salts were carried out in a three-necked flask equipped with a mechanical stirrer. All other reductions were carried out by heating under reflux without stirring.

The standard solutions of lithium aluminum hydride in tetrahydrofuran were prepared as follows: A mixture of 62 g. of hydride in 2 l. of solvent was heated under reflux for 6 hr., cooled overnight and then filtered through glass wool under nitrogen. The concentration of lithium aluminum hydride was determined by the addition of an excess of 0.1*N* hydrochloric acid, followed by back-titration with standard 0.1*N* sodium hydroxide solution and by the addition of an excess of a standard solution of iodine in benzene, followed by back-titration with a standard sodium thiosulfate solution.[18]

Reduction of benzyl chloride in tetrahydrofuran. To a stirred solution of 6.3 g. (0.166 mole) of lithium aluminum hydride in 300 ml. of tetrahydrofuran, heated under reflux, was added a solution of 20.0 g. (0.158 mole) of benzyl chloride in 50 ml. of tetrahydrofuran over a 30-min. period. After the solution had been heated under reflux for an additional 5.6 hr., 270 ml. of tetrahydrofuran was removed by distillation through an 18-inch, helix-packed column over a 5-hr. period. The residue was diluted with 300 ml. of ether and cooled in an ice bath while 400 ml. of a 20% sodium potassium tartrate solution was added. After the aqueous layer was extracted with two 75-ml. portions of ether, the combined ether layers were dried over magnesium sulfate. The solvents were removed by distillation through a 10-inch, helix-packed column to yield 25.3 g. of a residue which was shown by vapor-phase chromatographic analysis to contain 12.1 g. (0.163 mole) of *n*-butyl alcohol and 12.5 g. (86%) of toluene as well as 0.7 g. of tetrahydrofuran.

A similar experiment with acetone in place of benzyl chloride gave no amount of *n*-butyl alcohol detectable by vapor-phase analysis, as described above.

Cleavage of tetrahydrofuran with a lithium aluminum hydride–aluminum chloride mixture. To a standard solution containing 1.52 g. (0.04 mole) of lithium aluminum hydride in 66 ml. of tetrahydrofuran was added as rapidly as possible with shaking a mixture of 1.78 g. (0.0133 mole) of aluminum chloride in 40 ml. of tetrahydrofuran. During the addition the solution became warm and a white fog (not hydrogen chloride) was produced. After the mixture had been heated under mild reflux for 26 hr. in an oil bath (105–110°),[19] most of the tetrahydrofuran was removed by distillation under reduced pressure (15 mm.) at room temperature over a 30-min. period. The residue was added to dilute sulfuric acid (prepared from 15 ml. of concd. sulfuric acid, 60 g. of ice and 86 ml. of water), and the resulting solution was extracted with three 50-ml. portions of ether. The ether extracts were then extracted with 40 ml. of a 5% sodium bicarbonate solution and two 20-ml. portions of water. The combined aqueous extracts were neutralized and extracted with 30 ml. of ether. After the combined ether layers had been dried over magnesium sulfate, the ether plus some tetrahydrofuran was removed by distillation through a 10-inch, helix-packed column. An analysis of the residue by vapor-phase chromatography showed the presence of 3.96 g. (0.0535 mole) of *n*-butyl alcohol. (In a similar vapor-phase analysis of the distillates, no additional *n*-butyl alcohol was detected.) If it is assumed that 1.78 g. (0.0133 mole) of aluminum chloride can yield 1.6 g. (0.0532 mole) of aluminum hydride and that 1 mole of *n*-butyl alcohol is produced for every mole of aluminum hydride present, 3.95 g. (0.0532 mole) of *n*-butyl alcohol is expected. On this basis, the actual amount of *n*-butyl alcohol obtained was 100.3% of the theoretical amount.

Cleavage of tetrahydrofuran with aluminum hydride. A solution of 1.72 g. (0.04 mole) of lithium aluminum hydride in 100 ml. of dry ether was heated under reflux for 5 hr. and then transferred through a fritted-glass filter into a solution of 1.72 g. (0.0133 mole) of freshly sublimated aluminum chloride in 200 ml. of dry ether. After the mixture had been allowed to stand for 10 min., it was filtered and the ether was removed from the filtrate by distillation under reduced pressure at 0°. To the dry residue was added 100 ml. of tetrahydrofuran, and the resulting solution was heated for 24 hr. at 100°. (The solution then contained a small amount of a gray precipitate.) When the solution was worked up as described above, the vapor-phase chromatographic analysis showed the presence of 2.52 g. (0.034 mole) of *n*-butyl alcohol. With the stated assumptions, this corresponds to a 64% yield.

COLLEGE PARK, MD.

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[18] H. Felkin, *Bull. soc. chim. France*, [5] **18,** 347 (1951).

[19] After the mixture had been heated for about 2 hr., there was observed a gray voluminous precipitate which was not dissolved by the dilute sulfuric acid during decomposition of the mixture. Wiberg and Gösele[15] observed a similar precipitate from the heating of a solution of aluminum hydride in tetrahydrofuran.

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

Polymers. III. Synthesis of Optically Active Stereoregular Polyolefins[1-3]

WILLIAM J. BAILEY AND EDWIN T. YATES[4]

Received February 8, 1960

Polymerization of optically active 3-methyl-1-pentene, $[\alpha]_D^{25}$ +33.49°, with a Ziegler catalyst gave a low melting atactic fraction, $[\alpha]_D^{23}$ + 94.9°, and a high melting isotactic fraction, $[\alpha]_D^{25}$ − 257°. The high melting fraction, m.p. 271–278°, was insoluble in boiling xylene but soluble in boiling 1,1-ditolylethane and was almost entirely crystalline. In contrast, the polymer from *dl*-3-methyl-1-pentene melted at 229–237°, was soluble in boiling 1,1-diphenylethane, and was composed of equal parts of amorphous and crystalline phases. Copolymerization of a mixture containing 40% *d*-3-methyl-1-pentene and 60% 4-methyl-1-pentene gave a copolymer with $[\alpha]_D^{26}$ +112.4°.

In a program to determine the correlation of chemical structure with physical properties of polymers, the effect of symmetry on the crystallinity of polymers has been of particular interest. Earlier

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[1] Previous paper in this series, *J. Org. Chem.*, **24,** 545 (1959).

[2] Presented before the Division of Polymer Chemistry at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

[3] This work was supported in part by a grant from the National Science Foundation.

[4] Office of Naval Research Fellow, 1955–57; Goodyear Tire and Rubber Co. Fellow, 1957; Dunlop Research Fellow, 1957–58.

work[5] has shown that the symmetrical poly-1,2-dimethylenecyclohexane was a highly crystalline material melting at 165°. However, the introduction of a methyl group in an asymmetric manner in the 4-position, even though it decreased the extent of crystallinity, did not appreciably affect the melting point.[6] It was of interest, therefore, to determine how asymmetry in the side chain affects the crystallinity of polymers. In addition to these derivatives of the cyclic dienes, the crystalline polyolefins were an interesting series for the study of the relationship. Natta, *et al.*,[7] have shown that by the use of stereospecific catalysts a series of highly crystalline isotactic polymers from *alpha* olefins could be prepared. It was shown by x-ray studies that these isotactic polymers contained long sequences, if not the entire chain, of similar configurations of the asymmetric carbon atoms. When the side chain was increased from methyl to *n*-butyl, the melting point of the isotactic polymer decreased from 160° to below room temperature. Also, the effect of a branched side chain was quite large; the change of the side group from *n*-propyl to isopropyl increased the melting point of the isotactic polymer from 80 to 240°. A very curious phenomenon occurred with the introduction of a second asymmetric center in the side chain of an isotactic polyolefin. For example, the stereoregular polymer derived from *d,l*-4-methyl-1-hexene melts at 188, while the polymer from the related 5-methyl-1-hexene, which is symmetrical, melts at 130°. At first glance this high melting point would be difficult to explain unless there was some order of the asymmetric centers in the side chains as well as in the main chain. However, Natta[8] feels that, on the basis of relatively high solubility and inferior sharpness of the x-ray photographs, the side chains have a random distribution of *d* and *l* configurations.

In order to determine just what effect this asymmetry in the side chain had on the physical properties of the polymers, it was necessary to prepare the polymers from both a racemic and an optically active olefin. The simplest optically active olefin for this purpose appeared to be 3-methyl-1-pentene. This olefin seemed to be an excellent candidate for study, as it would produce an optically active polymer with the asymmetric center in the side chain immediately adjacent to the asymmetric center in the main chain to produce a notable effect on the properties.

A preliminary study of the method of preparation of the Ziegler catalyst from triisobutylaluminum and titanium tetrachloride showed that aging the catalyst at an elevated temperature gave a very active catalyst for the production of a stereoregular polymer. With such a catalyst a polypropylene that consisted of 95% of ether-insoluble isotactic material was produced. In a similar manner, polymers were obtained from 1-octene and a mixture of isomeric hexenes and *d,l*-3-methyl-1-pentene. When pure *d,l*-3-methyl-1-pentene,[9] which had been treated with sodium, was used, a 12% yield of solid polymer was obtained. This material was separated into four fractions by successive extractions with cold benzene, hot xylene, hot *p*-cymene, and hot 1,1-diphenylethane. The major fraction that was soluble in refluxing 1,1-diphenylethane was shown to melt at 229–237°[10] with the aid of a polarizing microscope. X-ray studies indicated that this polymer was composed of about equal portions of a crystalline phase and an amorphous phase. Even though the exact configuration of this fraction is not known, it appears not to be an isotactic polymer with a random distribution of the asymmetric carbons in the side chains as reported by Natta for poly-5-methyl-1-hexene.[8] The relatively low solubility and high melting point indicate that this fraction probably is an isotactic polymer with at least long sequences of regularity of configuration of the asymmetric centers in the side chain. The more soluble fractions of this racemic polymer probably contain some crystalline isotactic polymer with a random distribution of configurations in the side chain.

In order to determine the effect on the rotation of the incorporation of an optically active olefin into a polymer, the copolymerization of *d*-3-methyl-1-pentene and 4-methyl-1-pentene was studied. As a mixture of isoamyl and active amyl alcohols was more readily available than the pure active amyl alcohol, a mixture containing 40% *d*-3-methyl-1-pentene and 60% 4-methyl-1-pentene was prepared in a series of model reactions for the preparation of the pure optically active olefin.[9] Thus, the mixture of alcohols was treated with thionyl chloride to give a mixture of the corresponding chlorides, which was converted to the Grignard reagents. Treatment of the Grignard reagents with formaldehyde, followed by esterification with butyric anhydride, gave a mixture of *d*-3-methylamyl and 4-methylamyl *n*-butyrates. Pyrolysis of this mixture of esters gave the mixture of olefins. Copolymerization with an aged catalyst gave a 5% yield of a benzene-soluble copolymer, $[\alpha]_D^{26}$ +112.4°.

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[5] W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.*, **76**, 5418 (1954).

[6] W. J. Bailey, Proceedings of Joint Army-Navy-Air Force Elastomer Research and Development Conference, Washington, D. C., 1954, p. 113.

[7] G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc.*, **77**, 1708 (1955).

[8] G. Natta, *Stereospecific Catalysis and Isotactic Polymers* (English translation of a review article), Milan, Italy, 1957.

[9] W. J. Bailey and E. T. Yates, *J. Org. Chem.*, in press.

[10] Gaylord and Mark (N. G. Gaylor and H. F. Mark, *Linear and Stereoregular Addition Polymers: Polymerization with Controlled Propagation*, Interscience Publishers, Inc., New York, N. Y., 1959, p. 321) list the specific gravity for poly-3-methyl-1-pentene as 0.83 but give no other data.

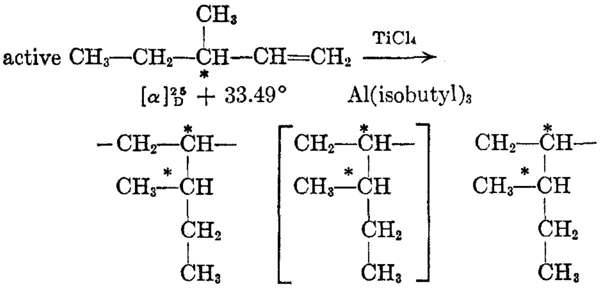
An infrared study indicated that the copolymer was composed of about equal portions of the two monomeric units. It is interesting that polymerization causes such a significant increase in rotation. One cannot be sure whether part of this change is due to asymmetric induction in the polymer chain or to the change of the groups around the active center, but at least part of it must be due to the retention of a helical conformation of the polymer chain in solution.

When a sample of *d*-3-methyl-1-pentene, which was estimated from vapor-phase chromatography and rotational values to be at least 96% pure,[9] was polymerized with an aged catalyst, an 11% yield of polymer was obtained. Extraction of this material with xylene produced a small amount of a fraction, $[\alpha]_D^{23}$ +94.9, that was only partially crystalline. As its properties were quite similar to those of the copolymer described, it was assumed that this fraction was mostly atactic. The major portion, m.p. 271–278°, was soluble in refluxing 1,1-ditolylethane. It was shown by x-ray studies as well as by observations with the polarizing microscope that the xylene-insoluble fraction was almost entirely crystalline; in fact, it was so crystalline that it was completely soluble in 1,1-ditolylethane only at temperatures above its melting point. This limited solubility made it extremely difficult to determine the optical rotation with any degree of accuracy with the instruments available. However, when a hot solution of this fraction was cooled, a small portion remained in solution and had an $[\alpha]_D^{25}$ −257°. Because the amount that remained in solution was small, it was not possible to determine whether this soluble portion is representative of the crystalline fraction or is only a minor component. However, x-ray studies indicate that the xylene-insoluble fraction is almost entirely crystalline and the crystalline phase present is different from the crystalline phase of the poly *d,l*-3-methyl-1-pentene. (Of course, different crystalline structures are possible even if the structures of the polymers are related.)

Of the possible configurations of the crystalline phase, three isotactic systems are considered to be the most likely, with the same configurations in the side chain in every monomer unit but different end groups—all *d* configurations in the main polymer chain, all *l* configurations, and a block copolymer of the two. As two of the isotactic polymers are diastereoisomers, they have different rotations and solubilities and should be separable. Of course, the presence of an asymmetric center in the monomer will favor the formation of one of the configurations in the polymer chain so that one of the diastereo forms will predominate. If the crystalline fraction can be separated into two or more different polymer forms, an insight into the structure of isotactic polymers could be obtained. From the high crystallinity of the xylene-insoluble fraction one would conclude that it is probably not a block copolymer of equal portions of the two diastereo forms. Of course, asymmetric induction would favor a block copolymer containing predominantly one form or the other.

Thus the presence of the asymmetric atom in the monomer had considerable influence on the formation of the asymmetric centers in the polymer chain, and accordingly had a profound influence on the properties of the final polymer.

It is interesting that, although the molecular weights of these polymers are not known with any accuracy, the molecular rotation of these materials must be extremely high.



atactic fraction, $[\alpha]_D^{23}$ +94.9°; isotactic fraction, $[\alpha]_D^{25}$ −257°

EXPERIMENTAL[11]

Polymerization procedure. Triisobutylaluminum was removed from a rubber-capped bottle with hypodermic syringe. A medicine dropper was used to handle titanium tetrachloride. Reasonable care was taken to keep all air and moisture from the polymerization flask. The materials were tested by the polymerization of propylene, 1-octene, and a mixture of isomeric hexenes. To a 200-ml. flask were added 100 ml. of dry xylene, 2.0 ml. of triisobutylaluminum, and 10 drops of titanium tetrachloride. The flask was swept with nitrogen and then stoppered and heated in an oil bath at 59–62° for 30 min. Propylene, dried by passage through a column of activated alumina, was bubbled through the mixture for 1.5 hr. while the temperature was kept at 60–65°. The reaction mixture was cooled and poured into 100 ml. of a 50:50 acetone-concd. hydrochloric acid solution. The crude polymer was removed by filtration and extracted with boiling methanol. The yield was 2.0 g. of isotactic polypropylene, m.p. 156–161° (reported[12] m.p. 158–160°).

Freshly distilled 1-octene (10.6 g.) was heated under reflux with sodium for 1 hr. and polymerized in a manner similar to that described above. The polymerization was carried out with stirring in a stoppered flask heated at 93–96° for 27 hr. To remove the catalyst, the cooled reaction mixture was poured into 100 ml. of a 50:50 acetone-concd. hydrochloric acid solution. When the xylene layer was added to methanol cooled in an ice bath, a gummy polymer coagulated. The polymer was extracted with boiling methanol and then placed in a vacuum desiccator to remove the last trace of solvent. The yield of polymer was 1.4 g. (13%). The approximate molecular weight, determined by the Rast method, was 1400.

A mixture of olefins, shown by vapor-phase chromatography to be a four-component mixture containing 4-methyl-

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(11) The authors are grateful to Dr. E. R. Lippincott, C. E. White, and W. R. Feairheller for the infrared spectra and aid in their interpretation. The spectra were obtained on a Beckman IR-4 spectrometer.

(12) G. Natta, *A New Class of Polymers from Alpha-Olefins Having an Exceptional Regularity of Structure,* paper presented in Rome, Italy, December 11, 1954.

1-pentene, *n*-1-hexene, 3-methyl-1-pentene, and 2-methyl-1-pentene, was treated in a similar manner. In an 8-ounce, screw-capped bottle were placed 50 ml. of dry xylene, 2 ml. of triisobutylaluminum, and 25 drops of titanium tetrachloride. After the bottle was swept with nitrogen, it was stoppered and heated in an oil bath at 100–111° for 1 hr. The mixture was cooled to room temperature, and 5.22 g. of the mixed olefins, which had been treated with freshly cut sodium for 2 hr., was added. The bottle again was swept with nitrogen, and the cap was replaced and sealed with paraffin. The reaction mixture was stirred with a magnetic stirrer and heated at 110–120° for 50 hr. When the reaction mixture was poured into a large volume of methanol, a white polymer precipitated. The copolymer, which was removed by filtration, amounted to 0.85 g. (16%).

Polymerization of d,l-3-methyl-1-pentene. In an 8-ounce, screw-capped bottle were placed 50 ml. of dry xylene, 1.6 ml. of triisobutylaluminum, and 25 drops of titanium tetrachloride. After the bottle was swept with nitrogen, it was capped and heated in an oil bath at 115–126° for 1 hr. The catalyst mixture was cooled to room temperature and 4.85 g. of *d,l*-3-methyl-1-pentene,[9] which had been treated with freshly cut sodium for 2 hr., was added. After the bottle again was swept with nitrogen, the cap was replaced and sealed with paraffin. The mixture was stirred with a magnetic stirrer and heated at 120–132° for 7 days. After the cooled reaction mixture was poured into a large volume of methanol, 0.60 g. (12%) of a white polymer was removed by filtration. Fractionation of the polymer resulted in the following fractions: benzene-soluble, 0.09 g.; xylene-soluble, 0.05 g.; hot *p*-cymene-soluble, 0.03 g.; and refluxing 1,1-diphenylethane-soluble, 0.12 g. The fraction of polymer which was soluble in refluxing 1,1-diphenylethane appeared to be highly crystalline and melted at 229–237°.

Polymerization of d-3-methyl-1-pentene. The procedure was similar to that described for the polymerization of the corresponding racemic olefin. Dry nitrogen was bubbled through 50 ml. of dry xylene in an 8-ounce, screw-capped bottle for 1 hr., followed by the addition of 1.6 ml. of triisobutylaluminum and 25 drops of titanium tetrachloride. The bottle was swept with nitrogen, capped, and stirred at 112–118° for 1 hr. The catalyst mixture was cooled to room temperature and 6.28 g. of *d*-3-methyl-1-pentene,[9] which had been treated with freshly cut sodium for 1 hr., was added. The bottle was swept with nitrogen, capped, and sealed. The reaction mixture was stirred while it was heated on an oil bath at 125–130° for 7 days. When the cooled mixture was added dropwise to a large volume of stirred methanol, a white polymer precipitated and was removed by filtration. The yield of crude polymer was 0.69 g. (11%). Fractionation yielded 0.08 g. of xylene-soluble polymer and 0.45 g. of a xylene-insoluble, crystalline polymer. The specific rotation of the xylene-soluble polymer, as determined in xylene, was $[\alpha]_D^{23}$ +94.9°. The xylene-insoluble polymer, m.p. 271–278°, was soluble in hot 1,1-ditolylethane. When a solution of this polymer in hot 1,1-ditolylethane was allowed to cool to room temperature, most of the polymer precipitated and was removed by filtration with the aid of Celite. The filtrate had a negative optical rotation. Evaporation of the solvent and weighing of the residual polymer led to calculation of an apparent specific rotation of $[\alpha]_D^{25}$ −257.2°.

Synthesis of a mixture of d-2-methyl-n-amyl n-butyrate and 4-methyl-n-amyl n-butyrate. By use of the procedure of McKenzie and Clough,[13] 201.2 g. (2.29 moles) of a mixture of about 60% *d*-amyl alcohol and 40% isoamyl alcohol (α_D^{25} −2.98°, 1:1.0) in 300 ml. of anhydrous ether was allowed to react with 286 g. (2.40 moles) of thionyl chloride in the presence of 5 ml. of pyridine. Distillation of the reaction products yielded 180.9 g. (74%) of the corresponding amyl chlorides, b.p. 97–99°, $[\alpha]_D^{25}$ +0.86° (1:1.0).

By the use of the procedure described previously,[9] the Grignard reagent from 123.6 g. (1.15 moles) of a mixture of *d*-2-methyl-*n*-butyl chloride and isoamyl chloride (α_D^{25} +0.77°, 1:1.0) was treated with formaldehyde. Distillation of the reaction products through a 6-inch, helix-packed column yielded 56.7 g. (48%) of a mixture of the corresponding hexyl alcohols, b.p. 147–154°, α_D^{26} +3.61° (1:1.0). This mixture of isomeric hexyl alcohols was esterified with 130 ml. of chloroform, 73.9 g. (0.94 mole) of pyridine, and 95.9 g. (0.90 mole) of butyryl chloride. The reaction mixture was treated as described previously.[9] Distillation of the residue yielded 95.0 g. (94%) of a mixture of about 60% *d*-3-methyl-*n*-amyl *n*-butyrate and 40% 4-methyl-*n*-amyl *n*-butyrate, b.p. 86–91° (18–23 mm.), α_D^{24} +3.89° (1:1.0).

Pyrolysis of a mixture of d-3-methyl-n-amyl n-butyrate and 4-methyl-n-amyl n-butyrate. Five separate pyrolyses were run on 53.0 g. (0.31 mole) of the mixture of esters (α_D^{24} +3.89°, 1:1.0) by essentially the same method that was employed in the pyrolyses of the *d,l*- and the *d*-3-methyl-*n*-amyl *n*-butyrates[9] at 515–530°, with an addition rate of 20 drops per minute. Distillation of a washed and dried *n*-butyl ether solution of the combined pyrolysates through a 6-inch, helix-packed column yielded 8.0 g. (31%) of a mixture of *d*-3-methyl-1-pentene and 4-methyl-1-pentene, b.p. 51–53°, α_D^{25} +13.15° (1:1.0); and 13.0 g. (25% recovery) of unpyrolyzed starting material. The yield of olefin, based on unrecovered butyrate, was 44%. On the basis of the observed optical rotation of the mixture of olefins relative to that of pure *d*-3-methyl-1-pentene,[9] the composition was approximately 40% *d*-3-methyl-1-pentene and 60% 4-methyl-1-pentene.

Copolymerization of d-3-methyl-1-pentene and 4-methyl-1-pentene. To 50 ml. of dry xylene in an 8-ounce, screw-capped bottle were added 1.6 ml. of triisobutylaluminum and 25 drops of titanium tetrachloride; a brown precipitate formed. The catalyst mixture was activated by heating at 119–129° for 75 min. To the mixture was added 2.55 g. of the previously described mixture of olefins which had been treated for 1 hr. with freshly cut sodium. After it was stirred at 130–137° for 7 days, the reaction mixture was poured into a large volume of methanol and 0.13 g. (5%) of precipitated copolymer was removed by filtration. The crude product was purified by solution in boiling xylene and reprecipitation with methanol to yield 0.11 g. of white polymer. A melting point determination on a hot-stage microscope with crossed Nicol prisms showed that the copolymer started to shrink at 68° and was melted at 193°. The copolymer was completely soluble in benzene; the specific rotation, as determined in benzene solution, was $[\alpha]_D^{26}$ +112.4°. The copolymer was melted on a salt plate and the infrared spectrum of the film was determined. Bands at 1360 and 1380 cm.$^{-1}$ indicated the presence of isopropyl groups contributed by 4-methyl-1-pentene units in the polymer. The infrared spectrum of a film of the xylene-soluble fraction of the polymer of *d*-3-methyl-1-pentene[9] had one band at 1380 cm.$^{-1}$ but otherwise was similar to that of the copolymer.

X-ray diffraction studies.[14] Attempts to pull fibers from the xylene-insoluble fraction of poly-*d*-3-methyl-1-pentene failed because of the high melting point; apparently, decomposition occurs at these elevated temperatures. For these reasons, powder patterns were run on both the active polymer and the corresponding racemic polymer. The crystalline phases of the two polymers were not the same but the amorphous regions of each appeared quite similar. Dr. Ashby reports: "The *d,l* polymer has both crystalline and noncrystalline phases present in about equal proportions. The optically active polymer also has both crystalline and

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(13) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, 699 (1913).

(14) The authors are grateful to Dr. George Ashby and Dr. Frank X. Werber of the Washington Research Center, W. R. Grace and Co., for the X-ray studies as well as their interpretation.

noncrystalline material present, but in this case most of the sample is crystalline. In both samples the noncrystalline phases have the same interchain distance, suggesting that these phases are very similar. Because of the magnitude of the interchain distance (9.4 Å) large pendant groups are probably on the polymer chain."

College Park, Md.

[Contribution from the Midwest Research Institute]

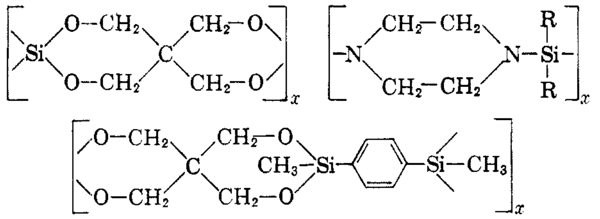
Reactions of Silanes with Pentaerythritol and Piperazine[1]

L. W. BREED, WILLIAM J. HAGGERTY, Jr., and JOHN HARVEY

Received January 7, 1960

Possible reactions for the preparation of linear polymers containing the alternate silane-pentaerythritol and silane-piperazine groups were investigated. Although prototype compounds were prepared by several procedures, attempted polymerization reactions failed to yield the desired polymers.

In the search for new polymer systems with good thermal stability, certain condensation products of silanes with pentaerythritol or piperazine could provide linear, rigid chains. For example:



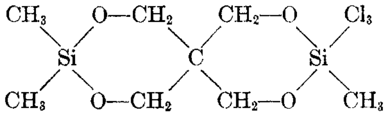
Several U. S. patents[2-4] report that the addition of pentaerythritol in varying amounts to silicone resins as a cross-linking agent gives resins which are superior to the unmodified resins, but no evidence was found that pentaerythritol has been used as an integral part of a silane polymer. In such a polymer, the absence of a β-hydrogen, as well as the rigidity of the chain, may contribute to thermal stability. No piperazine polymers containing silicon have been reported. The silicon-nitrogen bond is known to be very thermally stable if no hydrogen is attached to the nitrogen atom.[5] Polymers containing silicon-nitrogen bondings have been described by Cheronis.[6,7,8]

We obtained the prototype compound, 3,3,9,9-tetramethyl-2,4,8,10-tetraoxa-3,9-disilaspiro[5.5]-undecane by three procedures. Procedure No. 1 was previously described by Davydova.[9] None of these syntheses is a high yield reaction likely to produce high molecular weight materials during polymerization.

1. $C(CH_2OH)_4 + 2(CH_3)_2Si(OAc)_2 \xrightarrow{61.5\%}$

2. $C(CH_2OAc)_4 + 2(CH_3)_2Si(OC_2H_5)_2 \xrightarrow[Al(OisoPr)_3]{40.4\%}$

3. $C(CH_2OH)_4 + 2(CH_3)_2Si(OC_2H_5)_2 \xrightarrow[p\text{-toluene-sulfonic acid}]{\text{low yield}}$



A fourth method used in the attempted preparation of dioxasilacyclohexane ring structure gave only a polymer. It is reported that chlorotrimethylsilane and pentaerythritol, in the presence of pyridine, gave a 90% yield of the tetrakistrimethylsilyl derivative.[10] However, when we treated pentaerythritol and dichloromethylphenylsilane in the presence of pyridine, a polymer rather than the bicyclic compound, 3,9-dimethyl-3,9-diphenyl-2,-4,8,10-tetraoxa-3,9-disilaspiro[5.5]undecane was obtained.

A portion of the polymer that flowed at 170° had a molecular weight of about 2000. The largest part, however, was benzene insoluble and could be drawn into fibers. The ratio of elements calculated from elementary analyses indicated that the amount of cyclization in the polymer was low.

Polymerization reactions generally resulted in the formation of insoluble and infusible products containing unchanged functional groups. The properties of the polymers suggest that a highly crosslinked structure is formed in preference to the

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[1] This research was supported in whole or in part by the United States Air Force under Contract AF 33(616)-3675, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] J. E. Dereich, U. S. Patent **2,684,354** (July 29, 1954).

[3] J. T. Goodwin, Jr., U. S. Patent **2,686,740** (Aug. 17, 1954).

[4] J. L. Speier, U. S. Patent **2,576,486** (Nov. 27, 1951).

[5] R. R. McGregor, *Silicones and Their Uses*, McGraw-Hill Book Co., Inc., New York, 1954, p. 228.

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