From the reaction of 1.5 g. of II with 1.0 g. of *p*-nitrobenzoyl chloride in 6 cc. of anhydrous pyridine there was obtained by the usual procedures 2.1 g. (80%) of **3-phenyl-4,5-dimethylphenyl *p*-nitrobenzoate**, needles from ethanol, m.p. 97.2–98°. *Anal.* Calcd. for $C_{21}H_{17}O_4N$: C, 72.61; H, 4.93. Found: C, 72.93; H, 4.79.

Bromination of II in ethanol gave by the usual procedures **2,6-dibromo-3-phenyl-4,5-dimethylphenol** as colorless needles from ethanol-water, m.p. 116–116.5°. *Anal.* Calcd. for $C_{14}H_{12}Br_2O$: C, 47.22; H, 3.40; Br, 44.89. Found: C, 47.38; H, 3.33; Br, 44.65.

(b) By **Condensation and Decarboxylation.**—Acetophenone was condensed with ethyl acetate by the action of sodium in ether to give in 50% yield benzoylacetone of m.p. 57–58.8°; reported[18] m.p. 59–60°. Benzoylacetone was methylated in 76% yield to 3-benzoylbutanone-2, b.p. 139–140° at 12 mm., $n^{22}D$ 1.5312, by the general procedure of Sprague, Beckham and Adkins[11]; reported[19] b.p. 150–152° at 20 mm.

A solution of 2.83 g. of sodium in 40 cc. of absolute ethanol, 21.27 g. of 3-benzoylbutanone-2 and 24.26 g. of ethyl acetonedicarboxylate stood at room temperature for 2 days, after which the ethanol was removed under reduced pressure. The residue was poured into water, acidified and extracted with ether. The combined ether extracts were washed with 5% sodium bicarbonate solution, then with water until the washings were neutral to litmus, and finally dried over anhydrous magnesium sulfate. After removal of the ether, distillation of the residue gave a forerun of unchanged reactants and a very pale yellow oil, b.p. 181–183° at 0.08 mm., which in the receiver set to a colorless solid of m.p. 84–86°. The solid (7.99 g., 19.2%) was recrystallized from petroleum ether (30–60°) or ethanol and sublimed *in vacuo* to give colorless crystals of diester VII (**ethyl 3-phenyl-4,5-dimethylphenol-2,6-dicarboxylate**) of m.p. 88.4–89.6°.

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.41; H, 6.41.

Diester VII (2.5 g.) was saponified by refluxing with 30 cc. of 15% methanolic potassium hydroxide for 12 hours. By the usual procedures there was obtained a dry ether solution of a fraction insoluble in water but soluble in 5% sodium bicarbonate solution. The residue from removal of the ether was decarboxylated by heating at 190–210° in 5 cc. of quinoline until carbon dioxide evolution ceased. The cooled reaction mixture was taken up in ether, washed thoroughly with 5% hydrochloric acid and with water, and dried over anhydrous magnesium sulfate. The residue from removal of the ether was crystallized twice from heptane, then sublimed to give 0.34 g. (23.5%) of colorless crystals of **3-phenyl-4,5-dimethylphenol** (**II**), of m.p. 107.8–108.2°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.89; H, 7.09.

This phenol on mixing with the phenol from the sulfonic acid rearrangement gave no depression of the m.p.

The ultraviolet absorption spectrum of this phenol was superposable on that of the phenol from rearrangement of the sulfonic acid (see above).

An α-naphthylurethan prepared as described above melted at 171.3–172.5° and showed no depression of m.p. on mixing with the previously described sample prepared from the phenol obtained by rearrangement of VI.

Summary

A previous synthesis of 3-phenyl-5,5-dimethylcyclohexenone has been confirmed and a new synthesis developed. The conversion of this ketone by way of its sulfonic acid to 3-phenyl-4,5-dimethylphenol, the structure of which is proved by its independent synthesis, exemplifies the synthetic possibilities of a recently reported method of aromatization and rearrangement.

BROOKLYN 2, NEW YORK RECEIVED JULY 5, 1950

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[18] Sprague, Beckham and Adkins, THIS JOURNAL, **56**, 2665 (1934).

[19] Dieckmann, *Ber.*, **45**, 2685 (1912).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Effect of Structure on the Fiber Properties of Linear Polymers. I. The Orientation of Side Chains[1]

BY JAMES H. BREWSTER[2]

It would be expected that the size, distribution and steric orientation of side-chains attached to the backbone of a linear polymer would affect those properties of the polymer which are a function of its crystallinity, *i.e.*, melting point, solubility and especially ability to form oriented fibers. The present study concerns the effect of the stereochemical configuration of the side chains on polymer properties.

Side chains on polymer molecules appear to interfere with the formation of strong oriented fibers.[3] There is some evidence that polymers whose side chains are distributed according to a regular and recurrent pattern are more crystalline than isomeric polymers having irregularly distributed side chains. Polymers with regularly spaced side chains may be prepared from symmetrical bifunctional reactants or from pure unsymmetrical monomers which must condense in a head to tail fashion (*e.g.*, ω-amino acids).

A polymer having n unpaired side chains attached to the polymer chain has n asymmetric carbon atoms. If the steric configuration of these asymmetric atoms is not uniform (as in polymers made from symmetrical bifunctional reactants or from racemic α-amino acids), the number of molecular species theoretically possible is 2^n (assuming that all polymer chains are of the same length). The disorder produced by lack of stereochemical uniformity of side chain orientation might well interfere with polymer crystallinity and cause modifications in polymer properties. That such is, indeed, the case is indicated by the work of Astbury and co-workers,[4] who noted that polymers of *dl*-alanine are water soluble, while those of *l*-alanine are not. It is further suggestive that silk, wool and other proteins[5] form strong oriented fibers despite the fact that numerous side chains are attached to the polypeptide backbone of a protein. This may well be due, at least in part, to the uniform steric configuration of the naturally-occurring amino acids.[6]

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[1] This work was supported by a grant from the Samuel S. Fels Fund.

[2] Chemistry Department, Purdue University, Lafayette, Ind.

[3] Hill and Walker, *J. Polymer Sci.*, **3**, 609 (1948).

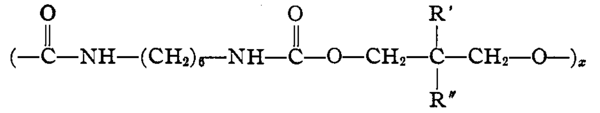
[4] Astbury, Dalgleish, Darmon and Sutherland, *Nature*, **162**, 596 (1948).

[5] Lundgren, in "Advances in Protein Chemistry," V. Interscience Publishers, New York, N. Y., 1949, p. 305.

[6] Neuberger, *ibid.*, IV, 1948, p. 297.

Polyurethans (I) were prepared from hexamethylene diisocyanate and three symmetrical glycols: 1,3-propanediol (Ia), 2,2-dimethyl-1,3-propanediol (Ib) and 2-methyl-1,3-propanediol (Ic). The last named glycol was prepared from 1,3-dibromo-2-methylpropane, which was formed by peroxide-catalyzed addition of hydrogen bromide to methallyl bromide.

The polyurethan having no side chains (Ia) and that having only paired and regularly spaced side chains (Ib) were crystalline and formed oriented fibers. The polyurethan which had only unpaired, but regularly spaced, side chains of indeterminate steric orientation was much lower melting and behaved like a very viscous liquid at room temperature; it formed filaments which could be stretched to one hundred times their original length without suffering any change in appearance or properties and which fused together when stored.



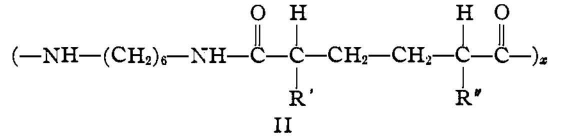
$$(-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{R'}{\underset{R''}{C}}-CH_2-O-)_x$$

I

Ia, R' = R'' = H
Ib, R' = R'' = CH_3
Ic, R' = H; R'' = CH_3

Nylon analogs (II) were prepared in order to study the effects of uniform steric orientation of unpaired side-chains on fiber properties. Racemic, *meso* and *dextro* α,α'-dimethyladipic acids were prepared by modifications of the method of Noyes and Kyriakides.[7] Pyridine decarboxylation[8] of 2,2,5,5-tetracarboxyhexane provided higher yields of the racemic dimethyladipic acid than could be obtained by thermal decarboxylation.

All of these stereoisomers of dimethyladipic acid formed polymers with hexamethylenediamine and all of the polymers formed oriented fibers. Filaments of the racemic polymer (IIa) were the weakest of all and could be cold-drawn only immediately after they had been spun and with exercise of great care (tensile strength, c. 0.6 kg./mm.^{2}). Filaments of the *meso* (IIb) and "dextro" (IIc) polymers could easily be cold-drawn and were of roughly equal strength (tensile strengths, c. 3.5 kg./mm.^{2}; c. 3.9 kg./mm.^{2}). Nylon (IId) filaments from a sample of polymer prepared in the same way were quite strong and very easily cold-drawn (tensile strength, c. 45 kg./mm.^{2}).



$$(-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{R'}{C}}-CH_2-CH_2-\overset{H}{\underset{R''}{C}}-\overset{O}{\overset{\|}{C}}-)_x$$

II

IIa, R' = $\pm CH_3$, R'' = $\pm CH_3$ (racemic)
IIb, R' = $\pm CH_3$, R'' = $\mp CH_3$ (*meso*)
IIc, R' = $+ CH_3$, R'' = $+ CH_3$ ("dextro")
IId, R' = R'' = H (Nylon)

These Nylon analogs exhibited interesting properties which clearly indicated that they were considerably less crystalline than the parent polymer. In all cases when cold-drawn fibers of the "dimethyl Nylons" were let stand, under no tension, for a week it was found that they had undergone a nearly complete reversal of the cold-drawing process. Aged *meso* (IIb) and "dextro" (IIc) cold-drawn fibers could be redrawn to about the same extent as freshly spun filaments of these polymers. Aged racemic (IIa) cold-drawn fibers, however, behaved like a viscous liquid and could be stretched without cold-drawing to 1400% of their original length before becoming so thin that they could not be handled.

In addition to suffering disorientation, these Nylon analogs exhibited a secondary cold-drawing just prior to breaking. When cold-drawn fibers of these polymers were subjected to additional tension, they "necked-down" to form *opaque and non-lustrous* regions which developed along the fiber in precisely the same way that the clear and lustrous regions develop along the fiber in normal cold-drawing. Breakage of the fiber under gradually increased tension always occurred within an opaque non-lustrous region. When the tension required for this secondary cold-drawing was released, the opaque areas disappeared within a few seconds and the fiber reverted to the clear, lustrous and, presumably, oriented state.

Clearly, the low tensile strength and the reversibility of both primary and secondary cold-drawing exhibited by these "dimethyl Nylons" indicate that even regularly spaced methyl side chains interfere strongly with polymer crystallinity. This interference is strongest when the steric orientation of the side-chains is indeterminate, as in the racemic polymer (IIa).

Little difference was noted between the "dextro" and *meso* polymers; it had been anticipated that the former, having more uniformly oriented side-chains, would be the more crystalline of the two polymers. It is possible that partial racemization occurred during the polymerization; if so, it was not complete, for the "dextro" polymer was levorotatory in glacial acetic acid solution. Base-catalyzed racemization would occur only at carbon atoms adjacent to amide groups; as amide groups formed, the base was consumed. Furthermore, as neutral salts of the adipic acids with hexamethylene diamine were used, there was little if any free base present in the system. No explanation other than that of partial racemization has been found for the lack of appreciable differences in crystallinity between the *meso* and "dextro" polymers.

Some aspects of this problem are under further study at Purdue University.

Experimental

Hexamethylene diisocyanate[9] was purified by preliminary distillation followed by distillation through a 14" heated Vigreux column, the fraction coming over at 105.0–105.5° at 5 mm. being taken.

Trimethylene glycol was dried and purified by distillation through a 14" heated Vigreux column, the fraction distilling at 96° at 8 mm. being collected.

2,2-Dimethyl-1,3-propanediol was prepared by reaction of isobutyraldehyde with excess formaldehyde in the presence of potassium hydroxide.[10] The product was purified by sublimation at 7 mm., the vapors passing over at 105–110°. The white solid melted at 127–128° (cor.).

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[7] Noyes and Kyriakides, THIS JOURNAL, **32**, 1057 (1910).

[8] Grigsby, Hind, Chanley and Westheimer, *ibid.*, **64**, 2606 (1942).

[9] Generously donated by the E. I. du Pont de Nemours & Co. (Inc.).

[10] Just, *Monatsh.*, **17**, 76 (1896); Franke, *ibid.*, **26**, 43 (1905); Bincer and Hess, *Ber.*, **61**, 537 (1927).

Methallyl Bromide.—It has been reported that methallyl chloride reacts with sodium bromide in refluxing acetone to form methallyl bromide[11]; no experimental directions were given. In a number of experiments in which this method was employed only minute amounts of methallyl bromide were obtained. Lithium bromide, which is very soluble in acetone, was found to give this reaction.

Methallyl chloride[12] was redistilled to free it of dimeric materials,[13] the fraction boiling at 71–72° being taken. To a solution of methallyl chloride (452.5 g., 5.0 mole) in acetone (500 ml.) was added freshly fused lithium bromide (465 g., 5.35 mole). The mixture was heated under reflux with stirring for 12 hours and then allowed to cool. Water (500 ml.) was added and the lighter organic layer separated, washed several times with water (the organic layer is denser than water but lighter than the lithium chloride solution) and dried over magnesium sulfate. The mixture of methallyl halides was fractionally distilled, affording methallyl chloride, b.p. 71–75° (76 g., 16.8% recovery) and methallyl bromide b.p. 91–94° (360 g., 53.5%). The remainder of the material was found in intermediate fractions (103 g.) and in high-boiling residues, which were probably dimers of the halides.

In smaller runs, somewhat higher yields of methallyl bromide were obtained by use of larger amounts of lithium bromide in more dilute acetone solution.

2-Methyl-1,3-dibromopropane.—It has been reported that methallyl chloride, in the presence of peroxides, adds hydrogen bromide to form 1-bromo-3-chloro-2-methylpropane in 97% yield[14]; no experimental details were given.

In a three-necked 500-ml. round-bottomed flask, fitted with a mechanical stirrer, a reflux condenser and a gas inlet tube and cooled in an ice-bath was placed 270 g. (2.0 moles) of methallyl bromide. A slow stream of dry air was passed through the liquid for one-half hour to form olefin peroxides. Then a rapid stream of hydrogen bromide (from a tetralin generator), which passed through a tetralin scrubber and a safety bottle, was passed into the stirred cooled methallyl bromide. A rapid stream of hydrogen bromide is required to prevent suck-backs, particularly in the early stages of the reaction. The hydrogen bromide formed from 680 g. of bromine was added over a period of 12 hours, until hydrogen bromide was no longer absorbed. The product was washed twice with an equal volume of water, then quickly with an equal volume of 5% potassium carbonate solution and again with water. The liquid was dried over magnesium sulfate and distilled through a heated column. There was obtained 362 g. (81.2%) of 1,3-dibromo-2-methylpropane, distilling at 175–177°, d^{25} 1.7995, n^{25}_{D} 1.5068; *MR* calcd. 36.20, found 35.80.

1,3-Dibromo-2-methylpropane (b.p. 177.5–178° at 765 mm.; d^{20}_{0} 1.8027) has previously been prepared, by thermal rearrangement of 1,2-dibromo-2-methylpropane (b.p. 150° at 750 mm.).[15]

Diacetate of 2-Methyl-1,3-propanediol.—(Adaptation of the method of Faworsky and Sokownin[15]). Silver acetate (87 g., 0.522 mole) was added to a solution of 1,3-dibromo-2-methylpropane (56.5 g., 0.261 mole) in acetic acid (300 ml.) and the mixture was heated with stirring under gentle reflux for 48 hours. During this time the suspended solid became dense, granular and yellow-green in color. The mixture was cooled and filtered and the filter cake was washed repeatedly with glacial acetic acid. The combined filtrate was distilled, first to remove acetic acid and then to separate the diol diacetate from unreacted dibromide. There was obtained 36 g. (79.5%) of the diacetate of 2-methyl-1,3-propanediol, distilling at 100–102° at 15 mm., n^{25}_{D} 1.4192, d^{25} 1.0436, *MR* calcd. 42.46, found 42.16.

2-Methyl-1,3-propanediol.—Sodium (0.5 g., 0.022 mole) was dissolved in absolute ethanol (130 ml., 103 g., 2.24 moles). To this solution was added 2-methyl-1,3-propanediol diacetate (39 g., 0.224 mole). The mixture was slowly distilled through a 14" Vigreux column to remove the ethyl acetate–ethanol azeotrope (b.p. 71.8°, 30.8% ethanol by weight).[16] Density measurements of the distillate were taken to determine the amount of ethyl acetate formed by the ester exchange reaction. When 98% of the theoretical yield of ethyl acetate had been obtained, the solution was cooled and treated with one gram of Dry Ice to neutralize the sodium ethoxide. The solution was then distilled, finally under vacuum, to yield 14.7 g. (73.3%) of 2-methyl-1,3-propanediol, b.p. 107–109° at 12 mm. (lit.,[15] 110–111° at 14.5 mm.).

Preparation of Polyurethans.—Roughly equivalent amounts of glycol and hexamethylene diisocyanate were weighed into a new, freshly cleaned and dried test-tube. The test-tube was heated in a Wood's metal-bath at 110–120° until a homogeneous solution was obtained and the polymerization reaction began. The temperature was slowly raised during the course of the reaction in order to keep the polymer in a clear liquid state. When it was necessary to heat the polymer above 150°, a slow stream of dry oxygen-free nitrogen was passed over the melt. Heating was continued until two hours of heating produced no further apparent change in the nature of the fibers which could be spun from the melt. This required from 3 to 7 hours. Some of the properties of the polymers so obtained are summarized in Table I.

TABLE I

POLYURETHANS PREPARED BY REACTION OF VARIOUS GLYCOLS WITH HEXAMETHYLENE DIISOCYANATE (DATA FROM TYPICAL EXPERIMENTS)

Diol	Glycol Wt., g.	Glycol Mole	Diisocyanate Wt., g.	Diisocyanate Mole	Final temp., °C.	Softening temp. of polymer, °C.
1,2-Ethane-	1.1538	0.01859	3.1115	0.01852	185	c.170
1,3-Propane-	1.0305	.01354	2.2706	.01349	175	c.155
1,5-Pentane-	2.4496	.02350	3.9453	.02342	250	c.235
2-Methyl-1,3-propane-	1.2641	.01402	2.3580	.01403	150	c. 50
2,2-Dimethyl-1,3-propane-	1.7490	.01679	2.8073	.01668	145	c.120

Filaments were readily obtained from all the polyurethans studied. None of the filaments could be cold-drawn as well as the polyamides and in many cases it appeared that the fibers merely stretched without cold-drawing. It seems probable that some of these filaments had undergone cold-drawing during the spinning process since the "undrawn" filaments frequently resembled Nylon fibers in being fairly strong, lustrous, flexible and capable of being tightly knotted. No good method for obtaining sharp or reproducible melting points of these polymers was found.

High melting polymers which formed strong fibers were obtained from ethylene glycol and pentamethylene glycol[9] in control experiments; cold-drawn fibers formed from these polymers were flexible, lustrous and somewhat elastic. The polymer formed from trimethylene glycol was lower melting (c. 150°) and formed fibers which, while fairly strong and lustrous, were less flexible and not appreciably elastic.

The polymer prepared from 2,2-dimethyl-1,3-propanediol melted at about 120°. Fibers spun from this polymer were not very strong and were non-lustrous, but could be cold-drawn to produce stronger, lustrous, flexible fibers. Some care was required in the cold-drawing process as the fibers were more fragile than, for example, Nylon fibers or those mentioned above.

Anal.[17] Calcd. for $(C_{13}H_{24}N_2O_4)_x$: C, 57.33; H, 8.88. Found: C, 57.06; H, 8.90.

Filaments of the polyurethan prepared from 2-methyl-1,3-propanediol were much lower melting (c. 50°) and behaved more like threads of softened glass than like true fibers. The filaments were somewhat rubbery in nature and contracted slowly after they had been stretched; rods of this material could be stretched to 60–100 times their original length before the threads became too fragile to handle.

Anal.[17] Calcd. for $(C_{12}H_{22}N_2O_4)_x$: C, 55.79; H, 8.57. Found: C, 55.90; H, 8.50.

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[11] Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

[12] Generously donated by the Shell Development Co., Emeryville, Calif.

[13] Wilzbach, Mayo and van Meter, THIS JOURNAL, **70**, 4069 (1948).

[14] Burgin, Hearne and Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

[15] Faworsky and Sokownin, *Ann.*, **354**, 364 (1907).

[16] Horsley, *Ind. Eng. Chem.*, *Anal. Ed.*, **19**, 508 (1947).

[17] Microanalyses by Mr. William Saschek, University of Chicago, Chicago, Ill.

1,1,4,4-Tetracarbethoxybutane was prepared from diethyl malonate and ethylene bromide, using magnesium ethoxide as the condensing agent.[18] Low yields were obtained when the reaction was run on a large scale; extensive tar formation was noted.

2,2,5,5-Tetracarbethoxyhexane.—The method of Noyes and Kyriakides[7] was used in the dimethylation of 1,1,4,4-tetracarbethoxybutane by means of methyl iodide in the presence of sodium ethoxide. The product was purified by recrystallization from low boiling petroleum ether and melted sharply at 54°.[19]

2,2,5,5-Tetracarboxyhexane.—A solution of 2,2,5,5-tetracarbethoxyhexane (97 g., 0.259 mole) and potassium hydroxide (87 g., 1.55 mole) in methanol (800 ml.) was heated under reflux for 24 hours. A solid separated soon after the boiling started, first as a gelatinous mass, then as a white powder. At the end of the heating period, water (600 ml.) was added and the solution was distilled until the temperature of the distilling vapors was 100°. The solution (about 500 ml.) was let cool to room temperature and then made acid to congo red by the addition of 37% hydrochloric acid, whereupon crystallization began. After the solution had stood at room temperature for several hours, it was filtered and the white solid that was collected was washed with a little cold water and dried in air. This material could be burned, but left an alkaline ash; it was, therefore, dissolved in water (200 ml.) and the solution was made strongly acidic by the addition of 50 ml. of 37% hydrochloric acid. A small amount of insoluble material was removed by filtration and the filtrate was thrice extracted with 150-ml. portions of ether. The combined ether was dried over magnesium sulfate and then evaporated to dryness. There was obtained 52.2 g. (77%) of 2,2,5,5-tetracarbethoxyhexane melting at 200° with decomposition and the evolution of gas.[19]

Decarboxylation of 2,2,5,5-Tetracarbethoxyhexane. (a) **Thermal Decarboxylation.**—One gram of the acid was heated in a Wood's metal-bath at 225–230° for several minutes until decarboxylation was complete. The white solid weighed 0.675 g. (100%) and melted at 80–115°. It is probable that this material was mainly *meso*-α,α'-dimethyladipic acid, as previous workers obtained a preponderance of this form by thermal decarboxylation.[19]

(b) **Pyridine Decarboxylation.**[8]—A solution of 2,2,5,5-tetracarboxyhexane (50 g., 0.191 mole) in pyridine (225 ml.) was boiled under reflux for 16 hours. The solution was distilled almost to dryness and water (200 ml.) and 37% hydrochloric acid (200 ml.) were added to the residue. The strongly acidic solution was cooled in ice for 3 hours, during which time crystals formed. The solid (fraction A) was collected by filtration, washed with 100 ml. of cold water and dried in air. It weighed 19.0 g. (57.3%) and melted at 110–121°. (The *meso* form of the acid melts at 143°[7] and is less soluble in water than is the racemic acid.[19]

The aqueous solution was extracted five times with 100-ml. portions of ether. The combined ether extract was dried over magnesium sulfate and then evaporated to dryness. The yellow residual oil crystallized after several days, yielding 10 g. (30%) of material (fraction B) melting at 59°.

***meso*-α,α'-Dimethyladipic acid** was obtained from fraction A by exhaustive repetition of the following procedure. The solid was digested with fifty parts by weight of benzene and the solution was decanted from the solid while hot. The residue was suspended in another equal portion of hot benzene and the mixture was filtered. The white solid so obtained was nearly pure *meso*-α,α'-dimethyladipic acid, m.p. 142–143°. When cooled, the mother liquors from the digestion and washing deposited crystals melting at 112–126°, which were treated as above. The process was continued until no more material melting at 112–126° could be obtained. The combined product was crystallized from water whereby 9.5 g. (28.6%) of *meso*-α,α'-dimethyladipic acid melting at 143.5–144.0° (cor.) was obtained.

***dl*-α,α'-Dimethyladipic Acid.**—The mother liquors from the operations described above were combined with fraction B and the solution was filtered and evaporated to dryness. The residual oil was treated with a little ether and was eventually obtained as a solid (18 g.) melting at 55–73°. The material was suspended in benzene (25 ml.) and the residue collected by filtration. This residue was treated in the same manner three additional times at the end of which it weighed 2.5 g. and melted at 101–106°. The combined digestion solution was boiled with charcoal, filtered and evaporated to dryness. Ether was added to the residual oil to promote crystallization. There was obtained 15 g. (45.2%) of *dl*-α,α'-dimethyladipic acid melting at 75–76° (cor.).

Resolution of *dl*-α,α'-Dimethyladipic Acid.—In general, the method of Noyes and Kyriakides was followed,[7] modified only in that fractional crystallization methods were employed. From 13.5 g. of the racemic acid there was obtained 10 g. (45%) of the brucine salt of *d*-α,α'-dimethyladipic acid. The solid was treated with 10% sodium hydroxide solution and the precipitated brucine was removed by filtration. The solution was made strongly acidic with 37% hydrochloric acid and was extracted with ether. The ether solution was dried over magnesium sulfate and then evaporated to dryness, yielding 3 g. of the *d*-acid, m.p. 104.5–105.0° (cor.), $[\alpha]^{27}\text{D}$ +30.75 ± 0.22° (*c*, 4.520, 95% ethanol); (lit.[7] $[\alpha]^{27}\text{D}$ +31.3 (*c*, 10, 95% ethanol)).

Neutral Salts of Hexamethylenediamine and Dimethyladipic Acid Isomers.—A hot solution of hexamethylenediamine[9] (2.32 g., 0.02 mole) in 95% ethanol (20 ml.) was added to a hot solution of *meso*-α,α'-dimethyladipic acid (3.48 g., 0.02 mole) in 95% ethanol (30 ml.). The solution was cooled and the solid which separated was collected by filtration, washed with 5 ml. of hot 95% ethanol and then with two 10-ml. portions of cold 95% ethanol and dried in a vacuum desiccator. There was obtained 5.05 g. (87%) of white crystalline salt, which melted at least as high as 186°. The melting point varied considerably, depending on the rate at which the sample was heated; the highest value was obtained by plunging the melting point tube into a bath at 180° and raising the temperature of the bath two degrees per minute. Melting seemed to be accompanied by the evolution of a gas, probably water formed by polymerization of the salt.

Anal.[17] Calcd. for $C_{14}H_{30}N_2O_4$: C, 57.90; H, 10.41. Found: C, 58.24; H, 10.43.

The neutral salt of hexamethylenediamine and adipic acid was obtained in the same way.

The hexamethylenediamine salts of *dl*- and *d*-α,α'-dimethyladipic acids did not crystallize from alcoholic solution under the conditions employed in the preparation of the *meso* isomer, but could be precipitated in crystalline form by slow addition of acetone (10 ml. per 50 ml. of alcohol) to the cold solutions. The salts were collected by filtration, washed twice with cold 1:2 acetone–alcohol mixtures and dried *in vacuo* (yields 83–85%). A sample of the salt of the *meso* acid prepared in the same mixture of solvents, appeared to be identical with that prepared in the absence of acetone (mixed melting point). The hexamethylenediamine salts of *dl*- and *d*-α,α'-dimethyladipic acids melted sharply in the range 180–187°, depending on the rate at which the sample was heated. Depressions of melting point (10–20°) were observed with mixtures of salts prepared from different stereoisomers of the dimethyladipic acid.

Anal.[17] (*dl* salt). Calcd. for $C_{14}H_{30}N_2O_4$: C, 57.90; H, 10.41. Found: C, 57.97; H, 10.77.

Polyamides of Hexamethylenediamine and Dimethyladipic Acids.—Polyamides were prepared from the hexamethylenediamine neutral salts of adipic acid, *meso*-, *d*- and *dl*-α,α'-dimethyladipic acid by a procedure that was identical throughout. Two samples of each polymer were prepared; in each case, the two polymers seemed to be identical.

The neutral salt (1.0–1.5 g.) was placed in a new, carefully cleaned side-arm test-tube. The test-tube was closed with a rubber stopper through which ran a nitrogen inlet tube with a stopcock. The test-tube was evacuated to 1–2 mm. and then dry oxygen-free nitrogen was introduced into the tube. This procedure of flushing was repeated five more times. The connection to the pump was broken and a slow stream of nitrogen was run into the tube while the salt was melted by careful application of a soft flame to the walls of the test-tube. The tube containing the molten salt was plunged into a Wood's metal-bath heated to 200°, and the salt was heated at 200–220° for 2 hours under a slow stream of nitrogen.

At the end of this time, the tube, while still being heated,

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(18) Meincke, Cox and McElvain, THIS JOURNAL, **57**, 1133 (1935).

(19) Lean, *J. Chem. Soc.*, **65**, 995 (1894); Kitzing, *Ber.*, **27**, 1578 (1894).

was cautiously evacuated and flushed with nitrogen six times. The thick clear, colorless liquid had a tendency to froth during the first evacuation. The stopcock of the nitrogen inlet tube was closed and the polymer was heated in the bath at 280–290° for 3 hours at 1–2 mm. of pressure.

The tube was again repeatedly flushed with nitrogen while being heated at 280°. The nitrogen inlet tube was removed and a stirring rod was introduced into the thick but clear and colorless polymer melt. Long colorless filaments could be spun by withdrawal of the rod.

The polymer derived from *d*-α,α′-dimethyladipic acid was soluble in glacial acetic acid; it was found to be levo-rotatory; $[\alpha]^{30}\text{D}$ $-11.2 \pm 2.0°$ (*c*, 0.187, glacial acetic acid). *Anal.*[7] Calcd. for $(C_{14}H_{26}N_2O_2)_x$: C, 66.10; H, 10.30. Found: (*dl*-polymer) C, 65.42; H, 9.91. (*d*-polymer) C, 65.37; H, 10.43. (*meso* polymer) C, 65.69; H, 10.72.

Properties of Polyamide Fibers. (a) **Adipic Acid Polyamide (Nylon)**.—Nylon fibers, prepared as described above, were readily spun from the hot melt. These fibers could be cold-drawn to about 500% of their original length. The undrawn fibers were not particularly fragile, nor did they change in their cold-drawing properties when let stand for several weeks. The cold-drawn fibers were only slightly elastic, but were strong and flexible and could be tied into strong tight knots. A crude determination of the tensile strengths of these fibers was made by measuring the weight required to break vertically suspended fibers (gradual addition of mercury to a small cup) and by measuring the cross-section of the fiber at the point of break immediately after the break by use of a traveling microscope; values of 45 ± 5 kg./sq. mm. were obtained. No change in the properties of the cold-drawn fibers was noted when they were let stand three weeks.

(b) *meso*-α,α′-**Dimethyladipic Acid Polyamides.**—Fibers of the polyamide derived from the *meso*-dimethyladipic acid could be cold-drawn readily in the same manner as Nylon fibers. The undrawn fibers were slightly more fragile than undrawn Nylon fibers, but no particular care was needed in conducting the cold-drawing process. The fibers could be cold-drawn to about 300% of their original length; these fibers were appreciably elastic and could be stretched to about 350% of the length of the undrawn fibers. When tension was released, the fibers slowly contracted to about 300% of the length of the undrawn fibers. The cold-drawn fibers were clear and lustrous.

When undrawn fibers of this polyamide were let stand for a week, they could be cold-drawn to 400% of their length. The fibers first "necked down" as in the ordinary cold-drawing process to yield segments of the clear lustrous oriented fiber. Under further tension, necessary to extend the cold-drawn regions of the fiber, a second, less-pronounced, "necking down" process, giving rise to opaque, non-lustrous, non-elastic segments, occurred. When the cold-drawing was complete, the fiber had been converted entirely to this opaque form. The opaque, cold-drawn fiber neither stretched nor broke until considerably more tension was applied to it. When the tension was released, the opaque form of the fiber reverted quickly to the clear lustrous state of the cold-drawn fibers. In non-uniform fibers, wherein breakage of the fiber occurred before cold-drawing was complete, the break was always preceded by formation of an opaque area.

When cold-drawn fibers of this polymer were let stand, under no tension, for a week, it was found that the cold-drawing process had been almost completely reversed. The fibers resembled undrawn fibers in most respects and could be cold-drawn to 320% of their original length. Opaque areas formed when these fibers were sufficiently stretched but seemed to be more difficult to form than in the case of the aged undrawn fibers. Breaks always occurred in opaque areas. The opaque areas disappeared when tension was released.

The tensile strength of freshly spun and freshly cold-drawn fibers, determined as for the Nylon fibers was 3.5 ± 0.4 kg./sq. mm. (about 7.7% of the value found for Nylon).

(c) *d*-α,α′-**Dimethyladipic Acid Polyamide.**—Fibers of the polyamide derived from the *d*-acid could readily be spun into long fibers. These fibers resembled those formed from the *meso*-polymer in that they could be cold-drawn to 315% of their original length and in that the undrawn fibers did not become fragile on standing.

Aged undrawn fibers from the *d*-polymer behaved like freshly spun fibers. Opaque areas were formed after the cold-drawing process was complete, and these opaque areas disappeared when tension was released. The fibers always broke in an opaque area.

Aged cold-drawn fibers of the *d*-acid could be recold-drawn to about 250% of their original length and then stretched another 50% before opaque areas appeared and the fiber broke.

The tensile strength found for freshly spun and cold-drawn fibers of the *d*-acid polymer was 3.9 ± 0.5 kg./sq. mm., essentially the same as that found for the *meso*-acid polymer.

(d) *dl*-α,α′-**Dimethyladipic Acid Polyamide.**—Fibers of this polyamide differed greatly from those prepared from the *meso*- and *d*-acids although long, clear fibers could readily be spun from a hot melt of the polymer. It was necessary to cold-draw the fibers immediately after spinning as they rapidly became too fragile to cold-draw. Considerable care was required during the cold-drawing process, even when the fibers were freshly spun, but elongations of 300% could be obtained.

When undrawn fibers of the *dl*-acid polymer were let stand for a week they lost some of their brittleness and could then be stretched *without cold-drawing* to 315% of their original length. No sign of true cold-drawing could be detected during this process, which appeared to be reversible.

Cold-drawn fibers of this polymer were let stand a week under no tension. The fibers were weak but could be stretched *without cold-drawing* to 1400% of their original length.

The tensile strength of the freshly cold-drawn fibers of the racemic polymer was difficult to determine, but values of 0.6 ± 0.1 kg./mm.^{2} were obtained. These fibers appear to be about 20% as strong as fibers from the *meso*- and *d*-acid polyamides.

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Summary

1. The theory of the influence of the stereochemical orientation of side-chains on polymer properties is discussed.

2. The polyurethans formed from 1,3-propanediol and 2,2-dimethyl-1,3-propanediol by reaction with hexamethylene diisocyanate are more crystalline than is that formed from 2-methyl-1,3-propanediol and the diisocyanate. The last-named polymer possesses unpaired side-chains with random steric orientation.

3. The polyamides of hexamethylenediamine and *meso*-, *d*- and *dl*-α,α′-dimethyladipic acid all form oriented fibers. All of these fibers are much weaker than is Nylon; the polymer from the racemic acid is much the weakest of the three. All of the "dimethyl Nylons" appear to suffer a slow reversion from the oriented state to the unoriented state.

4. The "dimethyl Nylons" undergo a secondary, rapidly reversible cold-drawing when subjected to stress greater than that required for primary cold-drawing. The fibers in this new state of orientation are opaque and lusterless; breakage of fibers always occurred in opaque, lusterless zones.

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