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Polyamides from 2,2'-Bis-[5(4H)-oxazolones]

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The synthesis and properties of a little studied class of polyamides are described. The polymers are formed at room temperature by polymerization of 2,2'-bis-[5(4H)-oxazolones] with diamines. An unusual repeating unit results which contains regularly-spaced α-amino acid residues between the dicarboxylic acid and the diamine components and a regular arrangement of both "head-to-tail" and "tail-to-tail" amide groups.

Polyamides may conveniently be divided into two classes. Class I is composed of polymers with amide groups in a regular "tail-to-tail" arrangement, resulting from the condensation of dicarboxylic acids with diamines.[1]

$$(\text{—NHCORCONHR}_1\text{—})_x \qquad \text{I}$$

Class II polyamides are characterized by a "head-to-tail" arrangement of the amide groups and result from the condensation of (a) α-amino acid N-carboanhydrides[2,3] or (b) amino-substituted acids, such as, ε-aminocaproic acid.[4]

$$\underset{\text{IIa}}{(\text{—CR}_1\text{R}_2\text{CONH—})_x} \qquad \underset{\text{IIb}}{(\text{—RCONH—})_x}$$

This paper describes the preparation and properties of several members of an interesting type of polyamide[5] containing a regular arrangement of both "head-to-tail" and "tail-to-tail" amide groups (III). These polymers are made up of a regular arrangement of dicarboxylic acid, α-amino acid and diamine units, and represent a "cross" between such conventional polyamides as polyhexamethyleneadipamide and the more recently described α-amino acid homopolymers.

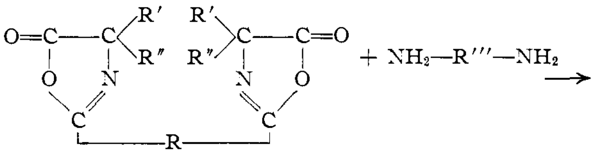
TABLE I

POLYMERS FROM DIAZLACTONES

No.	Repeating unit: α-Amino acid	Repeating unit: Dibasic acid	Repeating unit: α-amino acid	Repeating unit: Diamine (or glycol)	Polymn. conditions hr. at 25°, followed by hr. at 61–65°	Polymer properties: Inherent viscosity[k]	Polymer properties: Stick-point, °C.
1	AIB[a]	- adipic	- AIB[a]	- HMD[b]	0, 4[c]	0.55 (0.3%)	140
2	ACC[d]	- adipic	- ACC[d]	- HMD[b]	0, 48[c]	0.36 (0.3%)	140
3	glycine	- terephthalic	- glycine	- HMD[b]	1, 17[e]	1.03 (0.1%[f])	312 dec.
4	alanine	- terephthalic	- alanine	- HMD[b]	3/4, 1/4[e]	1.81 (0.3%)	218–220
5	alanine	- terephthalic	- alanine	- DMP[g]	0, 24[e]	0.08 (0.5%)	.....
6	alanine	- terephthalic	- alanine	- DID[h]	0, 24[e]	0.11 (0.5%)	.....
7	AIB[a]	- terephthalic	- AIB[a]	- HMD[b]	2, 3[e]	0.46 (0.1%)	197–199
8	leucine	- terephthalic	- leucine	- HMD[b]	0, 19[e]	1.07 (0.3%)	270
9	leucine	- terephthalic	- leucine	- MPD[i]	2, 20[e]	0.13 (0.1%)	225–230
10	leucine	- terephthalic	- leucine	- HMG[j]	0, 144[e]	0.20 (0.1%)	50

[a] α-Aminoisobutyric acid. [b] Hexamethylenediamine. [c] In benzene. [d] 1-Aminocyclohexanecarboxylic acid. [e] In chloroform. [f] In dichloroacetic acid. [g] 2,6-Dimethylpiperazine. [h] N,N'-Diisobutylhexamethylenediamine. [i] m-Phenylenediamine. [j] Hexamethylene glycol. [k] In m-cresol at 25°; concentration of solution in parentheses.

The general route to such polyamides, briefly mentioned previously in the literature,[6,7] is by condensation of 2,2'-diazlactones with diamines as shown in the equation



$$(\text{—COCR'R''NHCORCONHCR'R''CONHR'''NH—})_x$$

III

This route to a polyamide is unusual in two respects: (a) no smaller molecules such as water, ammonia or carbon dioxide are lost during polymerization, and (b) unusually mild reaction conditions (25–60°) afford polymers of high molecular weight.

A variety of these α-amino acid-containing polyamides have been prepared at room temperature by simply adding solutions of diamines to solutions of 2,2'-diazlactones.[8] The specific diazlactones, diamines, conditions of polymerization and properties of the polymers are collected in Table I. The technique of polymerization was similar in most cases, and a typical example is given in the Experimental Section (Section 1). Additional remarks concerning the polymerizations are given below.

Influence of Diazlactones.—The reaction of 2,2'-*alkylene*bis-[5(4H)-oxazolones] with aliphatic primary diamines evolved more heat and deposited polymer more rapidly than did the same reaction of 2,2'-*arylene*bis-[5(4H)-oxazolones]. However, the reaction of all 2,2'-diazlactones with primary diamines was very rapid, quantitative, and generally afforded high molecular weight polymers.

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[1] D. D. Coffman, G. J. Berchet, W. R. Peterson and E. W. Spanagel, *J. Polymer Sci.*, **2**, 306 (1947).

[2] E. Katchalski, "Advances in Protein Chemistry," Vol. VI, Academic Press, Inc., New York, N. Y., 1951, p. 123.

[3] R. B. Woodward and C. H. Schramm, THIS JOURNAL, **69**, 1551 (1947).

[4] W. H. Carothers and G. J. Berchet, *ibid.*, **52**, 5289 (1930).

[5] W. E. Hanford, U. S. Patent 2,293,388 (1942).

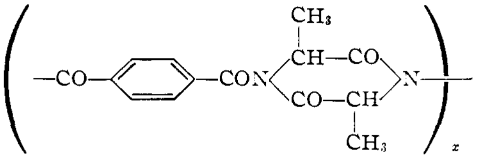
[6] I.G. patent application 79,859-IVc/39c, 11/11/41; P.B. Report 19,922; issued as French Patent 887,530 (1943).

[7] B.I.O.S. Final Report No. 1472, Item No. 22.

[8] C. S. Cleaver and B. C. Pratt, THIS JOURNAL, **77**, 1544 (1955).

Influence of Diamine.—It was observed that N-substituted aliphatic diamines, such as N,N′-diisobutylhexamethylenediamine and 2,6-dimethylpiperazine, gave polymers of lower molecular weight than did primary aliphatic diamines (Table I, no. 5, 6). Similarly, diazlactones reacted with aromatic diamines such as *m*-phenylenediamine, and with aliphatic glycols such as hexamethylene glycol to yield low molecular weight polymers (Table I, no. 9, 10). High molecular weight polymers which incorporated these difunctional compounds were difficult to obtain even in the presence of a variety of acidic and basic catalysts or at high polymerization temperatures.

The failure of acids or bases to catalyze the reaction of diazlactones with glycols and thereby produce high molecular weight polymers was unexpected in view of literature statements[9] that such reagents catalyze the reaction of azlactones with alcohols. A partial explanation may reside in an interesting base-catalyzed rearrangement and dimerization of azlactones which has been mentioned elsewhere recently[10a] and was verified during this work. When a chloroform solution of 2-phenyl-4-methyl-5(4H)-oxazolone was refluxed in the presence of catalytic amounts of triethylamine, an excellent yield of di-N-benzoyl-3,6-dimethyl-2,5-diketopiperazine rapidly formed. When a chloroform solution of the diazlactone, 2,2′-*p*-phenylenebis-[4-methyl-5(4H)-oxazolone], was similarly treated, a quantitative yield of orange amorphous solid formed, for which structure IV is suggested, by analogy with the reaction product from the monoazlactone.

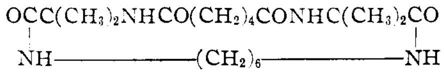

IV

The low inherent viscosities[11] (0.08 at 0.5% in *m*-cresol) of this suggest that (a) the polymer was of low molecular weight or (b) that *m*-cresol caused degradation during viscosity measurements. The base-catalyzed formation of this material or other similar rearrangement products possibly prevented the production of high molecular weight glycol-containing polymers. Similarly, since aromatic diamines reacted with diazlactones very slowly, they probably simultaneously catalyzed the rearrangement of the diazlactone and thus also unbalanced the desired polymer-forming reaction.

Effect of Polymerization Medium.—The polymers of highest molecular weight were formed in inert media such as benzene, pyridine and chloroform. Although the polymers were generally insoluble in such reagents, apparently the polymer surface was wet sufficiently to permit good reaction between polymer and unreacted monomers, and between growing polymer chains. Polymers of lower molecular weight were formed in acetic acid and *m*-cresol media, in which several final polymers were soluble.

Concentration of Monomers.—The concentration of monomers for each polymerization was governed by the solubility of the diazlactone in the polymerization medium. Polymerization was usually carried out at a concentration corresponding to a saturated solution of the diazlactone, generally 2–10%. To obtain homogeneous, soluble products, the diazlactone was always completely dissolved, if possible, before adding the diamine. A fibrous, insoluble, cross-linked material was obtained from one experiment wherein the diamine was added to a *slurry* of the diazlactone.

One unusual concentration effect was noted. At high dilution, the product from 2,2′-tetramethylenebis-[4,4-dimethyl-5(4H)-oxazolone] and hexamethylenediamine was a mixture of crystalline material and amorphous polymer. The crystalline material has tentatively been assigned structure V based on analytical data. It represents an unusual twenty-membered cyclic tetramide.



$$\begin{array}{l}\mathrm{OCC(CH_3)_2NHCO(CH_2)_4CONHC(CH_3)_2CO} \\ \ \ | \hspace{27em} | \\ \mathrm{NH}\text{———————}\mathrm{(CH_2)_6}\text{———————}\mathrm{NH}\end{array}$$

V, 1,4,11,14-tetraaza-3,3,12,12-tetramethyl-2,5,10,13-cycloeicosatetraone

Somewhat similar cyclic polyamides containing up to 20 members have been formed by reaction of certain aromatic diamines with aliphatic diacyl chlorides[12] and by combination of several dicarboxylic acid esters with various diamines.[13] Crystalline material was not observed in the products resulting from the reaction of other diazlactones with diamines.

Temperature and Time of Polymerization.—In general, several hours at room temperature followed by a few minutes at 60° sufficed to produce very high molecular weight polymer. Occasionally, longer times and higher temperatures were tried in attempts to obtain higher molecular weight products, but insignificant improvements resulted.

Polymer Stick-point.—The polymers, as a class, failed to melt without degradation. Presumably amide interchange[14] occurred at high temperatures resulting in diketopiperazine formation among other reactions. The *stick-point* of the polymer has therefore been used as an indication of the polymer's useful upper temperature limit as a solid and corresponds to the temperature at which a few particles of polymer on a heated Maquenne block either partially coalesced or left a smear when pressed with a spatula. While polymers containing terephthalic acid had higher stick-points than did those incorporating adipic acid, other consistent relationships did not appear to exist between stick-points and the structures of the various polymers.

Polymer Solubility.—The polymers in general were soluble only in polar solvents, such as formic acid and *m*-cresol, and were therefore more similar to the conventional polyamides such as polyhexamethyleneadipamide in this respect than to the α-amino acid polymers. The polymer composed

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(9) "Organic Reactions," Vol. III, John Wiley and Sons, Inc., 1946, p. 215.

(10) (a) H. T. Clark, J. R. Johnson and R. Robinson, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., p. 768; (b) p. 742.

(11) L. C. Cragg, *J. Coll. Sci.*, **1**, 261 (1946).

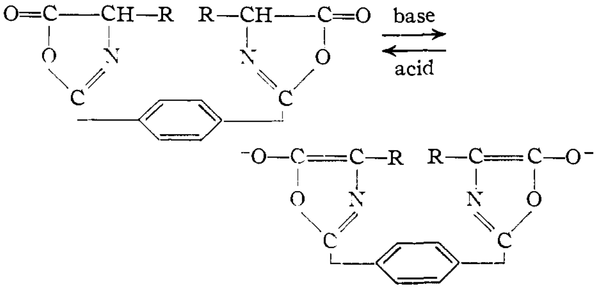
(12) P. Ruggli, *Ann.*, **392**, 92 (1912); **399**, 174 (1913).

(13) A. L. Lippert and E. E. Reid, U. S. Patent 2,156,300 (1939).

(14) L. F. Beste and R. C. Houtz, *J. Polymer Sci.*, **8**, 395 (1952).

of adipic acid, α-aminoisobutyric acid, and hexamethylenediamine (Table I, no. 1) was unusual in that it was very soluble in cold water, but precipitated from solution upon warming. The effect was reversible with temperature and thus did not resemble the somewhat similar denaturation behavior of proteins.

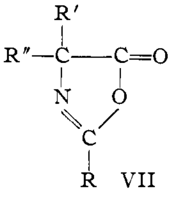
Color Changes During Polymerization.—A brilliant orange color instantly appeared upon addition of diamine solutions to solutions of certain diazlactones. The diazlactones that gave the color were those containing one or more hydrogen atoms at position 4 of the oxazolone ring in conjunction with a *p*-phenylene linkage of the oxazolone rings. Thus, the diazlactones derived from terephthalic acid and glycine, alanine or leucine produced the color in the presence of the diamines. The diazlactones derived from aliphatic dicarboxylic acids, such as adipic and succinic acids, or those from terephthalic acid and α-amino acids which contained no α-hydrogen atoms, such as α-aminoisobutyric acid, failed to produce a color in the presence of the diamine. It was suggested[15] that the color was due to structure VI which might readily form in the presence of bases



VI

Structure VI contains a completely conjugated system with conceivably enough chromophoric groups to absorb visible light. The diazlactones derived from aliphatic dicarboxylic acids or those containing α-amino acids with no α-hydrogen atoms cannot form a similar conjugated system and thus would not be expected to give a color in the presence of bases.

The formation of such ions would explain the difficulty observed[10b] in preparing optically active amides from optically active azlactones and amines, since enolization and racemization probably destroyed asymmetry. However, optically active azlactones of structure VII should afford an optically active amide since such enolization and racemization would not be possible.



VII

(R' and R'' are different alkyl groups)

X-Ray Diffraction Patterns.—X-Ray diffraction patterns of three polymers (1, 4 and 8) were taken with the beam perpendicular to the polymer films. All three polymers were amorphous or very poorly crystalline as undrawn films. Polymers 4 and 8 became slightly oriented upon cold-drawing 2.5×, but retained their amorphous character. Although polymer 4 could be cold-drawn only 2.5×, it could be drawn in steam 10×, and films were then highly oriented and crystalline.

The generally amorphous structure of these three representative polymers even after cold-drawing is unusual and they are quite different in this respect from conventional polyamides. Presumably, the side chains of the α-amino acid units and the combination of both "tail-to-tail" and "head-to-tail" amide groups in the repeating units prevent crystallization and a high degree of orientation during cold-drawing.

Experimental

Section 1. Polymerization.—Under anhydrous conditions, 60 g. (0.223 mole) of 2,2'-*p*-phenylenebis-[4-methyl-5(4H)-oxazolone] was dissolved in 1.5 l. of warm ethanol-free chloroform. Under carbon dioxide-free conditions, 25.60 g. of pure hexamethylenediamine (0.223 mole) was dissolved in 500 ml. of ethanol-free chloroform. The diamine solution was rapidly added to the diazlactone solution, under both anhydrous and carbon dioxide-free conditions, with swirling to obtain good mixing. The diamine flask was washed twice with 40 ml. of ethanol-free chloroform, and the washings were added to the diazlactone solution to ensure quantitative transfer of the diamine. Upon addition of the diamine, a brilliant orange color instantly developed in the reaction mixture, and the temperature rose to approximately 50°. Within 15 seconds, the orange chloroform solution became turbid and rapidly gelled to a thick orange paste.

After one hour at room temperature, the contents of the reaction vessel were light cream in color. The thick gel was broken with a spatula to a thick slurry to prevent bumping during the subsequent "finishing" cycle. The polymer was "finished" by warming at 60° on a steam-bath for 15 minutes, during which time the color completely disappeared and a white slurry of swollen polymer remained. The polymer was filtered from the vessel and dried in a vacuum oven at 65° (20 mm.) to a fine white powder (quantitative yield).

Section 2. Preparation of VI.—To a solution of 10 g. of 2,2'-tetramethylenebis-[4,4-dimethyl-5(4H)-oxazolone] (0.0358 mole) in 500 ml. of purified pyridine was added a solution of 4.15 g. of hexamethylenediamine (0.0358 mole) in 200 ml. of purified pyridine. The mixture stood at room temperature for 15 hours and then at 60° for seven days. After cooling, the solution was filtered to yield 4.5 g. of polymer, $\eta_{\text{inh}} = 0.28$. One liter of petroleum ether was added to the filtrate, and the solution was filtered to yield 7.0 g. of amorphous material, $\eta_{\text{inh}} = 0.06$. Crystals slowly formed on the sides of the flask containing the final filtrate. They were filtered from solution after 24 hours (2.0 g.). The crystalline material was recrystallized from a methanol–acetone mixture; m.p. 258–259°. The melting point of crystals manually extracted from polymer 1, Table I, was 258°.

Anal. Calcd. for $C_{20}H_{36}N_4O_4$: C, 60.60; H, 9.09; N, 14.14; mol. wt., 396; Van Slyke N, 0.00; neut. equiv., ∞. Found: C, 60.50; H, 9.15; N, 13.80; mol. wt., 320; Van Slyke N, 0.53; neut. equiv., 950.

The Van Slyke analysis and neutral equivalent suggest that the material was slightly contaminated with low molecular weight polymer. By conducting an identical polymerization in one-tenth as much pyridine, a quantitative yield of material was obtained, $\eta_{\text{inh}} = 0.56$. Continuous pyridine extraction of this material afforded a polymer fraction with $\eta_{\text{inh}} = 1.2$ and lower molecular weight fractions which contained small amounts of crystalline material. Thus, it appears that polymer formation is favored in concentrated solution while cyclization is favored in dilute solution.

Acknowledgment.—The authors wish to thank Dr. W. A. Gregory of the Grasselli Chemicals Department for suggesting this route to diazlactone polymers.

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(15) C. Niemann, personal communication, 1950.