

CONDENSATION MONOMERS

**Edited by John K. Stille and
Tod W. Campbell**

CONDENSATION MONOMERS

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AND

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PREFACE

This book is one of several volumes of a series devoted to the synthesis, purification, and properties of monomers; its purpose is to provide chemists working in the field with an accurate—as far as possible—and practical reference source. We do not intend to make an extensive survey of the polymerization reactions of the monomers and the structure and the properties of the resulting polymers; instead, only a brief treatment of the kinds of polymerization reactions into which the monomers will enter is outlined.

Early in 1967, Tod W. Campbell took over the editorship of this volume on condensation-type monomers. Tod selected the group of authors and prepared a set of guidelines for them. Three years ago today, Tod passed away at his home in Tucson, Arizona, and shortly thereafter, I agreed to assume the responsibility for completing this volume.

This book originally contained 16 chapters, including discussions of inorganic monomers and silicone monomers and chapters on lactams, lactones, cyclic ethers, and carboanhydrides. Later it was decided that the cyclic monomers, which can undergo polymerization by typical addition-type or chain-growth polymerization, should be the subject of a separate volume.

The authors of each chapter have followed the format guidelines as closely as possible. Of course, differences in the commercial availability, the knowledge of the synthesis and properties each monomer, etc., have necessitated deviations from the format. In each chapter, however, the authors have attempted to provide the following information:

1. A historical introduction, including the commercial utility and production data.
2. A survey of the chemistry of all the practical synthetic routes to each monomer.
3. Details of the more important synthetic routes, including the commercial synthesis when feasible, or a practical laboratory synthesis in which pound quantities of the monomer can be prepared and purified.
4. The physical properties of the monomer.
5. Analytical procedures for determination of purity.
6. Storage and toxicology.
7. Polymerization and polymerizability.

In any book conceived in this way, featuring a number of contributors, the chapters are usually completed at widely different times. Unfortunately,

this volume is no exception; the first chapters were received in the spring of 1968 and the last in the spring of 1971. Some of those chapters received early may not contain some of the more recent significant information.

Many thanks are due to the authors who have contributed these chapters; the burden of the work is theirs. I owe special gratitude to those many reviewers who so willingly gave excellent critiques of individual chapters.

JOHN K. STILLE

*Iowa City, Iowa
May 9, 1971*

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1. ALIPHATIC DIBASIC ACIDS

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I. THE ALIPHATIC DIBASIC ACIDS

A. Introduction

Aliphatic dibasic acids include straight-chain, branched, saturated, unsaturated, and, for the purposes of this chapter, alicyclic dicarboxylic acids. Of these, the most important commercially are the α -, ω -alkanedioic acids, especially adipic acid. Their importance arises chiefly from their bifunctionality, which permits them to undergo various polycondensation reactions for the preparation of certain polymers and plastics. Several of the most accessible acids along with pertinent references are listed in Table 1, and the most important of these are discussed in individual sections as indicated. The unsaturated dicarboxylic acids listed have been reviewed adequately elsewhere and, of the cyclic acids listed, only dimer acid is discussed here. The remaining cyclic acids were mentioned because of interest in them as monomers and their potential availability.

The alkanedioic acids constitute an interesting homologous series; yet major differences in their properties point out the fallacy of considering them to have complete uniformity. Carbonic acid is listed as the initial member of the homologous alkanedioic acids, being a dibasic although not a dicarboxylic acid. It is, of course, not usable in the free acid form because of its instability. However, it is available as a monomer in the form of the acid chloride (phosgene), the ester chloride (chloroformate), and the amide (urea).

B. Chemistry

Thermal stability is essential, both in the preparation of polymers by melt polymerization and in the polymer itself. Under comparable conditions, the following order of decreasing stability has been reported by Korshak and Rogozhin (22) for several acids (decarboxylation temperatures given in $^{\circ}\text{C}$): sebacic (360) > suberic (350) > azelaic (330) > adipic (340) > succinic (300) > glutaric (285) > oxalic (170) > malonic (150). These decarboxylation temperatures are even lower under conditions of polymerization; that is,

TABLE I
The Aliphatic Dibasic Acids as Monomers

Total number of carbon atoms	Common name	Geneva name	Formula	Reference	Comments
Saturated Acids					
1	Carbonic	—	HOC(O)OH	1-3	Unstable, used as a monomer in the form of esters, acid chlorides, amides
2	Oxalic	Ethanedioic	HOOC-COOH	Section II	Polyoxamides not now commercial but have potential
3	Malonic	Propanedioic	$\text{HOOC-CH}_2\text{-COOH}$	Section III	Too unstable, both thermally and oxidatively
4	Succinic	Butanedioic	$\text{HOOC-(CH}_2\text{)}_2\text{-COOH}$	Section IV	Used to a minor extent
5	Glutaric	Pentanedioic	$\text{HOOC-(CH}_2\text{)}_3\text{-COOH}$	Section V	Not commercially important at present
6	Adipic	Hexanedioic	$\text{HOOC-(CH}_2\text{)}_4\text{-COOH}$	Section VI	The most important of all the dibasic acids; used for nylon-6/6
7	Pimelic	Heptanedioic	$\text{HOOC-(CH}_2\text{)}_5\text{-COOH}$	Section VII	Not commercially important
8	Suberic	Octanedioic	$\text{HOOC-(CH}_2\text{)}_6\text{-COOH}$	Section VIII	Not commercially important but may have potential
9	Azelaic	Nonanedioic	$\text{HOOC-(CH}_2\text{)}_7\text{-COOH}$	Section IX	Important commercially for uses other than polyamides
10	Sebacic	Decanedioic	$\text{HOOC-(CH}_2\text{)}_8\text{-COOH}$	Section X	Important commercially as in nylon-6/10

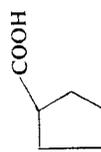
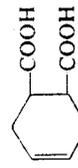
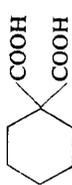
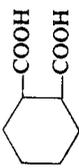
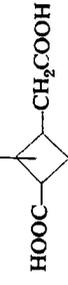
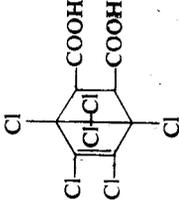
11	Undecanedioic	$\text{HOOC}(\text{CH}_2)_9\text{COOH}$	Beilstein,* 4	Not commercially important
12	Dodecanedioic	$\text{HOOC}(\text{CH}_2)_{10}\text{COOH}$	Section XI	Has recently become commercially important
13	Brassylic	$\text{HOOC}(\text{CH}_2)_{11}\text{COOH}$	Section XII	Not commercially important but may have potential
14	Tetradecanedioic	$\text{HOOC}(\text{CH}_2)_{12}\text{COOH}$	Beilstein ^a	Not important
15	Pentadecanedioic	$\text{HOOC}(\text{CH}_2)_{13}\text{COOH}$	Beilstein ^a	Not important
16	Hexadecanedioic	$\text{HOOC}(\text{CH}_2)_{14}\text{COOH}$	Beilstein ^a	Not important
21	Henicosanedioic	$\text{HOOC}(\text{CH}_2)_{19}\text{COOH}$	Beilstein ^a	Not important
Unsaturated acids				
4	Maleic	$\text{HOOCCH}=\text{CHCOOH}$	5, 6	Used mainly in unsaturated polyester resins
4	Fumaric	$\text{HOOCCH}=\text{CHCOOH}$	5, 6	Used mainly in unsaturated polyester resins
5	Citraconic	$\text{HOOC}(\text{CH}_2)=\text{CHCOOH}$	7	Used as a comonomer
5	Itaconic	$\text{HOOC}(\text{C}=\text{CH}_2)\text{CH}_2\text{COOH}$	7, 8	Used mainly as a comonomer in latex polymers
Cyclic acids				
6	1,1-Cyclobutanedicarboxylic		9, 10	Has potential value in polyesters and polyamides
7	Norcamphoric		11-13	Has potential value in polyesters and polyamides
8	Tetrahydrophthalic 4-Cyclohexene-1,2-dicarboxylic		7	Used in alkyd resins

TABLE 1 (continued)

Total number of carbon atoms	Common name	Geneva name	Formula	Reference	Comments
8	—	1,1-Cyclohexanedicarboxylic		14	Has potential value in polyesters and polyamides
8	Hexahydrophthalic	1,2-Cyclohexanedicarboxylic		15	Has potential value in polyesters and polyamides
8	—	1,4-cyclohexanedicarboxylic		16-18	Has potential value in polyesters and polyamides
9	Pinic	2,2-Dimethyl-3-carboxycyclobutylacetic		19	Has potential value in polyesters and polyamides
9	Chlorendic	1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic		20	Has potential in nonflammable polymer applications
10	—	1,4-Benzenediacetic		21	Has potential value in polyesters and polyamides
36	Dimer	—	Mixture of acyclic, mono-, and bicyclic compounds	Section XIII	Important for certain polyamides

^a For acids that do not have specific references cited, the best source of general information is *Beilsteins Handbuch der Organischen Chemie*, 4th ed., 1918—to date, Beilstein-Institut für Literatur der Organischen Chemie, Springer Verlag, Berlin.

in the presence of glycols and diamines, which doubtless serve as catalysts. Decomposition temperatures as measured by derivatographic thermal analysis are somewhat at variance with those given by Korshak and Rogozhin (23): sebacic (330) > azelaic (320) = pimelic (320) > suberic (290) = adipic (290) = glutaric (290) > succinic (255) > oxalic (200) > malonic (185).

Anhydride formation is one example of the difference in chemical properties that can be displayed by alkanedioic acids. Oxalic and malonic acids do not form anhydrides. Succinic and glutaric acids form cyclic anhydrides when heated. When heated, adipic acid forms cyclopentanone, but when treated with acetic anhydride, it forms a polymeric anhydride. A cyclic anhydride also exists for adipic acid. Polymeric anhydrides are the normal products for the higher alkanedioic acids, but some produce fairly stable cyclic monomers or dimers when molecularly distilled (24). Pimelic acid also forms a cyclic ketone—cyclohexanone—when heated. This characteristic cyclization of succinic and glutaric acids to an anhydride and of adipic and pimelic acids to a ketone by application of heat is frequently expressed as Blanc's rule (25).

Oxidative degradation studies have been described for several reagents including chromium (VI) oxide (26,27), nitric acid (28), and hydrogen peroxide in the presence of a copper salt (29). Succinic acid is the most stable, with the higher acids progressively less stable according to number of carbon atoms. Mareš and Roček (27) give the oxidation rate constants, $k \times 10^{-3}$ in $\text{M}^{-1} \text{sec}^{-1}$, as follows: succinic, 0.0071; glutaric, 0.044; adipic, 0.32; pimelic, 0.80; suberic, 4.1; azelaic, 8.0; sebacic, 12; undecanedioic, 16; dodecanedioic, 24; and brassylic, 28. The effect of the carboxyl group in retarding oxidation of methylene groups decreases progressively up to the δ position.

Half-esters of the alkanedioic acids are useful chemical intermediates. Depending on the particular acid, they may be prepared by one of three different methods (30). For those acids forming cyclic anhydrides (succinic and glutaric), reaction of the anhydride with an alcohol forms the half-ester in good yield. For those acids between and including adipic and sebacic acids, partial esterification is used to best advantage. For the higher acids, the dimethyl ester is partially saponified with barium hydroxide; this method precipitates the barium salt of the half-ester and thereby removes the half-ester from further reaction. Half-esters tend to disproportionate with time, particularly when heated. The half-ester acid chlorides are readily prepared with thionyl chloride.

Cyclization reactions of the higher alkanedioic acids are characteristic and well known (31,32). For preparation of cyclic ketones having 5–6 ring atoms, the Dieckmann condensation of diesters is preferred. For those with 7–8 ring atoms, the Hantzsch-Wegler reaction of dinitriles is used; for those