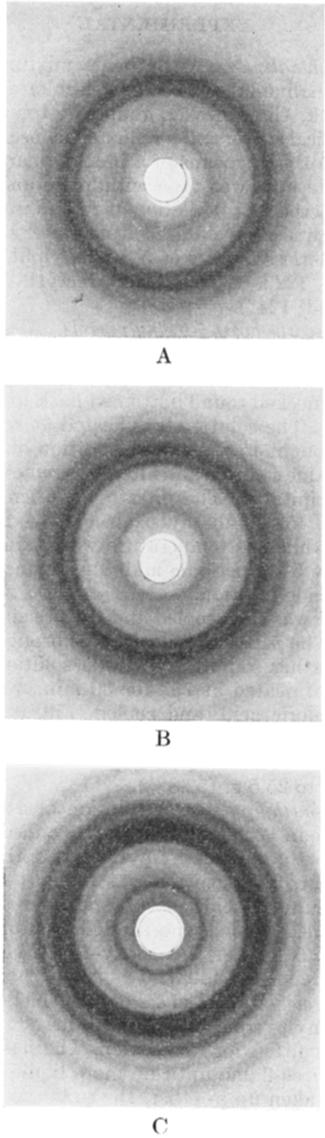

Fig. 1. X-ray diffraction photographs of polystyrenes (CuKα radiation). *A*. Alfin polystyrene crystallized by heating 14 hours in heptane at 90°. *B*. Triphenylmethylpotassium-catalyzed polystyrene crystallized by heating 14 hours in heptane at 90°. *C*. Modified-Ziegler-catalyzed polystyrene extracted and crystallized in boiling acetone

highly crystallizable polystyrene in very low yields. By use of a pressure bottle to contain the reaction system, good yields of highly crystallizable polystyrene were obtained, employing triisobutylaluminum-titanium tetrachloride as catalyst.

It appears that the organo-alkali-metal-catalyzed polystyrenes are block polymers consisting of interlinked atactic and isotactic regions. By extraction with methyl ethyl ketone, it is not possible to raise the crystallinity as high as is obtainable from the Ziegler-type polymer. This statement also applies to organo-alkali-metal-catalyzed polymer which has been degraded to inherent viscosities as low as 0.75. Such degradations release low-viscosity, amorphous polymer, which, after extraction, precipitation, and crystallization, has very low crystallinity.

In contrast, the Ziegler-type polystyrene lends itself readily to the fractionation of isotactic from the atactic materials, partly because the atactic polymers are mainly of low molecular weight and hence are easily extracted. When Ziegler-type polystyrene ($[\eta]=1.6$) and high-molecular-weight atactic polymer ($[\eta]=1.8$) were precipitated together from a dilute solution in benzene, extraction of the crystallized intimate mixture gave a high yield of isotactic polymer. This extracted residue was as highly crystalline as the polymer before dilution with atactic polystyrene and more highly crystalline than any extracted residue obtained from polystyrene which was polymerized with an organo-alkali-metal catalyst.

EXPERIMENTAL

Polymerizations.[4] Polystyrenes were prepared using Alfin-type catalyst and triphenylmethylpotassium, as previously described.[2,3] Modified Ziegler[5]-type polymerizations were carried out as follows:

Run 1. The apparatus consisted of a three-necked, one-liter flask equipped with a sintered glass disk in the bottom, high-speed, stainless-steel stirrer, reflux condenser, thermometer, dropping funnel, and nitrogen inlet tube. The reaction flask was heated in an oil bath.

A solution of 7.045 g. of trimethylaluminum in 70 ml. of heptane was placed in the flask and heated to 70° under an atmosphere of dry nitrogen. A solution of 7.6 g. of titanium tetrachloride in 20 ml. of heptane was added over a period of 10 min., with efficient stirring, during which time gas was evolved and a black precipitate formed. Heating was continued for 30 min. after the addition was complete and, using the porous glass disk, the precipitate was then filtered by means of nitrogen pressure upon the surface of the liquid. The precipitate was washed three times with a 2% solution of trimethylaluminum in heptane. The coarse precipitate was then suspended in 250 ml. of heptane containing 7.05 g. of trimethylaluminum. After the suspension was transferred (under nitrogen) to a one-liter, three-necked flask, the catalyst mixture was heated to 65°, and 150 g. (166 ml.) of freshly distilled styrene was added dropwise, with efficient stirring, over a 15-min. period. The polymerization mixture was then heated at 70–75° for 4 hr. The reaction mixture was cooled, poured into methanol, and the inorganic products were dissolved by the addition of hydrochloric acid. Two layers were formed; the flocculent product was present in the upper layer. After the precipitate was collected, it was purified by boiling in acetone containing hydrochloric acid. The polymer was filtered, and then washed several times with fresh acetone. The highly crystalline polymer had a melting point of 228° and an inherent viscosity of 1.14. The yield was 0.2 g. (0.13%). The crystallinity was extremely high.

Run 2. A 375-ml. pressure bottle was flushed with dry nitrogen and capped using a Neoprene-line, self-sealing cap. A solution of 5.7 g. of triisobutylaluminum, diluted with dry heptane to a total volume of 42.3 ml., was injected into the bottle by means of a hypodermic syringe. The bottle

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(4) Trimethylaluminum and triisobutylaluminum were used in these experiments, whereas triethylaluminum[7] was employed by Ziegler.[5] All-glass equipment was used rather than steel autoclaves.

(5) K. Ziegler, Australian Patent **14116**, example 44 (1955).

was immersed in a 70° water bath for 10 min. and a solution of 3.8 g. of titanium tetrachloride, diluted with dry heptane to a volume of 12.2 ml., was added in small amount over a 5-min. period, using a hypodermic syringe. The bottle was vented from time to time in order to relieve the pressure. The reaction bottle was then tumbled for 30 min. at 70°, after which time 42.3 ml. of triisobutylaluminum-heptane solution and 75 ml. of freshly distilled styrene were added. The bottle was then tumbled in a 70° water bath for 24 hr. After the bottle was cooled to room temperature, the contents were poured into methanol. Hydrochloric acid was added to dissolve the inorganic materials, and the mixture allowed to stand for 16 hr. The polymer was collected and then suspended in acetone containing hydrochloric acid. The polymer was washed by decantation several times with a fresh acetone and subsequently boiled in acetone for 18 hr., to give a 72% yield of polystyrene having an inherent viscosity of 4.42, a melting point of 230°, and extremely high crystallinity.

KODAK RESEARCH LABORATORIES
COMMUNICATION NO. 1922
ROCHESTER, N. Y.

An Improved Synthesis of 3-Methylpyrrole[1]

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Received December 16, 1957

The simple compound 3-methylpyrrole is only very poorly characterized in the chemical literature. Earlier methods of synthesis[2-7] gave either low yields, small amounts of impure material, or an inseparable mixture of isomers.

The present paper reports the synthesis of pure 3-methylpyrrole in 37.8% yield starting with potassium phthalimide by condensation of aminoacetone with diethyl oxalacetate and subsequent hydrolysis and decarboxylation of the product, 2-carboxy-3-carbethoxy-4-methylpyrrole, essentially by the method of Piloty and Hirsch.[2] Our contribution consists in the development of a new method for the *in situ* synthesis of aminoacetone (hydrolysis of *N*-acetonylphthalimide) and in the improvement of the subsequent steps, as well as in a more complete characterization of 3-methylpyrrole.

EXPERIMENTAL

N-Acetonylphthalimide. An intimate mixture of 250 g. of potassium phthalimide with 200 g. of 1-chloropropanone was added to a 2-l., three necked round bottomed flask fitted with a mechanical stirrer and a reflux condenser. The mixture was heated gently by means of a heating mantle until reaction began; the heat was then withdrawn and the reaction allowed to proceed to completion at room temperature. The solid product was recrystallized from water to yield 269 g. (98.2%) of colorless needles of *N*-acetonylphthalimide, m.p. 116.0–116.8°, 122.9–123.5° after recrystallization from water (reported[8] 124°).

2-Carboxy-3-carbethoxy-4-methylpyrrole. A solution made from 150 ml. of concentrated hydrochloric acid and 75 ml. of water was added to 50.0 g. of crude *N*-acetonylphthalimide in a 500-ml., one necked round bottomed flask fitted with a reflux condenser. The solution was heated at reflux for 4 hr., cooled and brought to *p*H 1.5 by addition of 30% aqueous sodium hydroxide solution and filtered to remove the phthalic acid that precipitated. The filtrate was then added slowly to a solution of 45 g. of diethyl oxalacetate sodium salt in 400 ml. of water while the temperature was maintained at 75° and the *p*H at 5 by periodic addition of small amounts of sodium hydroxide solution.

The mixture was then cooled and the precipitate removed by filtration. The *p*H of the filtrate was brought to 8 by the addition of further sodium hydroxide solution and the resulting solution heated at 75° for 30 min., reacidified with dilute hydrochloric acid, and cooled. Filtration afforded a second crop of 2-carboxy-3-carbethoxy-4-methylpyrrole to bring the total yield of product, m.p. 195.7–196.8° (reported[3] 196°), to 25.5 g. (52.8%).

3-Carboxy-4-methylpyrrole. A solution of 440 g. of potassium hydroxide in 1250 ml. of water was added to 67 g. of 2-carboxy-3-carbethoxy-4-methylpyrrole and the mixture refluxed for 24 hr. The solution was brought to *p*H 9 with concentrated sulfuric acid, cooled, and filtered. The filtrate was then acidified, cooled, and filtered to afford a quantitative yield (42.5 g.) of 3-carboxy-4-methylpyrrole, m.p. 152.6–153.7° (reported[3] 149°).

3-Methylpyrrole. A total of 22.0 g. of finely powdered 3-carboxy-4-methylpyrrole was placed in a 200-ml. round bottomed flask fitted for distillation. The flask was heated gently with a free flame until no more liquid distilled. The distillate was taken up in ether, the solution dried over anhydrous magnesium sulfate and redistilled to yield 10.6 g. (73.1%) of pure 3-methylpyrrole, b.p. 142–143° (740 mm.) n^{20}_{D} 1.4970, n^{25}_{D} 1.4949.

Anal. Calcd. for C_5H_7N: C, 74.0; H, 8.7; N, 17.3. Found: C, 74.0; H, 8.8; N, 17.3.

The absorption bands in the infrared spectra of 3-methylpyrrole and 2-methylpyrrole[9] are compared in Table I and the respective infrared spectra of 12.25% solutions in chloroform taken with a Perkin Elmer Model 21 double beam spectrophotometer in 0.05 mm. sodium chloride cells are shown in Figs. 1 and 2.

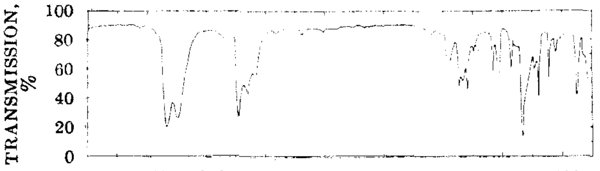

Fig. 1. Infrared spectrum of 3-methylpyrrole

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[1] This investigation was performed as a part of American Petroleum Institute Research Project 52 on *Nitrogen Constituents of Petroleum,* which is conducted at the University of Kansas in Lawrence, Kan., and the Bureau of Mines Experiment Stations in Laramie, Wyo., and Bartlesville, Okla.

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