Hans Kricheldorf

Polycondensation

History and New Results

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Leo Hendrik
Baekeland 1863–1944

Wallace Hume
Carothers 1896–1937

The grandfathers of polycondensation chemistry.

Contents

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Abbreviations

DA	Donor-acceptor complex
DP	Degree of polymerization of an individual chain
DPn	Average number degree of polymerization
DPw	Average weight degree of polymerization
IMC	Initial monomer concentration
KC	Kinetically controlled (irreversible)
MWD	Molecular weight distribution
M_n	Number average degree of polymerization
M_w	Weight average degree of polymerization
$N_{a0,}N_{at}$	Number of "a" (end) groups at time zero or later
N_{b0},N_{bt}	Number of "b" (end) groups at time zero
n_c	Number fraction of all chains
n_r	Number (mole) fraction of all rings
PBT	Poly(butylene terephthalate)
PET	Poly(ethylene terephthalate)
ROP	Ring-opening polymerization
RZDP	Ruggli-Ziegler dilution principle
TC	Thermodynamically controlled (involving equilibration)
w_c	Weight fraction of all chains
w_r	Weight fraction of all rings

Chapter 1
Introduction

For three reasons polycondensation is a polymerization process, which plays a unique role in the history of chemistry in general, and in the history of polymer science in particular. Polycondensation was the first polymer forming reaction sequence which existed on the early earth before living organisms appeared. It is clear from the experiments of Stuart Miller [1, 2] and other authors that whenever organic molecules were formed on earth, α-and ß-amino acids were formed together with α-hydroxy acids, such as glycolic and lactic acid. Heating and drying of their aqueous solutions might have yielded their oligomers and polymers. The second reason for the unique role of polycondensation is the fact that the first polymer synthesized in a laboratory (although not intentionally) was poly(D,L-lactic acid) which was obtained by heating of lactic acid in vacuo (see Sect. 2.1 in Chap. 2). The third reason is the fact that the first commercialized synthetic polymers, namely Novolac and Bakelite, were polycondensates (see Chap. 2).

The main purpose of this introduction is to present and discuss the definition of the term "polycondensation", because in recent years an increasing number of authors published misleading or definitely incorrect applications of his term. The experimental and theoretical basis of step-growth polymerizations, in general, and polycondensation, in particular, was elaborated by W. H. Carothers (see Chap. 3) and by P. J. Flory (see Chap. 4). Their results and conclusions are still valid nowadays (for partial revisions see Chaps. 4, 5 and 7) and form in all textbooks the framework for chapters dealing with step-growth polymerizations. Polycondensation and polyaddition are the two branches of step-growth polymerization, which were defined by Flory via a kinetic scheme [3], which complements the kinetic definition of chain-growth polymerization (see Chap. 16). In connection with step-growth polymerizations the term polyaddition should be used instead of addition polymerization, because the latter term is frequently applied to chain-growth polymerizations of vinyl monomers and a-olefins. Polycondensation and polyaddition differ formally by the fact that each growing step of a polycondensation involves elimination of an (usually) small molecule, such as H_2O, HCl, MeOH etc. This difference does not affect the kinetic course of both polymerization processes, but it marks an enormous difference for the thermodynamic properties. A normal polycondensation of non-cyclic monomers is characterized by a reaction entropy

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(ΔS) close to zero, so that even a low reaction enthalpy suffices to promote the polycondensation. In contrast, polyaddition is characterized by a large negative reaction entropy, so that a highly exothermic reaction is needed to effect the polymerization. The requirement of a highly exothermic reaction strongly limits the number of addition reactions suited for a successful polymerization. In the case of polycondensations even a reaction enthalpy around zero may allow for the synthesis of a high molar mass polymer, when the byproduct is transferred into another phase (e.g., evaporization of CO_2 or crystallization of NaCl). From the thermodynamic point of view polycondensations of cyclic monomers represent an intermediate case, as discussed in Chap. 9.

Flory outlined [3] that the definition of polycondensation is necessarily based on kinetic aspects and not on the structure of polycondensates, because numerous polycondensates can also be prepared by ROP which usually proceeds as chain-growth polymerization. Flory's definition of step-growth polymerization is limited to polycondensations and polyadditions in the melt or in solution, and does not include solid-state polycondensations. Flory's definition of step-growth polymerizations is based on point 1.

(1) The course of a normal step-growth polymerization is characterized by the fact that monomers, oligomers and polymers can react with each other at any time This course necessarily requires that the reactivities of the functional groups does not significantly depend on the size of the molecules. This kinetic scheme has the unavoidable consequence that the molar mass distribution of the linear chains obey the most probable distribution (also called Schultz-Flory distribution), even when equilibration reactions take place. This distribution has, in turn, the consequence that the linear chains alone (cyclics not included) have a polydispersity (M_w/M_n) of 2. Slight deviations from this standard scheme are tolerable for the definition of polycondensation. For instance, the reaction of a_2 with b_2 may be slightly slower or faster than reactions with oligomers and polymers. Yet, when one monomer reacts faster with oligomers and polymers than with the second monomer, the kinetic course changes dramatically and may finally obey the definition of a chain-growth polymerization (see Chap. 8).

Theoretical and experimental research of the past 40 years allow for a more precise definition of step-growth polymerization by addition of to more points:

(2) Cyclization competes with chain growth at any monomer concentration and at any stage of the polymerization (see Chaps. 5 and 7).

(3) The molar concentration of all linear species together (monomers, oligomers and Polymers) steadily decreases with higher conversions (p in Eq. 1) [4].

The implications of this "Law of Self-Dilution" with regard to reaction rates and cyclization reactions are discussed in Chaps. 5 and 7.

$$[L]_t = [L]_0(1 - p) \tag{1}$$

$[L]_0$,$[L]_t$ = molar concentration of all linear species at time zero or later

The occurrence of condensation (elimination) steps together with points (1)–(3) yield a clearcut definition of the term polycondensation, and allow for an easy distinction from polymerizations which at first glance show similarities, but differ from the definition given above. For instance, the term polycondensation was recently misused in numerous publications [4–9] dealing with chain-growth polymerizations involving condensation steps. Such polymerizations are correctly termed “condensative chain polymerizations” according to IUPAC, and a detailed discussion is presented in Chap. 16. Confusion in the opposite direction also frequently occur. For instance, handful of papers has recently been published [10–15] on polyadditions of functional olefins or lactones under the terms “self-polycondesation” or “self-condensing polymerization”. Those polymerizations obey a step-growth kinetic, but condensation (elimination) steps are totally lacking. Such a confusion of polycondensation and polyaddition is particularly strange, as the meaning of condensation and addition reactions has been clarified in organic chemistry about hundred years ago.

Furthermore, it should be mentioned that throughout this book the following three terms coined by Flory [3] are used.

“Linear Polycondensation”. This term is used for polycondensations exclusively yielding linear reaction products. Flory originally assumed [3] that cyclization reactions do not play any role in step-growth polymerizations and used this term instead of “Two-dimensional polycondensations”.

“Two-dimensional Polycondensations” this term means polycondensations of $a - b$ and $a_2 + b_2$ polycondensations regardless, if cyclics are formed or not.

“Three-dimensional Polycondensations” this term includes polycondensations of all multifunctional monomers such as $a - b_n$ and $a_2 + b_n$ with $n > 2$

Finally, the concept of this book needs a short explanation. According to the title, this work focuses on two aspects. It is aimed at presenting an as complete as possible history of polycondensation experiments. A lot of information about Carothers work and life is available from numerous sources including the internet. Despite the outstanding work of Carothers the early history of polycondensation is not limited to his work. Information about earlier experiments is scattered over numerous original papers, patents and scarce comments in books. For example, Flory wrote a few sentences about early polycondensation experiments in his famous book “Principles of Polymer Chemistry” [16]. A broader and more detailed description of the history of polycondensation chemistry was presented by H. Morawetz in his excellent book “Polymers-The Origins and Growth of a Science” [17]. Yet, step-growth polymerization played a minor role in that work, and all the important inventions and contributions made by various polymer chemists around or after 1940 were not considered.

The second purpose of this book was the presentation of new working fields which emerged over the past fifty years. These working fields were selected under the aspect of a broader and deeper understanding of polycondensations with regard to the theoretical background and with regard to new preparative applications.

However, although the author has attempted to cite as many as possible original papers and review articles concerning these new working fields, this book was not designed as handbook of polymer syntheses.

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Part I
History

Chapter 2
Experiments Before World War I

2.1 Early Formulas and Terminology

The nineteenth century has witnessed the gradual transformation of alchemy into modern chemistry. In a simplified view of this process one may say that this evolution mainly proceeded on two tracks. Definition of elements, detection of elements, and elaboration of the periodic table represent one track. Syntheses of organic molecules in the laboratory and the elaboration of formulas allowing for a correct three-dimensional description of organic molecules represent the second track. In the first half of the nineteenth century isolation and purification of organic substances by fractionated distillation or crystallization had become standard methods. The characterization of the purified substances was performed by elemental analyses, cryoscopic determination of the molar masses (e.g., in water, benzene, or camphor), and by derivatization of functional groups. The results challenged the organic chemist to find formulas allowing for an adequate representation of chemical structures.

The confusion about structure and formulas which still existed around 1860 among the best chemists of that time is illustrated by the three formulas proposed for lactic acid [1–3] (see Formula 2.1). Two-dimensional formulas analogous to those used today were first proposed by Crum-Brown in 1863 [4] and strongly recommended by other authors [5]. These formulas were based on an important publication of Kekule (1829–1896) in which he stated [6] that carbon atoms are tetravalent and that “carbon atoms bind themselves to one another, whereby part of the affinity of one carbon is naturally engaged with an equal part of the affinity of another carbon”. He also stated that “the number of H-atoms attached to n C-atoms which are linked to each other is $2n + 2$”. In 1865 Kekule also “invented” the famous formula of the benzene ring [7]. Considering this progress in the “formula language” it is amazing that Kekule himself and other chemists [8] did not consider their formulas as constitutional formulas of stable molecules, where the atoms are in fixed positions relative to each other. Kekule wrote in his textbook: “which of the rational formulas should be used depends on the purpose…(they) are only transformations and not constitutional formulas….and in no

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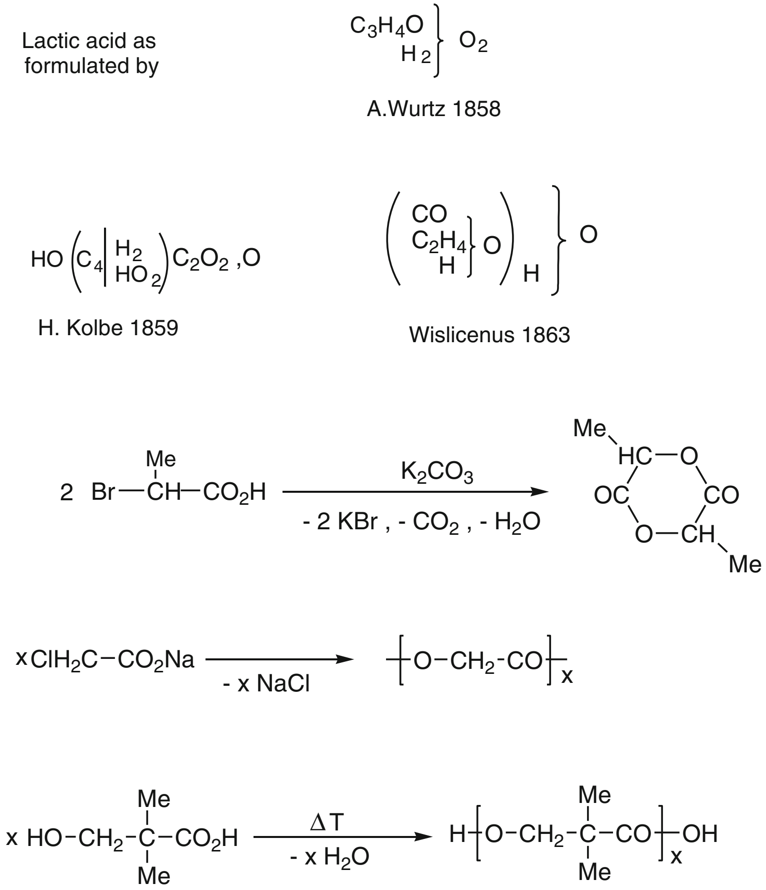
way express the positions of these atoms in the compounds”. Therefore, several types of formulas coexisted in the literature for at least two decades.

A final and decisive progress was contributed by Pasteur [9–11] (1822–1895) and van t’Hoff (1852–1908) [12]. Pasteur was troubled as a student by a report that salts of tartaric acid and paratartaric acid (i.e., the racemate) differed from each other by the optical rotation of tartrate solutions and absence of optical rotation in the case of “paratartrates”, although these salts had identical properties in all other aspects. Careful examination of numerous salts of racemic tartaric acid led to an extremely important discovery. In the case of sodium–potassium or sodium ammonium salts he found equal amounts of hemihedral crystals which contained either the laevorotatory or the dextrorotatory molecules. In other words, he was able to separate the optical enantiomers in their crystalline form. About 20 years later Paterno published a rarely cited paper [13] in which he presented a tetrahedral



Formula 2.1

arrangement of the four carbon valences. The genial van t'Hoff combined in 1874 (before completion of his Ph.D., thesis!), all these pieces of information in a famous paper which explained the stereochemistry of organic compounds, including their chirality, by three-dimensional formulas. Assuming a rotational barrier of the C–C double bond he also explained the different properties of fumaric and maleic acid by cis–trans isomerism. With van t'Hoff's concept all fundamental problems concerning the correlation between formulas, constitution, and properties of organic compounds were solved. In 1901, van t'Hoff was awarded with the 1st Nobel Prize of chemistry.

Long before rational and correct formulas for organic compounds were elaborated, first reports on polymerization processes were published. In 1839 E. Simon [14], a pharmacist in Berlin, distilled "storax resin" a natural product, under alkaline conditions and isolated an oil which he called "styrol" (since then the German name of styrene). He obtained correct elemental analyses, but he had no idea about the structure of his oil. Kekule's formulation of the benzene ring did not exist yet, and the correct formula of "styrol" as vinyl benzene was published by Erlenmeyer in 1866 [15]. Simon noted that "with old oil the residue that cannot be vaporized without decomposition is greater than with fresh oil undoubtedly due to a steady conversion of the oil by light and heat to a rubber-like substance". In a detailed study of styrene Blyth and Hofmann [16] confirmed Simon‘s elemental analyses and noted that this ratio was the same as that of benzene or cinnamol, an oil obtained by distillation of cinnamic acid [17]. They assumed that Simon‘s styrol and cinnamol are identical substances and they confirmed that the transition of styrol to the solid metastyrol is catalyzed by heat and sunlight and proceeds without any change of the elemental composition. This transition was discussed in 1866 by Berthelot (the most influential French chemist at that time) [18] as a polymerization which was understood as a special case of isomerism. The term isomerism was coined by Berzelius in 1832 "I suggest that substances of identical composition, but different properties, should be called isomers" [19]. One year later, Berzelius used for the first time the term "polymeric" for an isomerism which is defined by an equal elementary composition but with a different absolute number of atoms [20].

2.2 First Syntheses of Polyesters

First experiments dealing with (poly)condensations of difunctional compounds concerned aliphatic hydroxyl acids such as lactic acid, glycolic acid, or tartaric acid. In 1833, [21] GayLussac and Pelouze reported that dehydratization of (racemic) lactic acid solution at temperatures up to 140 °C yielded a non-crystalline residue with was sirupy in the heat but solid at room temperature. This residue was insoluble in water, soluble in ethanol or diethyl ether and yielded lactic acid on hydrolysis [22]. This residue was called "water free lactic acid", and the elementary formula $C_6H_5O_5$ was noted. Yet, the molar mass was not determined and no structural formula was presented, a logical consequence of the fact that even the formula of lactic acid itself was unknown at that time (see Formula 2.1) [1–3]. Synthetic route and properties of this material perfectly agree with poly(D,L-lactide) having a random stereosequence. As it became known much later, such a polylactide is an amorphous mass with a Tg of 45–50 °C (depending on the molar mass). Hence poly(D,L-lactide) represents not only the first polycondensate, but also the first synthetic polymer at all, a fact, which is largely ignored in the literature of polymer science. It is one of the numerous ironies in the history of polymer science that the usefulness of the first polycondensate was ignored for almost 150 years.

In 1849 [23] Engelhardt reported that the distillation of lactic acid yields a residue which was identical with the "water free lactic acid" of GayLussac and Pelouze. A cyclic dimeric ester called lactide was first identified by Henry in 1863 [24] who published a correct determination of its molar mass. However, the term lactide was known before and was the reason why later several authors coined the terms "glycolide" and "salicylide" for the condensation products of glycolic acid and salicylic acid, respectively. By distillation of lactic acid in a stream of air around 150 °C Wislicenus [25] found small amounts of both L,L- and racemic D,L-lactide. He did not measure their optical rotations, but he reported their different melting points: 97 and 125–126 °C, respectively. Racemic D,L-lactide was later prepared by Bischoff and Walden in two ways, namely by heating the sodium salt of a-bromo propionic acid in vacuo [26, 27] or by heating of K_2CO_3 with the anhydride of a-bromo propionic acid [28] (see Formula 2.1). A detailed study of all stereoisomers of lactide was later published by Jungfleisch and Godchot [29, 30], but nobody showed interest in polylactides before the end of World War I.

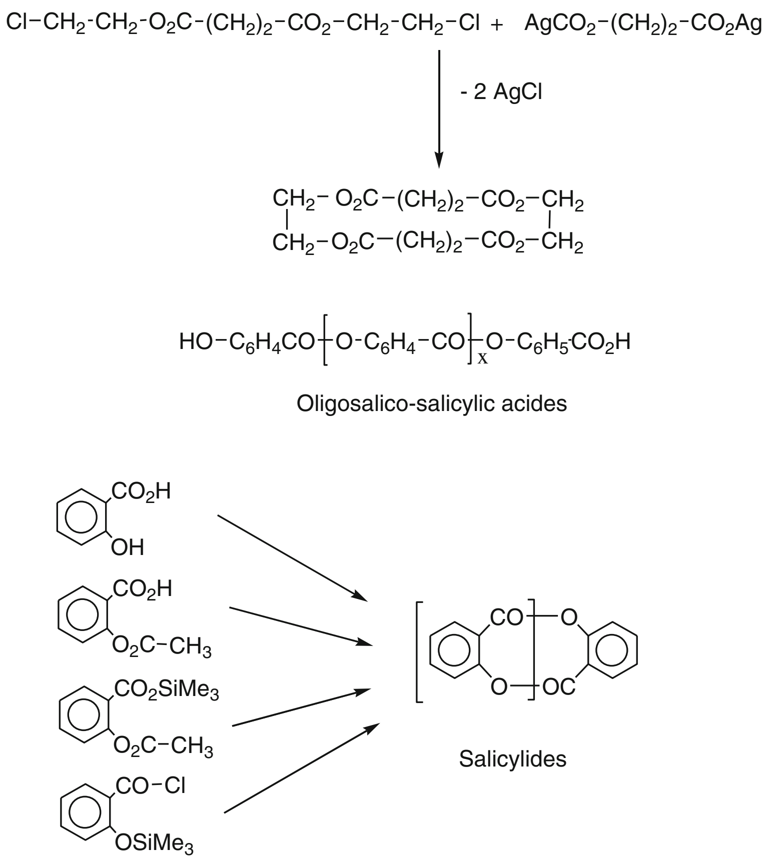
The first synthesis of a polyglycolide was reported by Desaignes in 1854 [31], who heated tartaric acid to 300 °C and obtained a crystalline high melting solid (Tm = 220 °C) which upon hydrolysis yielded glycolic acid. Desaignes called this product glycolide and did not recognize its polymeric structure. A few years later Kekule [32] and Norton and Tschaerniak [33] obtained a high melting polyglycolide by heating potassium or sodium chloroacetate (see Formula 2.1), and assumed again that a low molar mass polyglycolide was formed, but no molar mass measurements were performed. More than 30 years later, Anschütz and Schroeder suspected that these so-called glycolides possess a polymeric structure and began to study the (poly)condensation of glycolic acid [34–36]. Upon heating in vacuo they were able to isolate a crystalline, dimeric glycolide melting at 82–83 °C which confirmed their suspicion. Finally Bischoff and Walden [37] prepared the cyclic, dimeric glycolide by heating sodium bromoacetate in vacuo. They also observed that this glycolide yields the high melting polyglycolid upon heating with traces of water or zink chloride. Furthermore, they found, that heating of polyglycolide in vacuo allows for a depolymerization yielding the cyclic dimer. With these results the relationship between glycolide and polyglycolide was clarified, but the structure of polyglycolide with regard to end groups or cyclic character was not elucidated yet.

Meanwhile it was found that ß-hydroxy carboxylic acids eliminate water upon heating yielding unsaturated acids, whenever a proton existed in a-position. Therefore Blaise and Marcilly [38] focused their experiments on the dehydratization of ß-hydroxy pivalic acid (see Formula 2.1).Upon heating to 200 °C or upon treatment with conc. sulfuric acid at 60 °C they obtained an almost insoluble solid which was purified by washing with water and diethyl ether. They found a Tm of 165 °C and elemental analyses agreeing with the values of poly(pivalolactone). They presented formulas of linear chains having one CH_2OH and one CO_2H end group. From cryoscopic measurements in phenol they estimated a molar mass of 620 Da or a DP of 6 (presumably underestimating the real DP). Like all other researchers before Word War I these authors believed that their products were monodisperse. Polydisperse mixtures of cycles or linear chains were never taken into account. Concerning polyester of aliphatic hydroxy acids preparation and polymerization of δ-valerolactone should also be mentioned. δ-Valerolactone and the polylactone were prepared by Cloves [39] from δ-chloro valeric acid, and he also found that heating of γ-chloro-, γ-bromo-, and γ-iodo butyric acid exclusively yields γ-butyrolactone. One year later Fichte and Beiswenger [40] reported that δ-valerolactone spontaneously polymerizes when stored at room temperature and that the lactone can be recovered by heating the polylactone in vacuo.

(Poly)condensations of ethylene glycol and succinic acid were first studied by Lourenco [41–44] who heated these monomers under various reaction conditions with temperatures up to 300 °C. He isolated oligoesters having carboxylic end groups, but he also obtained a neutral polyester giving elemental analyses in agreement with those of the repeat unit. Apparently the same product ($Tm = 90$ °C) was prepared by Davidoff [45] from silver succinate and dibromoethane. Molar mass measurements were not conducted and the structure of these products remained unclear. About 8 years later polycondensations of ethylene glycol and various dicarboxylic acids were studied by Vorländer [46]. From the experiments outlined in Formula 2.2 he concluded that the neutral ethylene succinate melting at 90 °C is most likely a cyclic dimer, but he did not exclude the formation of a linear polyester.

Not only aliphatic, but also aromatic hydroxyl acids and diphenols were subjected to condensation experiments, and salicylic acid was in the focus of several research groups. In 1859, Gerhardt [47] observed that the treatment of sodium salicylate with $POCl_3$ yielded a mixture of products which was fractionated by washing and extraction with water, ethanol, and diethyl ether. An almost insoluble white powder remained the elemental analyses of which agreed with those of a repeat unit. This product was called salicylide and speculatively interpreted as analog of lactide. Yet a structural formula was not presented, and the structure of lactide was still unclear at that time.

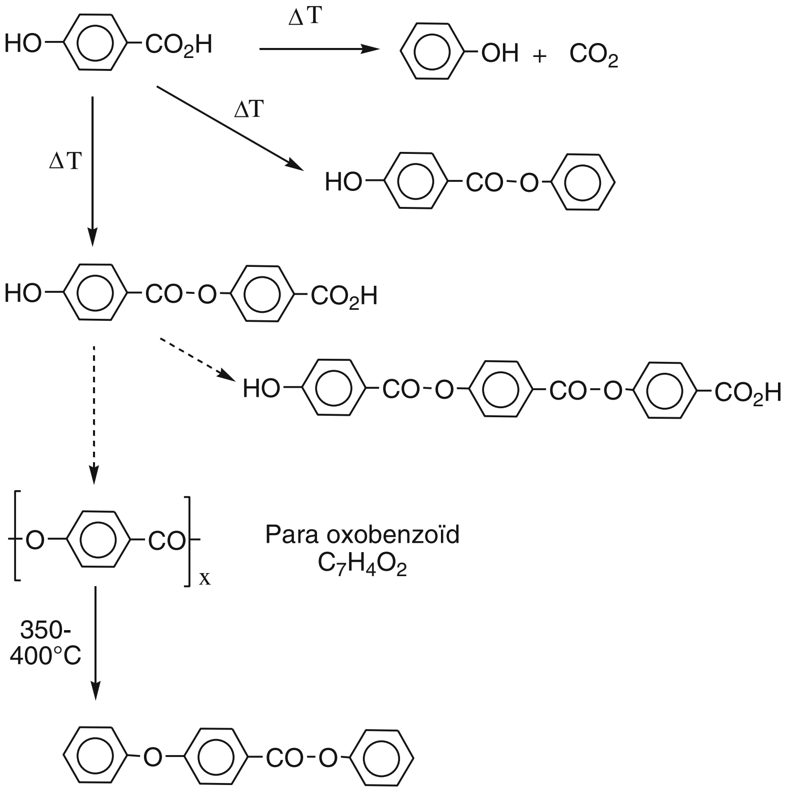
In a detailed study of salts and derivatives of salicylic acid Kraut [46] heated salicylic acid with acetyl chloride under variation of the reaction conditions. He isolated products which were interpreted as linear oligoesters called salico salicylic acid and trisalico salicylic acid (see Formula 2.2). He also reinvestigated the condensation of sodium salicylate with $POCl_3$ and interpreted the resulting salicylide as



Formula 2.2

linear heptameric oligoester (see Formula 2.2). Schiff [48] repeated the condensation of salicylic acid with $POCl_3$ and criticized the interpretation of Kraut Schiff concluded that the C_6H_4 units are connected by ether and not by ester groups. About 20 years later Anschütz [34, 49–52] launched a comprehensive study of salicylic acid derivatives and their condensation products. He synthesized salicyl chloride by means of thionylchloride (which became available after 1890), but he also performed polycondensations of salicylic acid and $POCl_3$. From his numerous results, Anschütz concluded that the main reaction products of all polycondensations are cyclic oligoesters which he called again salicylides. He believed that the crystalline α- and ß-salicylide he had isolated from several experiments were two isomers of the cyclic dimer. He also isolated a cyclic tetramer which formed a complex with chloroform, and he called a less soluble fraction of higher molar mass "polysalicylide". In 1951, three British chemists [53] re-examined the work of Anschütz. They used various methods for reliable determination of the molar masses and they included X-ray measurements of pure crystalline substances. They reached the conclusion that the so-called α-salicylide was indeed a cyclic dimer, but ß-salicylide a cyclic trimer. The identification of the cyclic tetramer was confirmed and a cyclic hexamer was isolated from the high molar mass fraction. Their experimental work also included the new synthetic methods of Einhorn [54, 55] who had performed condensations of salicylic acid with $COCl_2$ or $POCl_3$ in pyridine, reaction conditions which favor the formation of low molar mass cyclics. Again 50 years later Kricheldorf et al. [56] examined the crude reaction products of several monomers and condensation methods (see Formula 2.2) by Fast Atom Bombardment mass spectrometry and found that cyclic oligoesters were the main reaction products of all experiments. In addition to the before mentioned rings the cyclic pentamer, heptamer, octamer, and nonamer were identified. Furthermore, it was found by means of MALDI-TOF mass spectrometry [57] that salicylic acid imparts a high cyclization tendency in copolyesters derived from m-hydroxybenzoic acid or other aromatic monomers. Hence, Anschütz's understanding of polycondensations of salicylic acid and its derivatives was eventually confirmed, and Kraut's assumption of linear oligoesters as main reaction products (favored by previous reviewers of the history of polymer science [58, 59]) was disproved. Finally, it should be mentioned that in 1862 Märker [60] reported on the pyrolysis of salicylide. A product with the elemental formula C_6H_4O was isolated. This finding was confirmed by Kraut [61] and this polymer was called phenyleneoxide, but its molar mass and structure were never characterized.

Polycondensations of m-hydroxybenzoic acid or its para isomer were less intensively studied Schiff [62] conducted polycondensations of both hydroxybenzoic acids with $POCl_3$ at 40–50 °C. The linear dimer was extracted from the reaction product of m-hydroxybenzoic acid and the insoluble reminder was considered to consist of the linear octamer, but convincing evidence for this conclusion was not presented. The only product isolated from analogous condensations of p-hydroxy benzoic acid was speculatively interpreted as tetramer. Two more research groups [62, 63] performed "dry distillations" of p-hydroxy benzoic acid, but the intractable reaction products were not characterized. A more informative study was presented by Klepl [64, 65] who analyzed the reaction products of the "dry distillation" in more detail. He observed that the melt loses phenol and carbon dioxide above 300 °C. In vacuo phenyl p-hydroxy benzoate distilled out of the reaction mixture and a solid residue was left. When the heating was stopped after 15 min, the dimer was found as the main component of the reaction mixture and a trimer was also isolated (see Formula 2.3). The insoluble and infusible residue remaining after intensive extraction with ethanol was correctly interpreted as polyester and called "paraoxibenzid". Heating of this polyester to 400 °C yielded the phenyl ester of p-phenoxy benzoic acid (see Formula 2.3). All these products were confirmed in later studies (see Chapter 14). Particularly interesting is the observation of Klepl that "paraoxibenzid" is rather stable up to 350 °C, but decomposes rapidly at higher temperatures. In later studies, it was found by DSC and X-ray measurements that poly(p-oxybenzoate) has a phase transition from a crystalline to a smectic state around 330–340 °C.



Formula 2.3

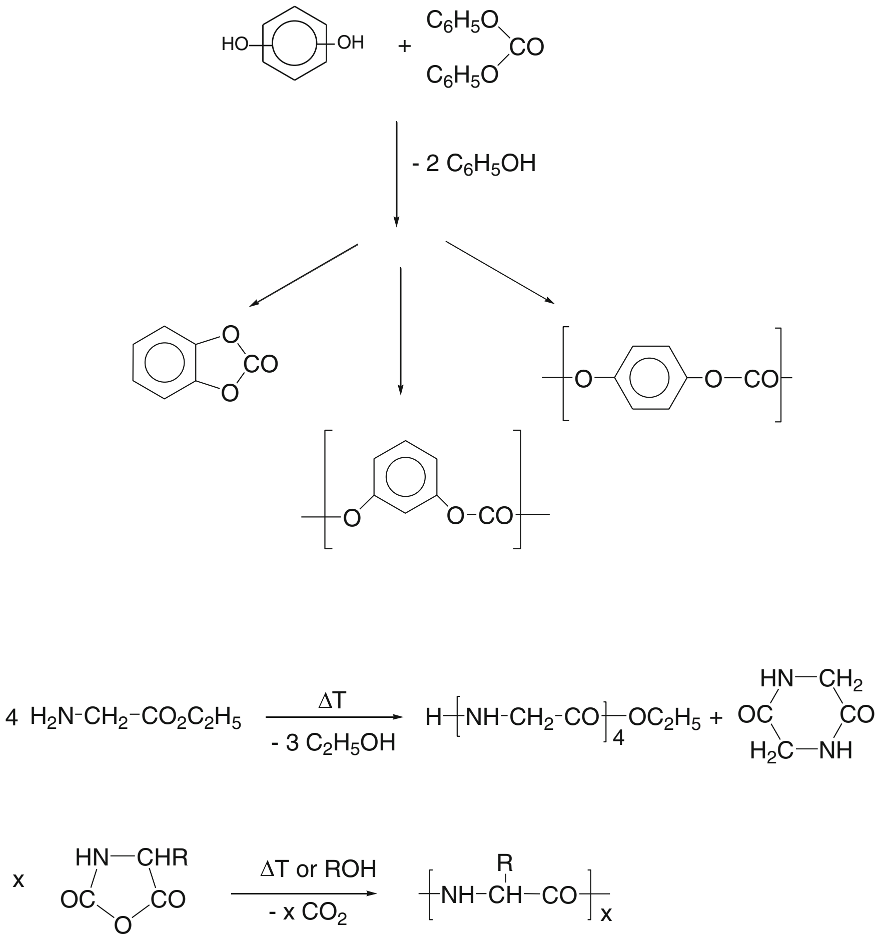
Although the smectic state is a solid phase, it is characterized by a high segmental mobility which favors chemical reactions.

Another class of aromatic polyesters, namely polycarbonates, was first prepared by Bischoff and Hedenström [66]. Those authors studied syntheses and properties of diphenyl carbonate, diphenyl oxalate and diphenyl esters of higher dicarboxylic acids. In this context, they performed polycondensations of diphenyl carbonate with catechol, resorcinol, and hydroquinone. The diphenols were heated with diphenyl carbonate up to 250 °C, and above 195 °C the liberation and distillation of phenol was observed. In the case of catechol the crystalline, monomeric, cyclic carbonate was isolated (see Formula 2.4). From resorcinol and hydroquinone insoluble, high melting residues were obtained which were purified by intensive washing with ethanol and hot diethyl phthalate. It was noted that the elemental analyses agreed with the "neutral carbonates" of the diphenols, but no comments on structure or molar mass were made. Oligomeric carbonates were also prepared by Birnbaum and Lurie [67] from resorcinol either by reaction with phosgene or by heating with cyanuric acid. A cyclic formula was presented, but molar mass measurements were not conducted.

2.3 Polypeptides and Polyamides

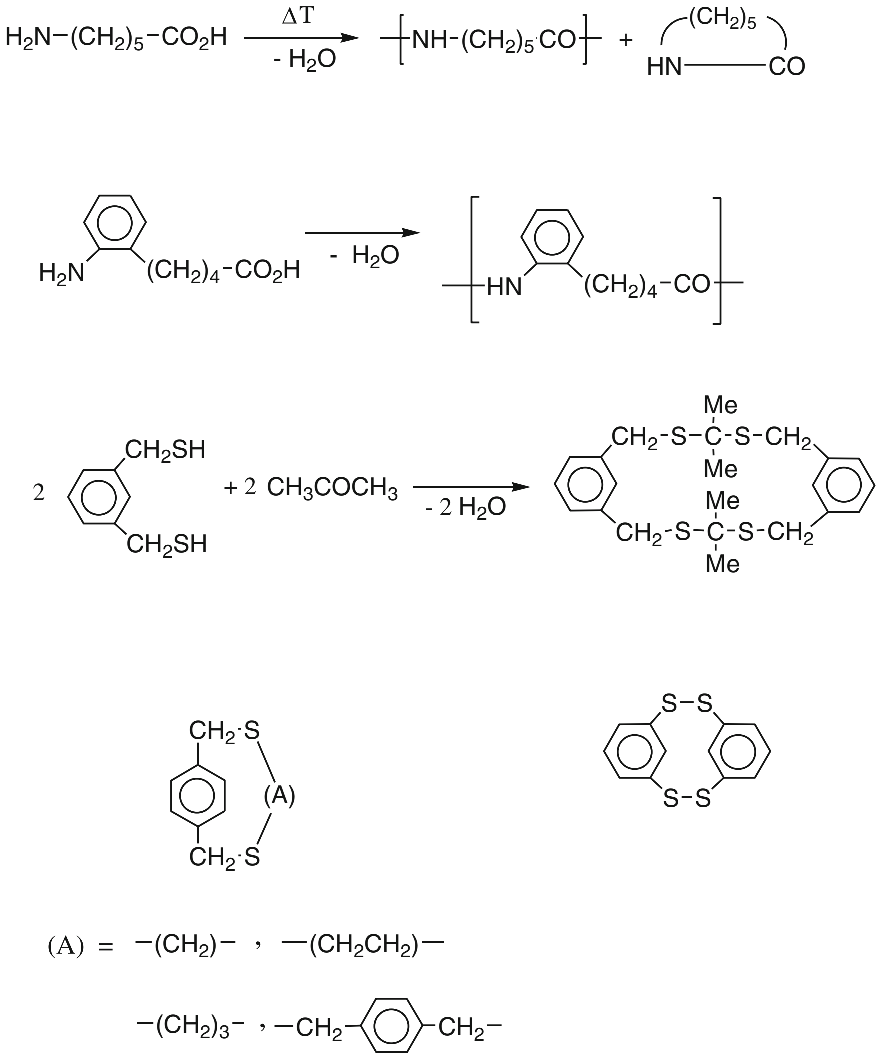
Experiments yielding oligopeptides and polypeptides were also reported before World War I. Curtius [68, 69], who systematically worked on amino acid and peptide chemistry, observed that the ethyl ester of glycine undergoes a spontaneous condensation process upon storage at room temperature. He also observed that two products were formed, the cyclic dimer (2,5-diketopiperazine) and the ethyl ester of the linear tetraglycine (see Formula 2.4). Higher oligomers were not found, seemingly, because the precipitation of the tetramer in the form of a ß-sheet structure hindered the further chain growth. He also found that for unknown reasons the presence of moisture favors the formation of the cyclic dimer at the expense of the linear tetramer. Two more research groups [70–72] obtained undefined oligoglycines by heating glycine in glycerol to 150–170 °C. However, Maillard [72] speculated that the high molar mass fraction of his reaction products mainly consisted of the cyclic octamer. High molar mass polypeptides were certainly obtained by Leuchs et al. via ring opening polymerization of a-amino acid N-carboxyanhydrides (NCAs) also called Leuchs's anhydrides [73–75]. Despite the elimination of carbon dioxide in every growing step (see Formula 2.4), the polymerization of NCAs is not a polycondensation, but a special case of chain growth polymerization labeled condensative chain polymerization according to IUPAC and is discussed in Chap. 16.

In addition to oligo- and polypeptides a several oligo- and polyamides were also prepared before World War I. (Poly)Condensations of diamines were mentioned by six research groups [76–81]. Hofmann noted in 1872 the formation of an intractable, apparently amorphous mass upon heating of 1,2-diaminoethane with diethyl oxalate [76]. Again 1,2-diaminoethane or a mixture of phenylene diamines were heated by Freund with the diethylester of malonic acid [77]. Yet, with exception of nitrogen elemental analyses he did not provide any characterization of his solid, poorly soluble reaction products. Michler and Zimmermann [78] reported that condensation of phosgene with m-diaminobenzene yielded a cyclic monomeric urea having softening temperature above 300 °C. Yet, a cyclic monomeric urea is for steric reasons impossible, and the authors certainly synthesized a mixture of cyclic and linear oligoureas. Meyer studied numerous condensations of various aromatic o-, m-, and p-diamines with esters or chlorides of aliphatic dicarboxylic acids [79]. Surprisingly he only described the isolation of crystalline cyclic monomers and dimers without mentioning polymeric byproducts. Ruggli [80] studied (poly)condensations of ω,ω'-diamino tulane with phosgene or dicarboxylic acid dichlorides. He purposely worked at low monomer concentration to favor the formation of cycles at the expense of polyamides. Fischer [81] correctly formulated formation of a polyurea prepared by heating of 1,4-diamino butane with CO_2 under pressure to 220 °C. In 1899, Gabriel and Mass [82] studied (poly)condensations of ω-amino acids. Upon heating of γ-aminobutyric acid or δ-aminovaleric acid to temperatures above 200 °C those authors



Formula 2.4

exclusively isolated the corresponding lactams, but from 6-aminohexanoic acid (called ε-leucine at that time) 20–30 % ε-caprolactam was obtained and an insoluble hard mass, a polyamide which was later called Nylon-6 or Perlon (see Chap. 6). Manasse [83] prepared shortly later Nylon-7 analogously from 7-aminoheptanoic acid and noted that in this case no lactam was detectable. Five years later von Braun [84] confirmed the results of Gabriel, Mass, and Manasse. Furthermore, he prepared a new polyamide by heating of 5-(o-aminophenyl)valeric acid (see Formula 2.5), whereas the seven-membered lactam was the main product, when 4-(o-phenyl)butyric acid was heated.



Formula 2.5

2.4 Various Polycondensates

Three research groups[85–88] worked on syntheses and characterization of oligo- and poly(ethylene glcol)s. Lourenco [85, 86] heated ethylene glycol and 1,2-dibromoethane to 120 °C for several days, and isolated oligo(ethylene glycol)s up to the hexamer by fractionated distillation. He also concluded that continuation of this series might in principle result in the formation of poly(ethylene oxide). Wurtz [87] prepared oligo(ethylene glycol)s or their acetates by heating oxirane with acetic acid or its anhydride. Yet, these polymerizations involved condensation steps only during fractionated distillation of the reaction products at temperatures up to 300 °C. Oligo(ethylene glycol)s and true poly(ethylene glycol) (*Tm* = 56 °C) were also obtained by Roithner via ring-opening polymerization of oxirane [88].

Condensation reactions yielding cyclic and/or linear oligosulfides were studied by four research groups [89–93]. In 1863, Husemann [89] prepared an intermediate by condensation of 1,2-dibromoethane with sodium sulfide. By heating he obtained the cyclic dimer, dithiane, as a volatile degradation product. Mansfeld [90] reinvestigated this reaction and interpreted the intermediate as polymer, but he speculatively assigned the formula of a cyclic trimer. Husemann also prepared poly(methylene sulphide) from dibromomethane and sodium sulfide. Furthermore, he performed condensations of dibromomethane and dibromoethane, respectively, with sodium trithiocarbonate, which was easily obtained from sodium sulfide and carbon disulfide. He isolated a five-membered cyclic ethylene trithiocarbonate, but a polymeric methylene trithiocarbonate the molar mass of which remained obscure.

In the years 1900–1909, Autenrieth, Beuttel, and Kötz [91–93] studied syntheses and reactions of the α,α-dimercaptanes of ortho-, meta-, and para-xylene. The main purpose of the condensation reactions with aldehydes, ketones, and dibromoalkanes was the isolation of cyclic compounds. For instance, oligomeric condensates were obtained when the meta dimercaptane was reacted with aldehydes, whereas a crystalline cyclic dimer was isolated with acetone as reaction partner (see Formula 2.5). In the case of the para dimercaptane crystalline dimeric cycles were also obtained with aromatic aldehydes. The condensations of the para dimercaptane with dibromoalkanes yielded several crystalline compounds which were interpreted as cyclic monomers (see Formula 2.5), although in most cases the monomeric structure is unlikely for reasons of ring strain. Another unlikely ring structure, namely a dimeric disulfide, was postulated by Zincke and Krüger [94] for the oxidation product of meta-dimercaptobenzene (see Formula 2.5).

Finally, it should be mentioned that Braun and Sobecki reported in 1911 [95] about the preparation of oligoalkanes. They extended the Grignard reaction to α,ω-dibromoalkanes. Starting out from 1,5-dibromopentane, decane, pentadecane and eicosane were isolated by fractionated distillation and characterized by elemental analyses and cryoscopy in benzene. The analogous dimer were obtained from 1,7-dibromoheptane and 1,10-dibromodecane. Twenty years later Carothers et al. [96] replaced magnesium by sodium and isolated pure alkanes up to heptakontane.

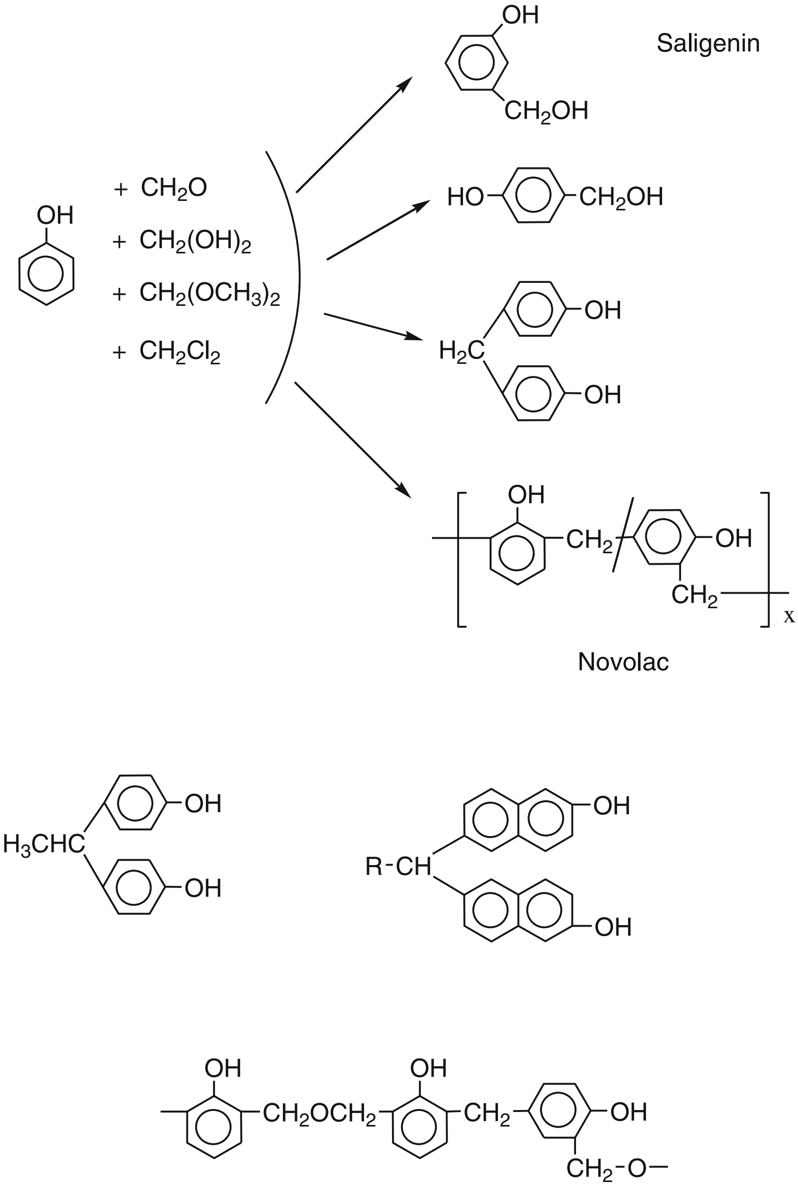
2.5 Bakelite and Related Polymers

The most intensively studied types of (poly)condensation studied before World War I were reactions between phenols and aldehydes. The interest in this field of chemistry like the interest in reactions of salicylic acid was partially motivated by the fact that extracts from the bark of willow trees have a pain-stilling effect (what was already known to the ancient Greeks). From willow trees and other plants saligenin was extracted (see Formula 2.6) which was understood as condensation product of phenol and formaldehyde. As early as 1861 Beilstein and Seelheim [97] observed that treatment of saligenin with $POCl_3$ yields a resinous product, the first synthesis of what was later called “Novolac”. The first study of phenol-aldehyde condensations was published in 1872 by von Bayer [98, 99] who was professor of organic chemistry at the universities of Berlin, Staßburg and München. Because of his numerous merits in the field of synthetic organic chemistry (including the first synthesis of indigo) he was awarded with the Nobel Prize in 1905. However, his contribution to the field of phenol-aldehyde condensations was of minor importance, because he was not able to identify reaction products. von Bayer used dimethoxymethane as reaction partner of phenol, because formaldehyde was not available before 1890. Regardless, if HCl or H_2SO_4 was used as catalyst, he obtained a resin similar to that described for the condensation of saligenin with $POCl_3$ [98].

Eight more research groups performed studies of phenol-aldehyde condensations before 1895 [99–106]. Their interest was focused on the isolation and characterization of low molar mass crystalline phenol, cresol, and naphthol derivatives, such as those outlined in Formula 2.5. The formation of resins was an undesired side reaction. Particularly remarkable was the finding of Manasse [101] that not only acids, but also bases catalyze condensations of phenols and aldehydes. With the work of Manasse two different reaction mechanisms became evident. Acid catalyzed condensations are based on the enhanced electrophilicity of aldehydes (or their derivatives) resulting from protonation or complexation with Lewis acids. The bases enhance the nucleophilicity of the phenol by deprotonation, because the phenoxide anions react easily with non-activated aldehydes. The different reaction mechanisms entail somewhat different chemical structures. Acid catalyzed resins, called “Novolac”, are produced from an aldehyde/phenol ratio <1.0 and contain only few ether groups (i.e., $CH_2–O–CH_2$). For base catalyzed syntheses aldehyde/phenol ratios around 1.5 are typical, and the “Resol” called resins contain a high percentage of ether groups (see Formula 2.6, bottom). Both types of resins are still used in the twenty-first century for a variety of applications [107].

After 1895 several scientists began to explore preparation, application, and commercialization of phenol-formaldehyde resins, and numerous patents were filed [108–124]. The motivation for these activities came from various sides. For wood and metal surfaces a chemically stable coating material was desired. And for the rapidly expanding application of electricity large amounts of insulating lacquers were needed. Mainly for the latter application shellac was used, a secretion of the “shellac beetle”. Due to this biogenic origin shellac was a relatively rare and expensive material. The name “Novolac” indicates that the phenol-formaldehyde resins were designed as new substitutes of the “old” shellac.

Other scientists were interested in a solid plastic as substitute of wood, metal, or celluloid [115–124]. To ease the molding or shaping process, these inventors kept small amounts of the reaction medium, glycerol, or camphor in the resins before or during the curing process. Furthermore, the curing temperature was kept <100 °C



typical segment of a "Resol" resin

Formula 2.6