

Review article

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Ring-opening polymerization

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Abstract: Ring-opening polymerization is defined by IUPAC (Penczek, S., Moad, G. (2008). Glossary of the terms related to kinetics, thermodynamics, and mechanisms of polymerization. (IUPAC Recommendations 2008), *Pure and Applied Chemistry*, 80(10), 2163–2193) as (cit.) “Ring-opening polymerization (ROP): Polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer”. The large part of the resulting polymerizations is living/controlled; practically all belong to chain polymerizations. After the introduction, providing basic information on chain polymerizations, the paper presents the concise overview of major classes of monomers used in ROP, including cyclic ethers, esters, carbonates, and siloxanes as well as cyclic nitrogen, phosphorus, and sulfur containing monomers. There are discussed also thermodynamics, kinetic polymerizability, and major mechanisms of ROP. Special attention is concentrated on polymers prepared by ROP on industrial scale.

Keywords: chain polymerization; heterocyclic monomers; ring-opening polymerization; thermodynamics of polymerization.

Introduction

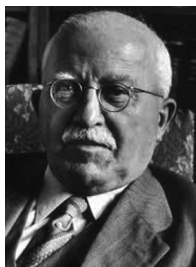
Polymers are macromolecules that are often compared to the string of pearls. Thus, there is a backbone, in which there are repeating units – former monomers. Monomers are the low molar mass molecules, joined one by one in the process called polymerization eventually forming macromolecule.

The first scientist who came with an idea of existence of macromolecules was a German Chemist Hermann Staudinger (Nobel Prize in 1953) (Staudinger, 1920).

There is no sharp definition how many of these repeating units have to be in a chain in order to constitute a macromolecule. A macromolecule that obeys Gaussian statistics can then theoretically be defined as a polymer (Ding, Kistiuk, & Sokolov, 2004). There is also a rather useful “behavioral” definition of a polymer as a large molecule that behaves differently from the typical low molar mass compounds. Thus polymers, whether in plastics, rubbers or fibers, could be extended to a certain length when a force is applied. Only the polymeric materials could behave this way. Thus, the formation of the polymer molecules requires, putting together a certain, usually large, number of monomer molecules.

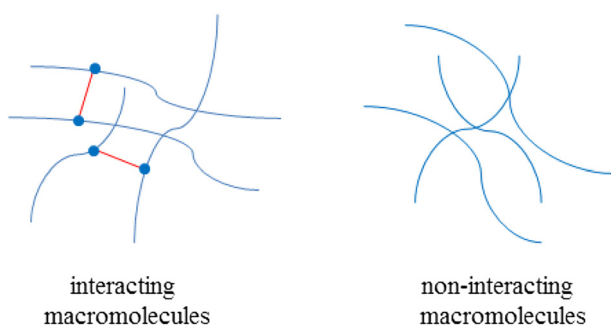
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Hermann Staudinger

It is seldom, that this number is lower than 1000, although, as it usually happens, there are exceptions with. There are certain polymer molecules having the lower limit of the molar mass around 10,000. We are giving this number being aware, that there are large differences in required sizes, depending on the molecular structures. This number is larger, when macromolecules do not interact one with another. In the case of molecular interactions the lengths of the individual macromolecules could be lower. This is illustrated in Figure 1.

**Figure 1:** Interaction of macromolecules with themselves.

As it will be shown further in the text, the ROP is a versatile method of preparing systems with interacting macromolecules (Penczek & Grubbs, 2012).

There are two general methods of preparing macromolecules, both are in large family of reactions, called polymerization. This word comes from the Greek language and has two parts “polýs” – meaning many and “méros” – part. Then, there are two subgroups of polymerization, namely chain polymerization and polycondensation (Penczek & Moad, 2008). Ring-opening polymerization (ROP) mostly belong to the first subcategory. Chain polymerizations are, in turn, a part of the large group of chemical reactions known as chain reactions. Chain reactions were, discovered by Max Bodenstein in 1906, when he observed that one quantum of light, usually responsible for one chemical change, e.g., $A + B \rightarrow AB$, provided a chain of reactions, thus $n A + n B \rightarrow n AB$.

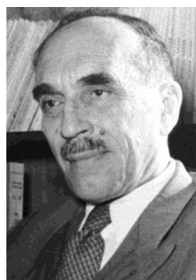


Max Bodenstein

This is because in every $A + B$, besides AB , there is an additional reaction, forming reactive A^* and/or B^* , able to further react with its counter component, without engaging additional activation. Chain polymerization was further elaborated by Sir Cyril Hinshelwood from England and Academician Nicolay Nikolaevich Semenov from Russia. They both received Nobel Prize in 1956 for their work.

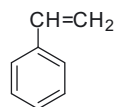


Sir Cyril Hinshelwood

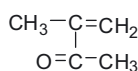


Nikolay Nikolaevich Semenov

There are two large groups of monomers that form polymers *via* chain polymerization (Penczek & Pretula, 2012). These are monomers with multiple bonds, mostly vinyl compounds, like styrene or methyl methacrylate (Scheme 1) and cyclic compounds used in ROP.



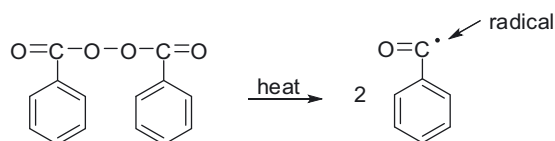
styrene



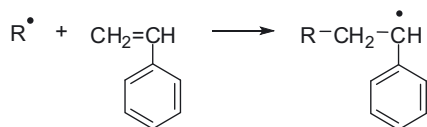
methyl methacrylate

Scheme 1: The most often studied vinyl monomers.

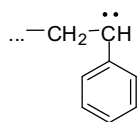
Formation of macromolecules from vinyl monomers proceeds, by multiple reactions of double bonds, in a series of identical reactions, starting from initiation and then chain growth. Initiation involves reaction of a compound with an unpaired electron, very often resulting from low energy dissociation of a given radical initiator (Scheme 2).

**Scheme 2:** Dissociation of the benzoylperoxide – formation of a primary radical.

This radical (R^\bullet) reacts with the first monomer molecule. Then addition of the next monomer additions lead to the formation of a macromolecular radical (Scheme 3).

**Scheme 3:** Reaction of the radical R^\bullet with a styrene molecule.

Mutual reaction of two macroradicals, after a certain number of propagation steps, interrupts the polymer growth. This is the termination reaction. However, when, the reactive species for polymerization are ions, unable to react between themselves to form a covalent bond, there are usually some side reactions responsible for the termination of the chain growth. In 1956 Michael Szwarc discovered general conditions in anionic vinyl polymerization that allow for the elimination of the side reactions. Macromolecules, fitted with anions at their ends (an anion – two electrons, like in Scheme 4) are still active, when the monomer is fully reacted and addition of a portion of another monomer leads to the formation of “block copolymers”.

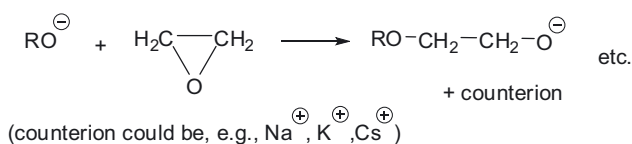
**Scheme 4:** Macroanion in polymerization of styrene.

“Living polymerization”, is defined by IUPAC in agreement with a term coined by Szwarc (Szwarc, 1968), and finally formulated in the IUPAC document (Penczek & Moad, 2008) (cit.): “**living polymerization:** *Chain polymerization* in which *chain termination* and irreversible *chain transfer* are absent”. Thus, in the living polymerization process there is only initiation and propagation. Termination is excluded. When a given portion of a monomer is converted into a polymer, then a new portion of the same or another monomer may be added and further polymerized, attached to the previously formed macromolecule.



Michael Szwarc

In ROP monomers are cyclic, mostly heterocyclic, and polymerization requires ring opening, preceding addition of the monomers to the growing macromolecules. Almost all ROP occur via ionic reactions, since opening the bond between the heteroatom and carbon atom, involves groups differing substantially in their electronic structures. Thus, e.g., in anionic polymerization of ethylene oxide, initiated by an alcoholate anion (aka, alkoxide anion), ring opening regenerates the anion that becomes the active species (Slomkowski & Duda, 1993). This is shown in Scheme 5.



Scheme 5: Anionic polymerization of ethylene oxide.

It could be mentioned at this point that the first quantitative studies of the anionic polymerization of ethylene oxide were performed by Paul Flory, in 1940s. This process was shown to proceed without termination, thus is a living polymerization process, although this expression was not used at that time. Paul Flory developed theories of chemical physics of polymerization and major theories in polymer physics. He was awarded Nobel Prize in 1974.

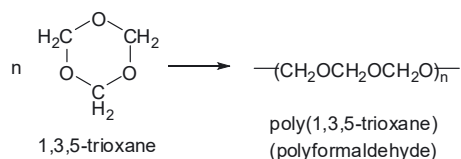
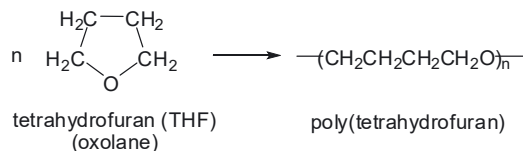
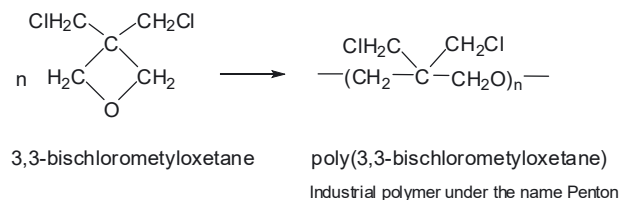
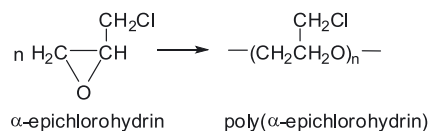
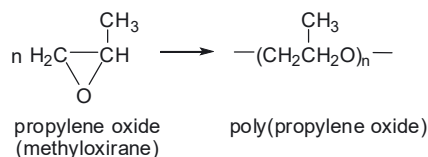
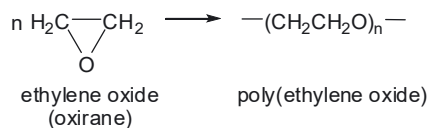


Paul Flory

Monomers that most often are used in ROP

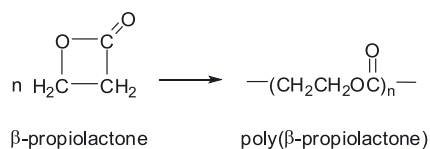
In this section the chemical formulae of the most typical monomers used in ROP are given. Properties and some applications of the polymers resulting from ROP are described later in the text (Penczek, Duda, Kubisa, & Slomkowski, 2007a).

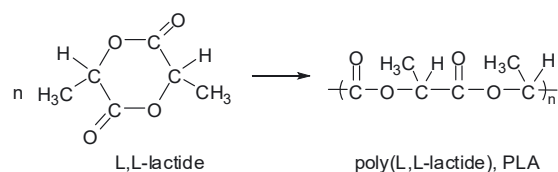
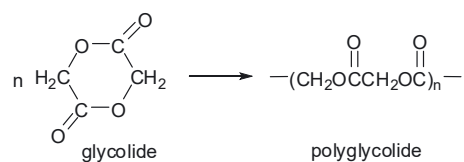
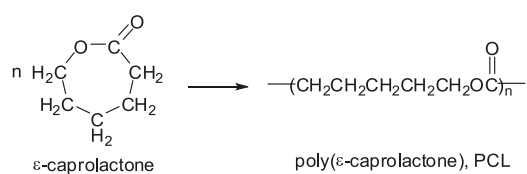
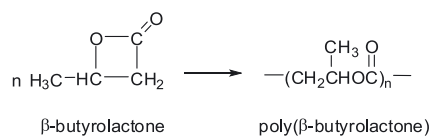
Cyclic ethers



Cyclic esters

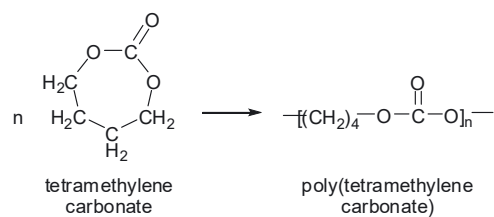
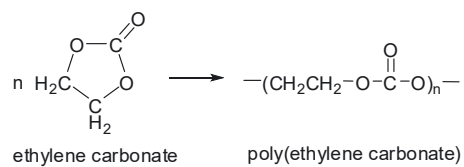
Due to the biodegradability of polyesters (aliphatic) there is a large number of cyclic esters (hundreds) that have been polymerized. Nevertheless, there are only a few that remain more than historical event. For example, β -propiolactone was extensively studied in the 1960s and 70s but studies were stopped when it was found to be cancerogenic.



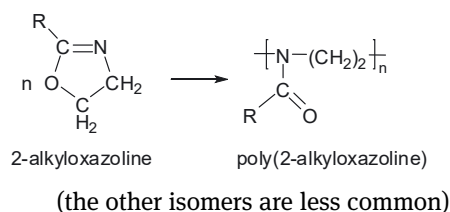
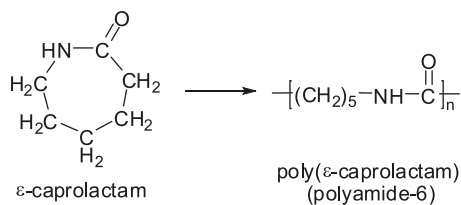


The D,D-isomer is also industrially available, although large scale production of polylactide is poly(L,L-lactide), prepared by biotechnological methods. Synthetic lactide (D,L-lactide) is a racemic mixture.

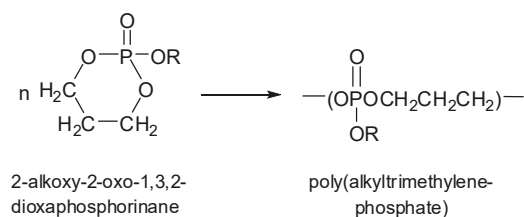
Cyclic carbonates



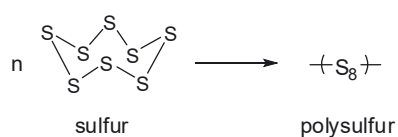
Nitrogen containing monomers



Phosphorus containing monomers



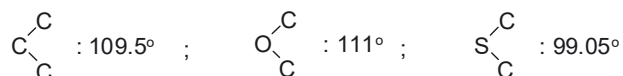
Sulfur containing monomers



Thermodynamics

Polymerization, as any other chemical reaction, is driven (the involved elementary reactions) either by specific chemical structures that are enthalpic, related to energy or entropic, stemming from the probabilistic features (Penczek & Kaluzynski, 2012).

ROP proceeds (mostly) exothermically, because cyclic monomers are usually strained species. There are certain bond angles that are known to be free of strain due to their geometry.



For several cyclic monomers it is not possible to avoid strain because to their structure. For instance, in the three membered rings, like ethylene oxide, the average angles for the C–O–C bonds are close to 60° angle being far the strain free angle of 111° . Examples of ring strain are given for cyclic ethers and cyclic esters are given in Tables 1 and 2.

Table 1: Ring strain in cyclic ethers.







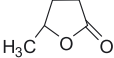


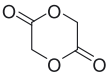
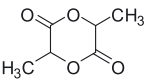
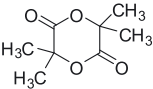
Cyclic ether					
	ethylene oxide	oxetane	tetrahydrofuran	pentamethylene oxide	hexamethylene oxide
Strain in kJ/mol in ΔH_p	–114	–107	–23	–5	–33

Table 2: Ring strain in cyclic esters.

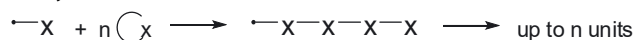
Cyclic ester	ΔH_p , calcd. in kJ/mol
 γ -butyrolactone	–15.4
 γ -valerolactone	–7.1
 δ -valerolactone	–26.8
 ϵ -caprolactone	–35.9
 glycolide	–23.0
 lactide	–20.9
 tetramethyl glycolide	–13.5

The strains given above are the results of superposition of several strains. These include:

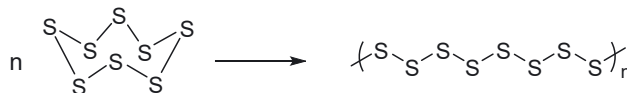
- Deviation from strainless angles in the ring,
- Deviation from distances between atoms from the strainless ones,
- Conformational perturbations (e.g., difference between the staggered and eclipsed conformations),
- Transannular strain due to the repulsion of the groups across the ring.

However, in poly(tetramethyl glycolide), listed in Table 2, repulsion between the methyl groups is stronger in the polymer than in the parent monomer, resulting in lower exothermicity than in the unsubstituted glycolide. Another factor influencing the total change of energy between the two ground states is related to entropy. Entropy can be related to:

- Translation: conversion of a certain number of monomer molecules into a macromolecule, thus decreasing the total mobility of the system:



- Rotation: different rotation of the segments in monomer and polymer unit. The monomer is not strained, but “stiffer” than the corresponding polymer unit. This is a case of sulfur. The monomer is the stiff eight-membered ring but polymer units are more mobile:



Polymerization of sulfur is an entropy driven, endothermic processes. Similar entropy dependent processes are known for some six-membered rings.

The features described above are part of the general thermodynamics of polymerization. Formally it is described by the corresponding thermodynamic functions; when a chemical change takes place at given conditions, the change of its Gibbs function (free energy), ΔG , has a negative value. One can also say that when calculated ΔG is negative, taking into consideration the energetic and entropic factors described above, then there is no thermodynamic restriction and thermodynamically the process is allowed. These energetic and entropic parts of the ΔG change are given by the following dependence:

$$\Delta G = \Delta H - T\Delta S$$

Usually, as described above, ROP are exothermic, thus $\Delta H < 0$. There is usually decrease of entropy, $\Delta S < 0$. Therefore, at the given temperature T , if polymerization takes place, then it means that the absolute value of ΔH is larger than $T\Delta S$ and polymerization is exergonic. Sulfur, and some cyclic monomers mentioned above, behave differently: $\Delta H > 0$ and $T\Delta S < 0$. Thus, sulfur starts to polymerize only at a certain high enough temperature (159 °C).

Kinetic polymerizability

Polymerization process is composed of three elementary reactions; “elementary” means that could not be broken down into other type composing reactions. These elementary reactions are: initiation, propagation (chain growth) and termination. In some polymerizations there is also chain transfer: inter- or intramolecular. For certain ionic polymerizations there is no termination and, as described above, these polymerizations are called living.

Basic principles of ROP kinetics

Several ROP can be realized as a living process (Dubois, Coulembier, & Raquez, 2009; Sisson, Ekinici, & Lendlein, 2013). Then, the basic kinetic equation is independent of the actual mechanism. The rate of reactions is usually the starting point of the kinetic studies, leading eventually to the subtle understanding of the process. Any kinetic study expresses the rate of polymerization as a function of the variables involved. These, first of all, are the structures of monomers and active species which interact to build the polymer chain. Therefore, the rate of polymerization in a given moment is expressed by the rate of monomer consumption (or polymer unit formation) and is proportional to the product of the momentary concentrations of a monomer and active species (P^*).

$$-d[M]/dt = k_p \cdot [M] \cdot [P^*]$$

In this equation k_p is a coefficient and is called the propagation rate constant. It is equal to the rate of polymerization when the product $[M]_0 \cdot [P^*] = 1.0$. If polymerization is living, and the active species P^* were formed quickly, before much monomer was reacted, then this coefficient may be easily found from the integrated form of the above equation.

The integrated equation is shown below:

$$\ln ([M]_0/[M]) = k_p \cdot [P^*] \cdot t$$

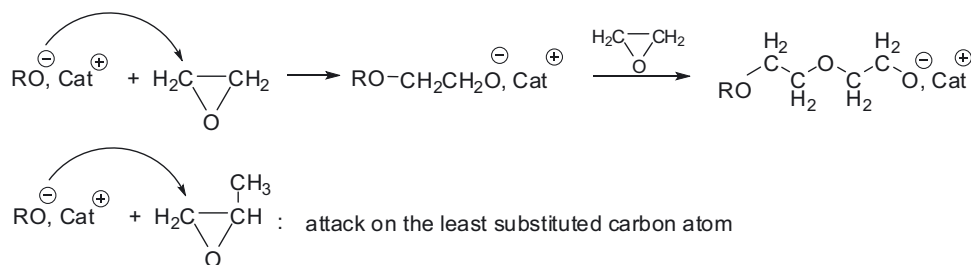
If dependence of $\ln([M]_0/[M])$ on time is linear, then it does not mean that polymerization is living; linearity requires invariance of $[P^*]$. This linear dependence only means that the concentration of active centers does not change, but does not inform as to whether there is chain transfer to the low molar mass chain transfer agents, restoring active centers. Let us assume that polymerization is initiated by metal alcoholate, like R_2AlOR' (polymerization proceeds only on the $>AlOR'$ bond). Then, the number of growing polymer chains should be equal to the number of R_2AlOR' molecules and the degree of polymerization should be given by $P_n = [M]_0/[R_2AlOR']_0$. If, however, there is an alcohol $R''OH$ present in the system, chain transfer to alcohol takes place as the growing macromolecule reacts with the alcohol. Growth of the macromolecule is temporarily terminated, but its active center is transferred to the reacting alcohol. Thus a new active center is formed – let us assume that of the same reactivity.

It should be remembered that the word “chain” has two meanings in polymer chemistry, namely molecular chain and kinetic chain. Thus, the length of a polymer chain is given by its degree of polymerization and the kinetic chain length is defined as the average number of monomers that react with an active center. When there is a chain transfer, every act results in the formation of a macromolecule. However, the active center is restored and the kinetic chain length can be many times larger than the length of the molecular chains formed. Therefore, if there is a chain transfer to a given alcohol $R''OH$ in the system with a monomer M and initiator R_2AlOR' , then $P_n = [M]_0/([R_2AlOR']_0 + [R''OH]_0)$. Kinetic chain length is merely equal to $[M]_0/[R_2AlOR']_0$, since reaction with a chain transfer agent is not changing the number of active centers originally introduced.

The classical example, related to the process described above, is the anionic polymerization of ethylene oxide proceeding in the presence of an alcohol (compare Scheme 6). Thus, macromolecules are either active, i.e., having an alcoholate anion at the end, or temporarily inactive, having the hydroxyl groups at the end. In the latter case, after being inactive for some time, they can react reversibly with an alcoholate anion, regaining activity and converting the reacting alcoholate anion into an alcohol. Thus, such a polymerization is a living one, since every macromolecule does have an ability to grow; concentration of active centers is invariant.

We are describing these phenomena in some details, since living/controlled polymerizations have become standard methods in polymer synthesis, particularly in the ROP.

Besides cyclic ethers, acetals and cyclic esters, ROP also provided industrially important polymers synthesized from monomers with other heteroatoms, – mostly nitrogen: cyclic amides, oxazolines and cyclic siloxanes. The corresponding polymers are described in a later section, based to the large extent on our review in the Elsevier Reference Module in Chemistry (2016) (Penczek & Pretula, 2016).



Scheme 6: Anionic polymerization of cyclic ethers.

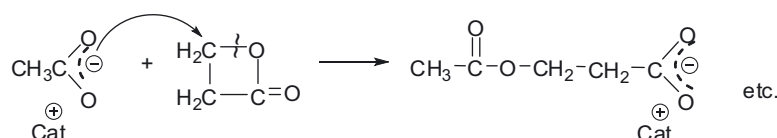
Major mechanisms of ROP polymerizations

There are two mechanisms of ROP ionic and pseudo ionic. In the latter ROP proceeds with formation of multicenter growing species without the formation of ions (Dechy-Cabaret, Martin-Vaca, & Bourissou, 2004).

Below a few examples demonstrate typical ionic and pseudo ionic processes. The ionic group has two subgroups: anionic and cationic ROP (AROP and CROP).

In the anionic processes initiation and then propagation involve alcoholate or carboxylate anions. Thus, polymerization of ethylene oxide, propylene oxide or ϵ -caprolactone are initiated and then propagate on alcoholate anions:

In these reactions nucleophilic attack on the monomer takes place. “Coma” in the formula in Scheme 6 indicates an ion-pair in contrast to free ions. An ion pair is electrically neutral. Cat^{\oplus} is a cationic counterion, often Na^{\oplus} , K^{\oplus} cations are used. There are also AROP that proceed with carboxylate active species, like in AROP of β -propiolactone (Scheme 7):



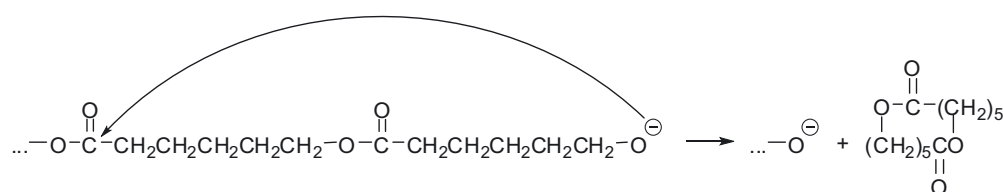
Scheme 7: Carboxylate active species.

In these AROP, as in the discussion below about CROP, ion-pairs are less reactive than free ions. Their proportions are measured by ion conductivity. Free alcoholate anions, although much more reactive than ion-pairs, are usually in the minority, because the two electrons constituting the anion are not dispersed and are concentrated on the oxygen atom. This results in a strong electronic attraction with its counterion.

In the AROP of cyclic esters there is an extensive chain transfer: intramolecular – i.e., within the macromolecule – and intermolecular – to the other macromolecules. Both lead to chain rupture. In the former, this will lead to cyclic formation, and in the latter only change the molar mass distribution.

Intramolecular chain transfer (back-biting) in polymerization of ϵ -caprolactone (CL) is shown in Scheme 8.

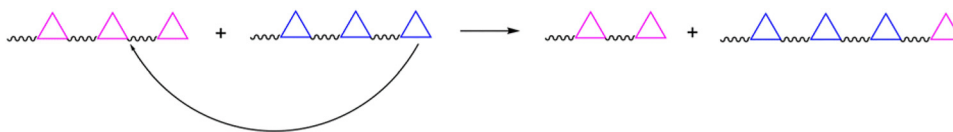
In the intermolecular process the number of macromolecules does not change, thus M_n is invariant and only M_w changes. This is because two macromolecules are interacting: one macromolecule attacks another one



Scheme 8: Formation of a cyclic dimer by back-biting in polymerization of CL (Penczek, Cypryk, Duda, Kubisa, & Słomkowski, 2009).

and, as the result, two macromolecules are formed. The extent of intermolecular chain transfer depends on conversion and may also proceed when propagation is over.

For a sake of clarity the intermolecular chain transfer is shown in a simplified way (Baran, Duda, Kowalski, Szymanski, & Penczek, 1997) (Scheme 9).



Scheme 9: Intermolecular chain transfer; triangles mean an ester groups.

There is also chain transfer to the low molar mass chain transfer agents, either adventitiously present or added intentionally in order to introduce required end groups. These processes may not disturb the 'living' nature of the process. For instance – chain transfer to an alcohol in AROP of ethylene oxide (Scheme 10):



Scheme 10: Chain transfer in AROP of ethylene oxide, providing required chain end.

The 'X' end group is introduced this way.

It has to be added that the back-biting process leads to the series of macrocycles of all degree of polymerization. Concentration of a macrocycle of a given degree of polymerization is given by the Jacobson-Stockmayer theory (Jacobson & Stockmayer, 1950; Volkenstein, 1963).

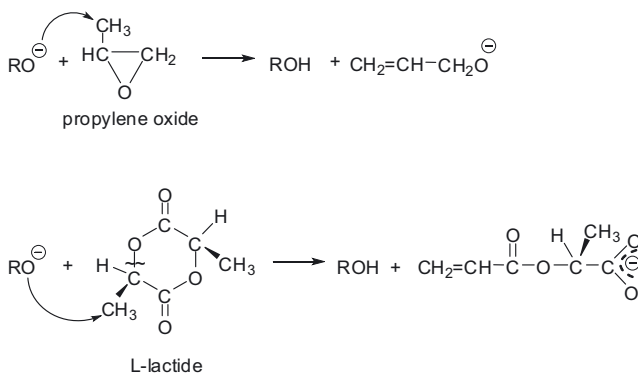
$$[(X)_n] = A n^{-5/2}$$

where 'n' is a degree of polymerization and 'A' is a coefficient of proportionality, dependent on conditions of polymerization and the monomer structure.

Sometimes the transfer processes can be observed directly. For instance: L,L-lactide is a dimer of lactic acid. Its molar mass is equal to 144.0 g/mol. Thus in MALDI peaks are separated by 144 g/mol. When there is chain transfer peaks separated by 72.0 g/mol appear. The frequency of these peaks indicates the extent of transfer.

We have devoted much attention to this transfer phenomena since these processes are most likely for AROP of cyclic esters, which are an important class of monomers for synthesizing (bio)degradable polymers.

There are also termination reactions involved in chain transfer. These are, e.g., for methyl substituted monomers: propylene oxide and lactide (Scheme 11).



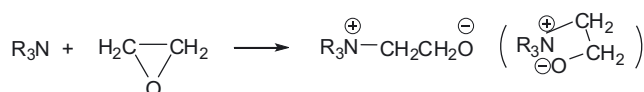
Scheme 11: Chain transfer leading to termination.

Zwitter-ionic polymerization

Starting in mid-1970s, a new kind of AROP was introduced: zwitter ionic polymerization with metal free initiators (Jaacks & Mathes, 1970). Initially it was studied with amines and phosphines. Later mostly strong-(super) bases have been used, initiating polymerization by forming zwitter ions, or abstracting a proton from a proton donating initiators:

(a) Zwitter ion formation

The most popular are DBU (1,8-diazabicyclo[5.4.0]undec-7-en) and TBD (1,5,7-triazabicyclo[4.4.0]dec-5-en). When used alone, lead to zwitterionic polymerization, in the same way as simpler strong bases, like trialkylphosphines or trialkylamines. Thus, in polymerization of ethylene oxide, initiated (catalyzed) by trialkylamine, there is the following chemical reaction (Scheme 12).

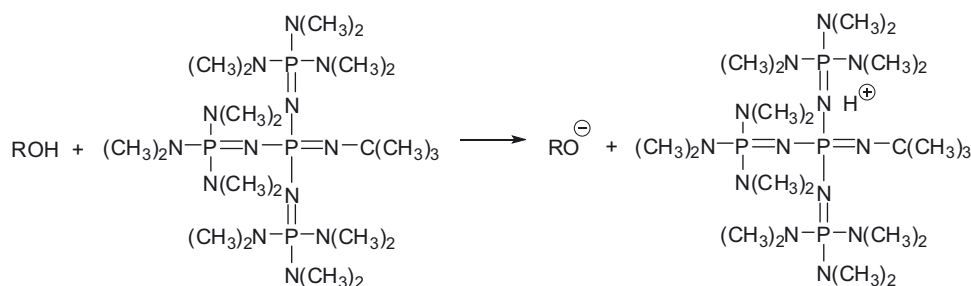


Scheme 12: Formation of a zwitter ion in polymerization of ethylene oxide initiated with tertiary amine.

In such a zwitterionic process, when the same strong bases are used, exclusively cyclic poly(L,L-lactide) are formed with $M_n \approx 3 \cdot 10^3$ g/mol.

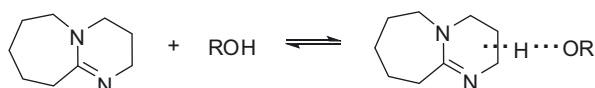
(b) Proton abstraction with non-nucleophilic strong bases like phosphazenes (Boileau & Illy, 2011)

Phosphazenes are superbases and abstract protons, converting e.g., alcohols into alcoholate (alkoxide) anions, accompanied by protonated phosphazene as a counterion (Scheme 13).



Scheme 13: Proton abstraction by a phosphazene perhaps *via* a zwitter-ion.

The very popular DBU are much less basic than large phosphazenes (over million times) and depending on the proton donor may either abstract protons or form strong hydrogen bonds, activating the -OH species (Nifant'ev & Ivachenko, 2019) (Scheme 14):



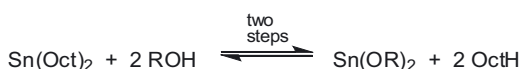
(DBU - diazabicyclo[5.4.0]undecene-7-ene)

Scheme 14: Hydrogen bonding to the strong base: DBU.

Pseudoanionic AROP

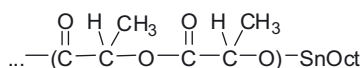
In this popular class of initiators those most often used are metal alcoholates (aka metal alkoxides) or their precursors. Almost all metal alcoholates were screened and $\text{Al}(\text{O}^i\text{Pr})_3$ was used the most extensively. $\text{Al}(\text{O}^i\text{Pr})_3$ and similar alcoholates exist in various aggregated forms, which differ in reactivity. $[\text{Al}(\text{O}^i\text{Pr})_3]$ (trimer) is reactive but the tetramer is much less reactive. Growing chains, that are also in the form of metal alcoholates, are usually less aggregated, since there are large substituents: polymer chains.

In polymerization of L,L-lactide very often tin II octoate ($\text{Sn}(\text{Oct})_2$) is used. This is salt of octanoic acid and is not reactive as such and has to be converted into the corresponding alcoholate, usually in reaction with an alcohol (Kowalski, Duda, & Penczek, 1998) (Scheme 15):



Scheme 15: Formation of the tin (II) alcoholate in reaction of tin (II) octoate with an alcohol.

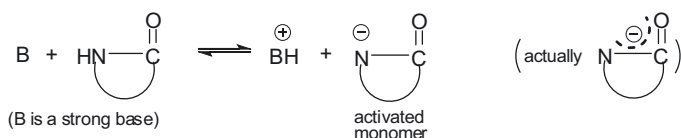
$\text{Sn}(\text{Oct})_2$ is used industrially, at the very low concentration (ca. 10 ppm), in a bulk polymerization process of L,L-lactide (~180 °C), as established by directly observing Sn in the macromolecules of poly(L,L-lactide) (Scheme 16):



Scheme 16: Polylactide catalyzed by $\text{Sn}(\text{Oct})_2$. Sn atoms are present in the polymer chains.

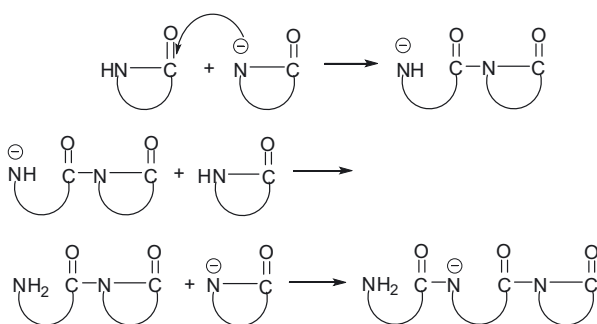
Activated monomer polymerization

Polymerization of lactams, initiated by strong bases, proceeds by a particular mechanism, in which monomer, activated by a strong base, is the actual ionic active species (O dian, 2004) (Scheme 17).



Scheme 17: Activation of a lactam monomer by a strong base.

Then, propagation takes place in the following, way (B^+H counterion is omitted) (Scheme 18):

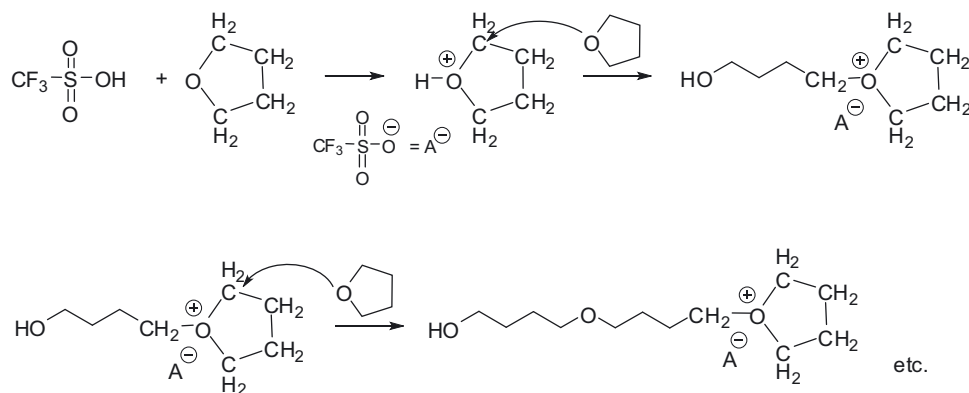


Scheme 18: Activated monomer (lactam) polymerization. Propagation step.

Cationic ROP (CROP)

In CROP there are two large subgroups: Active Chain End (ACE) and Activated Monomer Mechanism (AMM) (Lewinski, Sosnowski, Kazmierski, & Penczek, 2015).

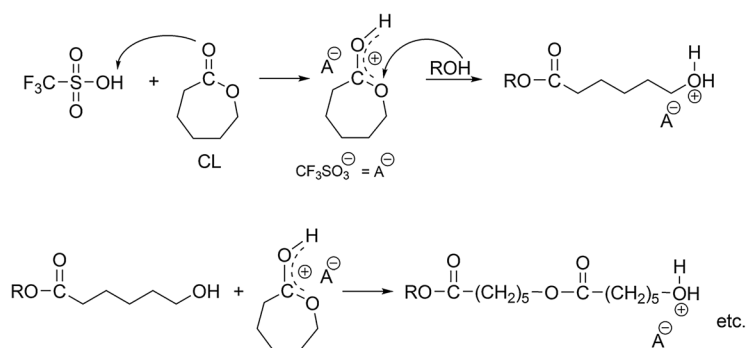
Polymerization of THF, initiated and catalyzed by trifluoromethanesulfonic acid: $\text{CF}_3\text{SO}_3\text{H}$ proceeds by ACE (Scheme 19).



Scheme 19: Active Chain End (ACE) polymerization of tetrahydrofuran (THF).

In initiation the less active secondary oxonium ion is formed, converted into the tertiary ion which becomes, the active species in propagation.

In contrast, polymerization of ϵ -caprolactone (CL) requires addition of an initiator, usually an alcohol. Then, polymerization proceeds by AMM, in which monomer is first protonated (activated) and then polymerization is finally initiated by nucleophilic ($\text{S}_{\text{N}}2$) reaction of an alcohol (water may also be used) with a protonated monomer, Scheme 20.



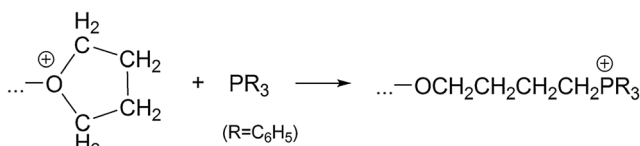
Scheme 20: Activated Monomer Mechanism (AMM) in polymerization of ϵ -caprolactone.

Then the proton moves to the next monomer molecule and the $-\text{OH}$ from the chain end adds to the same monomer molecule.

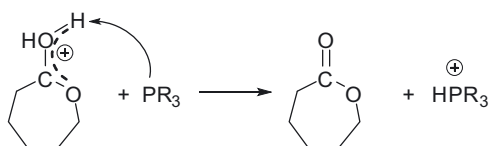
Thus, in ACE process proton from protonic acid is eventually converted into the $-\text{OH}$ end group and generates the active species, that could be an oxonium ion, as shown above, or a carbenium ion. In contrast to this process, in the AMM polymerization proton from protonic acid is not consumed and its concentration is invariable. Distinguishing between polymerization by ACE and AMM is possible by reaction with a base, forming the corresponding addition product. It is convenient to use, e.g., for phosphines ^{31}P NMR method can

be used for detection of the product. When low concentration of active species are present (e.g., 10^{-4} mol L $^{-1}$) only end groups with P atoms are observed in ^{31}P NMR.

\ACE polymerization of THF reaction with triphenylphosphine leads to the alkylated product (Scheme 21), whereas in reaction with the protonated CL, that can be considered as active species in the AMM, reaction with PR_3 leads to the protonated phosphine (Scheme 22).



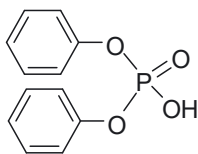
Scheme 21: Ion trapping with triphenyl phosphine allowing distinguishing between ACE and AMM.



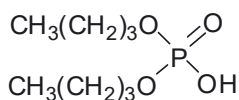
Scheme 22: Ion trapping in AMM polymerization: protonated phosphine is formed.

The alkylated and protonated PR_3 differ substantially in ^{31}P NMR spectra.

The most often used protonic acids in CROP of cyclic esters are derivatives of acids of phosphorus, like diphenylphosphate (DPP) or its derivatives, substituted in the ring (Makiguchi, Satoh, & Kakuchi, 2011).



Usually, unsubstituted DPP are not acidic enough to efficiently catalyze polymerization of L,L-lactide, a much weaker base than CL. However, DPP substituted in the ring with electron withdrawing groups ($-\text{NO}_2$) or, particularly at higher temperature, the dialkylphosphoric acid, like dibutylphosphate are sufficiently active.



Polymers prepared by ROP on industrial scale

As already indicated above, besides cyclic ethers, acetals and cyclic esters, ROP has provided industrially important polymers made from monomers with other heteroatoms. Mostly nitrogen: cyclic amides, oxazolines and cyclic siloxanes. The corresponding polymers are described in the next section, based to the large extent on our review in the Elsevier Reference Module in Chemistry (2016) (Penczek & Pretula, 2016). There are many papers, describing the *in spe* applications, but only small percentage of the expected products are achieved. Polymers of oxazolines and of cyclic compounds with phosphorus atoms are not yet in production. They have, however, sufficiently high potentials to be discussed in this part of review.

Polymers of ethylene oxide

Polymers of ethylene oxide are prepared (mostly) by anionic or coordination polymerization (Bailey & Koleske, 2000).

There is a large spectrum of molar masses of ethylene oxide polymers that have already found practical applications with molar masses equal to a few hundred to a few million. Traditionally, polymers with molar masses below $\sim 10^4$ are called poly(ethylene glycols) (PEG), whereas higher polymers are called poly(ethylene oxide) (PEO or POE). This differentiation is not rigid. IUPAC suggests two names poly(oxyethylene) (structure based) or poly(ethylene oxide) (source based). There are also several names given by producers. PEO are either (mostly) linear or specifically prepared as highly branched or star-like structures. These products are available in Adrich, Polymer Source (Canada), Shearwater Polymers (USA), Dow Chemical Co. SunBio Inc. (Walnut Creek, CA), JenKem Technology (Allen, USA), Nektar (Huntsville, AL, USA) and so on.

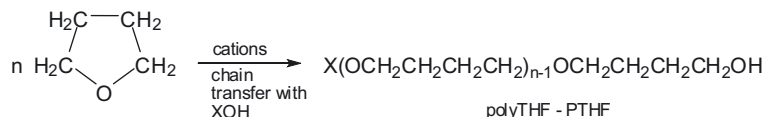
It is difficult to decide what kind of application is the most important and it is up to the reader to make their own decision. PEG are used for a process known as PEGylation, leading to attachment of PEG to other polymers. The most spectacular is PEGylation of proteins – biologically active polypeptides. PEGylation prevents bioactive polypeptides from premature degradation by enzymes. An example of PEGylation is an interferon, used to treat hepatitis C. Altogether there is already over 20 conjugates in practical applications. There is also a large number of other medical uses and several trials taking place on animals and not yet in clinical tests. However, it is indicated, that although PEG has been clinically proven and that more than 20 conjugates are already in the market, this polymer is not completely devoid of technical and commercial challenges. Particularly dangerous is an observation of development of specific antibodies against PEG in the serum of the patients treated with PEGylated products. Moreover, preexisting anti-PEG antibodies were identified in over 25% of patients who never received prior treatment with PEG drugs. The authors assumed that it could be result of using PEG_n in food, beauty and body care products.

PEG that is highly hydrophilic and when coupled to the hydrophobic macromolecules gives amphiphilic products, mainly used as nonionic surfactants. There are several large scale productions of copolymers (mostly block) with propylene oxide in a number of countries.

High molar mass PEO is also added to water to decrease friction and hence used by fireman and also to increase the speed of boats. Applications in cosmetics and various industrial applications are well documented, with numerous references.

Poly(tetrahydrofuran), polyTHF (PTHF)

PolyTHF is also known under the name poly(tetramethylene ether glycol), according to the source – based or the structure – based nomenclature (cf. PEO). It is prepared by cationic polymerization of tetrahydrofuran (THF) (Dreyfuss, 1982) (Scheme 23):



Scheme 23: Polytetrahydrofuran.

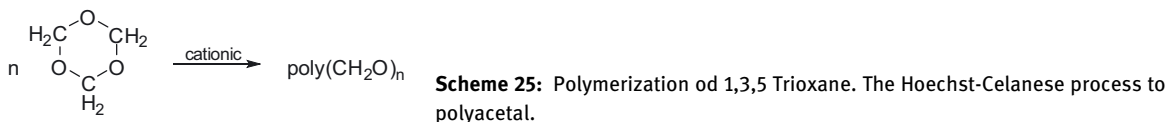
A monograph published by Dreyfuss in 1982 (Dreyfuss, 1982) describes the monomer, polymerization, properties and applications.

Polymerization of THF is a major source of information on the cationic ROP, with exclusion of the AMM, which does not operate for THF, because of its relatively high basicity.

Commercial products are usually α,ω -OH ended with molar masses from a few hundreds to a few thousand and are prepared in the presence of a glycol, in order to result as a macromolecular glycol. The main uses of HO(PTHF)OH are elastic blocks, either for polyurethanes or a multiblock copolymer with rigid blocks of polyterephthalates (e.g., butylene). There are well known commercial names of these products: elastic fiber Spandex[®], thermoplastic elastomer Hytrel (polyester) of DuPont Co., or Pebax (with polyamide 11–Rilsan), invented by E. Marechal from Sorbonne University and commercialized in France. These thermoplastic elastomers can be extruded or injection molded and perform also well at low temperature. Also, the 3M company developed PTHF of special molar mass, used in all the “postit” applications.

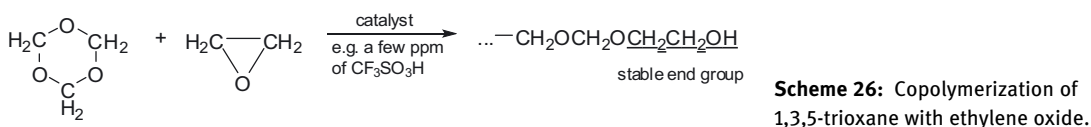
Polyacetal: polymer of CH_2O or copolymers of its cyclic trimer – 1,3,5-trioxane

Polyacetal – poly(oxymethylene) is either prepared by polymerization of formaldehyde (DuPont), Scheme 24 or by copolymerization of 1,3,5-trioxane, Scheme 25 (Lüftl, Visakh, & Chandran, 2014).



When formaldehyde or trioxane are polymerized and traces of water are present in the systems, then macromolecules have the hemiacetal end groups, from which there is an easy depropagation to formaldehyde (ceiling temperature for $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ is equal to 120 °C). Since the polymer is crystalline, with $T_m \sim 180$ °C, it could not be converted into a viscous liquid (needed for extrusion or injection molding) at or above its T_m ; thus, a useful object could not be produced from an unmodified polymer.

The early work on polyformaldehyde goes back to 1920s, when Hermann Staudinger could not find a way to stabilize the polymer. Since instability is due to the depropagation from the end-groups, two methods were eventually found in US (DuPont), and in Germany (Hoechst). In DuPont the polymer has two α,ω -OH end-groups and is reacted with (e.g.,) acetic anhydride, and converted into a polymer with more stable ester end groups. In Celanese/Hoechst, in copolymerization with 1,3-dioxolane or with ethylene oxide stable end groups are provided by units from comonomer at the chain end (depropagation would require formation of highly strained ethylene oxide) (Scheme 26).



In the technological process, conducted in the melted trioxane, in which polymer is not soluble, the unstable end groups, still present, namely $\dots \text{OCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{OH}$, are removed until depropagation reaches stability. Polyacetal is an engineering thermoplastic and can be injection molded with such a precision, that some time ago Hoechst (now Ticona) has shown that it is possible to produce internal mechanism for

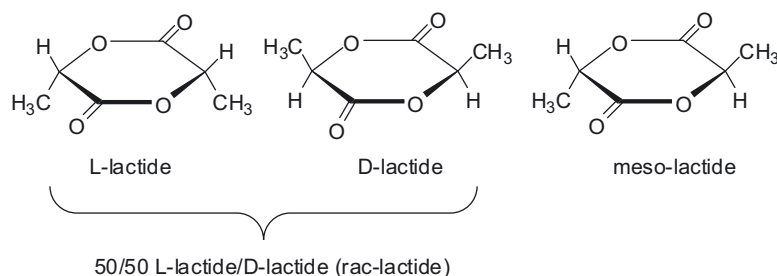
watches. Polymers also find applications in injection molded parts used in mechanical gears – e.g., in car industry, and sporting goods.

Polyesters: polyglycolide and polylactide

Poly(L,L-lactide) (PLA) has been known for a long time. Carothers, at DuPont, was preparing this polymer in the 1930s, but due to the PLA hydrolytic instability PLA was then of no industrial interest (Drumright, Gruber, & Henten, 2000; Steinbüchel, 2004; Vert, 2015).

Due to the more recent shift to biobased raw materials and ecological concern, PGL and particularly PLA have become important. Perhaps with some exaggeration PLA is sometimes called the “polymer of the XXist century”, since it is biobased, biocompatible and (bio) degradable. PLA is based on L,L-lactic acid, obtained by fermentation process, similar to the better known biotechnological synthesis of ethyl alcohol.

Lactic acid is a chiral compound. Although by the careful choice of microorganisms both L,L- or D,D-lactic acids could be prepared, the present technologies are based on L,L-lactic acid. PLA can either be prepared by polycondensation of lactic acid or by ROP of the cyclic dimer of lactic acid. The trivial name of the cyclic dimer is lactide. Depending on the chirality of the carbon atoms in the dimer there are L,L-; D,D- (both homochiral) or L,D-meso-lactides and also a fully synthetic racemic mixture. The corresponding formulae of lactides are given in Scheme 27.



Scheme 27: Isomers of lactide.

Traditionally the L and D formalism is used in works related to PLA, although, according to IUPAC, formalism based on the proper description of stereochemistry of the chiral centers, namely S and R should rather be used.

Industrial processes are based on the polymerization of LA in the melt of the polymer, i.e., most probably at ca. 180 °C. The catalyst used is Sn(Oct)₂.

The major producer is still Cargill Co., although there is also industrial activity in several countries.

PGL and its copolymers are mostly used as surgical sutures. Copolymers with LA are on the market for the drug deliveries.

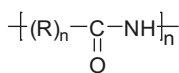
PLA has physical properties bearing resemblance to polystyrene. Since the homopolymer is rather stiff, there are several modifications, including polymer mixtures with other polyesters available industrially, like products from BASF Co. under the name Ecovio.

PLA and its mixtures with other polyesters are used for the production of films, used in agriculture and in the packaging industry. However, the most spectacular uses are biomedical applications. As quoted by Vert (2015), one of the pioneers, of biomedical applications of PLA: “After soft tissues, bone, drug delivery and packaging, PLA aims at blood”. Stents made of PLA are already in use in clinics and described in the above cited paper.

Polyamides

Polyamides have repeating units with amide bonds. Naturally occurring polyamides are (mostly) polyaminoacids-polypeptides – (proteins), such as (e.g.,) wool or silk (Not covered by this Review) (Kohan, 1995).

Synthetic polyamides (PA) are prepared by polycondensation of α,ω -aminoacids or by polycondensation of diamines with dicarboxylic acids. For instance PA66: product of polycondensation of hexamethylenediamine with adipic acid (i.e. two monomers with six carbon atoms each). An alternative method is ROP of cyclic amides-lactams. There are industrially available PA6, PA7, PA11, PA12 – numbers mean the number of carbon atoms in the cyclic monomer – a ring (Scheme 28).



Scheme 28: Repeating unit in a polyamide.

PA6 may be prepared by ROP melt anionic polymerization, allowing production of the multikilogram objects, like wheels, cogs and bearings. This is a thermoplastic material with $T_m = 200\text{ }^\circ\text{C}$. It is sometimes known as 'Nylon' – the name – was coined by Carothers; there are several tales what the letters separately mean.

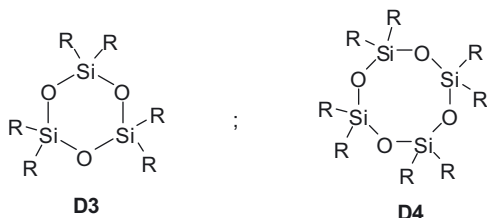
PA6 is also used in textiles for clothing, carpets, vehicle tyre cords and ropes including equipment for rock/ice climbers. PA6 constitutes up to 95% material for women's hosiery and for safety air bags. Almost every developed country has at least one producer of PA6.

Polysiloxanes – silicones

Silicones belong to the most versatile group of polymers and are used extensively throughout the world (Clarson, Fitzgerald, Owen, Smith, & Van Dyke, 2003).

Polymer molecules are built over chains with a simple sequence of atoms: polysiloxanes: -Si(<)-O-Si(<)- . Usually substituents at the Si atoms are methyl groups: poly(dimethyl siloxanes) (PDMS). The nonpolar methyl groups can rotate freely around the -Si-O- bonds, forming a shield around the polar backbone. Although PDMS are heat stable (silicone oils used for high temperatures), poly(diphenylsiloxanes) are even more stable. There are also chains with exclusively Si atoms, although these are less known.

PDMS are prepared either by polycondensation of $\text{Si(CH}_3)_2\text{(Cl)}_2$ (from reaction of Si with CH_3Cl discovered by Muller and Rochow, 1940) or by ROP of the cyclic trimer (D3) or cyclic tetramer (D4) (Scheme 29):



Scheme 29: Cyclic siloxane monomers. For $\text{R} = \text{CH}_3$: D3 is hexamethyl trisiloxane.

In these reactions both cationic and anionic polymerizations can be used. In the anionic process controlled/living conditions have been achieved.

Polysiloxanes, as industrial products, are used as liquids, reactive liquids and solid products (silicone rubbers).

Silicone rubber under the hood of a car protects the electronics against moisture and dirt, and in lacquer it provides gloss. PDMS are also used to prevent foaming and gives softness to garment fabric. Silicone sealants are very well known. However, the most versatile are uses for silicones in medicine, either externally (prostheses, tubing) or internally, e.g., to improve digestion.

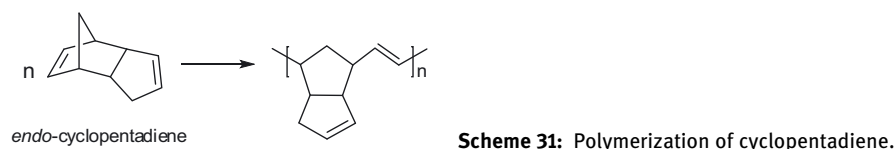
Polymers from ring-opening metathesis polymerization (ROMP) (described only in this section)

Catalysts were developed mostly by Grubbs and Schrock (Nobel Prize Winners for this development). The fundamental mechanism of the ROMP is based on conversion of the unsaturated monomers into polymers retaining double bonds in linear macromolecules and differing from the typical ROP (Davidson & Wagener, 1998).

The following are the best known industrial products synthesized by ROMP: polycyclopentene (Schemes 30 and 31):



and and polycyclopentadiene:



Polymerization of dicyclopentadiene can be realized in one step by reactive injection moulding (RIM) of very large objects, such as satellite dish antenna. Thus, the monomer is polymerized directly in the melt. The polymer has good properties from low temperatures ($-40\text{ }^{\circ}\text{C}$) up to $160\text{ }^{\circ}\text{C}$.

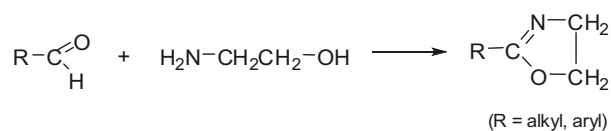
Particular progress in applications of ROMP has resulted from the development of ruthenium-carbenes catalysts that tolerate water. This opened a way for syntheses of bio-related polymers, like glucose – substituted polymers and several sulphated glucoconjugates with biological functions, including – potential cytostatic.

Polyoxazolines and related polymers

Oxazolines are cyclic five membered imino ethers (Dworak, Trzebicka, Kowalczuk, Tsvetanov, & Rangelov, 2014).

Studies of polymerization of this group of monomers started in 1960 when Saegusa, Ikeda, and Fuji (1972) and Kobayashi, Uyama, Narita, and Ishiyama (1992) mostly contributed to the development of the kinetics, mechanisms and synthetic applications of oxazolines and related monomers. The same Authors published extensive reviews covering practically all the aspects of oxazolines polymerization. It is not expected that large scale production would emerge from polymerization of rather expensive monomers. Nevertheless, it is highly possible that some representatives of this class of polymers will find practical applications, perhaps in biomedicine.

The most often used 2-oxazolines can be synthesized using a number of routes, e.g., (Scheme 32):

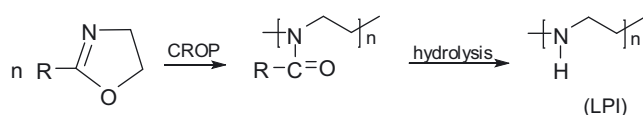


Scheme 32: Synthesis of a substituted oxazoline.

Besides five-membered oxazolines six-membered analogues, oxazines and seven-membered oxazepines were polymerized.

Polymerization of oxazolines is initiated by cationic initiators (anionic polymerization does not take place), like protonic acids and Lewis acids.

Polymerization of 2-oxazolines leads to linear poly(ethylene imines) (LPEI), polymer of particular interest because of its formation of bio-complex with DNA (Scheme 33):



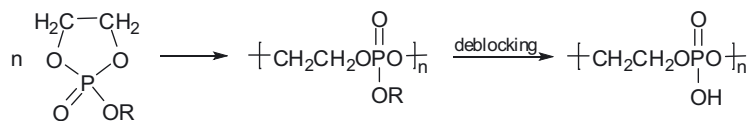
Scheme 33: Polymerization of substituted oxazoline to the linear polymer and further hydrolysis to the linear polyethylene imine.

As already mentioned, LPEI was used in numerous works for DNA complexation. Novel two triblock copolymers, LPEI-*b*-PEG-*b*-LPEI were shown to condense plasmid DNA effectively to give polymer/DNA complexes (polyplexes) of small sizes (<100 nm).

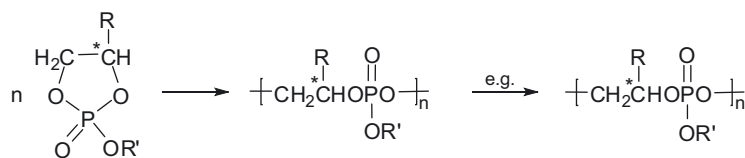
These examples strongly indicate expected practical application of polyoxazolines in the areas still dominated by PEG.

Polymers of cyclic phosphorus monomers

Although this section (Monge, Canniccion, Graillo, & Robin, 2011; Penczek & Lapienis, 1992) is devoted to the short presentation of ROP already used industrially, other monomers that have high potential are also described. ROP of phosphorus monomers belongs to this group. Their potential is amply seen from the recently published review, “Poly(phosphoesters): A new Platform for Degradable Polymers” (Steinbach & Wurm, 2015). Another review (Müller, Steinbach, & Wurm, 2015) (also published in 2015) describes polymers of poly(alkylene phosphates) prepared by (among other methods) polyaddition of H_3PO_4 with diepoxides (Penczek, Kaluzynski, & Pretula, 2007b). ROP involves the following processes, which takes advantage of the ring strain of the 5-membered monomers, e.g., (Schemes 34 and 35):



Scheme 34: Polymerization of the five-membered cyclic triester of phosphoric acid with further deblocking of the resulting polymer.



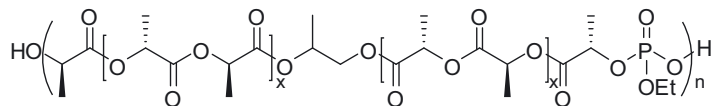
Scheme 35: Ring-opening route to the teichoic acid.

It also includes polymerization of chiral monomers, which lead to models of teichoic acids:

In polymerizations of chiral monomers the optical activity is retained, because in the chain growth attack takes place on the P atom, far enough from the center of chirality.

In several review papers biocompatibility *in vivo*, controlled degradability, and low cytotoxicity *in vitro*, were indicated by several research groups.

Microspheres of copolymer of PLA and ethylphosphate loaded with paclitaxel are in phase one of clinical trial as strong mitotic inhibitor. The molecular structure of the poly(ethylphosphate-co-lactide) copolymer used in Paclimer[®] (Zhao, Wang, Mao, & Leong, 2003) as drug carrier system for paclitaxel is shown in Scheme 36.



Scheme 36: Copolymer of L-lactide with ethyl-ethylene phosphate.

Concluding remarks

Heterocyclic compounds polymerize almost exclusively by ROP. Thus, the synthesized polymers contain heteroatoms in their main chains. The most important monomers include cyclic ethers, esters (of carboxylic and phosphoric acids), carbonates, amides, acetals, and cyclic siloxanes. These polymers have a number of properties not present in the vinyl polymers.

Comprehensive studies of mechanism and kinetics of ROP for many systems enable synthesis of polymers with well controlled molar masses and molar mass distributions as well as with controlled stereoregularity. For example, polylactides (polymers from monomers from renewable resources) were synthesized with molar masses in a range from a few thousand to a million g/mol. ROP processes are used for synthesis of polysiloxane sealants, substrates for silicone rubber and coatings, construction materials (polyamides), polymers used for production of drug formulations and temporary degradable implants, carriers of enzymes, nucleic acids and other biomolecules. ROP seems to be a mature field, however there continues to be a search for better catalytic systems and polymer post-polymerization modification. Recently there have been frequent efforts to use ROP for synthesis of copolymers with controlled architectures inducing controlled self-assembly of macromolecules into nanomaterials. These function as nanoreactors or drug carriers enabling more precise drug delivery. ROP is used for synthesis of aliphatic polyesters, which due to their degradability may help to reduced accumulation of plastic waste.

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