Cyclic and Macrocyclic Organic Compounds – a Personal Review in Honor of Professor Leopold Ružička*

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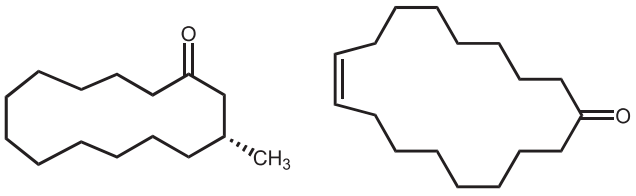
Ružička opened the field of cyclic molecules such as cyclic terpenes and cyclic ketones with up to 17 ring atoms. This work until now was extended in many directions such as cyclic paraffins, crown ethers and cryptands and cyclic ester amides. Cyclic molecules are formed upon electron transfer and intramolecular association of polymers with two active ends and they are synthesized by directed cyclization of bifunctional macromolecules. In the course of step growth polymerization and ring opening polymerization, ring chain equilibria may be established; the larger the monomer unit the easier is the separation of pure oligomers such as the heptamer of cyclododecene with 84 carbon atoms in the ring. Still many questions remain open, in particular whether there are macrocyclic catenanes in commercial polycondensates.

Keywords: *Cyclic compounds, macrocyclic compounds, synthesis*

Introduction

Leopold Ružička, born in Vukovar 121 year ago obtained his Ph. D. with Hermann Staudinger, joined Staudinger to ETH Zurich and worked as an assistant to Staudinger on pyrethroids, the insecticides in pyrethrum. For his habilitation, however, Ružička chose a topic of his own, which Staudinger disliked so much that he terminated the assistant position for Ružička. Hence, Ružička had to survive personally and scientifically on his own. This situation forced him to establish a model-like cooperation with industry. Since Ružička was familiar with pyrethrines which belong to the class of monoterpenes he was aware of their properties as insecticides as well as natural odoriferous products. Thus, it was obvious to cooperate with the perfumers Chuit, Naef Company and Firmenich, Geneva, and Haarmann & Reimer, Holzminden. His work at that time (1926) culminated in the analysis of the structure of muscone **1** and civetone **2**, two cyclic ketones with 15 and 17 carbon atoms, respectively (Fig. 1). These compounds were not only important for their odors but also their cyclic structure was quite unexpected.

After Kekulé had proposed the well-known simple ring structure for benzene with six ring atoms in 1865, the existence of cyclic molecules, in particular with more than eight atoms, was considered to be highly improbable. Ružička expanded his research to terpenes, found a number of cyclic compounds, built up by isoprene units, coined the expression polyprenes, and elucidated the structures of a number of sesquiterpenes, containing 3 isoprene units or 1,5 terpene units (Fig. 2).



1
muscone

2
civetone

Fig. 1 – *Structure of muscone and civetone*
Slika 1 – *Strukture muskona i civetona*

From there he worked out the chemical structure of the hormones androsterone and testosterone (Fig. 3) and synthesized them, almost at the same time as Butenandt.

Syntheses of cyclic compounds and polymerization reactions

The synthesis of cyclic compounds generally might be considered as an intramolecular reaction of bifunctional compounds with suitable functionalities. In most cases, however, the intramolecular reaction is in competition with the intermolecular reaction which results in the polymerization reaction. Therefore, one of the ingenious discoveries of Ružička was the oxidation of cyclic ketones (Fig. 4a) with Caro's acid (H_2SO_5) to give cyclic esters with the number of ring atoms increased by one.[1] A second discovery was the pyrolysis of α,ω-dicarboxylic acids using thorium(IV) or cerium(III) salts to yield – after decarboxylation – cyclic ketones with $n \leq 34$ (n: number of ring atoms) (Fig. 4b).[1] In 1933 Ziegler developed the intramolecular cyclization of

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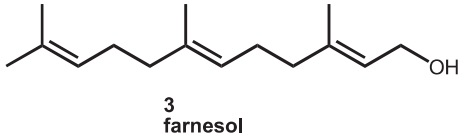
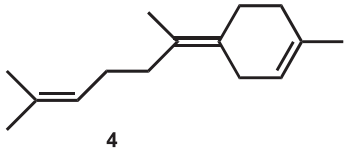
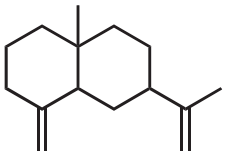


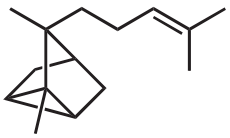
3
farnesol



4
bisabolene



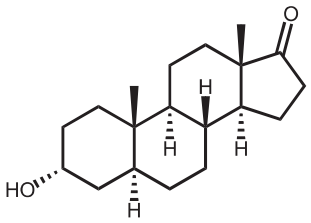
5
beta-selinene



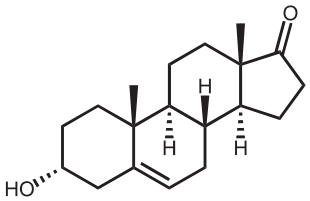
6
alpha-santalene

F i g. 2 – *Sesquiterpenes C15(H), "Polyprenes"*
S l i k a 2 – *Sesquiterpeni C15(H), "Polipreni"*

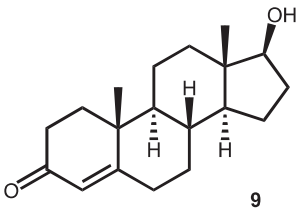
long chain dinitriles in the presence of e. g. lithium ethylanilide ($C_6H_5N(C_2H_5)Li$) in ether. Via the β-keto nitriles and the β-keto acids the cyclic ketones are formed with $14 < n < 33$ (Fig. 5). The intramolecular reaction is enhanced using the Ruggli-Ziegler high dilution principle.[1]



7
Androsterone

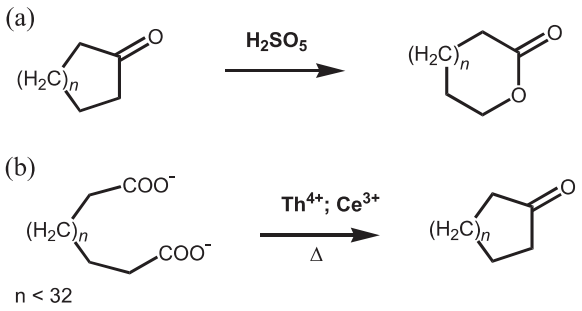


8
5-Dehydroandrosterone



9
Testosterone

F i g. 3 – *Structure of Androsterone, 5-Dehydroandrosterone and Testosterone*
S l i k a 3 – *Strukture androsterona, 5-dehidroandrosterona i testosterona*

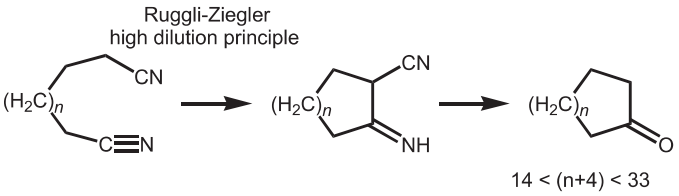


F i g. 4 – *Oxidation of cyclic ketones (a) and cyclization of dicarboxylates (b)*
S l i k a 4 – *Oksidacija cikličkih ketona (a) i ciklizacija dikarboksilata (b)*

In 1934 Stoll, Rouvé and Stoll-Comte[2] argued that the ratio *R* of cyclic compound to chain polymer is

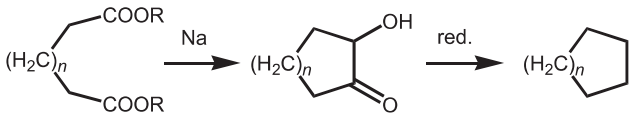
$$R = k_1 c / k_2 c^2 = C / c,$$

where *k* are the rate constants, *c* is the concentration, and *C* is the cyclization constant. Hence, the enhancement of intramolecular reaction is inversely proportional to the concentration. It should be mentioned that there is a number of other effects on the intramolecular reaction such as a template effect, a rigid group effect, a gauche effect etc.



F i g. 5 – *Cyclization of dinitriles*
S l i k a 5 – *Ciklizacija dinitrilnih spojeva*

Prelog and Stoll (1947) developed a very efficient method of cyclic compounds formation by dropping dicarboxylic esters into a hot suspension of sodium in xylene in nitrogen atmosphere while the sodium surface acts as the template (auxilary bond formation). Upon acid hydrolysis of the endiol the acyloin is formed which may be reduced to result the cyclic paraffines (Fig. 6).[1]

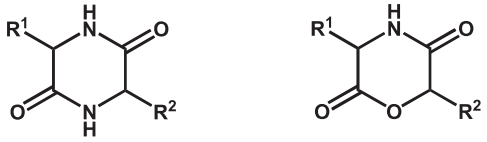


F i g. 6 – *Cyclization of diesters*
S l i k a 6 – *Ciklizacija diesterskih spojeva*

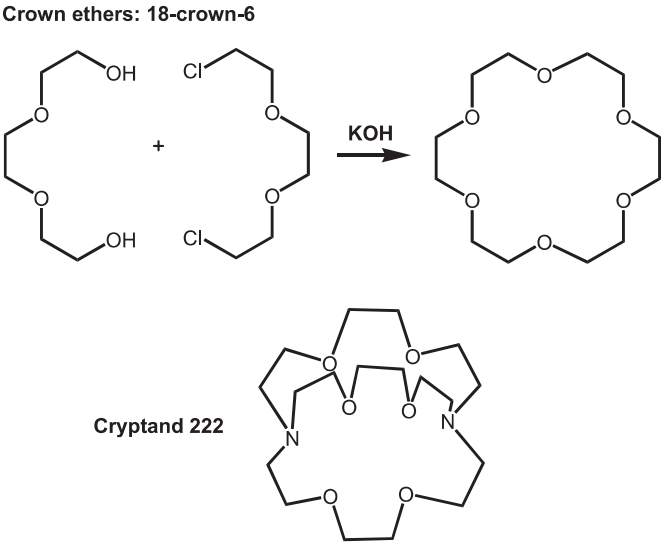
The 'auxilary bond' was also the clue when Pedersen in 1967 developed crown ethers, e. g. 18-crown-6, which was obtained by reaction of dihydroxy-dioxa-octane and dichloro-dioxa-octane with KOH (Fig. 7).[1] Later the threedimensional cryptands, bicyclic polyaminoethers with two nitrogen atoms bridged by three dioxa-octylene groups were synthesized.[3]

Macrocyclic compounds are quite frequent in nature.[4] Examples are cyclodepsipeptides, with the antibiotic valinomycine being a representative, and macrolides with nonactine being a representative. Moreover, cyclic DNA[5] is found, e. g., in viroids (Fig. 8).

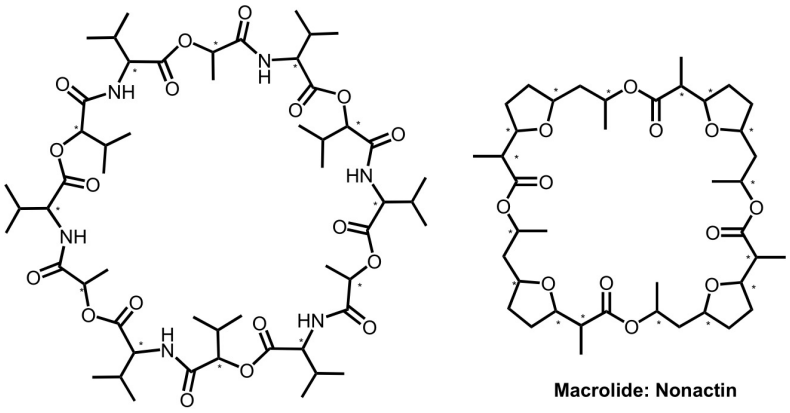
In carbon chemistry, penta- and hexacycles are easily formed.[6] Thus, from hydroxy butyric acid and hydroxy valerianic acid the cyclic esters are readily formed. Correspondingly, cyclic dipeptides, diketopiperazines, as well as cyclic condensation products of an α-amino acid and an α-hydroxy acid, cyclic depsipeptides, are readily obtained (Fig. 9). Cyclic esteramides with larger ring size are synthesized e. g., via an S_N2 substitution addition mechanisms from ε-caprolactam and bromopivalic acid chloride yielding 3,3-dimethyl-5-aza-1-oxacycloundecane-4,11-dione (Fig. 10).

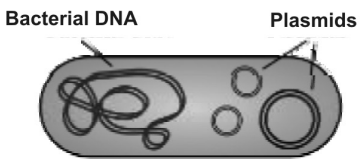


F i g. 9 – *Diketopiperazines and depsipeptides*
S l i k a 9 – *Diketopiperazini i depsipeptidi*

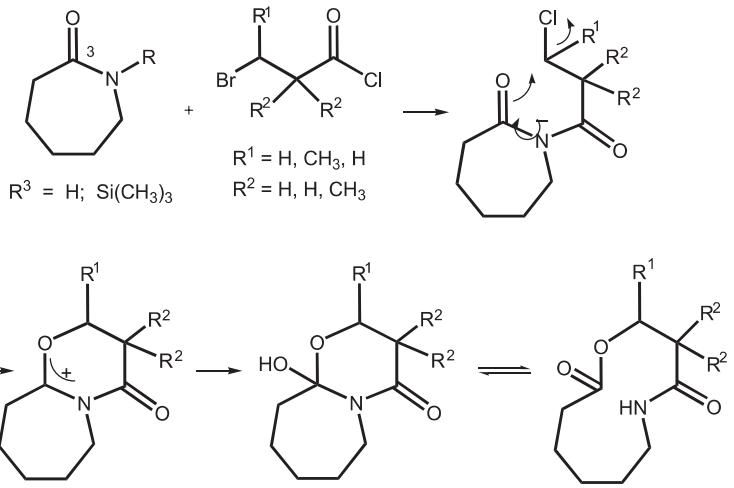


F i g. 7 – *18-Crown-6 and Cryptand 222*
S l i k a 7 – *18-kruna-6 i kriptand 222*





F i g. 8 – *Valinomycine, nonactin, and circular DNA*
S l i k a 8 – *Valinomicin, nonaktin i kružna DNA*

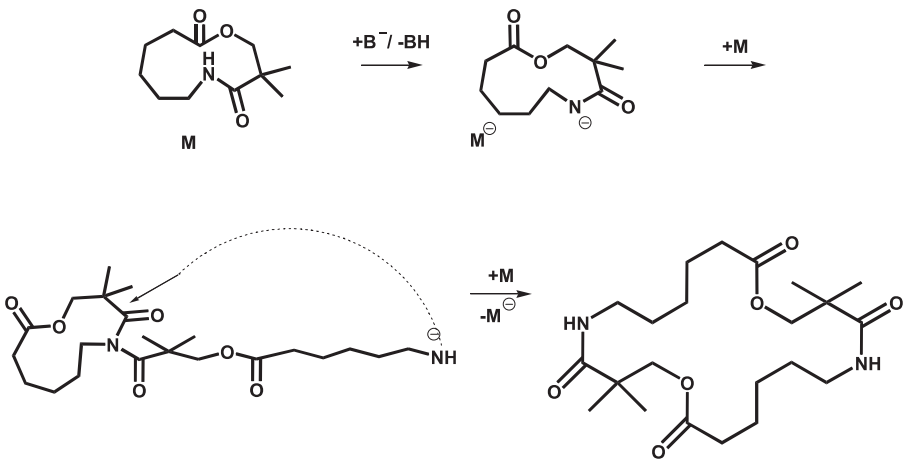


F i g. 10 – *Synthesis of 11-membered cyclic ester amides*
S l i k a 10 – *Sinteza 11-članog cikličkog esterskog amida*

The ring-expansion of *N*-(3-halogenoacyl)-ε-caprolactam occurs in the presence of water in alkaline medium. Under these conditions an intramolecular substitution of the halogen atom takes place which is induced by a nucleophilic attack of the carbonyl oxygen followed by addition of water and formation of the cyclol. The cyclol is in equilibrium with the cyclic ester amides. The yields of the corresponding cyclic ester amides are low for R^2 = H; in this case elimination of HX takes place with formation of *N*-crotonyl or *N*-acryloyl groups. In the absence of this side reaction the yields increase to 60 %.

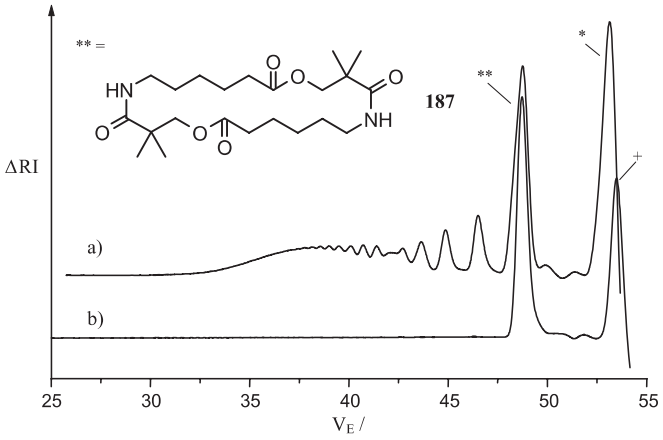
These monomers were polymerized anionically (Fig. 11). The initiation reaction is the deprotonation of the amide nitrogen. The anion formed adds to the amide carbonyl group of a second monomer molecule with ring opening and formation of an *N*-acylamide. In the contrast to the polymerization mechanism of ε-caprolactam the amide anion adds intramolecularly to the acylated amide carbonyl group under insertion and ring enlargement to form the cyclic tetraesteramide anion. Proton transfer and growth reactions result in strongly alternating macrocyclic polyesteramides.[7]

SEC (Size Exclusion Chromatography)-analysis of the oligomers prepared with K-naphthalin as initiator in bulk revealed no UV-absorption, showing that the naphthalin



F i g. 11 – *Polymerization mechanism of cyclic 11-membered ester amides*

S l i k a 11 – *Mehanizam polimerizacije 11-članog cikličkog esterskog amida*



F i g. 12 – *Size exclusion chromatogram (SEC) (refractive index, RI vs. elution volume, V_E) of cyclic ester amide oligomers*

S l i k a 12 – *Kromatogram isključenja po veličini (SEC) (indeks refrakcije, RI vs. volumen eluiranja, V_E) cikličkih ester-amidnih oligomera*

moiety is not incorporated into the polymer (Fig. 12). In addition, one of the oligomers has the same elution volume as the cyclic dimer. An SEC calibration plot of these oligomers shows a linear dependence of the degree of oligomerization on *n* on the elution volume. This calibration plot, however, is different from the plot obtained for the linear oligomers which are prepared via polycondensation reactions of a linear precursor. The elution volume of the cyclic oligomers is higher as compared to the linear oligomers of the same degree of oligomerization, this is what is to be expected from theoretical considerations.

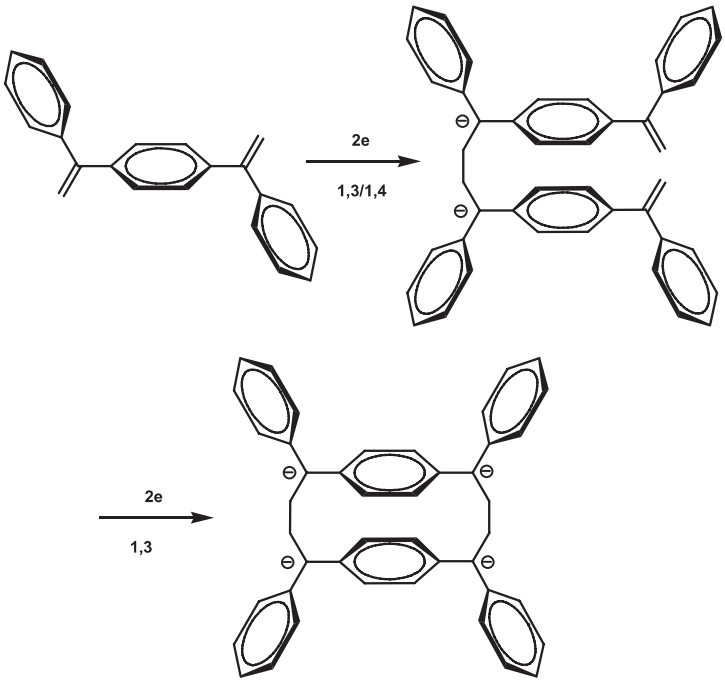
Cyclic compounds via electron transfer reactions

1,1-Diphenylethylene for steric reasons is not homopolymerizable. Electron transfer from e. g. sodium naphthalene yields the radical anion which under combination reaction forms the dimeric dianion. When molecules which comprise the 1,1-diphenylethylene structure twice with conjugated double bonds (1,4-bis(1-phenylvinyl)benzene) or with isolated double bonds (1,3-bis(1-phenylvinyl)benzene) are subjected to electron transfer, for the 1,4-compound (conjugated double bonds) the dimeric dianion is formed with the external double bonds being intact, however, now in isolated fashion. After protonation and isolation and upon electron transfer reaction, the two double bonds react independently of each other forming radical anions and undergoing intra- and intermolecular combination reactions resulting in a homologous series of cyclic oligomers and polymers (Fig 13).

In the case of the 1,3-compound (isolated double bonds) the two double bonds react independently of each other and thus the monomeric dianion diradicals are formed which undergo dimerisation reaction to yield the cyclic dimeric tetraanion which may be used as a tetrafunctional initiator for the living anionic polymerization of styrene.[8]

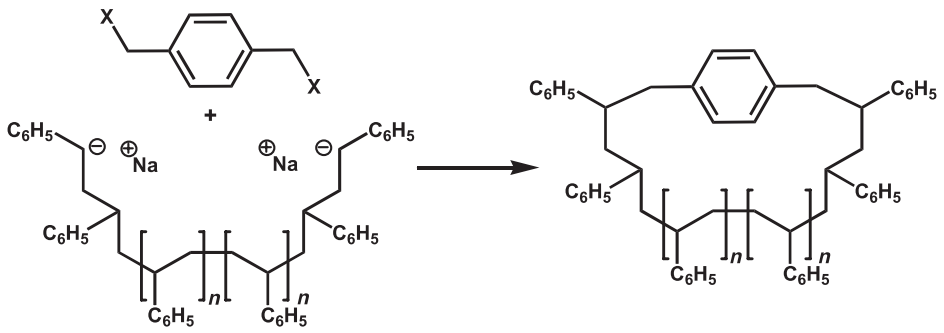
Macrocyclic polymers

When Staudinger analyzed the first macromolecules he was unable to find experimental evidence for the presence of end groups (because of their extremely low concentration) which mislead him to the conclusion that these macromolecules might be cyclic. Only when the end groups were successfully labeled with dye residues they could be ana-



F i g. 13 – *Cyclization of 1,4-bis(1-phenylvinyl)benzene induced by electron transfer reaction*

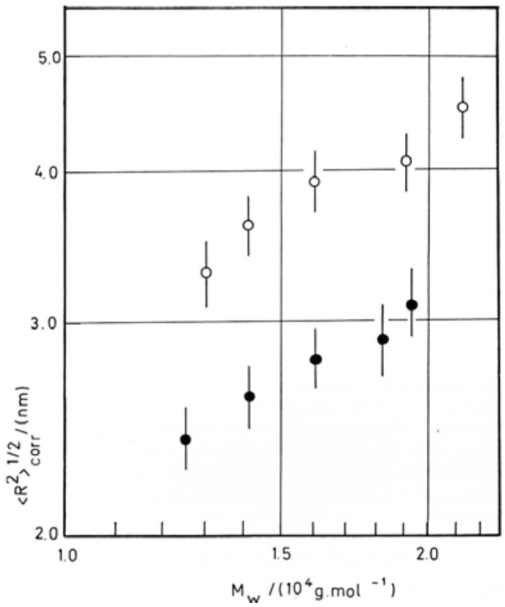
S l i k a 13 – *Ciklizacija 1,4-bis(1-fenilvinil)benzena uzrokovana reakcijom prijenosa elektrona*



F i g. 14 – *Synthesis of cyclic polystyrene*
S l i k a 14 – *Sinteza cikličkog polistirena*

lyzed and even used to determine the number average of the molecular weight. On the other hand, macrocyclic polymers are conceivable both for polyaddition and polycondensation polymerization[6] as well as for ring opening polymerization reaction. Before addressing this topic, however, the directed synthesis of macrocyclic polymers should be considered.

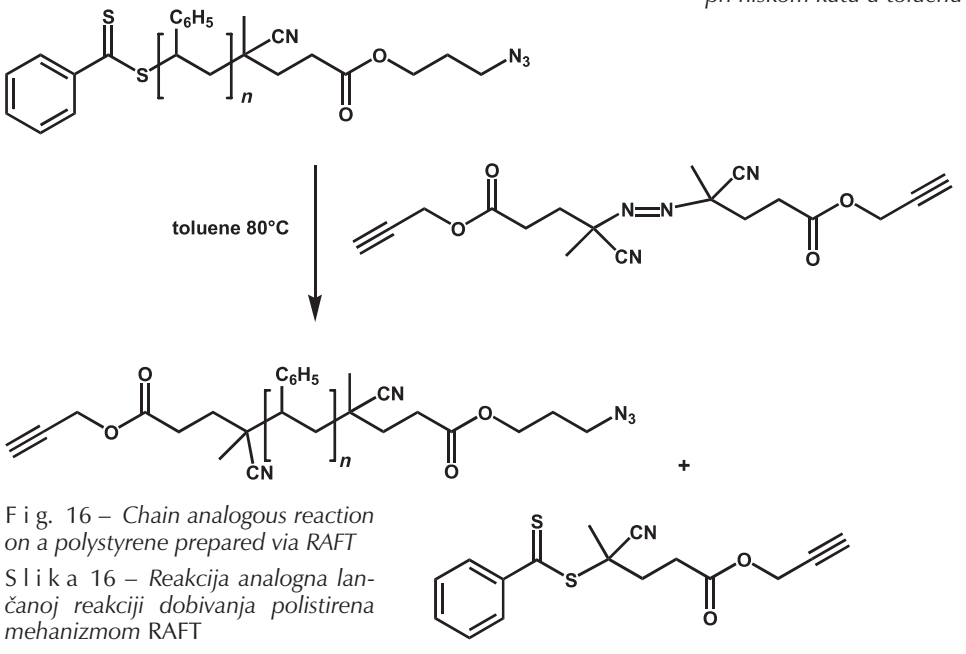
In 1980 three groups[9–11] almost simultaneously used the anionic polymerization of styrene (Fig. 14) with a bifunctional initiator to obtain bifunctionally living polystyrene which was reacted with 1,4-bis(chloromethyl)benzene under high dilution conditions – simultaneous addition of the living polymer and the cyclizing agent to a large volume of a suitable solvent. Molecular weights up to a few ten thousands was obtained. Polycondensation reaction could be excluded and the macrocycles were characterized by means of size exclusion chromatography, viscosity measurements in solution and low angle neutron scattering in toluene-d_8. The ratio of the mean square radius of gyration of cyclic and acyclic molecules (Fig. 15) was found to be 0.5 (as actually expected for a Θ-solvent).[12]



F i g. 15 – *Radius of gyration as a function of molecular weight for cyclic (●) and acyclic (○) polystyrene as obtained from low angle neutron scattering in toluene-d_8*

S l i k a 15 – *Polumjer vrtnje kao funkcija molekulske mase cikličkog (●) i acikličkog (○) polistirena dobiven raspršenjem neutrona pri niskom kutu u toluenu-d_8*

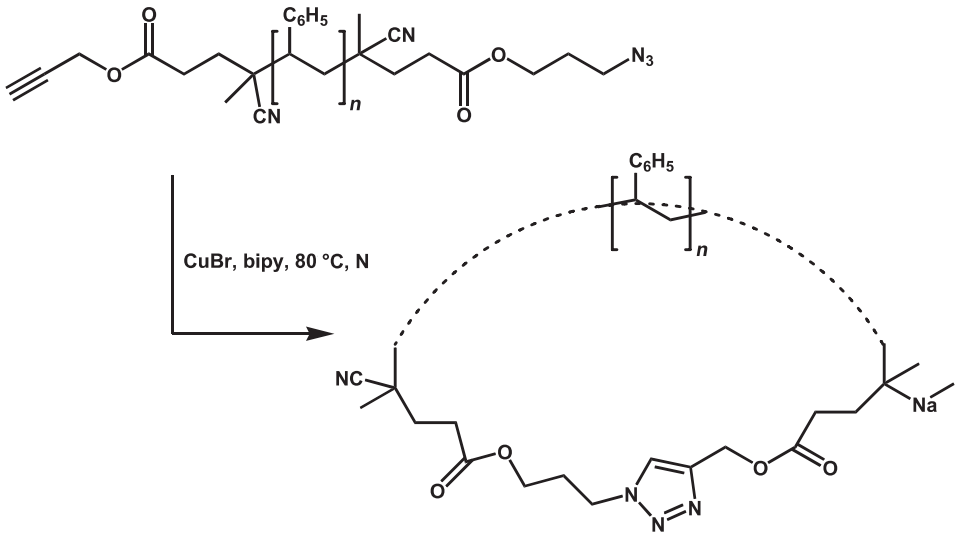
As a consequence, the SEC elution volume of cyclic molecules is larger than that of linear molecules of equal molecular weight (the ratio of molecular weights of cyclic and acyclic molecules eluted at the same elution volume was found to be ca. 1.4), the ratio of intrinsic viscosities of cyclic and acyclic molecules was found to be 0.66 which is close to the theoretically expected value.[9]



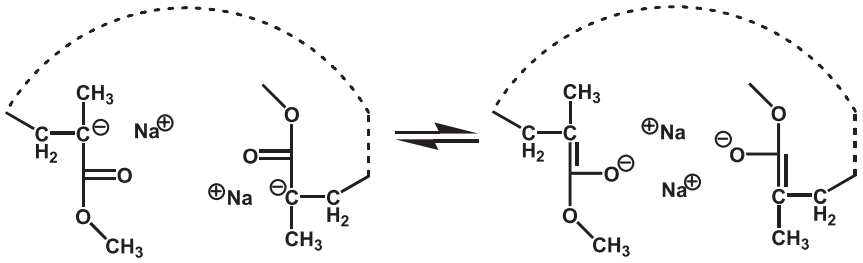
F i g. 16 – *Chain analogous reaction on a polystyrene prepared via RAFT*

S l i k a 16 – *Reakcija analogna lančanoj reakciji dobivanja polistirena mehanizmom* RAFT

Later on much larger macrocycles were synthesized and characterized by Roovers and Toporowski.[13] And the interest in macrocyclic polymers still continues when reversible addition fragmentation chain transfer (RAFT) polymerization is combined with the Huisgen 1,3-dipolar cycloaddition of an azido group to an alkyne group, called click chemistry by Sharpless (Figs. 16 and 17).[14] The azido end group is introduced via the azido



F i g. 17 – *Cyclization of telechelic polystyrene via click reaction*
S l i k a 17 – *Ciklizacija telekeličnog polistirena putem "click"-reakcije*



F i g. 18 – *Macrocyclic association of the chain ends of living poly(methyl methacrylate) (PMMA) initiated with a bifunctional initiator*
S l i k a 18 – *Makrociklička asocijacija krajeva lanca živućeg poli(metil-metakrilata) (PMMA) inicirana difunkcionalnim inicijatorom*

dithiobenzoate RAFT agent and the dithiobenzoate end group of the polystyrene is exchanged by means of an azo initiator with two alkyne end groups.

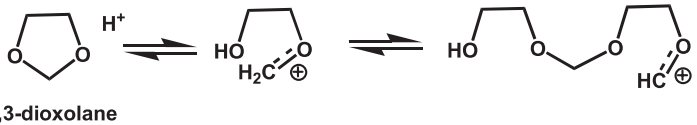
A very special case is the intramolecular complex formation of end groups of bifunctionally living polymers, such as polystyrene with two Cs^+ counter ions[15] or a Ba^{++} counter ion.[16] In a similar way we observed an intramolecular complex of a bifunctionally living poly(methyl methacrylate) with two Na^+ counter ions which is considerably stable up to high molecular weights and adds the monomer with a rate being by almost one order of magnitude smaller than that of the non-complexed monofunctionally growing chain (Fig. 18).[17]

Ring chain equilibria

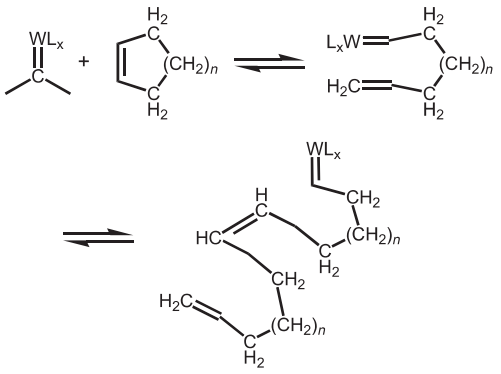
As mentioned already, the formation of cyclics beside linear polymer chains may be expected for step growth reactions such as the polycondensation of dicarboxylic acids and diols or of hydroxycarboxylic acids (except an intramolecular reaction to form a penta- or hexamembered cycle is possible) and of dicarboxylic acid chlorides and diamines, for polyaddition reactions such as diisocyanates and diols or diamines. In the following ring opening polymerization reactions will be considered such as the cationic ring opening of tetrahydrofuran[18] as well as of 1,3-dioxolane (Fig. 19), 1,3,6-trioxocane, 1,3,6,9-tetraoxacycloundecane and 1,3,6,9,12-pentaoxacyclotetradecane.[19]

In the same way cyclics and linear chains are obtained in the metathesis polymerization of cycloolefins (Fig. 20) such as cyclopentene, cyclooctene, cyclododecene etc. with carbene complexes as initiators. Cyclics are formed during the reaction both via back-biting and end-biting reactions.[20] Two 'famous' further examples are the polymerization of sulfur or S_8[21] and the polymerization of the trimer of dimethyl-siloxane or D3.[22]

In all cases a ring chain equilibrium is observed which was theoretically treated by Jacobson and Stockmayer[23] who came up with the relation that the equilibrium constant of a cycle with degree of polymerization x, K_x, or the equilibrium molar concentration of this cycle M_x is proportional to

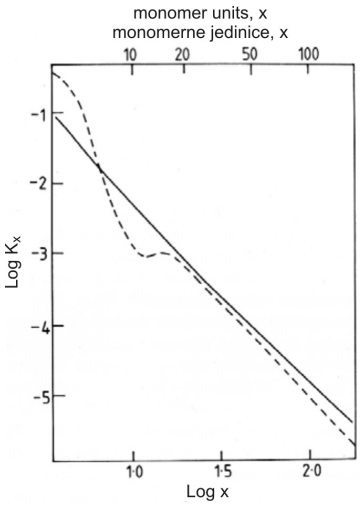


F i g. 19 – *Cationic polymerization of 1,3 dioxolane*
S l i k a 19 – *Kationska polimerizacija 1,3 dioksolana*



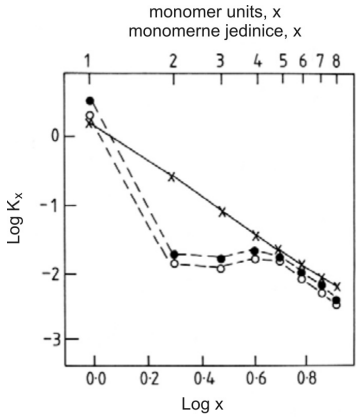
F i g. 20 – *Metathesis polymerization of cyclic olefins*

S l i k a 20 – *Polimerizacija metatezom cikličkih olefina*



F i g. 21 – *Molar cyclization equilibrium constant K_x (in mol/L) for cyclics $[Me_2SiO]_x$ in a ring-chain equilibrate in toluene solution (broken line) compared with calculated values*

S l i k a 21 – *Molarna ravnotežna konstanta ciklizacije K_x (mol/L) za prsten – lanac uravnotežene prstenove $[Me_2SiO]_x$ u otopini toluena (puna crta) uspoređena s izračunatim vrijednostima*

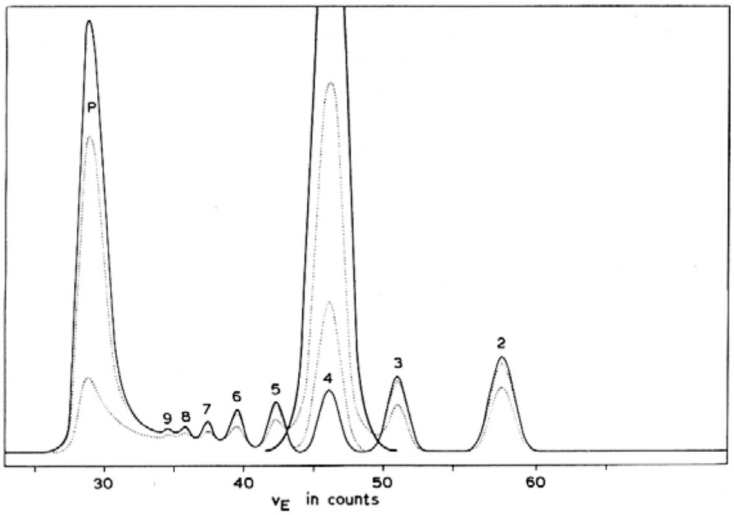


F i g. 22 – *Experimental molar cyclization equilibrium constants K_x (in mol/L) for cyclics $[CH_2OCH_2CH_2O]$ in undiluted (◦) and solution (•) equilibrates of poly(1,3-dioxolane) at 333 K compared with values calculated (x) by the Jacobson and Stockmayer theory*

S l i k a 22 – *Eksperimentalna molarna ravnotežna konstanta ciklizacije K_x (mol/L) za prstenove $[CH_2OCH_2CH_2O]$ u nerazrijeđenom mediju (◦) i otopini (•), uravnotežene poli(1,3-dioksolanom) pri 333 K uspoređena s vrijednostima (x) izračunatima prema Jacobsonovoj i Stockmayerovoj teoriji*

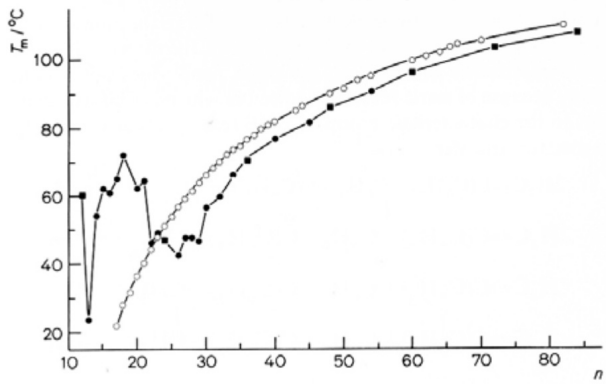
$x^{-5/2}$ (Figs. 21 and 22). Deviations from this relation for low molecular weight cycles indicate particular configurationally constraints.

To close the cycle of this review, I come back to cycloparaffines mentioned in the beginning. The metathesis reaction of cycloolefins, in particular of cyclooctene and cyclododecene, allows the preparation of cyclic oligomers as mentioned above. After synthesis and separation they were characterized in detail by means of infrared spectroscopy, size exclusion chromatography (Fig. 23) and mass spectrometry.[24] Finally the oligomers were hydrogenated to form cycloparaffines which were obtained up to 84 carbons in the cycle and which exhibit lower melting points than the linear alkanes from the cycle with 25 carbons on and – in the contrast to linear alkanes – a very individual behavior up to ca. 35 carbons in the cycle (Fig. 24).[25]



F i g. 23 – *Size exclusion chromatograms (SEC) of a homologous series of oligomers and polymers as generated from the tetramer of cyclododecene, $C_{48}H_{88}$; the broken lines show distributions before equilibrium is achieved*

S l i k a 23 – *Kromatogrami isključenja po veličini (SEC) homologne serije oligomera i polimera dobivenih iz tetramera ciklododekana, $C_{48}H_{88}$; isprekidane crte prikazuju raspodjele prije uspostave ravnoteže*



F i g. 24 – *Melting points of cycloalkanes (●) as compared with those of n-alkanes (○) based on the number of C-atoms, n*

S l i k a 24 – *Točke taljenja cikloalkana (●) uspoređene s vrijednostima za n-alkane (○) prema broju C-atoma, n*

Conclusion

The pioneering work of Leopold Ružička which nowadays is found in the textbooks of Organic Chemistry – beside many other subjects – opened the field of cyclic molecules which has been followed since then with great intensity up to these days where the cycles have become larger and larger and more and more complex as cubane, tetrahedrane or dodecahedrane. Still many questions remain open, in particular the question what the portion of cyclic structures is in networks or whether there is a significant amount of cyclics or even catenated cyclics in our commercial polymers obtained by means of step growth reactions or ring opening polymerization. Thus, the world is waiting for excellent chemists, chemist of Ružička's caliber.

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SAŽETAK

Ciklički i makrociklički organski spojevi – pregledni rad posvećen Lavoslavu Ružički

H. Höcker

Ružička je otvorio polje cikličkih organskih molekula kao što su ciklički terpeni i ketoni s do 17 atoma u prstenu. U međuvremenu se proučavanje područja proširilo u brojnim smjerovima kao što su ciklički parafini, krunasti eteri i kriptandi te ciklički esterski amidi. Cikličke molekule nastaju prijenosom elektrona i intramolekulskim asocijacijama polimera s dvije aktivne krajnje skupine, a sintetiziraju se izravnom ciklizacijom difunkcionalnih makromolekula. Tijekom stupnjevitih reakcija polimerizacije i polimerizacija otvaranjem prstena može doći do uspostave ravnoteže prsten – lanac pri čemu, što je veća monomerna jedinica tim je lakše odvajanje oligomera kao što je heptamer ciklododekana s 84 ugljikova atoma u prstenu. Ipak, brojna pitanja ostaju otvorena kao što su postojanje makrocikličkih katenana u komercijalnim polikondenzatima.

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