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Radical Polymerization of Methylene Heterocyclic Compounds: Functional Polymer Synthesis and Applications

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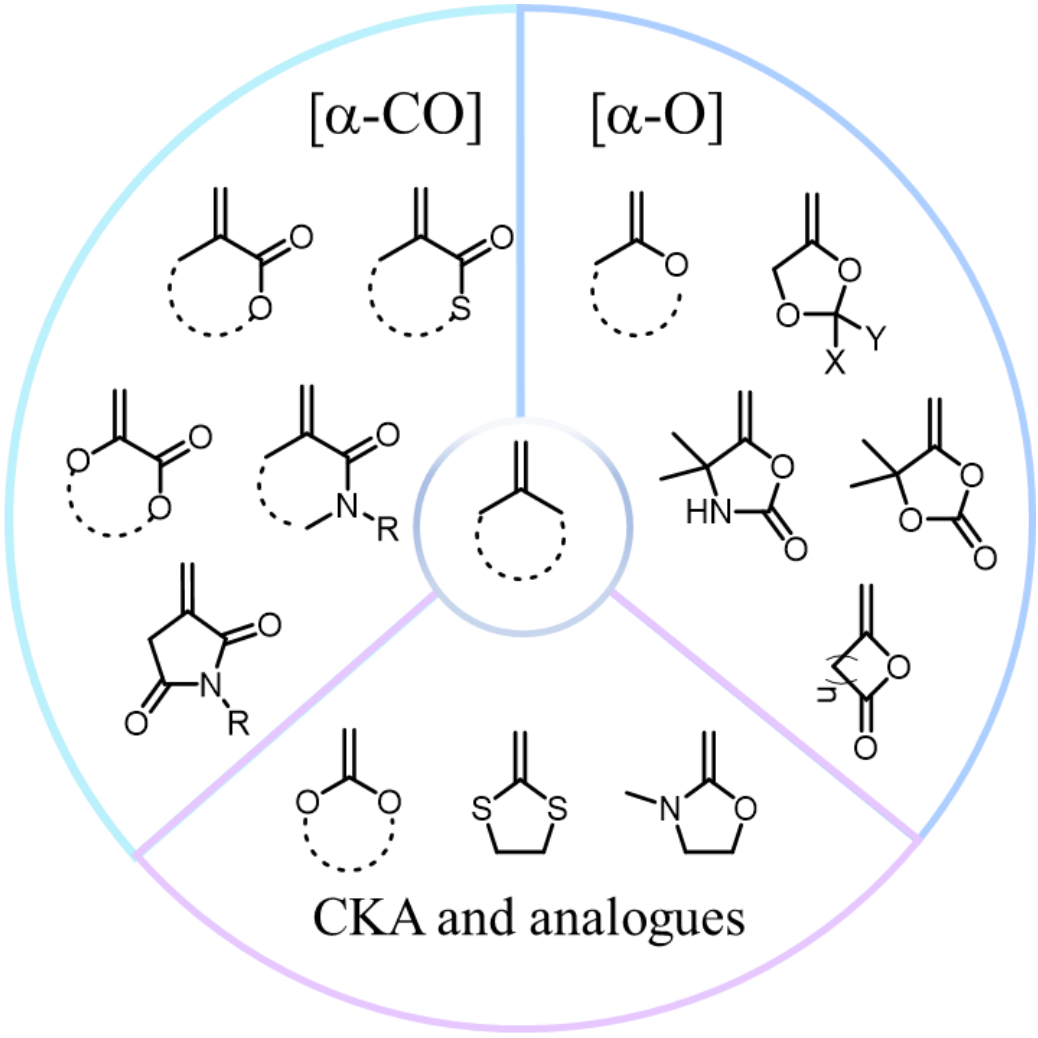

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Abstract

Synthetic polymers sustain a wide range of applications but the quest for further sophistication and functionalization of polymers remains topical to improve their scope and performance. In this respect, the radical polymerization of exo-methylene heterocyclic compounds (MHCs) is attractive. Compared to the classical acyclic vinyl monomers constrained to the vinyl-type polymerization process, MHCs can undergo different polymerization modes, namely the radical ring-retaining polymerization (rRRP) and the radical ring-opening polymerization (rROP). In rRRP, the cyclic group is preserved and inserted as side group of the polymer backbone offering a myriad of post-polymerization modifications whereas functional groups are incorporated within the backbone of linear polymers and confer them some degradability in rROP. Herein, recent advances in the radical polymerization of MHCs as well as the variety of macromolecular structures and applications it offers are highlighted. The reversible deactivation radical polymerization of MHCs leading to well-defined MHC-based macromolecular architectures, including multifunctional, stimuli-responsive and degradable polymers, is also discussed. The review emphasizes the current limitations of the radical polymerization of MHCs as well as future prospects including the development of innovative bio-based MHCs. Overall, the radical polymerization of MCHs represents a powerful macromolecular engineering tool and a broad field of exploration for polymer chemists.

1. Introduction

Polymer materials promote the development of our modern societies and touch almost every aspect of our daily lives from commodity polymers used in paints, packaging, containers,

clothing, adhesives, etc, to highly engineered polymers applied in medical, electronic and photonic technologies, to name a few. After several decades of progress, efforts to make polymerization techniques more efficient, versatile and sustainable, remain timely owing the increasing demand for innovative functional polymers able to address the requirements of today's applications.

Free radical polymerization (FRP) is one of the most widely used polymerization methods. It proceeds through a classic chain growth process and generates high molecular weight polymers. Its robustness, tolerance to moisture and high compatibility with many functional groups, make radical polymerization a tool of choice for producing synthetic polymers, especially in industry.[1] However, the inherent irreversible termination reactions leading to ill-defined structures prevent conventional FRP from being further used in cutting-edge applications which often require precise polymer architectures, predictable molecular weight and/or controlled chain-end functionalities.

In the past decades, the limitations of conventional free radical polymerization have been overcome by the development of controlled radical polymerization, preferentially referred to as reversible deactivation radical polymerization (RDRP).[2] In the latter, a controlling agent allows the temporary deactivation of the propagating radicals in the form of a dormant species which limits the extent of irreversible reactions and prolongs the life time of radicals. In other words, a dynamic equilibrium rapidly establishes between a small amount of active radicals and a large amount of dormant species.[3] In this case, fast and quantitative initiation reaction associated to a low propagation rate compared to the deactivation rate result in polymers with predictable molecular weights, low dispersity and high chain-end fidelity. This also paved the way to polymer with complex architectures including block, gradient, graft, star-shaped and telechelic copolymers to name a few. There are several RDRP techniques

that can be classified in three main categories based on their mechanism, namely the stable radical-mediated polymerization, atom transfer radical polymerization and degenerated chain transfer methods (**Figure 1**). Among the stable radical-mediated polymerizations, techniques based on the reversible capping of the radical chains by a controlling agent, are the nitroxide-mediated radical polymerization (NMP)[4–7] and the organometallic-mediated radical polymerization (OMRP)[8–11] involving nitroxides and transition metal complexes as controlling agents, respectively. Other systems involve the reversible transfer of atoms. The most emblematic example is the atom transfer radical polymerization (ATRP)[12–15] which uses a transition metal catalystto reversibly activate a terminal halogen moiety. Finally, two popular RDRPs involving a degenerated chain transfer mechanism are the reversible addition fragmentation chain transfer (RAFT)[16–21] and the tellurium-mediated radical polymerization (TERP)[22,23], using notably thiocarbonylthio groups and alkyl tellurides as chain transfer agents, respectively.

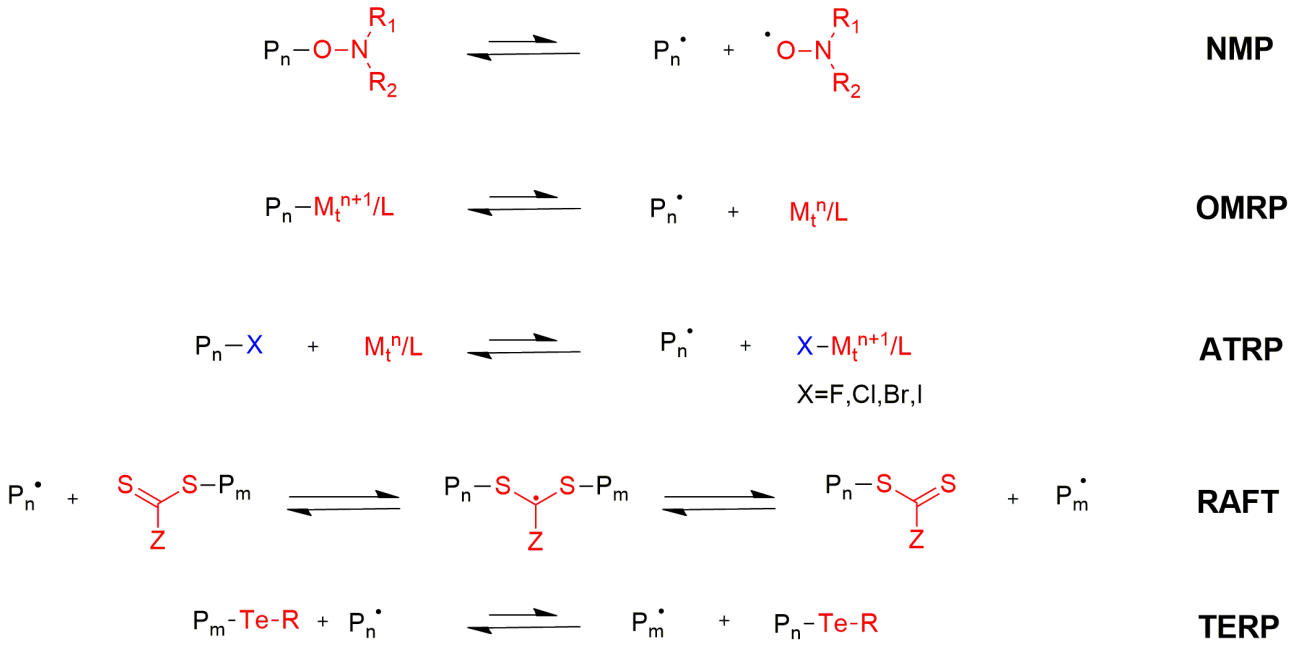

Figure 1: Main RDRP techniques

In the past decades, extensive research has been dedicated to control of radical polymerization of a large variety of monomers including the conjugated more activated monomers (MAMs) and the non-conjugated less activated monomers (LAMs). The former category includes monomers whose the vinyl group is conjugated to another unsaturated bond such as styrenics, (meth)acrylics or dienes. In these cases, the propagating radicals are stabilized by the side-group, which facilitates their formation from the dormant species in the RDRP equilibrium. However, the growing radicals derived from LAMs are deprived of radical stabilizing group. This makes the radical regeneration more difficult and implies the use of controlling agents able to make relatively weak bond at the polymer chain end. Emblematic examples of LAMs include vinyl esters, vinyl chloride, vinyl amides and ethylene.

Besides the common acyclic vinyl monomers, cyclic vinyl compounds are gaining more and more interest in the field of radical polymerization. It is notably the case of exo-methylene heterocyclic derivatives (MHCs) which feature heteroatoms in their ring as well as an exo-cyclic methylene group that can undergo radical addition reactions and polymerization. Their structure, and so reactivity, varies with the size of the ring but also by the nature and position of the functional groups which can be ester, amide, ether, carbonate and acetal for example.[24,25] As depicted in **Figure 2**, these MHC monomers can be divided into three categories, (i) the [α-CO] compounds bearing a carbonyl at the α position of the exo-methylene and belonging to the MAMs' family, (ii) the [α-O] derivatives having an oxygen at the α position of methylene and considered as LAMs and (iii) the cyclic ketene acetals (CKAs) and analogues where the exo-methylene group is adjacent to two heteroatoms (O, N or S).

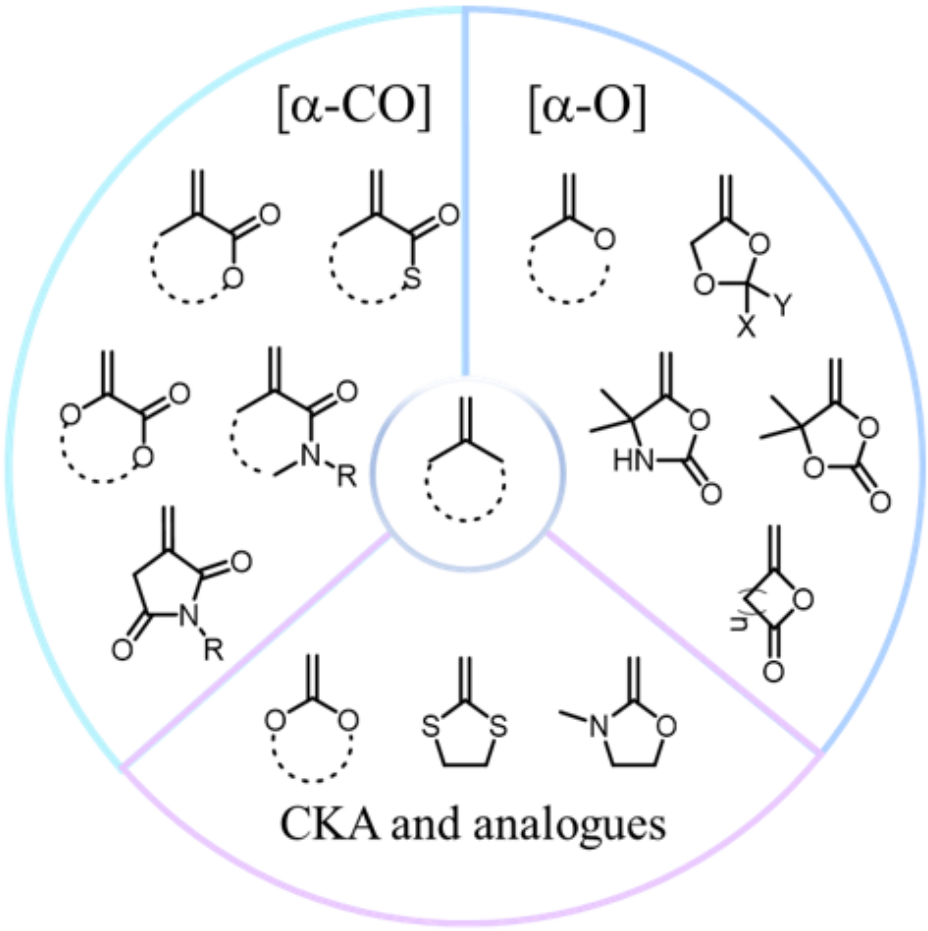

Figure 2. Categories of methylene heterocyclic monomers used in radical polymerization.

Compared to acyclic vinyl monomers which only follow the classical radical addition chain growth process, exo-methylene heterocyclic monomers can undergo different polymerization modes depending on the group adjacent to the methylene moiety of the MHC, namely the radical ring-retaining polymerization (rRRP) and the radical ring-opening polymerization (rROP) (**Figure 3**). These pathways lead to structurally diverse polymers which broadens the scope of their applications. The rRRP consists in a classical vinyl-type propagation and leads to aliphatic carbon-based skeletons with cyclic side groups. These rigid lateral cyclic groups tend to decrease the flexibility of the polymer chains which usually

exhibit high glass transition temperature and improved thermostability. In addition, some of these pendant heterocyclic groups can undergo post-polymerization modification leading to unique functional polymers. In this case, the cyclic moieties can be seen as protective groups during the polymerization which can generate two functions per MHC repeating units via post-polymerization modification instead of one for polymers derived from acyclic monomers. In the rROP mechanism, the radical addition onto the methylene group leads to a carbon-centered radical which undergoes a ring opening rearrangement before further monomer addition. As a result, heteroatoms or functional groups are incorporated in the polymer main-chain. Accordingly, weak bonds can be introduced into the backbone opening prospects in the field of degradable polymers.

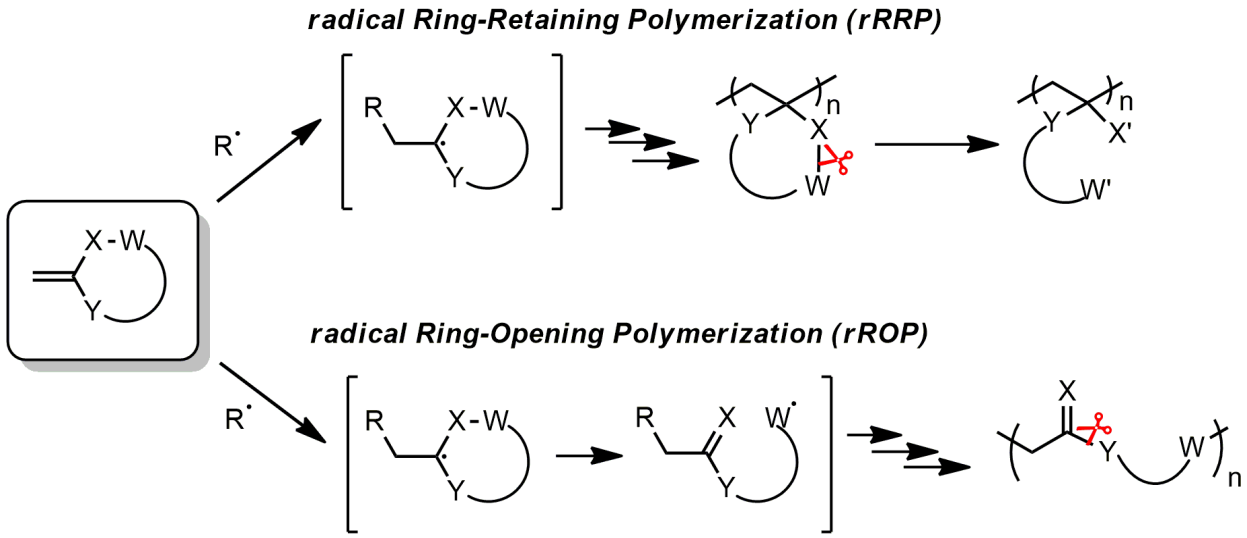

Figure 3: Radical ring-retaining polymerization vs radical ring-opening polymerization of MHCs.

The present review aims to provide an overview of the radical polymerization of methylene heterocyclic monomers and the variety of macromolecular structures and applications it offers. As will be emphasized, some MCHs are more reluctant to radical homopolymerization but their copolymerization with acyclic vinyl monomers is possible. The properties of these MCH-containing copolymers are discussed with respect to those of the polymers derived from the acyclic monomers alone. Besides FRP, we report on the RDRP of MHCs and the production of innovative well-defined macromolecular structures, including multifunctional, stimuli-responsive and degradable polymers. Throughout the review, special care is be devoted to emphasize the opportunities and limitations of the radical (co)polymerization of MCHs in terms of molar mass, conversion and compositions. Overall, it highlights the great potential of MCHs as building blocks for macromolecular engineering.

2. Discussion

2.1. [α-CO] Methylene heterocyclic monomers

2.1.1. [α-CO] Methylene cyclic ester

The [α-CO] methylene cyclic esters consist in an exo-methylene group conjugated to the carbonyl function of a lactone. Some representative derivatives of this class of monomers are shown in **Figure 4**. To some extent, the [α-CO] methylene cyclic esters are cyclic analogues of methacrylates but exhibit some peculiar polymerization features and offer unique functionalization opportunities compared to the latter, as discussed below.

The α-methylen-γ-butyrolactone **1** (α-MBL) and derivatives **2**-**4** are emblematic 5-member [α-CO] methylene cyclic esters. In line with the current challenge to render polymer synthesis more sustainable,[26–28] some [α-CO] methylene cyclic esters can be extracted or produced from biomass.[29–31] For example, α-MBL **1**, also known as tulipalin A, is a natural substance from tulips that is valued in the preparation of a wide variety of biosourced products.[30,32,33] α-MBL **1** and its derivatives can also be prepared via transformation of the biomass-derived levulinic acid[34] and itaconic acid[35,36], as shown in **Figure 5**.

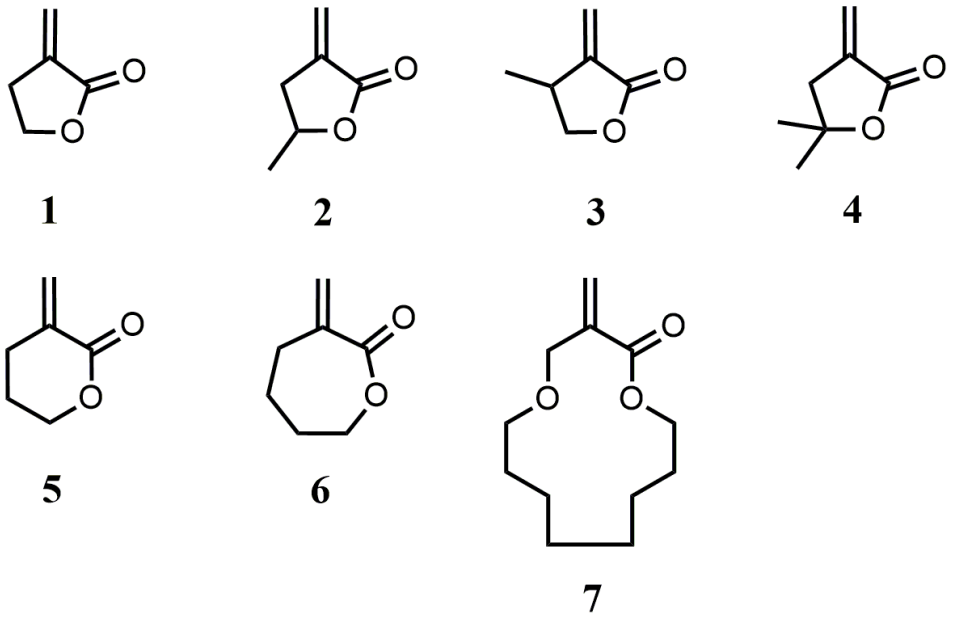

Figure 4:Typical examples of [α-CO] methylene cyclic esters

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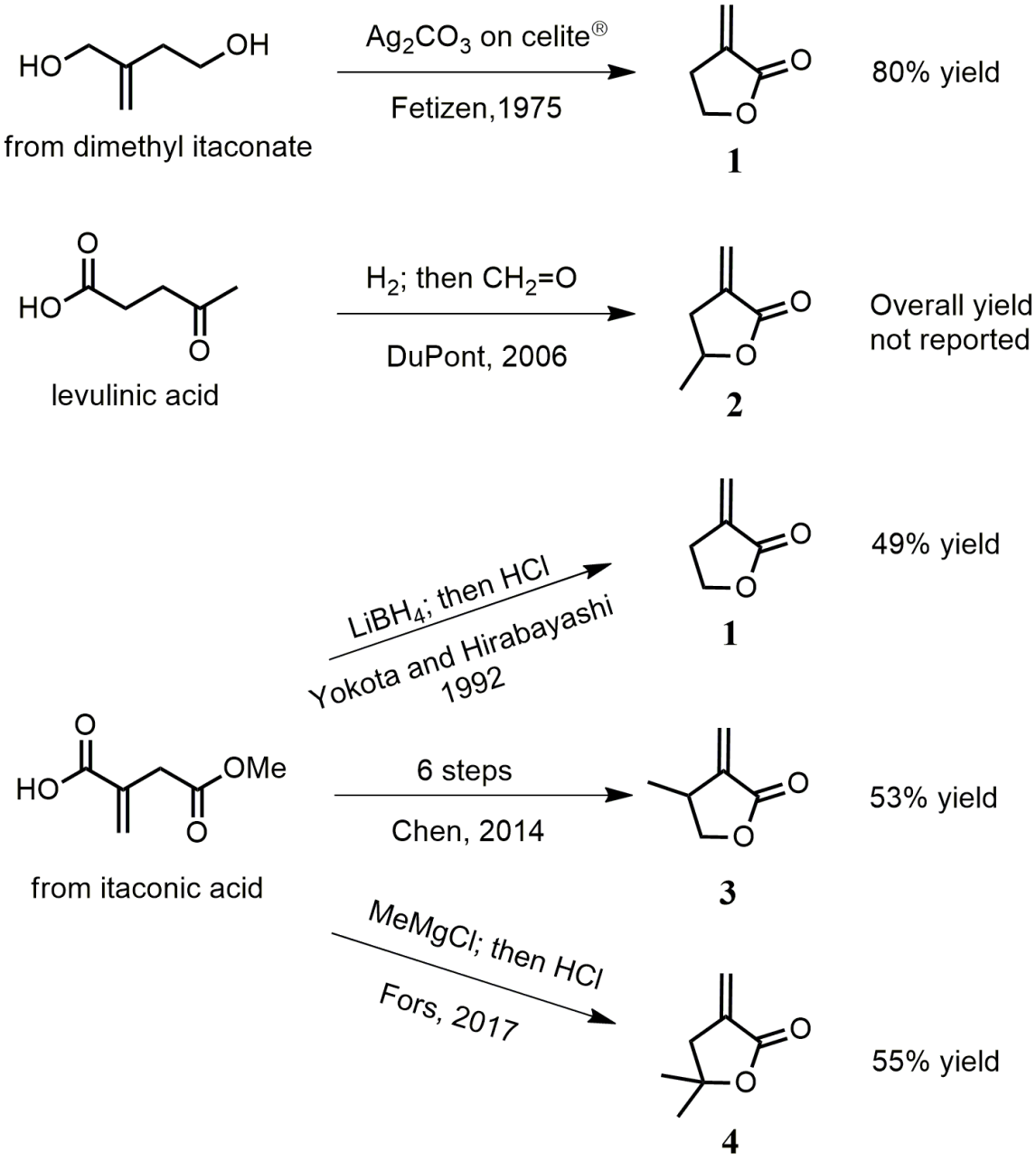


Figure 5: Synthesis of α-MBL and its derivatives from biomass-derived compounds.

The radical polymerization of [α-CO] methylene cyclic esters **1-4** exclusively proceeds in a vinyl type manner without ring-opening of the lactone under standard conditions, which is due to the low strain energy of the five-membered ring leading to a small negative change of enthalpy (ΔH_p^0) for its ring-opening polymerization.[37,38,39] The first example of free radical

polymerization of α-MBL **1** was reported by Akkapeddi et al and conducted at 60°C using AIBN as initiator.[40] The monomer conversion was limited to 72% when polymerization was conducted in bulk due to the slow translational diffusion of α-MBL and segmental diffusion of chain ends in its glassy state. Carrying the radical polymerization of **1** in DMSO ([α-MBL] =2.7 M) improved the monomer conversion (93%) compared to the bulk process performed under similar temperature and initiator concentration. The resulting amorphous poly(α-MBL) exhibited a higher thermal stability as well as better solvent resistance than PMMA owing to the rigid pendant cyclic structures along its backbone.[40,41,42] Poly(α-MBL) was thermally stable up to 320 °C40,42 and its glass transition temperature (Tg = 195 °C)40 was about 90 °C higher than that of atactic PMMA(Tg= 105 °C, Td = 176 °C).43 Furthermore, poly(α-MBL) resembles poly(MMA) in many properties including optical (refractive index=1.540) and mechanical properties, etc., indicating the potential of poly(α-MBL) as alternative to PMMA for high temperature applications. 44,45

The α-MBL also served as comonomer in radical copolymerization notably with MMA.[46,47] Even though the propagating radicals from both monomers are stabilized by an adjacent C=O group, α-MBL exhibits higher reactivity compared to MMA, r_{MBL}= 1.67 and r_{MMA}=0.6. In this case, the planar structure of α-MBL not only facilitates delocalization of the chain-end radical but also offers less steric hinderance between the growing chain radical and the approaching monomer compared to MMA.[40,42] The α-MBL was radically copolymerized with various other monomers, including styrene (St),[46,48] acrylamide,[46] acrylonitrile,[46] vinyl thiophene,[49] etc., to enhance thermal stability, solvent durability and scratch resistance of

the polymer materials.[50] Regarding the post-polymerization modification of poly(α-MBL), its pendant cyclic ester was not affected upon acidic treatment but could be hydrolyzed by strong alkali.[40,31] As shown in **Figure 6**, treatment of poly(α-MBL) with KOH 5 M for several hours at 100 °C promoted the ester hydrolysis and the release of one hydroxyl group and one carboxylate function per repeating unit leading to a highly hydrophilic but water insoluble potassium salt of poly(α-methylene-γ-hydroxybutyric acid).[40] Interestingly, acidification of the poly(α-methylene-γ-hydroxybutyric acid) suspension in water at 25 °C causes the complete lactonization.[40] The α-MBL was also incorporated in polyacrylates networks and the lactone functions of the latter were subsequently saponified leading to cross-linked ionomers with swelling percentage superior to 5000 %.[51] Superabsorbents were also produced by copolymerizing the saponified α-MBL with bisacrylamide.[31]

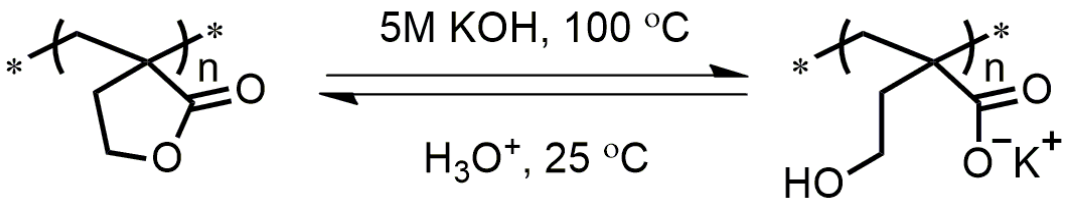


Figure 6: Acid/base treatments of poly(α-MBL).[40]

The RDRP of α-MBL was considered for the preparation of well-defined α-MBL-based structures, including block copolymers.[35,47,52,53] Like MMA, α-MBL is a conjugated monomer that can be polymerized in a controlled manner by atom transfer radical polymerization (ATRP).[52,47,53] ATRP of α-MBL was first reported by Matyjaszewski et al in DMF at 50 °C using the bromopropionitrile (BPN) initiator and the CuBr/$CuBr_2$ /bpy catalytic system.[53] Poly(α-MBL) with predictable molar mass (up to 18200 g/mol) and low dispersity (*Đ* = 1.09)

was obtained accordingly. The RDRP of α-MBL was also achieved by RAFT in benzene at 80 °C using 2-cyano-2propyl benzodithioate (CPBDTA) as CTA leading to poly(α-MBL) of moderate molar mass (15000 g/mol) and dispersity of 1.22.[35] Later on, a series of well-defined triblock copolymers containing a middle soft poly(*n*-butyl acrylate) (PBA) segment and outer hard blocks of poly(α-MBL) were synthesized via ATRP and valued as thermoplastic elastomers (**Figure 7**).[47] Given the high reactivity of the radical derived from α-MBL, an halogen exchange strategy (from Br to Cl) was implemented in the chain extension procedure to ensure proper block copolymerization. The poly(α-MBL)-*b*-poly(PBA)-*b*-poly(α-MBL) casted films showed various microphase separated morphologies where cylindrical or spherical hard block poly(α-MBL) domains arranged in the soft poly(PBA) matrix.[47] Dynamic mechanical analysis (DMA) exhibited a broad rubbery plateau extending up to 300 °C, associated with the high T_g and high thermal stability of poly(α-MBL), suggesting the suitability of these materials for high temperature applications.

High-density poly(α-MBL) brushes were also prepared through surface-initiated ATRP on the (2-bromo-2-methyl) propionyloxyhexyltriethoxysilane-immobilized silicon substrate, as shown in **Figure 8**.[54] Due to the highly stretched conformation and polar interactions between polymer chains, the poly(α-MBL) brushes exhibited higher elastic modulus and better friction resistance compared to their PMMA counterparts, highlighting the potential of the former for scratch resistant applications.

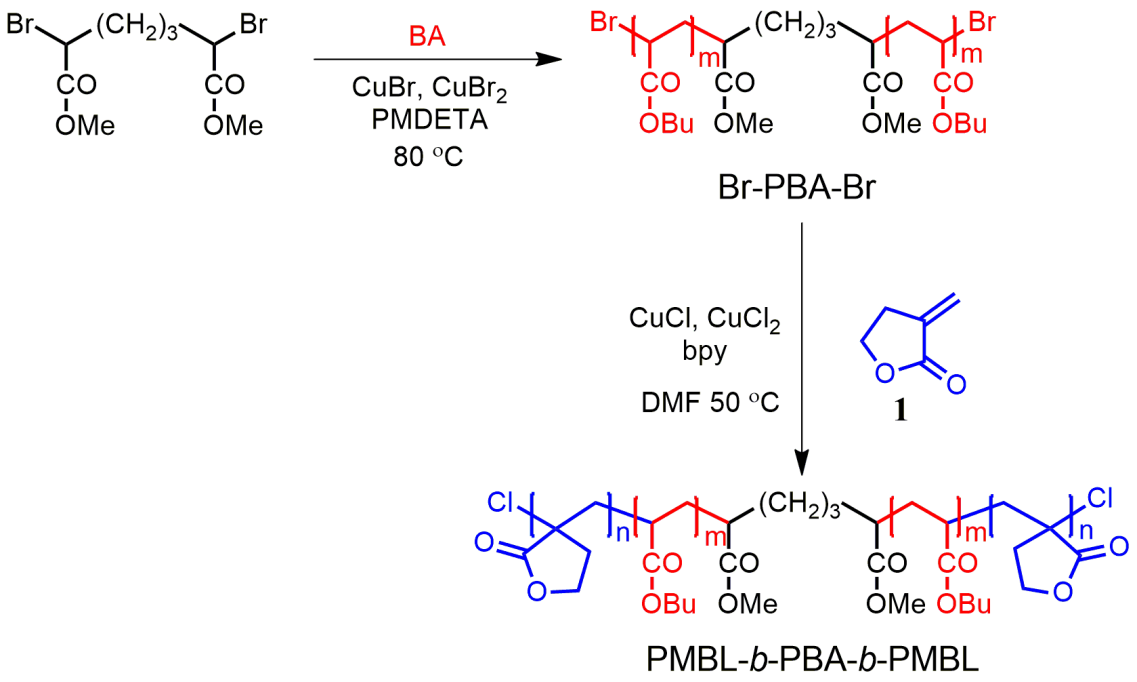


Figure 7: Synthesis of poly(α-MBL)-*b*-poly(PBA)-*b*-poly(α-MBL) triblock copolymers by ATRP.[47]

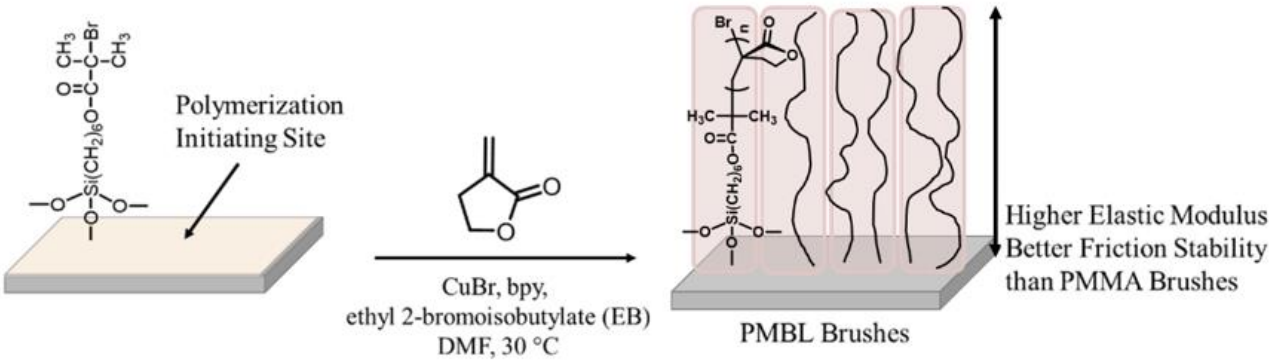


Figure 8: Poly(α-MBL) brushes synthesis via surface-initiated ATRP.[54]

In addition to bulk and solution polymerizations, the radical (co)polymerization of α-MBL was performed under emulsion[51] and precipitation[48] conditions. For example, poly(MBL-*co*-St)

particles were synthesized via precipitation copolymerization of α-MBL and St in isoamyl acetate for various monomer feed ratios.[48] Narrow size distributed spherical polymer particles with number average diameters in the range of 785–2620 nm were formed when the monomer feed ratio of MBL to St was 1:2.[48] As alternative to the petroleum-based acrylic acid, α-MBL was utilized in the production of superabsorbent via an emulsion process.[51] In practice, α-MBL, pentaerythritol tetraallyl ether (PETAE) and a small amount of AA (~5 wt% used as extra stabilizer for the growing polymer particles) were copolymerized under emulsion conditions. After treatment at 95 °C with NaOH, about 75% of the lactones were saponified and the resulting ionomer network exhibited enhanced absorbency for saline and deionized water compared to the corresponding cross-linked poly(AA), i.e. 1.28 and 2 times more saline solution and deionized water, respectively.[51]

Introduction of methyl substituents onto MBL as is the case for γ-methyl-α-methylene-γ-butyrolactone **2** (γ-MeMBL), β-methyl-α-methylene-γ-butyrolactone **3** (β-MeMBL) and γ,γ-dimethyl-α-methylene-γ-butyrolactone **4** (Me_2MBL), somewhat changes the monomer reactivity and the properties of the resulting polymers. For example, the conventional radical polymerization of β-MeMBL **3** exhibits a higher free energy of activation (ΔG) value than that of α-MBL **1** because of the more crowded transition sate for propagation resulting from the steric hindrance of the methyl group.[55] However, the five-membered ring β-MeMBL **3** remain planar, promoting resonance delocalization and so high polymerizability.[55] The most obvious variation between α-MBL and γ- or β-MeMBL concerns the stereoregularity of the produced polymers. While poly(α-MBL) prepared via FRP is an atactic polymer, an isotactic poly(γ-MeMBL) was obtained by conventional radical polymerization of enantiopure (R)-γ-

MeMBL.[41] However, annealing the isotactic poly(γ-MeMBL) above the glass transition temperature failed to develop any crystallinity. The racemic poly(γ-MeMBL) was also synthesized from the racemic monomers.[41] Regardless of the stereoregularity, the T_g of poly(γ-MeMBL)s (~215 °C) were about 20 °C higher than the T_g of poly(α-MBL) (195 °C). Finally, a series of well-defined (*Đ*~1.1) poly(Me_2MBL) with predictable molar masses ranging from 8800 to 61100 kg/mol were produced by RAFT of **4** using 2-cyano-2-propyl benzodithioate (CPBDTA) as CTA (**Figure 9**).[35] The obtained poly(Me_2MBL) exhibits enhanced solubility (notably in THF) and higher T_g (209 °C) compared with poly(α-MBL) as well as a high decomposition temperature (T_d = 337 °C).

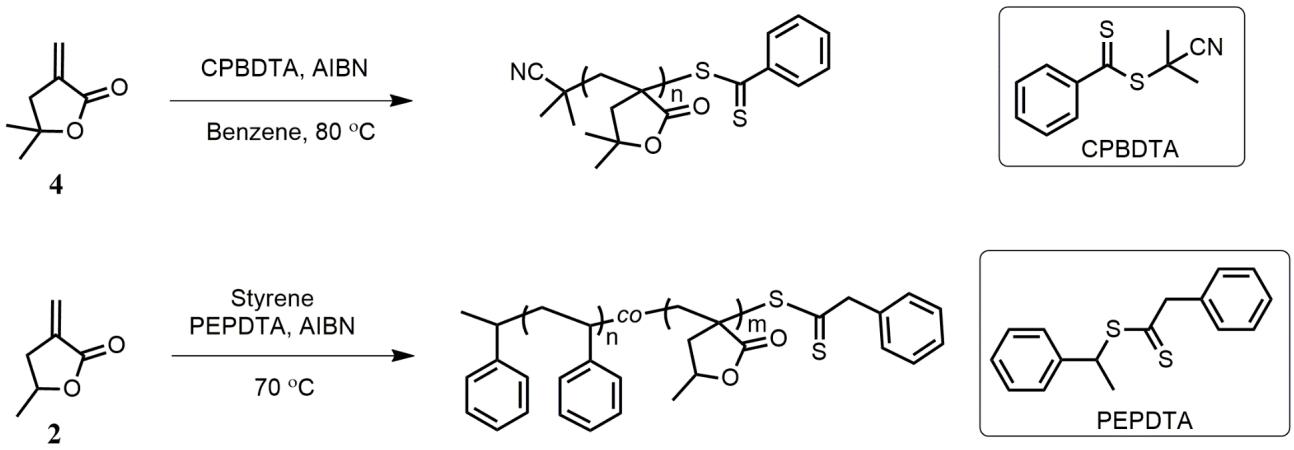


Figure 9: Synthesis of well-defined of poly(Me_2MBL)[35] and poly(γ-MeMBL-*co*-St)[56] by RAFT.

The copolymerization of β- or γ-MeMBL with styrene by FRP and RAFT was also reported.[55,56] As was the case for the α-MBL/styrene copolymerization ($r_{\alpha\text{-MBL}}$ = 0.70 and $r_{styrene}$= 0.09, in DMF at 60 °C),[46] the reactivity ratios of the binary systems β-MeMBL/styrene ($r_{\beta\text{-MeMBL}}$ = 0.74 and $r_{styrene}$= 0.22, in DMF at 60 °C) [55] and of γ-MeMBL/styrene ($r_{\gamma\text{-MeMBL}}$ = 0.70 and $r_{styrene}$= 0.09, in bulk at 70 °C)[56] were significantly in favor of the methylene

heterocyclic monomers. The copolymerization of γ-MeMBL/styrene was carried out via RAFT in bulk at 70 °C with 1-phenylethyl phenyldithioacetate (PEPDTA) used as chain transfer agent (**Figure 9**).[56]

The good solvent resistance and high T_g of poly(γ-MeMBL) can lead numerous process difficulties that can be addressed via miniemulsion polymerization and production of poly(γ-MeMBL) latex.[56] This miniemulsion approach was extended to the γ-MeMBL/styrene copolymerization by RAFT.[56] Although some rate retardation was observed in the aqueous dispersed RAFT polymerization process, well-defined copolymers with controlled compositions were achieved accordingly. Compared with the 5-membered ring α-MBL, [α-CO] methylene cyclic esters with higher lactone size are non-planar which provides less resonance delocalization of radicals and more hindrance between the growing chain radical and the approaching monomer.[55,57] These steric effects make depolymerization competitive with polymerization and result in low ceiling temperature (T_c). For example, the six-membered ring α-methylene-δ-valerolactone **5** (α-MVL) exhibits a T_c of 83 °C and was successfully radically homopolymerized in bulk at 60 °C (**Figure 10**).[57] Like poly(α-MBL), poly(α-MVL) is only soluble in aprotic polar solvents like DMF or DMSO but is thermally slightly less stable than the former (T_d of poly(α-MVL) = 280 °C and T_d of poly(α-MBL) = 320 °C). Subsequently, α-MVL was copolymerized with styrene in DMF with AIBN as the initiator leading to a marked preferential incorporation of the MHC monomer in the copolymer ($r_{\alpha\text{-MVL}}$ = 1.44 and $r_{styrene}$=0.096 at 55 °C).[58] The seven-membered ring α-methylene-ε-caprolatone **6** (α-MCL) was copolymerized with styrene under similar conditions, in DMF at 60 °C (**Figure**

10).[59] Some polymers having macrocyclic side chains shows valuable properties like selective alkali-ion extraction and ion transport abilities,[60,61] but their preparation by radical polymerization has been only minimally studied. So far, only 2-methylene-4-oxa-12-dodecanolide **7** was polymerized via FRP using (*i*-PrOCO$_2$)$_2$ as initiator in toluene at 30 °C (**Figure 10**).[62] Under these conditions, monomer conversion up to 62% was reached but some ring-opening side reactions occurred concurrently to the ring-retaining polymerization pathway.

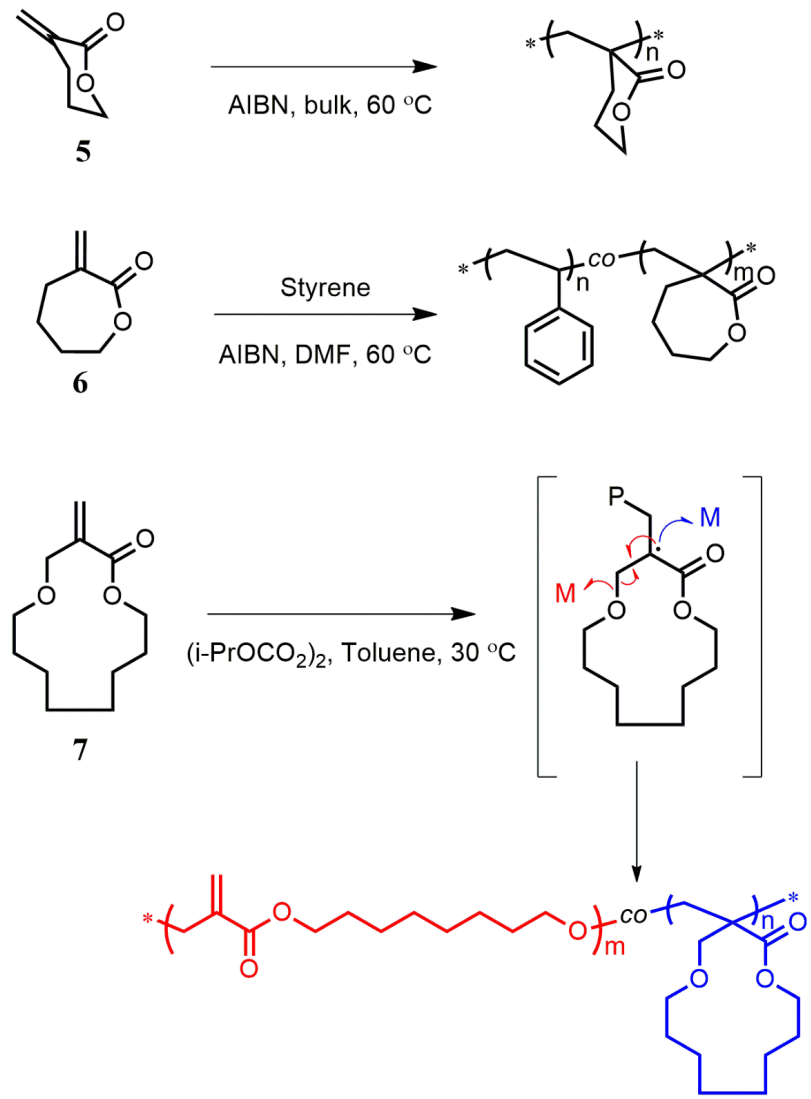


Figure 10: Radical (co)polymerization of 6-membered ring, 7-membered ring and macrocyclic [α-CO] methylene cyclic esters.

Among the [α-CO] methylene cyclic esters, some compounds include additional reactive groups in their ring which offers new derivatization opportunities as discussed below. It is notably the case of 5-methylene-2-phenyl-1,3-dioxan-4-one **8a** (MPDO), 2-isopropyl-5-methylene-1,3-dioxolan-4-one **8b** (IMDO) and 2,6-dimethyl-5-methylene-1,3-dioxa-4-one **9** (DMDO) which feature an acetal moiety in their lactone structure (**Figure 11**). MPDO **8a**, obtained by reaction of β-chlorolactic acid with benzaldehyde followed by dehydrochlorination with diisopropylamine, was homopolymerized at 60 °C by FRP via a rRRP pathway (**Figure 11a**).[63] The ATRP of MPDO was also successfully implemented at 70 °C in anisole in the presence of CuBr/$CuBr_2$ and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) using ethyl α-bromoisobutyrate as initiator.[63] Well defined poly(MPDO)s with M_n up to 50 kg/mol, low dispersity ($Đ$ =1.18) and no apparent T_g below 200 °C were prepared. Similar ATRP conditions were also used for the copolymerization of MPDO with MMA and St.[63] Expectedly, T_g of the poly(MPDO-*co*-MMA)s increased with the MPDO content in the copolymer. The poly(MPDO-*co*-St)s remained mostly unchanged after UV and hydrolytic treatment indicating the absence of weak ester bonds within the backbone and confirming that the (co)polymerization of MPDO proceeds exclusively via rRRP. The radical polymerization of **8b**, 2-isopropyl-5-methylene-1,3-dioxolan-4-ones, occurred via rRRP and was mainly used to prepare precursors of poly(α-hydroxy acrylic acid)s.[64] After alkali hydrolysis of lactone units on poly(**8b**), the obtained poly(α-hydroxy acrylic acid) exhibited excellent water solubility and capacity to undergo cyclodehydration under acidic condition as shown in **Figure 11b**.[64] St[65] and AA[66] were also copolymerized with **8b** through conventional radical polymerization in bulk at 60 °C. The RDRP of (*S*)- and (*R*)-2-isopropyl-5-methylene-1,3-dioxolan-4-ones (***S*-8b** and ***R*-8b**) was

successfully performed by reversible chain transfer catalyzed polymerization (RTCP) to produce a well-defined polymer with controlled tacticity and molecular weight. [67]

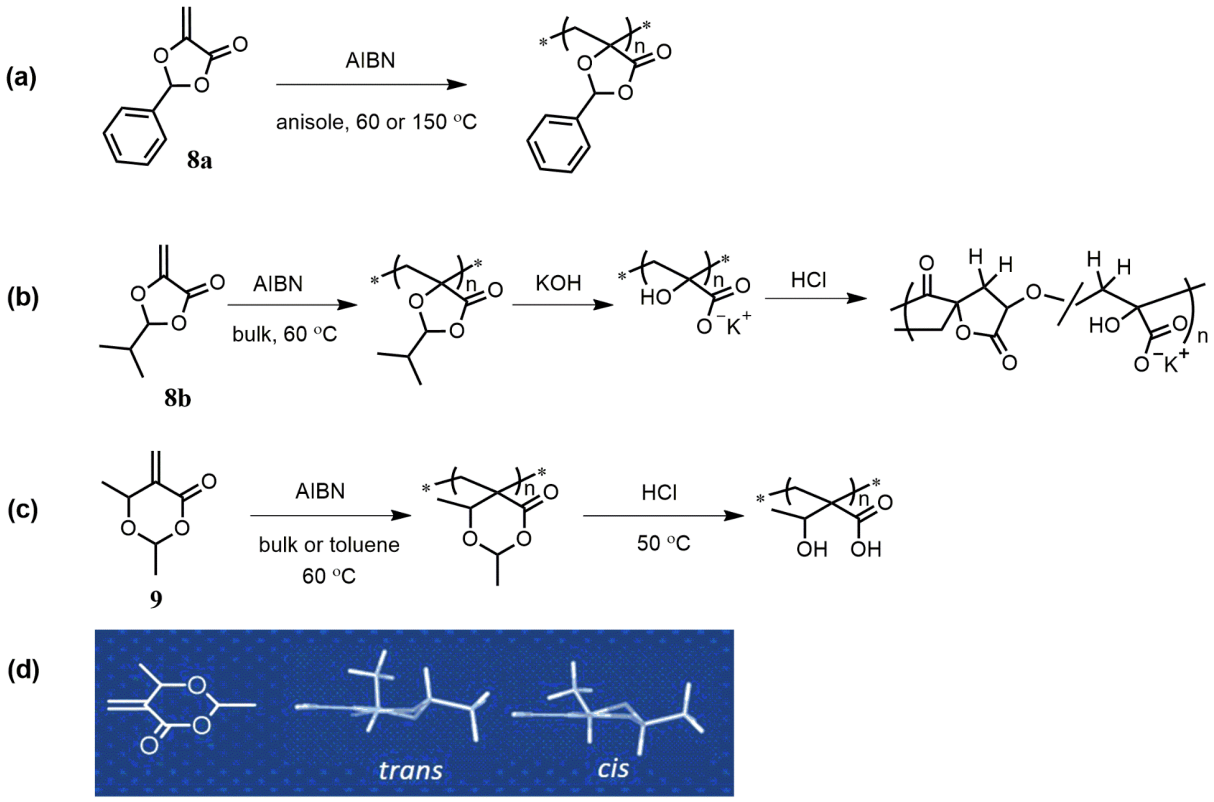


Figure 11: FRP of (a) MPDO, [63] (b) IMDO followed by alkali and acid treatment,[64] (c) DMDO followed by acid treatment[68] and (d) the most stable conformations of *cis*- and *trans*- DMDO.[68]

2,6-Dimethyl-5-methylene-1,3-dioxa-4-one **9** (DMDO) is another acetal containing in [α-CO] methylene cyclic esters (**Figure 11c**). The latter was prepared as a mixture of cis- and trans-isomers (95:5) through Baylis-Hillman reaction[68] and polymerized radically in toluene or bulk at 60 °C via a ring-retaining mechanism.[68] Interestingly, the *cis*-isomer was consumed faster than *trans*-isomer because the dihedral angle of vinyl and carbonyl groups in the *cis*-isomer is smaller than that in *trans*-isomer, as shown in **Figure 11d**, meaning that acrylate moiety in the *cis*-isomer was more planar resulting in higher reactivity in radical polymerization

(**Figure 11c**). Acid treatment of the poly(DMDO) at 50 °C allowed full deprotection of the acetal and release of one hydroxyl function and one carboxylic group per repeating unit leading to a water soluble poly[α-(hydroxymethyl)acrylate] (Figure 11c).[68]

Finally FRP of the exo-methylene-lactide MLA **10**, a biomass-based molecule derived from L-lactide,[69] led to atactic and thermally stable poly(MLA) with pendant lactide moieties (T_g ~ 230-250 °C, T_d ~ 305-320 °C) (**Figure 12**).[70] High polymerization yields and molecular weights were obtained at 75 °C in ortho-dichlorobenzene (*o*-DCB) (99% conv in 1h, M_w = 250 kg/mol). These conditions were successfully employed for the MLA/γ-MeMBL copolymerization. The binary copolymerization of MLA **10** with the di-exo-methylene-lactide **11** (DMLA) containing two methylene groups and the MLA/ γ-MeMBL/DMLA terpolymerization led to insoluble polymer networks, DMLA playing the role of the crosslinking agent.[70]

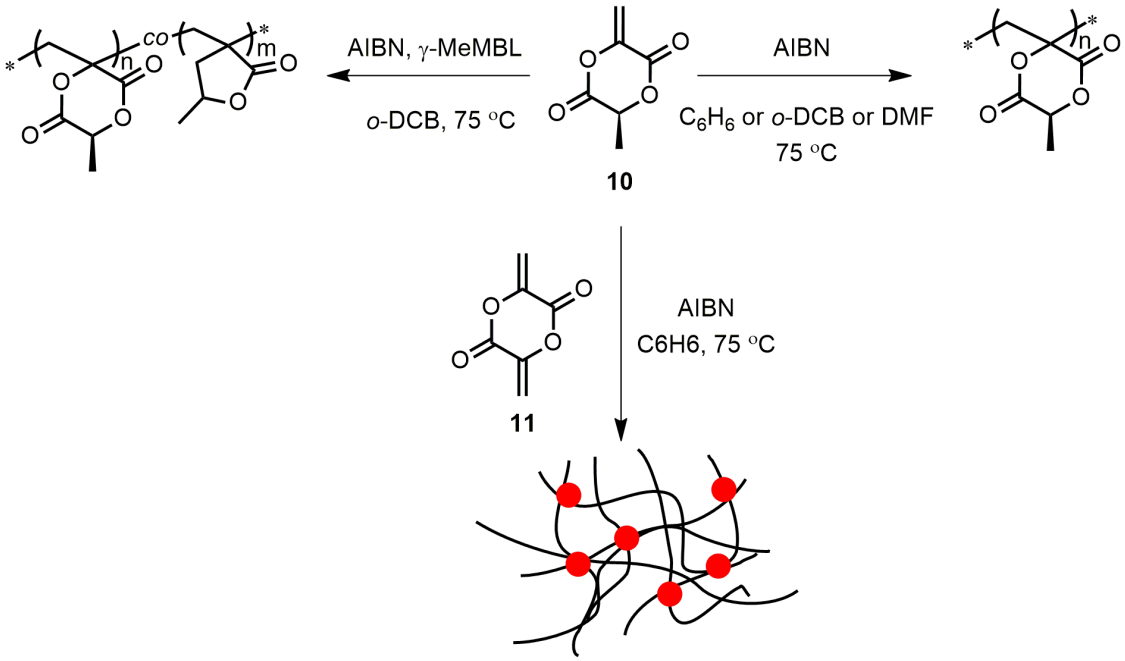
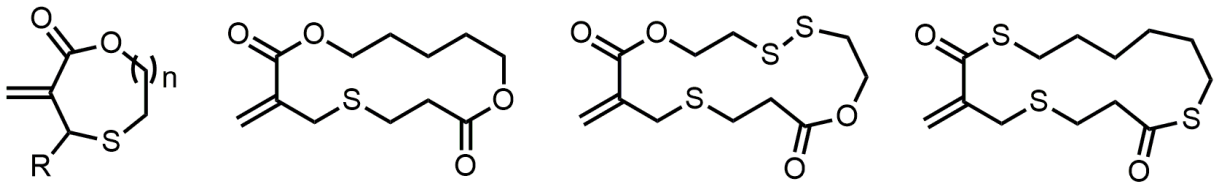


Figure 12: Homo- and co-polymerization of MLA through FRP.[70]

2.1.2. [α-CO] methylene cyclic esters with allylic sulfide or sulfone

The incorporation of heteroatoms within the lactone ring of [α-CO] methylene cyclic esters can deeply impact their polymerization path. For example, the radical polymerization of a series of methylene cyclic (thio)esters containing an allylic sulfide group in their ring **12**-**15** did not follow a ring retention mechanism but a radical ring opening pathway (**Figure 13**).[71–82] This produced a library of polymers having ester, thioester or disulfide bonds in their backbone which imparts some degradability to the polymer upon basic/acidic, reductive or enzymatic treatment, as discussed below.



12a: R=H,n=1
12b: R=H,n=2
12c: R=H,n=5
12d: R=CH_3,n=1

13 **14** **15**

Figure 13: Structure of [α-CO] methylene cyclic (thio)esters containing an allylic sulfide group.

The rROP of methylene cyclic esters **12** containing an allylic sulfide group is based on (i) addition of radical onto the alkene, (ii) ring opening with radical transfer to the sulfur atom and (iii) addition of the released thiyl radical onto the double bond of another monomer (**Figure 14**).[71,72,76] Note that double bonds generated along the polymer backbone during

the ring opening reaction also undergo radical addition followed by β-fragmentation reactions or crosslinking reactions leading to insoluble gels (**Figure 14**).[71,72] Substitution of a hydrogen atom in allylic position for a methyl group, as it is the case for compound **12d**, limits the crosslinking side reaction via steric hindrance effect.[71,72,76] The radical copolymerization of methylene cyclic (thio)esters containing an allylic sulfide with classical acyclic vinyl monomers were considered in order to introduce degradable/cleavable functions in the copolymer backbone notably for biomedical application purposes [25,77,78] The sulfide containing methylene cyclic (thio)esters were notably copolymerized with MMA (MHCs **12c**, **13**-**15**)[79] by RAFT and styrene (MHCs **12a**, **12d**)[80] by FRP, as illustrated in **Figure 15**. For copolymerization via RAFT, moderate dispersity (<1.5) and molecular weights in agreement with theoretical predictions were achieved when feed ratios of cyclic monomers were less than 5 mol%. Poorer control of the polymerization was observed for higher content of cyclic monomer due to the above mention side reactions involving the backbone double bonds. By integrating cyclic monomers into linear copolymer backbones led to systems with programmable degradation profiles upon base, reductive or thiolate treatments. For example, poly(**14**-*co*-MMA) possesses disulfides moieties in its backbone which are sensitive to either hydrazine[81] and tributylphosphine[82] at room temperature. Subsequently, MMA was substituted by the water soluble *N,N*-dimethylaminoethyl methacrylate (DMAEMA) and 2-hydroxyethyl methacrylate (HEMA) for the production of degradable materials dedicated to biological and medical applications.[79]

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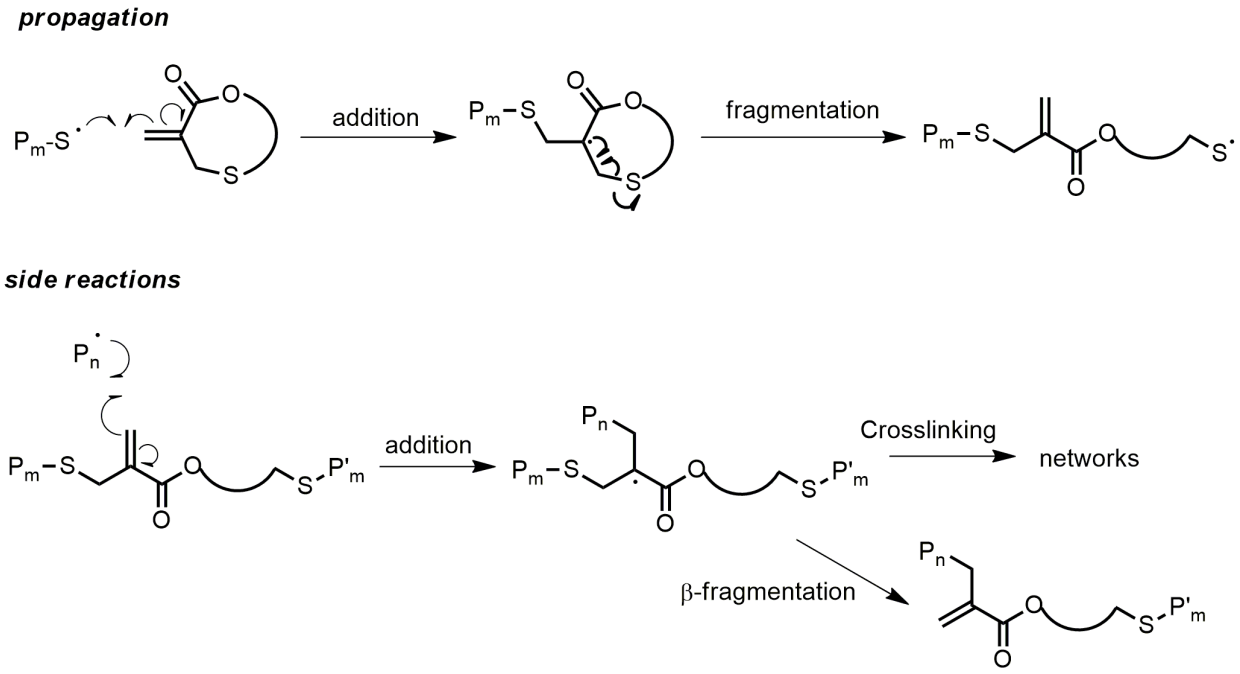

Figure 14: Polymerization mechanism of [α-CO] methylene cyclic (thio)esters containing an allylic sulfide group.

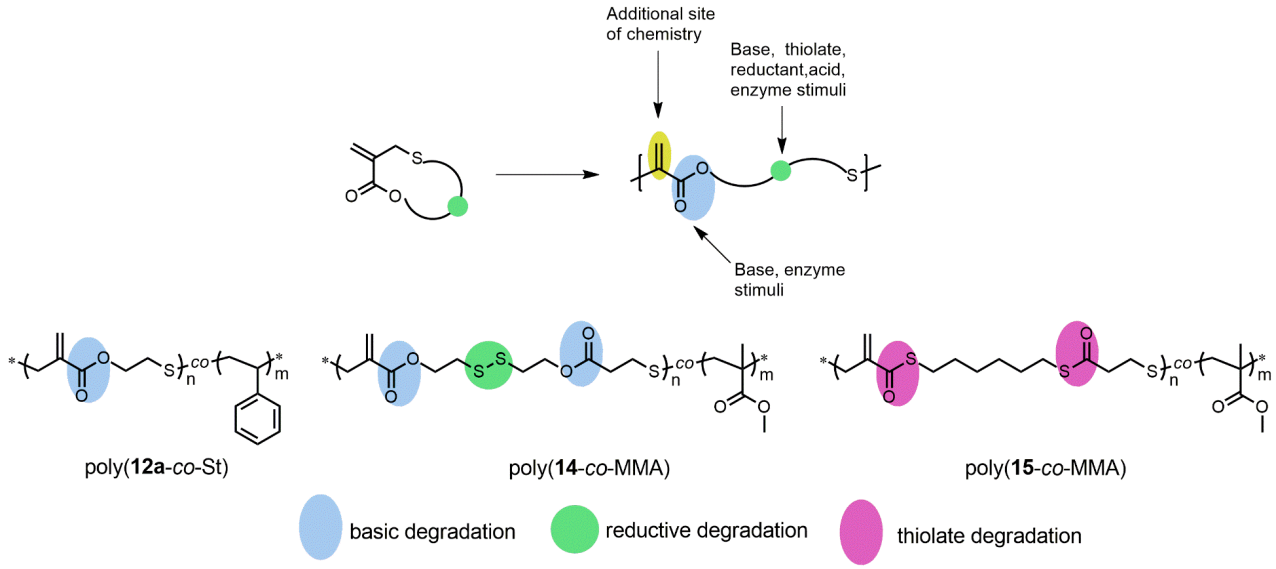

Figure 15: Degradable (co)polymers composed of allylsulfide containing methylene cyclic (thio)esters.[79,80]

Degradable amphiphilic diblock copolymer nano-objects of interest for drug delivery systems and responsive biomaterials were fabricated via polymerization-induced self-assembly (PISA) involving the disulfide-based compound **14** (**Figure 16a**).[73] The RAFT copolymerization of **14** with 2-hydroxypropyl methacrylate was performed in water using a poly(glycerol monomethacrylate) macro-CTA. Depending on the degree of polymerization, spheres, worms or vesicles containing disulfide bond in their hydrophobic region were formed. In the case of worms, the cleavage of the disulfide bonds resulted in a reduction of the copolymer molar mass sufficient to induce an irreversible worm-to-sphere transition. Paclitaxel-loaded amphiphilic diblock copolymer containing reduction-sensitive disulfide linkages were also prepared via RAFT copolymerization of **14** with a drug functionalized monomer and the pH-sensitive 2-(diisopropylamino) ethyl methacrylate (DPAEMA) using an oligo(ethylene glycol) methyl ether methacrylate (OEGMA) macro RAFT agent (**Figure 16b**).[74] The resulting poly(OEGMA)-*b*-poly(DPAEMA-*co*-PTXMA-*co*-**14**) was then self-assembled into dual pH- and redox-sensitive vesicles. Decrease of the pH and treatment with reducing agents promoted the disassembly of these carriers facilitating the release of the drug.

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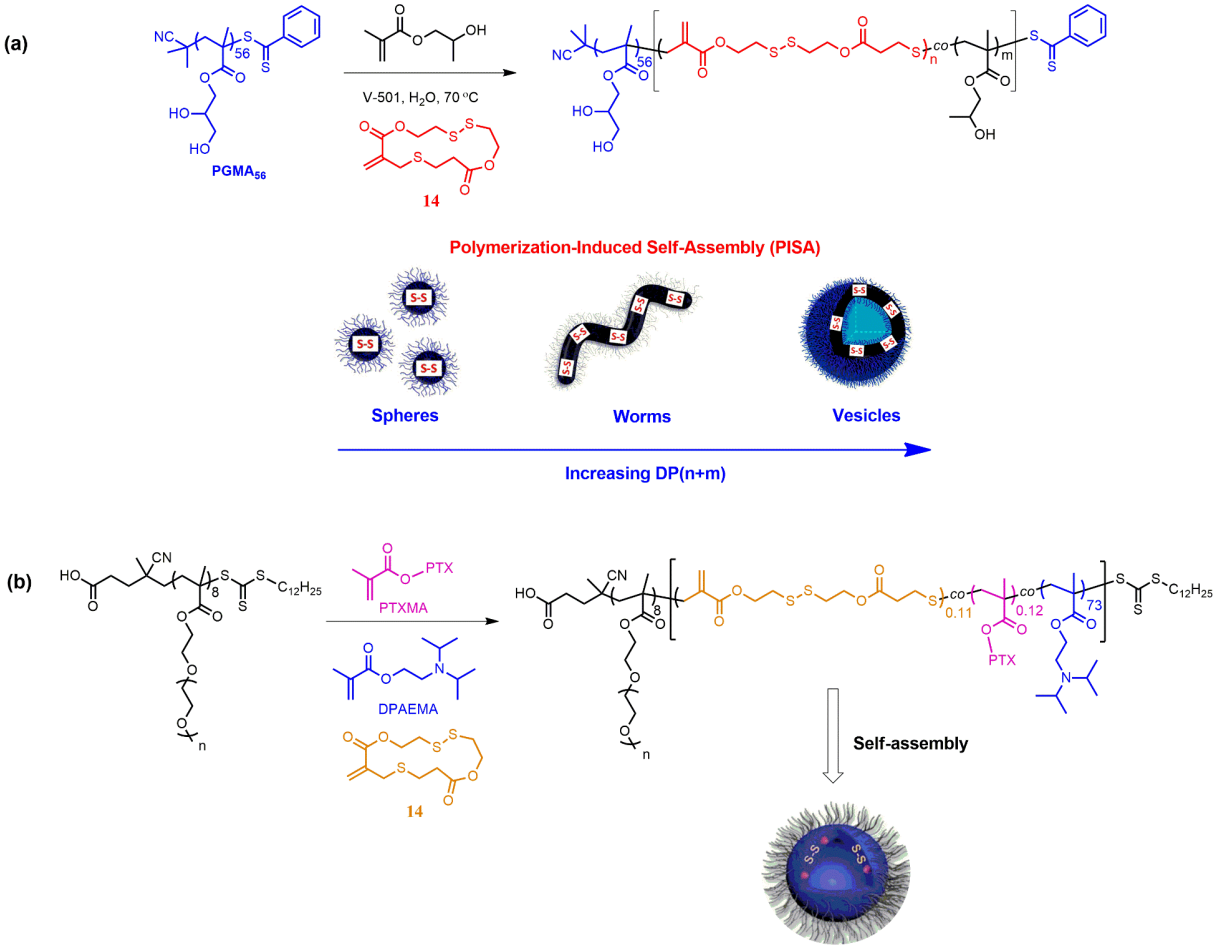

Figure 16: Use of the disulfide-based compound **14** for (a) the preparation of nanoobjects of different morphology by PISA[73]and (b) the design of dual pH- and redox-sensitive vesicles for drug delivery systems.[74]

One limitation of the allyl sulfide methylene cyclic esters mentioned above is the impossibility to control their radical ring opening homopolymerization involving thiyl radical species. To overcome this limitation, the radical ROP of allyl alkysulfone containing methylene cyclic esters, such as **16-19**, was developed (**Figure 17**). This process consists in a radical cascade process involving (i) radical addition on the methylene group, (ii) radical ring opening with β-elimination of alkylsulfone leading to an alkylsulfonyl radical, (iii) extrusion of SO_2 from the alkylsulfonyl radical and formation of carbon centered radical which can add a

new monomer.[83] The free radical polymerization of monomer **16** was achieved at 65 °C in DMF and yielded a polymer with molecular weight of 9.8 kg/mol and dispersity of 1.70.

Given the similarity of the propagating carbon centered radical generated during polymerization of allyl alkylsulfone-based monomers and acrylate propagating species, the RDRP polymerization of monomers **16-19** was successfully achieved by RAFT between 65 °C and 100 °C using various trithiocarbonates (**Figure 18a**).[83] A series of block copolymers made of the allyl alkylsulfone-based monomers **16-19** as well as statistical copolymers composed of **16** and methyl acrylate(MA) were also achieved by RAFT.[83] In these thermally initiated radical copolymerization, however, the allyl alkylsulfone macrocyclic esters exhibited a considerably faster rate of incorporation than methyl acrylate which precluded the formation of ideal random copolymers. Recently, a low temperature photoinduced electron/energy transfer-RAFT (PET-RAFT) process was investigated for the homopolymerization of the allyl alkylsulfone macrocyclic esters and their copolymerization with acyclic vinyl monomers (**Figure 18b**).[84] The reversible deactivation radical homopolymerizations of **16** and **19** were notably mediated by the ECTMPA CTA under 450 nm light irradiation in the presence of the *fac*-[Ir(ppy)$_3$] photocatalyst yielding polymers with dispersity below 1.2 (**Figure 18b**). These polymerizations were halted when the light was shut down and resumed efficiently after turning on the light. This PET-RAFT system also allowed the controlled copolymerization of **19** with various acrylates or acrylamides (**Figure 18b**).[84] In contrast to the thermal RAFT process, this photoinitiated RDRP approach led to mostly ideal random copolymers with reactivity ratios close to unity, e.g. r_{19}=1.07 ±0.03 and r_{MA} = 0.94±0.02. This conclusion was further supported by the narrow dispersity of the low molecular weight fragments produced by degradation of the copolymer upon treatment with sodium methoxide.

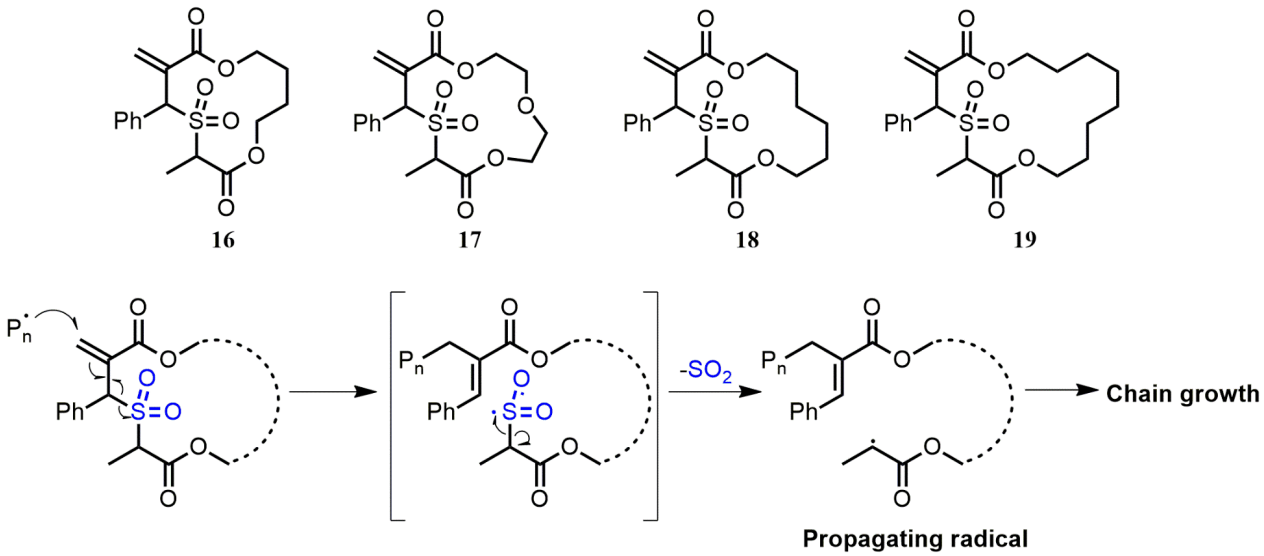

Figure 17: The structure and mechanism of polymerization of [α-CO] methylene cyclic esters with allylic sulfones.

2.1.3. [α-CO] Methylene cyclic amide and imide.

[α-CO] methylene cyclic amides are cyclic analogues of *N*-substituted methacrylamides. In general, the *N,N*-disubstituted methacrylamides are considered as poorly polymerizable monomers via radical pathway due to the twisted conformation between the vinyl group and the carbonyl moiety due to the presence of the α-methyl group.[85,86] In contrast, the planar lactam ring structure in [α-CO] methylene cyclic amides endows a higher reactivity and facilitates chain propagation due to the absence of serious steric hinderance between the propagating radical and the approaching monomer. Typical [α-CO] methylene cyclic amides involved in radical polymerization are presented in **Figure 19**.

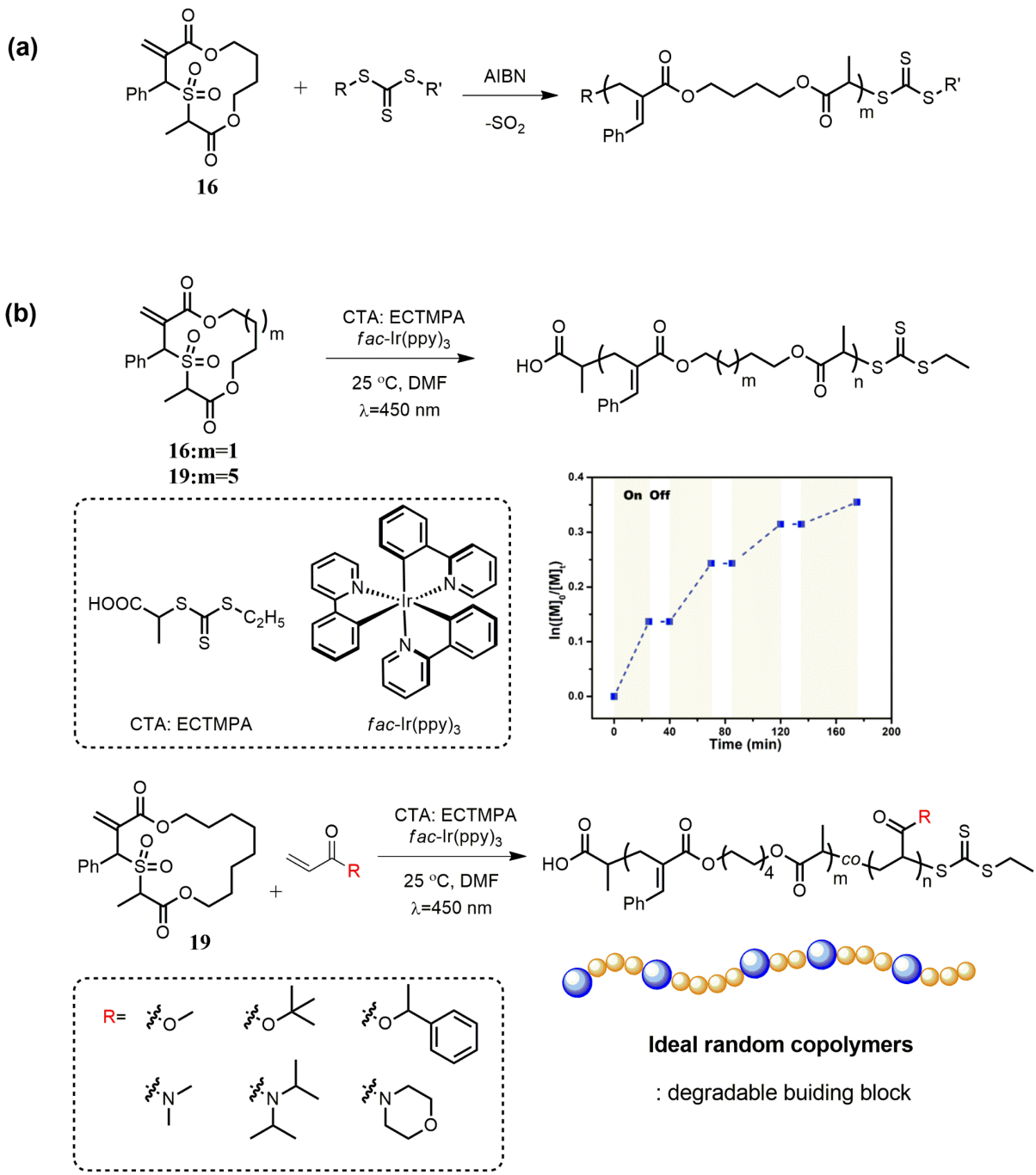

Figure 18: Controlled (co)polymerization of allyl alkylsulfone macrocyclic esters via (a) thermally initiated RAFT[83] and (b) PET- RAFT (co)polymerizations.[84]

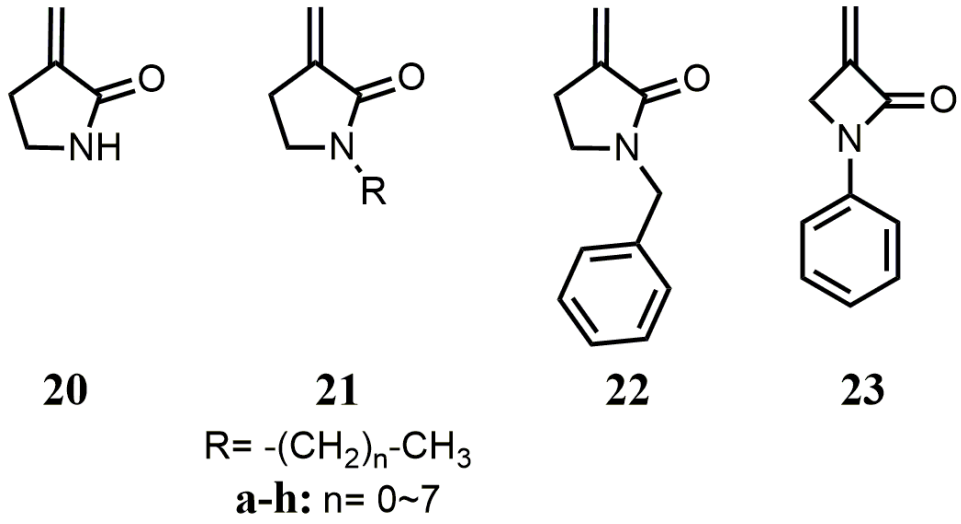

Figure 19: Structure of [α-CO] methylene cyclic amides.

As a rule, the FRP and RDRP of [α-CO] methylene cyclic amides follow a rRRP pathway. For example, the polymerization of 3-methylene-2-pyrrolidone **20** was demonstrated at 60 °C in DMSO leading to 82 % conversion and the formation of a polymer having pendant lactams with molar mass and dispersity of 6.7 kg/mol and 2.33, respectively (**Figure 20a**).[87] This homopolymer showed high thermal stability due to its lateral lactam groups and intermolecular hydrogen interactions (T_d ~ 400-500 °C, and T_g ~ 285 °C). The controlled radical polymerization of **20** was achieved by RAFT[87] and SET-LRP[87] giving access to well-defined poly(**20**) with narrow dispersity (RAFT: M_n=16 kg/mol, $Đ$=1.22; SET-LRP: M_n=11 kg/mol, $Đ$=1.16) (**Figure 20 b** and **c**). Cell viability tests demonstrated the absence of toxicity of poly(**20**) towards GT1−7 cultured hypothalamic mouse cell lines up to 1 mg/mL, emphasizing the interest of this water-soluble and biocompatible pyrrolidone-based vinyl polymers for biomedical applications.[87] The 3-methylene-2-pyrrolidone **20** was also copolymerized with MMA[88] or *N,N*-dimethylaminoethyl methacrylate (DMAEMA)[87] by FRP

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and low dispersity poly(*N,N*-dimethylaminoethyl methacrylate)-*b*-poly(**20**) block copolymers were also produced by RAFT.[87]

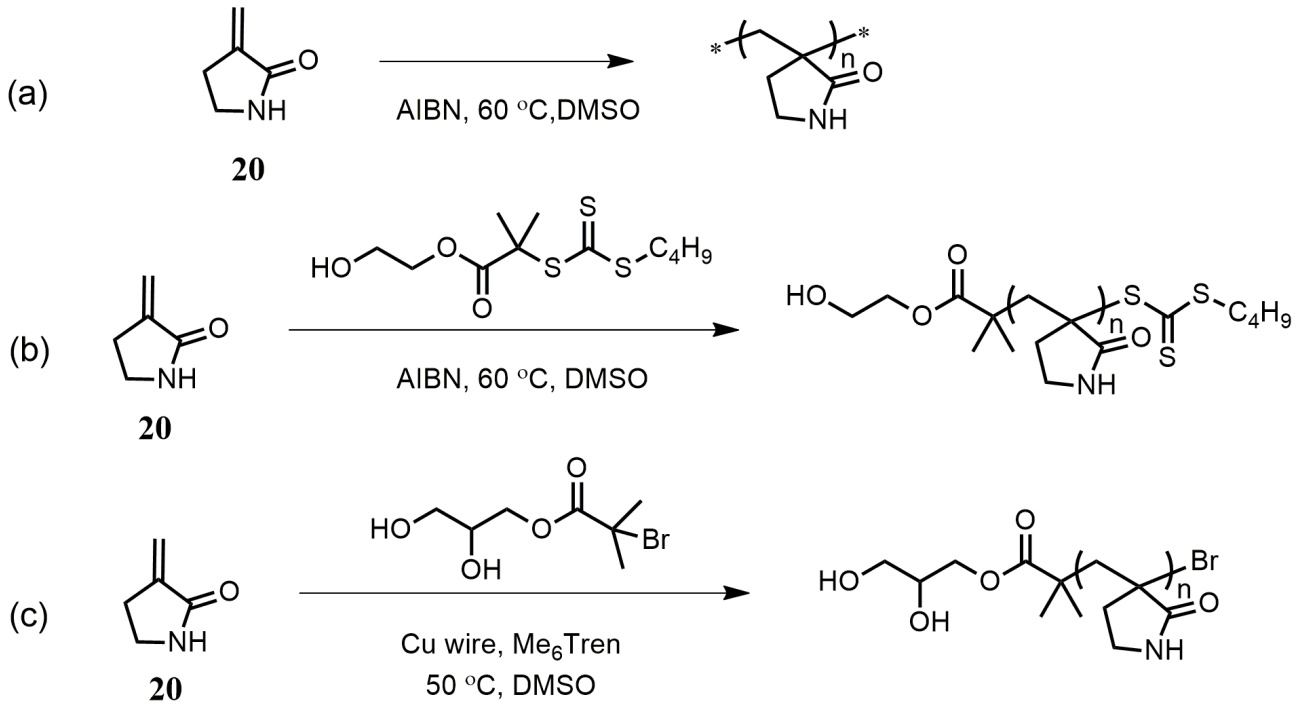

Figure 20: FRP (a), RAFT (b) and SET-LRP (c) of 3-methylene-2-pyrrolidone **20**.[87]

A series of poly(*N*-alkyl-3-methylene-2-pyrrolidone) with various hydrophobic/hydrophilic properties, solubility and thermal stability, was prepared via FRP of the corresponding *N*-substituted 3-methylene-2-pyrrolidone monomer (**21a-h**, **Figure 19**).[89,88,90] As the *N*-alkyl chain length of **21** increased from C_1 to C_8, T_g varied from 110 °C to -5 °C.[89] Contrary to poly(*N*-alky-3-methylene-2-pyrrolidone)s with long alkyl chains, those with shorter alkyl chains (C1-C3) were insoluble in common organic solvents but water soluble at room temperature. Expectedly, the equilibrium water content (EWC) of networks prepared from ethylene glycol dimethacrylate and *N*-alkyl 3-methylene-2-pyrrolidone compounds increased when decreasing of the *N*-alkyl chain length.[89]

Markedly, when the nitrogen atom of the 3-methylene-2-pyrrolidone was substituted by benzyl, namely *N*-benzyl-3-methylene-2-pyrrolidone **22**, mostly isotactic poly(*N*-benzyl-3-methylene-2-pyrrolidone) with a minor tendency to syndiotacticity was obtained via FRP as a result of the voluminous substituent and strong dipolar interaction between the amide functions (**Figure 21**).[90] Compared with the above mentioned poly(N-alky-3-methylene-2-pyrrolidone)s, the benzyl substituted poly(**22**) showed a slightly higher T_g (124 °C). Both **22** and the corresponding homopolymer are insoluble in water but the *N*-benzyl-3-methylene-2-pyrrolidone **22** formed a highly soluble complex with a methylated β-cyclodextrin allowing its radical polymerization in water using VA044® as initiator. The resulting polymer precipitated in water while the cyclodextrin slipped off step by step from the guest component. No information was provided about the tacticity of poly(*N*-benzyl-3-methylene-2-pyrrolidone) prepared in the presence of the cyclodextrin host.

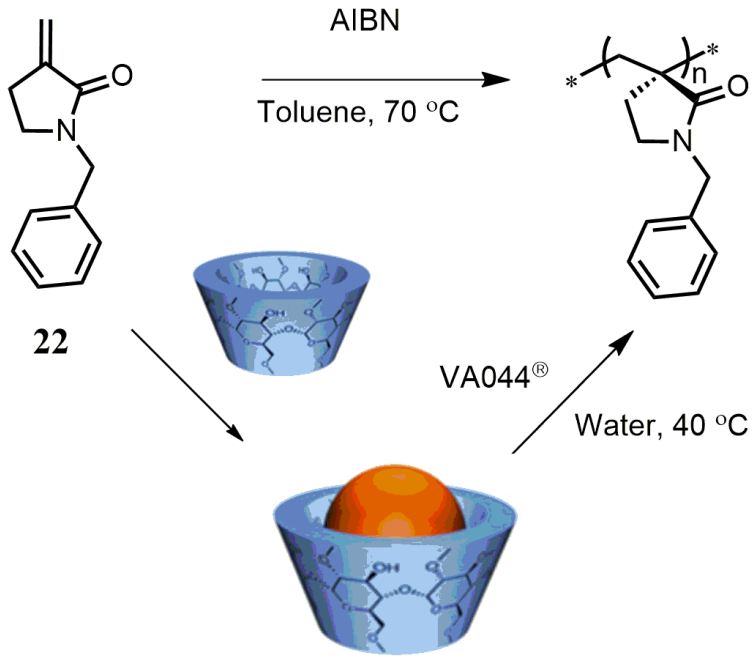

Figure 21: Radical polymerization of *N*-benzyl-3-methylene-2-pyrrolidone and its host-guest complex with methylated β-cyclodextrin.[90]

The radical polymerization of the 4-membered ring methylene lactam **23** (PML) was also reported. The resulting poly(*N*-phenyl-α-methylene-β-lactam) was highly syndiotactic (rr = 92%), possessed a T_g of 180 °C and was thermally stable until 330 °C in nitrogen.[91]

In addition to the MHCs bearing amides, those containing an imide moiety (**24**-**28**, **Figure 22**) were also used as monomers in radical polymerization with the aim to produce thermally stable vinyl polymers.[92]

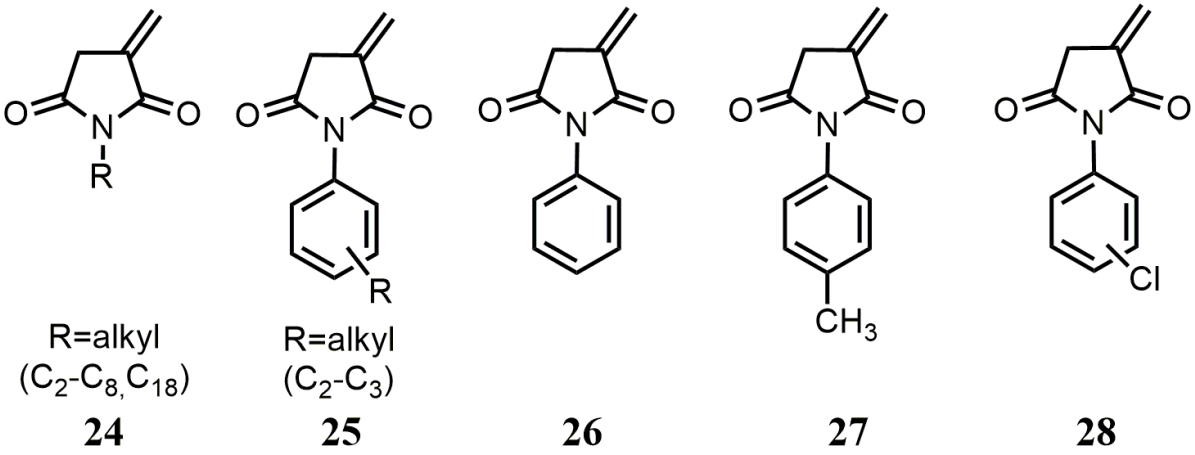

Figure 22: Typical examples of *N*-substituted itaconimides.

A series of *N*-alkyl itaconimides **24** with different alkyl groups were notably polymerized in bulk at 60 °C producing very high molar mass polymers (from 230 kg/mol to 997 kg/mol).[92] The highest yields and M_n were achieved with monomers having long alkyl chains such as $-(CH_2)_7CH_3$ and $-(CH_2)_{17}CH_3$. Moreover, monomers with bulky substituents, such as secondary and tertiary alkyl groups, also produced polymers in high yield indicating that the polymerization of *N*-alkyl itaconimides was weakly sensitive to the structure of substituents. The radical polymerization of *N*-(alkyl-substituted phenyl) itaconimides **25** was faster than

24. It was also found that the position, number and bulkiness of alkyl substituents on the phenyl ring significantly affected the reactivity of *N*-(alkyl-substituted phenyl) itaconimides. Higher yields were obtained for monomer substituted in the meta or para position of the phenyl ring.[92] For *N*-2,6-disubstituted phenyl monomers, the rate of polymerization decreased as the bulkiness of the alkyl substituents increased, due to the inhibition of conjugation with the phenyl ring and steric hindrance. Both the poly(*N*-alkyl itaconimides)s and poly(*N*-(alkyl-substituted phenyl) itaconimides)s exhibited excellent thermal stability with onset decomposition temperatures of 250-300 °C and 300-350°C, respectively.

The RDRP of plant-derived itaconic acid compounds such as *N*-phenylitaconimide **26** and *N*-(p-tolyl) itaconimide **27**, was also achieved by RAFT using cumyl dithiobenzoate as CTA (**Figure 23**).[93] This RAFT process gave access to the well-defined homopolymers but also allowed the production of novel itaconimide-based block copolymers.[93] For example, the sequential RAFT polymerization of dibutyl itaconate and *N*-phenyl itaconimide using difunctional CTA led a biobased thermoplastic elastomer consisting of hard itaconimide out block (T_g = 241 °C) and soft itaconate inner segment (T_g = 14 °C).[93] Block copolymers consisting in PMMA attached to a poly(*N*-aryl itaconimide)s segment from the *N*-tolyl or *N*-(chlorophenyl) itaconimides **27-28**, were also prepared by ATRP. In this case, however, only low fractions of *N*-aryl itaconimides were incorporated (<10 mol%) in the copolymer and the molecular weight of poly(N-aryl itaconimide) segments remained low (1~1.8 kg/mol) maybe due to isomerization of *N*-aryl itaconimides into *N*-aryl citraconimides or to termination via chain-transfer reactions.[94]

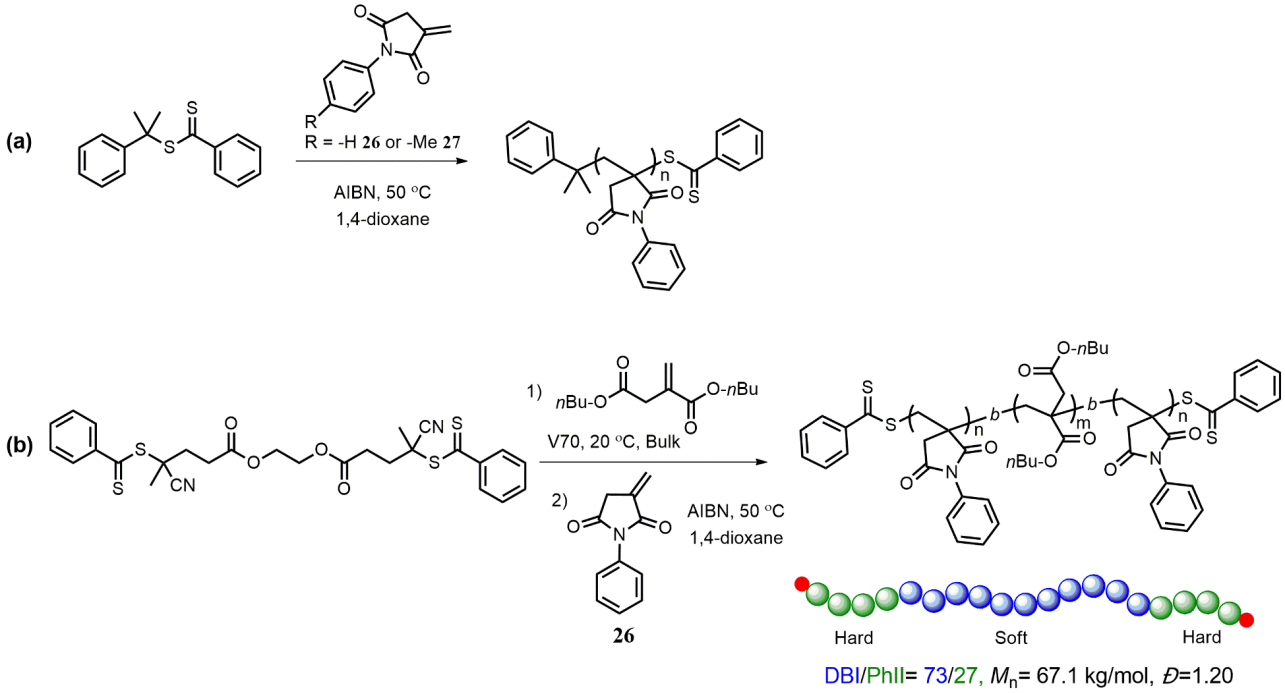

Figure 23: (a) RAFT polymerization of *N*-aryl itaconimides and (b) production of triblock elastomers.[93]

2.1.4. [α-CO] methylene cyclic ketone.

Pinocarvone **29** is a bicyclic vinyl ketone synthesized via photooxidation of α-pinene, the most abundant naturally occurring terpene (**Figure 24**). Upon radical polymerization of **29**, at 60 °C in bulk or in various solvents, two types of repeating units were detected in the polymer chain.[95] One of them was formed by rRRP and presented a bicyclic pendant group while the other resulted from the rROP pathway involving the β-scission of the four-membered ring and leading to unsaturated six-membered rings in the polymer chain (**Figure 24a**). The rROP pathway was dominant in all cases and was even selectively achieved (99 %) when conducting the radical polymerization at 60 °C in hexafluoroisopropanol (HFIP). Excellent thermal properties were recorded for the poly(pinocarvone) composed almost

exclusively by ring-opened units (T_g = 162 °C, T_d = 327 °C). Optically active polymers were also produced from the (+)-pinocarvone.[95] Finally, well-defined poly(pinocarvone)s containing 95% ring-opened units were synthesized by RAFT in HFIP.[95] This approach was implemented for the preparation of poly(pinocarvone)-*b*-poly(*n*-butyl acrylate)-*b*-poly(pinocarvone) copolymers of valuable interest as high service temperature thermoplastic elastomers (**Figure 24b**). [95]

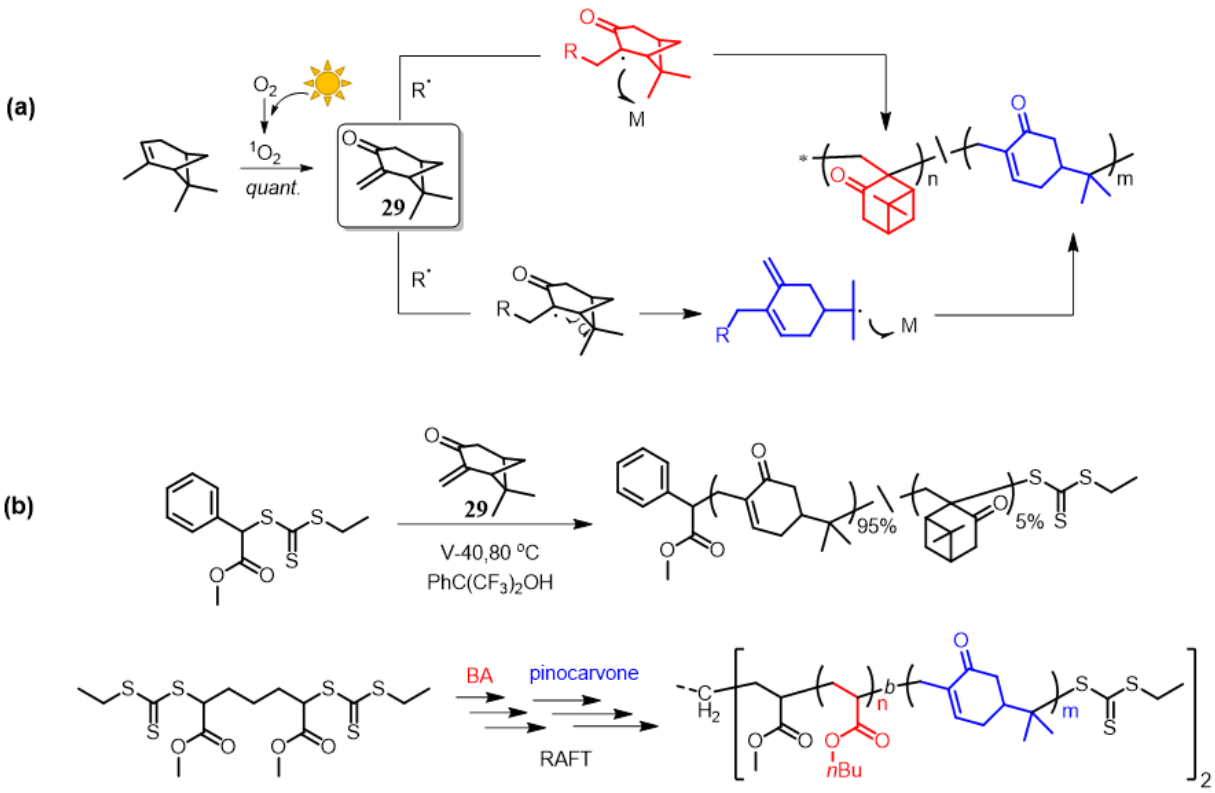

Figure 24: (a) Mechanism of radical polymerization of pinocarvone and (b) RAFT synthesis of pinocarvone-based (co)polymers.[95]

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2.1.5. [α-CO] alkylidene cyclic ester.

The use of carbon dioxide as building block for the synthesis of monomers and polymers is a topic of growing interest. In this respect, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one **30**, synthesized by palladium-catalyzed condensation of CO_2 and 1,3-butadiene, produced polymers with high molar mass and CO_2 content of 29 wt% via radical polymerization.[96] This [α-CO] alkylidene cyclic ester was first homopolymerized in bulk at 100 °C in the presence of V-40 leading to polymers with bicyclic structures in the main chain (α repeating units in **Figure 25a**). This polymerization proceeded with radical addition onto the substituted acrylate followed by cyclisation via addition of the tilgate radical onto the allyl group (See mechanism in **Figure 25**).[96] Interestingly, polymers synthesized via FRP in the presence of Lewis acid like $ZnCl_2$, not only presented the bicyclic α structures but also the repeating units β (with pendant cyclic ester groups) and γ (with cyclic ester functions within the polymer backbone). $ZnCl_2$ promoted the polymerization of the allyl esters leading to the structure β whereas coordination of the Lewis acid with the carbonyl oxygen of **30** reinforced the electrophilicity of the α-carbonyl radical from tiglate and the intramolecular hydrogen abstraction leading to the repeating unit γ. The synthesis and radical polymerization of **30** were also combined in a one-pot process as well as the terpolymerization of CO_2, butadiene and another 1,3-diene. Interestingly, reversible ring opening and ring closure phenomena were observed for poly(**30**) composed exclusively of α repeating units (**Figure 25b**). Treatment with KOH/18-crown-6 promoted the ring opening of the bicyclic structure (90 %) and cleanly reversible ring closure was achieved by simple heating at 180 °C.[97] The ring opening aminolysis of the bicyclic structure of poly(**30**) was also described, and the resulting modified polymers achieved 93% reversible ring closure at 260 °C.

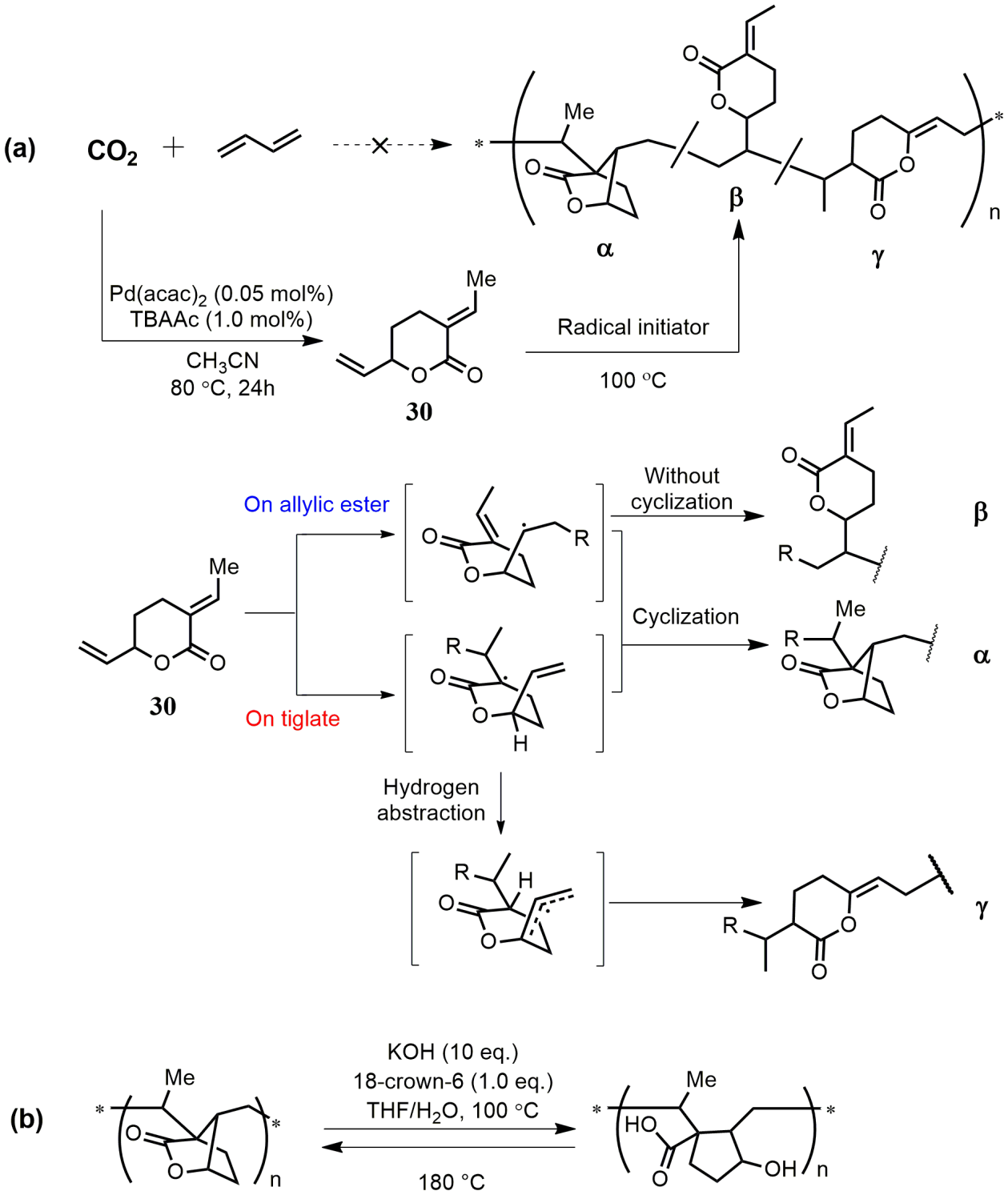

Figure 25: (a) Synthesis and radical polymerization of the lactone **30**[96] as well as (b) reversible ring-opening/closure post-polymerization modification of poly(**30**).[97]

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2.2. [α-O] Methylene heterocyclic monomers

2.2.1. [α-O] Methylene cyclic ester

Contrary to the [α-CO] methylene cyclic esters belonging to the conjugated vinyl monomers category, reports on radical polymerization of non-conjugated [α-O] methylene cyclic esters are scarce. One example concerns the four-membered ring ketene dimer **31** (**Figure 26**).[98] Due to the ring tension and the possibility to form a quite stable intermediate acyl radical, **31** polymerized via rROP at 120 °C. When polymerization was performed in closed vessel, the polymer was essentially composed of 1,3-diketone groups whereas copolymer with large proportion of 1,4-diketone groups was obtained for open flask polymerization due to substantial loss of carbon monoxide CO.

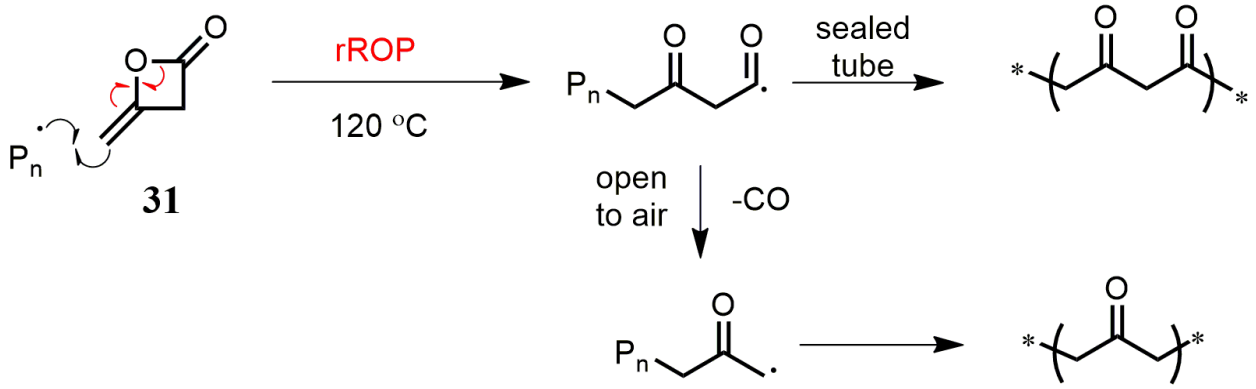

Figure 26: Radical ring opening polymerization of [α-O] methylene cyclic ester **31**.[98]

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Because *α*MγBL **1** is a conjugated vinyl lactone, its copolymerization with non-conjugated LAMs such as vinyl acetate (VAc) or α-olefins is precluded. From there, the five membered ring γ-methylene-γ-butyrolactone (γMγBL) **32**, a non-conjugated version of **1** and a cyclic structural analog of VAc, was prepared by Pd-catalyzed cycloisomerization of 4-pentyn-1-oic acid and used as comonomer in radical polymerizations for incorporating pendant lactones within LAMs-based copolymers (**Figure 27**).[99,100] The radical polymerization of **32** exclusively proceeded via rRRP and its organometallic-mediated radical copolymerization with VAc[99] or *N*-vinyl caprolactam (*N*VCL)[100] led to a series of well-defined γMγBL-containing copolymers with controlled compositions. Hydrolysis of their pendant lactones produced unique stimuli responsive materials including pH-sensitive hydroxy acid-functional poly(vinyl alcohol) (PVOHs)[99] as well as dual pH/thermo-responsive hydroxy acid-bearing P*N*VCLs.[100] In contrast to the previously reported acid-functional P*N*VCLs, this multi-responsive NVCL-based system emphasized a unique reversible pH-dependent ring opening/closure of the pendant lactones preventing aggregation via H-bonding upon reacidification.

2.2.2. [α-O] Methylene cyclic carbonate

α-Alkylidene cyclic carbonates (αCCs) is an important class of partially renewable compounds produced by catalytic carbonylation of propargylic alcohols with CO_2.[101,102] Compared to the classical five-membered cyclic carbonates, in αCCs **33**, the presence of an exo-methylene group activates the carbonate allowing its reaction with numerous nucleophiles[102,103] but it also paves the way to the radical polymerization of these [α-O] methylene cyclic carbonates (**Figure 28**).

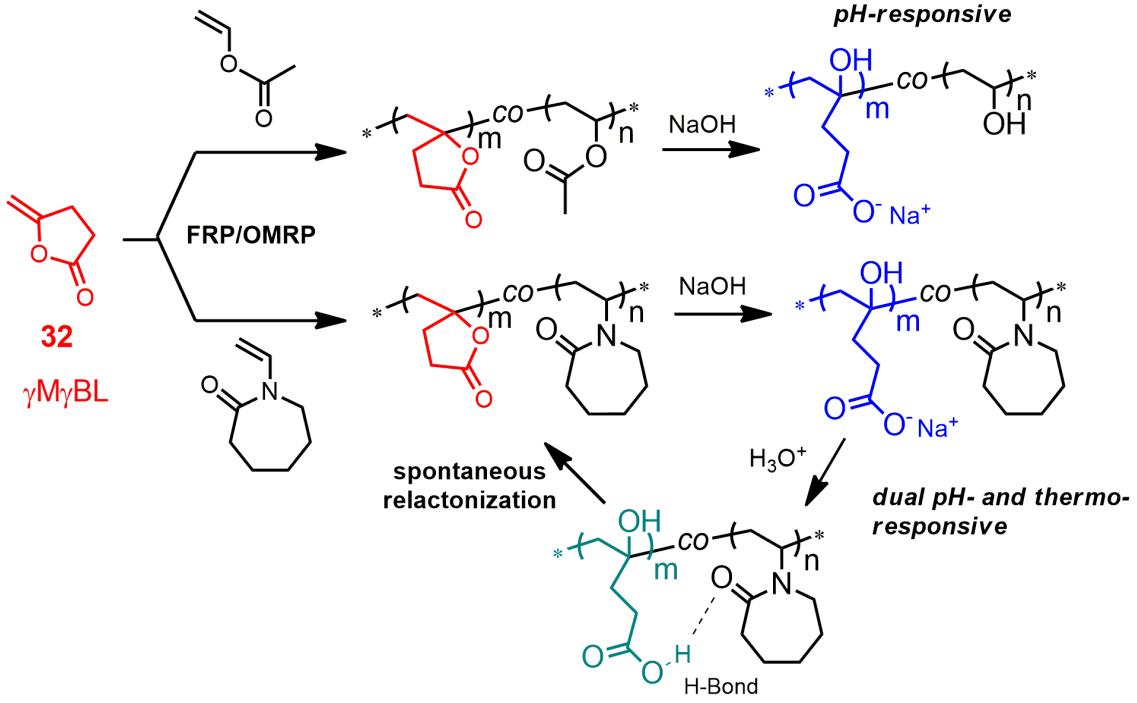

Figure 27: Radical copolymerization of γMγBL **32** with VAc[99] and NVCL[100] towards multi-responsive PVOH and PNVCL.

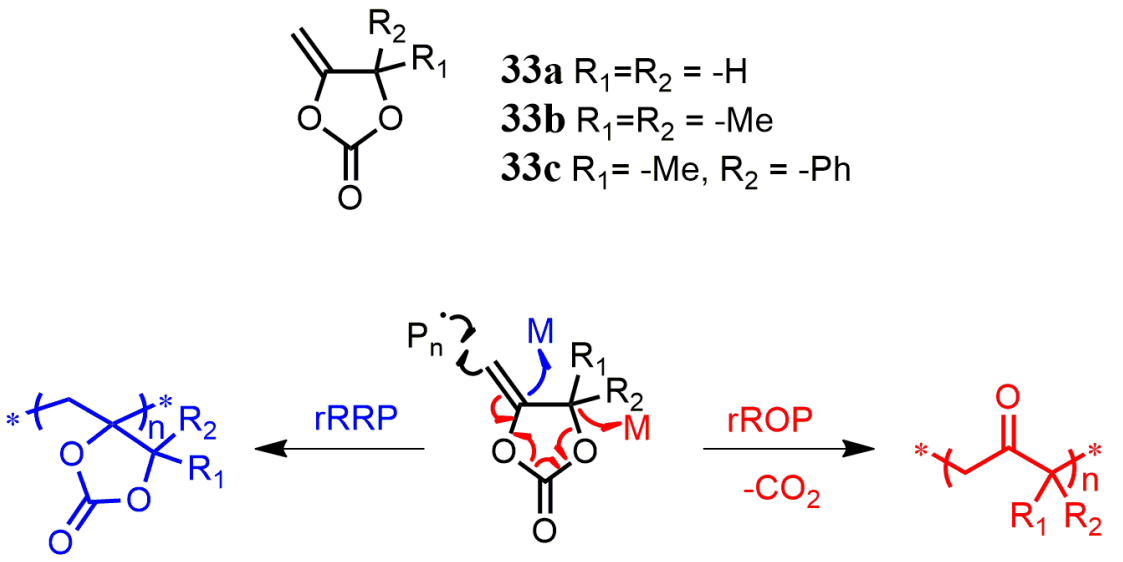

Figure 28: Typical [α-O] methylene cyclic carbonates and their possible radical polymerization pathways.

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The radical polymerization of αCCs (**33**) was notably carried out at temperatures ranging from 60 to 130°C.[104,105] At 60 °C, only poly(**33a**) was collected (>89%). The mechanism consisted in rRRP yielding polymers with pendant cyclic carbonates. The latter were further methanolized with sodium methoxide to generate a water-soluble hydroxy-functional polymers.[104,106] Due to steric hindrance, the presence of two substituents in monomers **33b-c** inhibited propagation. When conducted at 130 °C, the radical polymerization of **33b** reached 46% conversion but led to oligomers comprising nearly equal content of pendant carbonates formed by rRRP and ketone functions resulted from radical ring opening reaction followed by decarboxylation, as shown in **Figure 28**.[105] Poly(**33c**) could not be generated through radical polymerization due to the steric hindrance from phenyl group and to the stabilized styrenic propagating radical after decarboxylation,[104,105,106]

The controlled radical copolymerization of the methylene cyclic carbonate **33b** with another non conjugated monomer, namely VAc, was also achieved by organometallic-mediated radical polymerization (OMRP),[107] a RDRP well-adapted to less activated monomers (LAMs).[10] A series of low dispersity ($Đ$ < 1.3) poly(**33b**-*co*-VAc)s with different compositions (up to 40 mol% of **33b**) were prepared by bulk copolymerization at 40 °C using $Co(acac)_2$ as controlling agent (**Figure 29**).[107] In line with the poor radical homopolymerizability of **33b** at low temperature, the reactivity ratio measured for **33a** was close to 0 ($r_{\mathbf{33a}}$ = 0.03 and r_{VAc} = 1.11). The presence of bulky and rigid pendant cyclic carbonates in the copolymer significantly increased T_g compared to the PVAc, namely from 42 °C to 80 °C for PVAc and poly(**33b**$_{0.22}$-*co*-VAc$_{0.78}$), respectively. A series of post-polymerization modification reactions

were carried out onto these poly(VAc-*co*-**33a**)s including methanolysis under basic conditions of both the pendant esters and the carbonate groups leading to vicinal-diol containing PVOHs with improved water solubility as compared to classical PVOHs.[107]

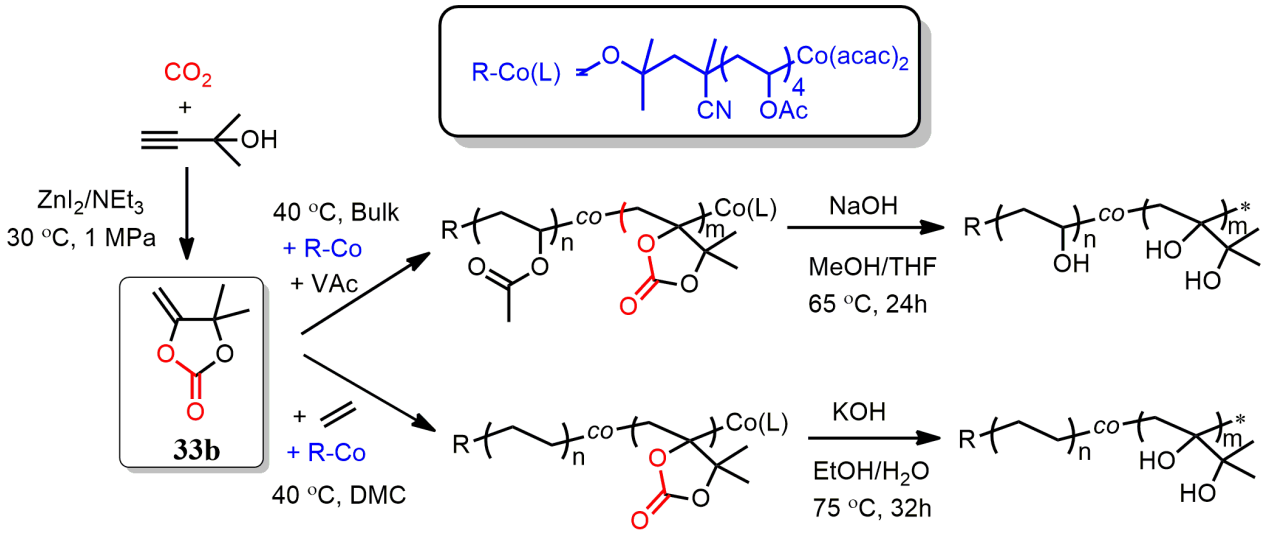

Figure 29: Organometallic-mediated radical copolymerization of **33b** with VAc and ethylene and the post-modification of resulting carbonate-containing copolymers.[107,108]

The CO_2-sourced cyclic carbonates **33b** was also incorporated into polyethylene (PE) via OMRP performed under ethylene pressure using an alkyl-Co(acac)$_2$ initiator at 40 °C in dimethyl carbonate (DMC) (**Figure 29**).[108] The molar mass and composition of the poly(E-*co*-**32b**)s was tuned by adjusting the monomer/alkyl-cobalt ratio and ethylene pressure, respectively. Increasing the ethylene pressure from 10 to 50 bar decreased the content of **33b** in the copolymer from 60 mol% to 22 mol%, while dispersity remained low in all cases ($Đ$ = 1.21-1.28). The T_g of poly(E-*co*-**33b**) also increased with the carbonate content (up to 27 °C for 60 mol% of **33b**) and semicrystalline behaviors were observed for copolymers with high ethylene content (F_E= 78 mol%, T_m= 49 °C). Finally, vicinal diol-bearing PEs were obtained by hydrolysis of the cyclic carbonate groups of poly(E-*co*-**33b**) under basic conditions (KOH, 75 °C).

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2.2.3. [α-O] Methylene oxazolidinone

Oxazolidin-2-one compounds sustain applications in many fields of applications[109–113] and several efforts were devoted to their incorporation into polymer structures[112,114,115]. In this respect, another CO_2-sourced MHC appeared as a valuable comonomer, namely 4,4-dimethyl-5-methyleneoxazolidin-2-one **34** (DMOx) (**Figure 30**).[116,117] The latter was produced via carboxylative cyclization of dimethylpropargylamine and copolymerized radically in a controlled manner with VAc and ethylene. Well-defined DMOx-containing PVAc[116] and EVAs[117] were prepared by OMRP and RAFT, but the latter technique appeared more suited for the production of copolymers with high DMOx content. Various post-polymerization modifications of these MHC-based copolymers, such as hydrolysis and aminolysis reactions, gave access to unique stimuli responsive materials including pH/thermo/metal ion-responsive amino alcohol-functional poly(vinyl alcohol) as well as unprecedented pH-responsive amino-functional ethylene/vinyl alcohol (EVOHs) copolymers.[116,117] A selective post-polymerization modification of the 1,2-amino alcohol functions into oxazolidines was also reported and exploited for the preparation of EVOH gels under mild conditions.[117]

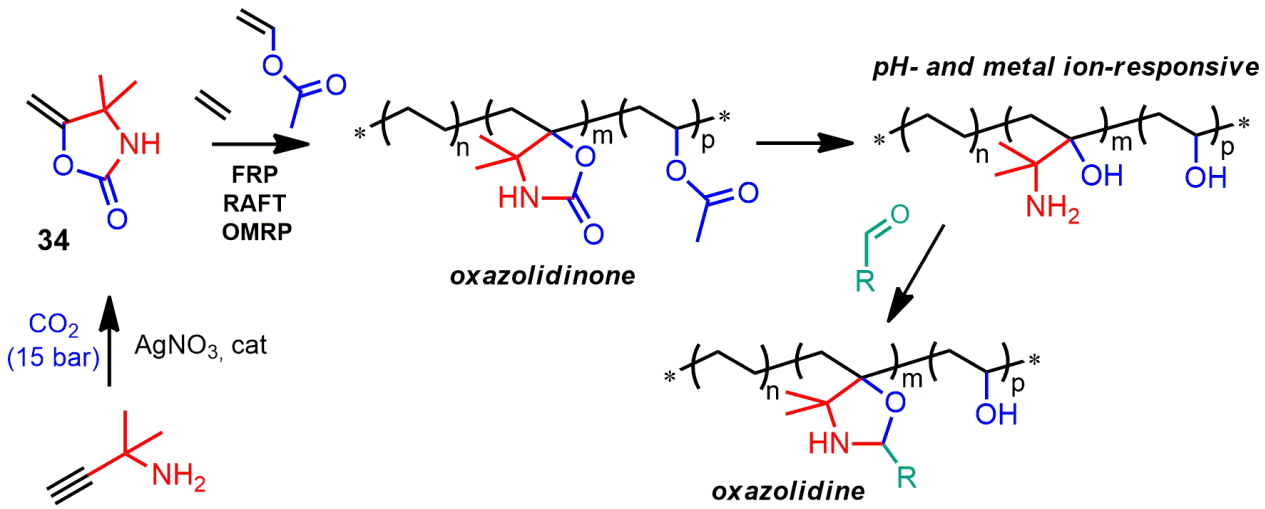

Figure 30: Radical copolymerization of DMOx **34** with ethylene and/or VAc towards multi-responsive PVOH and EVOH derivatives.[116,117]

2.2.4. [α-O] Methylene cyclic ether

The free radical polymerization of a series of [α-O] methylene cyclic ethers (**35**-**38**) was reported at 120 °C using di-tert-butyl peroxide (DTBP) as initiator (**Figure 31**).[98] In this case, the extent of ring opening during polymerization was governed by the ring size and substituents. The homopolymerization of the 5-membered ring methylene cyclic ether **36a** mainly proceeded via rRRP and polymers contained less than 10% of ring opened units.[98,118] Introduction of methyl and phenyl group at the ortho position of O atom (**36b** and **36c**), however, increased the extent of ring opening approximately to 20% and 50%, respectively, due to the higher stability of the radical generated via rROP in this case. In contrast, monomer **37** exclusively underwent rRRP due to the stable tertiary benzyl radical (with additional stabilization from oxygen) formed upon radical addition onto the vinyl bond.[98] Finally, the 6-membered ring methylene cyclic ether **38** showed similar polymerization behavior compared to its 5-membered ring counterpart **36a** with less than 10 mol% of ring opened units whereas the intrinsic strain effect of the 4-membered ring monomer **35** led to higher extent of ring opening (40 mol%).[98]

2.2.5. [α-O] Methylene cyclic acetal

The radical polymerization of [α-O] methylene cyclic acetal, also named 2-substituted-4-methylene-1,3-dioxolanes, composed of a cyclic structure containing a methylene adjacent to an acetal function, proceeds either via ring-retaining or ring-opening pathways depending on the acetal substituents (**Figure 32**).[119] In the case of [α-O] methylene cyclic acetal, the rROP process involves a radical rearrangement with release of a ketone and the formation of polyketones.

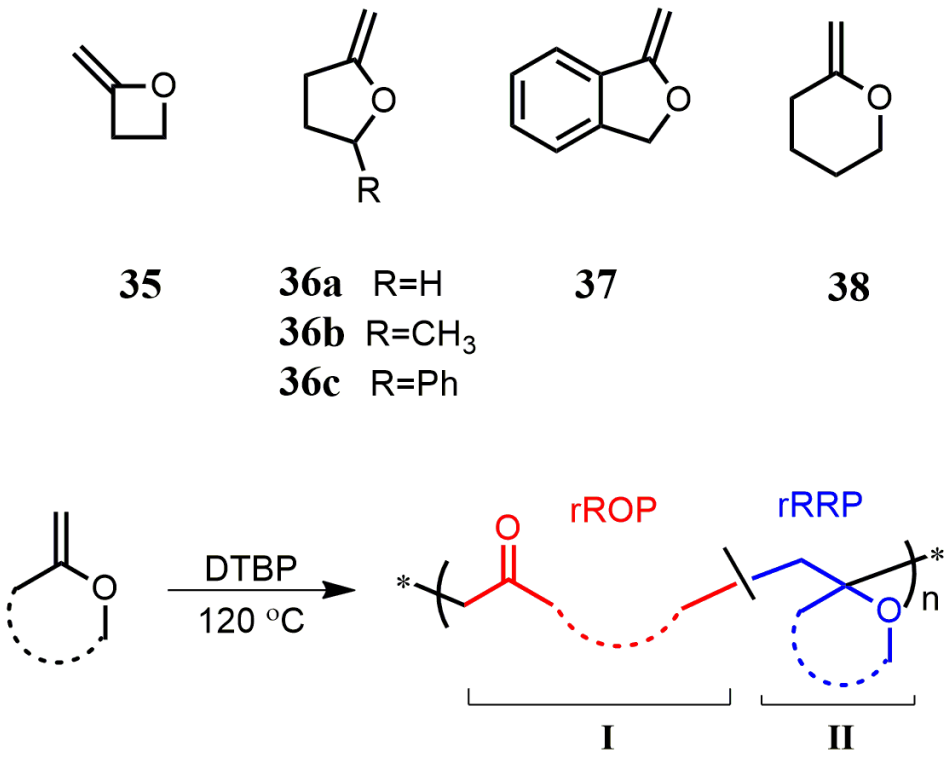

Figure 31: The typical [α-O] methylene cyclic ethers and their radical polymerization pathways.

As an illustration, a series of [α-O] methylene cyclic acetal with different alkyl or aryl substituents (**39a-i**) were polymerized in bulk at 120 °C using DTBP as initiator.[119,120,121] Typically, monomers **39a-h** underwent simultaneous ring-retaining and ring-opening polymerization and produced low molar mass polymers (1.3-2.7 kg/mol) with pendant acetals and ketones in the main chain.[119,120,121] Only compound **39i** with two phenyl substituents almost exclusively polymerized via rROP due to the formation of a stable and bulky diphenylmethyl intermediate radical (97% of ring opened units).[119,122] Later on, quantitative rROP of **39i** and elimination of benzophenone was reported in chlorobenzene leading to polyketones, alternating ethylene and carbon monoxide in its backbone, that was insoluble in organic solvents.[123] Several structural variations of the diphenyl methylene dioxolane **39i** were examined. First, introducing a methyl group on the methylene cyclic acetal, namely monomer **40**, led to poly(**40**) with improved solubility in common organic solvents such as DMF, THF and chloroform.[124] In contrast to **39i**, only partial ring-opening polymerization was observed for the fluorene containing compound **41** due to the locked

aromatic rings which decreases the steric hindrance between the monomer and the propagating radical and favors the radical ring retaining polymerization (up to 40-50 mol% in the copolymer).[125] On the other hand, para substituted diphenyl methylene dioxolane derivatives (**42a-d**) underwent predominantly rROP with elimination of the corresponding disubstituted benzophenones. While the copolymer composition was barely affected by the substituents, the polymer yield decreased as the electron-withdrawing character of the substituents increased.[126] As a curiosity, the styrenic moiety of the bifunctional monomer **43** was selectively polymerized in DMF at 60 °C and the resulting polymer served as template for the rROP of the pendant methylene acetals and the production of polyketones.[127,128]

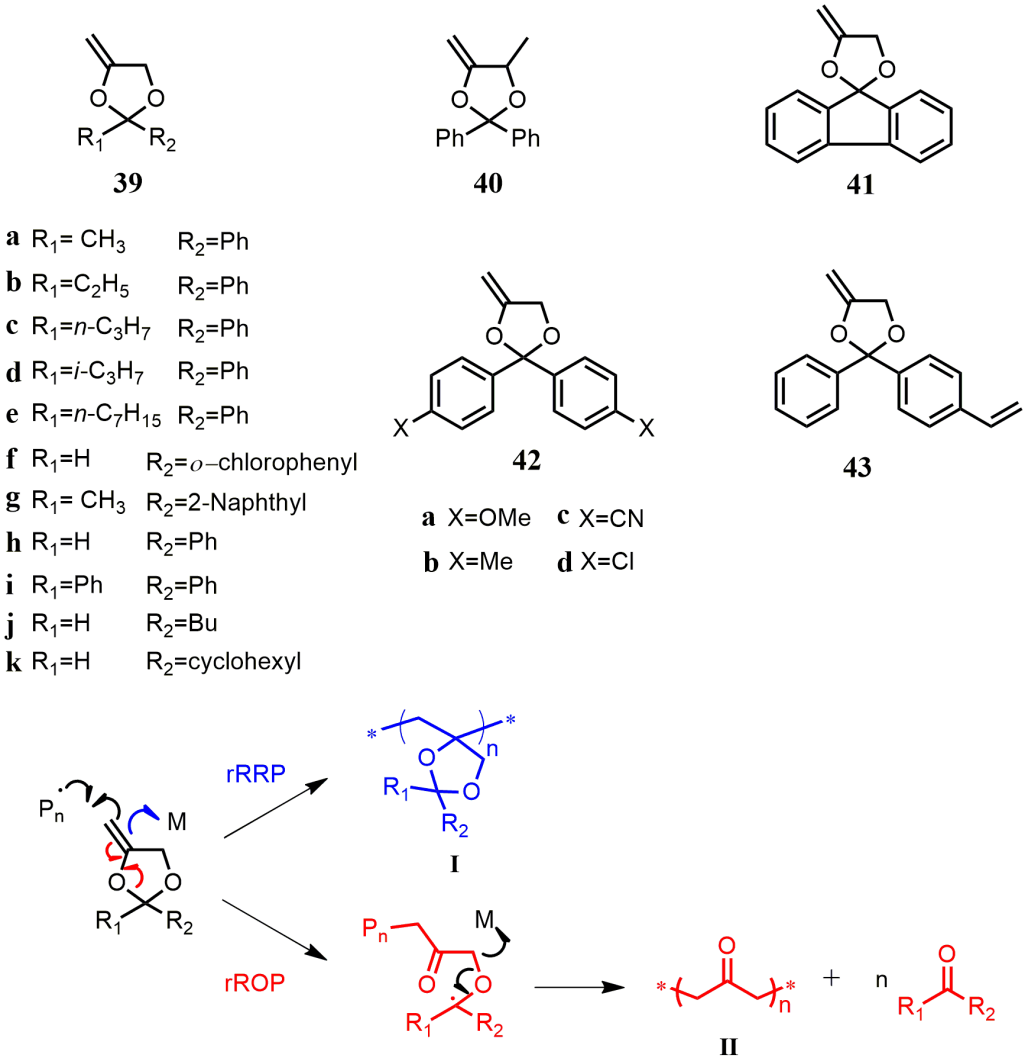

Figure 32: Examples of [α-O] methylene cyclic acetals and their rRRP and rROP mechanisms.

The diphenyl methylene dioxolane **39i** was also copolymerized with acyclic monomers and the polymerization pathway of the former varied with the nature of the comonomer. Indeed, **39i** essentially underwent ring opening polymerization when copolymerized with NVP, St and VAc,[129] whereas significant amount of ring retaining polymerization was observed for copolymerization with MMA[129] and AN.[130] Some cyclic vinyl ethers with acetal linkage and phenyl, butyl or cyclohexyl substituent (**39h**, **39j** and **39k**, respectively) were synthesized from glycerol and copolymerized through rRRP by FRP and RAFT with different vinyl monomers including MA.[131] The hydrophilicity of the resulting biobased copolymers could be tuned by conversion of the pendant acetal functions into diols upon deprotection reaction. Among the [α-O] methylene cyclic acetals, spiro-ring monomers such as **44**, **45** and **46**, follow a peculiar radical double ring-opening polymerization pathway leading to linear copolymers alternating ketone and ester in their backbone (**Figure 33**).[98,132] The radical polymerization of **46** involving a benzyl propagating radical was also performed at 125 °C in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).[132] Although low, the M_n increased linearly with the monomer conversion and the dispersity of poly(**46**) prepared by NMP was significantly lower than the one produced by FRP ($Đ$ = 1.8 and 6, respectively).

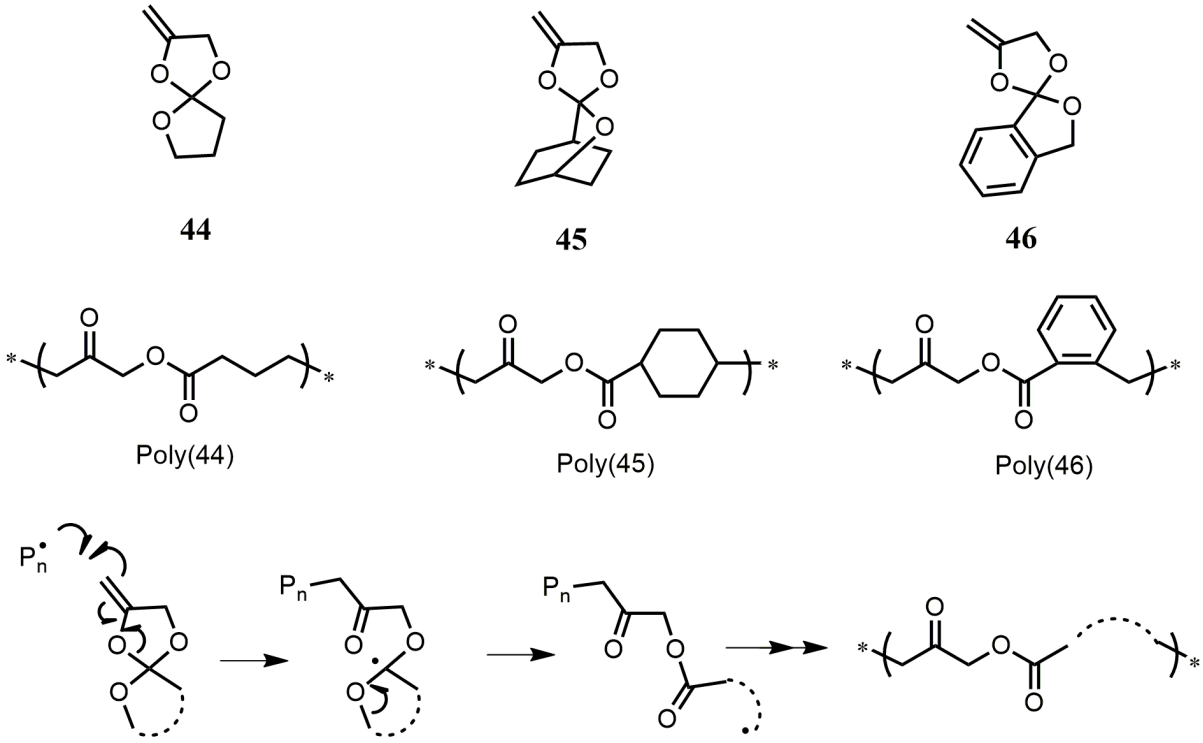

Figure 33: Structure of [α-O] methylene spiroacetals and their general rROP mechanism.

2.3. [α-2O] cyclic ketene acetal

Cyclic ketene acetals (CKAs) are a peculiar class of monomers whose doublets of the two oxygen atoms are delocalized on the double bond rendering the latter highly polarized and nucleophilic. As a result, CKAs are sensitive to electrophiles and easily undergo cationic polymerization.[25] Although slower than cationic polymerization, the radical polymerization of CKAs has also been largely investigated in the last decades, notably yielding degradable polyesters via rROP.[25] Because several recent comprehensive reviews already cover this field, [25,133–137] only key aspects of the radical polymerization of CKAs and the potential applications of the polymers resulting therefrom will be described in the present section.

The radical polymerization of CKAs can follow a ring opening pathway and/or a ring retaining process, as depicted in **Figure 34**. The rROP leads to the incorporation of degradable ester functions in the polymer backbone whereas rRRP generates pendant acetals which can be further converted into ketone. Mastering the competition between rROP and rRRP is a major challenge when considering the radical polymerization of these monomers. There are three main factors influencing the polymerization pathway,[136–138] namely ring size, substituents and reaction conditions (i.e. temperature, monomer concentration, etc…). The ring-opening ability of CKA monomers with various ring-size evolves in the order 7>5>6 membered ring.[136] The 6-membered ring monomers are known to be the most stable and difficult monomers to polymerize through a ring opening process as a result of their low ring-strain. For example, the radical polymerization of **48** at 65 °C yielded polymers containing only 7.7 mol% of ester units.[137] Under same conditions, the polymerization of the 5-membered ring compound **47** produced polymers containing 51 mol% of ester units.[137] Although the ester content increased with the reaction temperature, the occurrence of rRRP was unavoidable for **47** and **48**.[136,139] On the other hand, the 7-membered ring **49** exclusively underwent an addition-fragmentation mechanism and generated polyesters at temperature as low as 60 °C.[139] Nonetheless, backbiting side reactions leading to branching were not negligible in this case. For instance, the rROP of **49** was accompanied by 1,7-H-transfer and produced a polyester showing 15% of branching, as shown in **Figure 34**.[137,140] In addition, the ether-containing 8-membered ring **50** also followed exclusively a ring-opening pathway and produced ester-ether copolymers at 70 °C.[141,142]

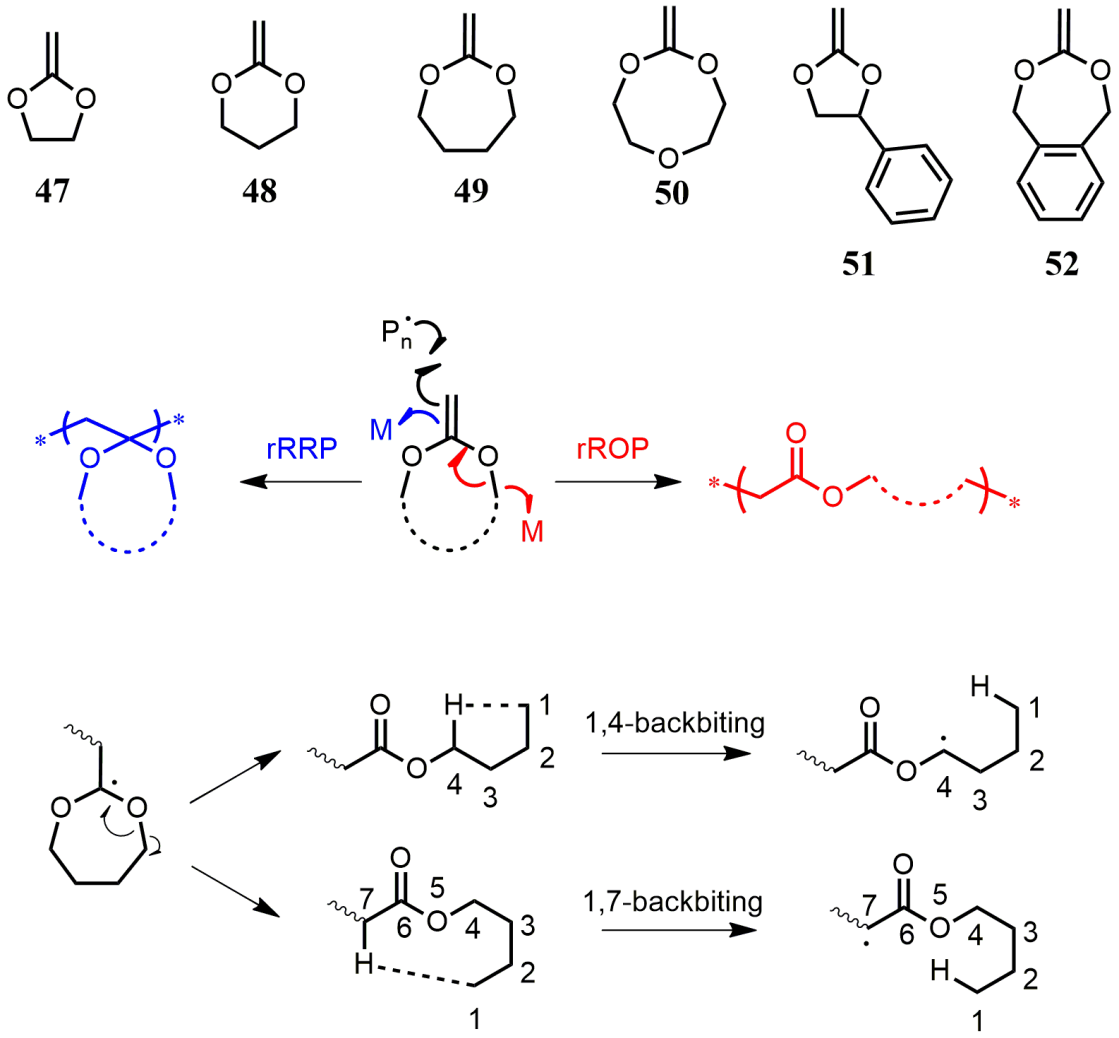

Figure 34: Structures, radical polymerization mechanisms and side reactions of CKAs.

The introduction of radical stabilizing substituents onto the CKA ring significantly favors its ring opening propensity. For example, the radical polymerization of the 5-membered ring **51** containing a phenyl substituent yielded only polyester whatever the polymerization temperature between 60-150 °C.[143] Compared to CKA **49**, the radical polymerization of the 7-membered ring CKA **52** containing an aromatic stabilizing group also proceeded via rROP but the polymerization rate was slower and backbiting side reactions were suppressed due to the higher stability of the propagating radicals.[133] The extent of rROP of CKAs can also be improved by adjustment of the polymerization conditions. In general, higher temperature and dilution of the polymerization medium favors the rROP pathway. So far, only **49**, **50** and **52** are known to exclusively promote radical ring opening polymerization under a broad

range of experimental conditions making the latter the most popular CKAs for the development of degradable polymers.

While degradable (co)polymers can be achieved via conventional radical ring-opening (co)polymerization of CKAs, combining RDRP with the rROP of CKAs gives access to more complex degradable polymer architectures. These includes functional and stimuli responsive materials of high interest for a wide range of applications, especially in the biomedical area. Several RDRP methods have been successfully used for the preparation of well-defined CKA-based polymers, including RAFT, ATRP, NMP and OMRP.[134] The choice of the RDRP method and of the controlling agent varied with the monomer structure.

Because a stabilized benzyl radical is generated in the radical ring opening polymerization of CKA **52**, efficient RDRP methods for **52** are inspired from those developed for styrene and other more activated monomers (MAMs). Polyesters with low dispersity and predictable molar masses were prepared by RAFT of **52** carried out in THF at 120°C in the presence of ethyl 2-((phenylcarbonothioylthio)butanoate and dicumyl peroxide (**Figure 35a**).[144] The ATRP of **52** initiated by the ethyl 2-bromobutanoate/bpy/CuBr system also afforded good control over M_n and dispersity ($Đ$=1.20-1.48) (**Figure 35b**).[145] Successful NMP of **52** was also reported with the BlocBuilder alkoxyamine initiator but the presence of dead polymer chains was observed above 50 % monomer conversion due to the trapping of the intermediate ketal-based macroradical (**Figure 35c**).[146] Moreover, the phenyl-functionalized CKA **51** was copolymerized in a controlled manner with oligo(ethylene glycol) methyl ether methacrylate (OEGMA) or MMA by NMP-mediated rROP.[147–149] In this case, **51** served as controlling comonomer for the NMP of methacrylic derivatives and conferred tunable degradability to the resulting copolymers. Cell viability tests demonstrated the absence of toxicity of the pristine (co)polymers highlighting the potential of these materials in the biomedical field.[147,149]

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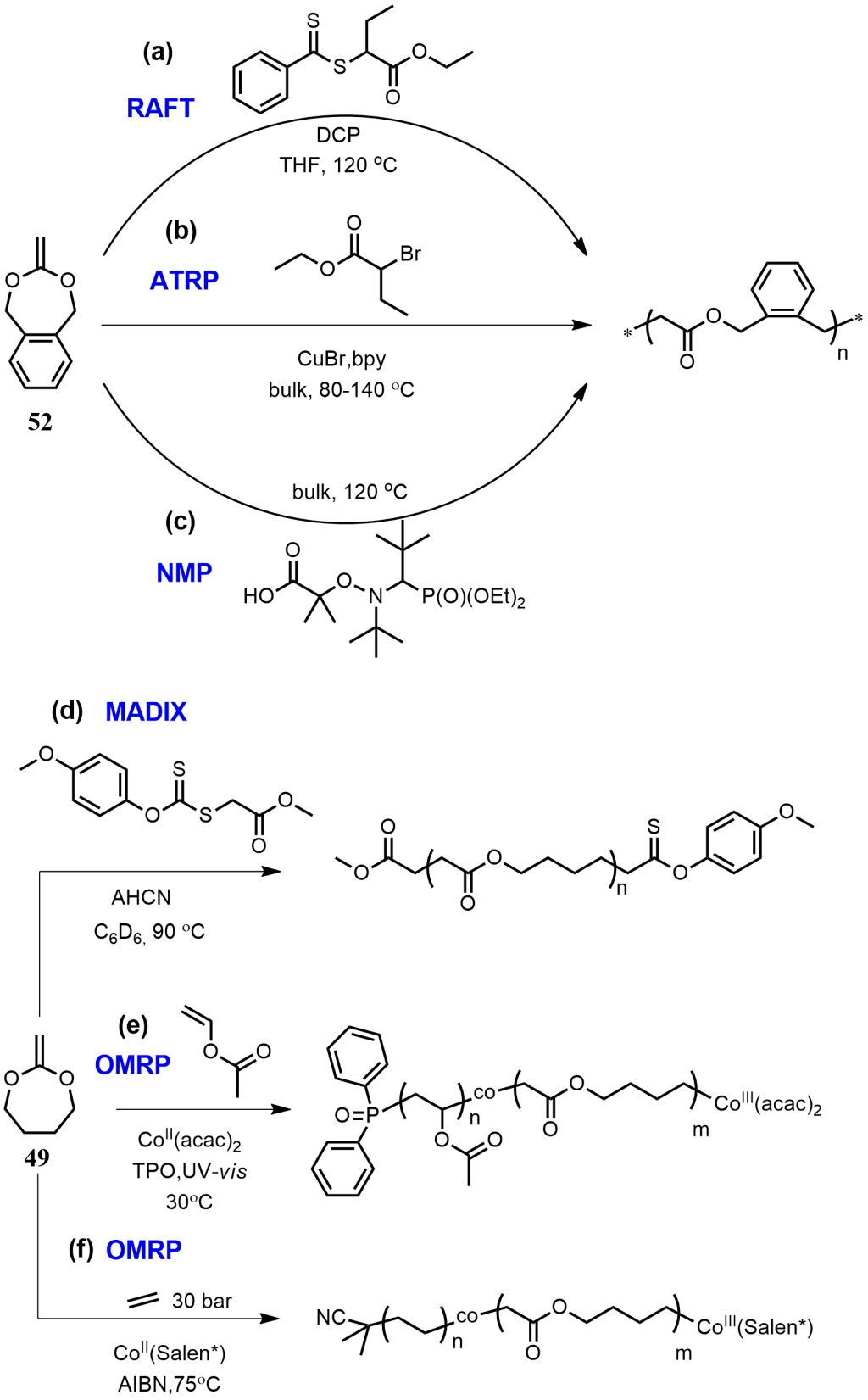

Figure 35: Examples of reversible deactivation radical ring opening (co)polymerizations of CKA.

In contrast to **52**, the propagating species involved in the rROP of **49** is deprived of radical stabilizing group similarly to less activated monomers (LAMs). For this reason, RDRP approaches typical of LAMs were applied to the rROP of **49**. The MADIX polymerization, involving a xanthate as CTA which favors the fragmentation step and the release of poorly stabilized radicals, displayed excellent control of the rROP of **49** leading to polyesters with low dispersity and high chain-end fidelity.[150] OMRP is another method of choice for the RDRP of LAMs. So far, the radical ring opening homopolymerization of CKAs hasn't been reported via OMRP but the VAc/**49** copolymerization was successfully mediated by $Co^{II}(acac)_2$ at 30 °C under UV irradiation with (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TPO) as the radical source (**Figure 35e**).[151] On the other hand, degradable polyethylene containing 10-35 mol% of ring-opened CKA units was obtained through controlled copolymerization of **49** and ethylene in the presence of Co^{II}(Salen*) complex (**Figure 35f**).[152]

Many other vinyl monomers were considered as comonomers of CKAs either to introduce functionalities into the degradable polyester chains to adjust their chemical/physical properties and allow post-modification reactions,[153–157] or to impart (bio)degradability to traditional vinyl polymers.[149,158–161] The 7- or 8- membered CKAs **49**, **50** and **52**, are most frequently considered as comonomers notably due to their excellent ability to undergo ring opening pathway. These CKAs were copolymerized with well-known vinyl monomers such as styrene,[162] methacrylates,[163,164] acrylates,[165] acrylamides,[166] vinyl acetate[167] and vinyl pyrrolidone.[156]

As main trend, CKA monomers exhibit moderate low reactivity when copolymerized with vinyl monomers excepted for VAc. Indeed, a feed fraction of 80 mol% of **49** was necessary to obtain a PS with only 10 mol% of ester units[162] whereas a random polymer containing 57 mol% ring opened **49** units and 53 mol% VAc units was attained in bulk at 70 °C.[167] For a feed fraction of 50 mol% 7-membered CKAs, up to 35 mol% of CKA units were incorporated during its copolymerization with MA,[165] MMA,[163,164] acrylamides[166] and acrylonitrile.[165] Alternating or alternating-rich copolymers were also obtained upon

copolymerization of **49** or **52** with an electron-deficient monomers such as N-ethyl maleimide,[168] 1-(trifluoromethyl)vinyl acetate[169] and pentafluorophenyl methacrylate.[170]

From an application point view, CKA monomers have been utilized to endow degradability to functional materials applied in several domains notably in the biomedical[171–174] and anti-biofouling[175] fields in order to avoid the accumulation of materials in human body and environment. As an illustration, an amphiphilic P(**49**-*co*-PEGMA-*co*-CMA) copolymer was synthesized via simple one-pot copolymerization of **49**, poly(ethylene glycol) methyl ether methacrylate (PEGMA) and 7-(2-methacryloyloxyethoxy)-4-methylcoumarin methacrylate (CMA) followed by self-assembly into biodegradable and biocompatible micelles (**Figure 36**).[172] The latter were core cross-linked upon UV exposure and loaded with doxorubicin for drug delivery application.[172] A water-soluble, degradable and pegylated polymer based on poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) with good p-DNA transfection efficiency was prepared by copolymerization of **52** with 2-dimethylaminoethyl methacrylate (DMAEMA) initiated from a PEO macro-azoinitiator.[173] The resulting poly(PEG-*co*-(**52**-*co*-DMAEMA))s contained alkaline hydrolysable ester linkages in their backbone, which overcome the nondegradable limitation of the use of PDMAEMA with high molecular mass for DNA transfection application.[173] As a final example, degradable poly(ester-*co*-acrylate) copolymers with antifoulant pendant groups were prepared by radical polymerization of **49**, methyl methacrylate, and *N*-methacryloyloxy methyl benzoisothiazolinone (**Figure 36**).[175] The final copolymer exhibited not only tunable enzymatic and hydrolytic degradation but also excellent antifouling capacity against marine bacteria *Pseudomonas sp.* and marine diatom Navicula incerta.[175]

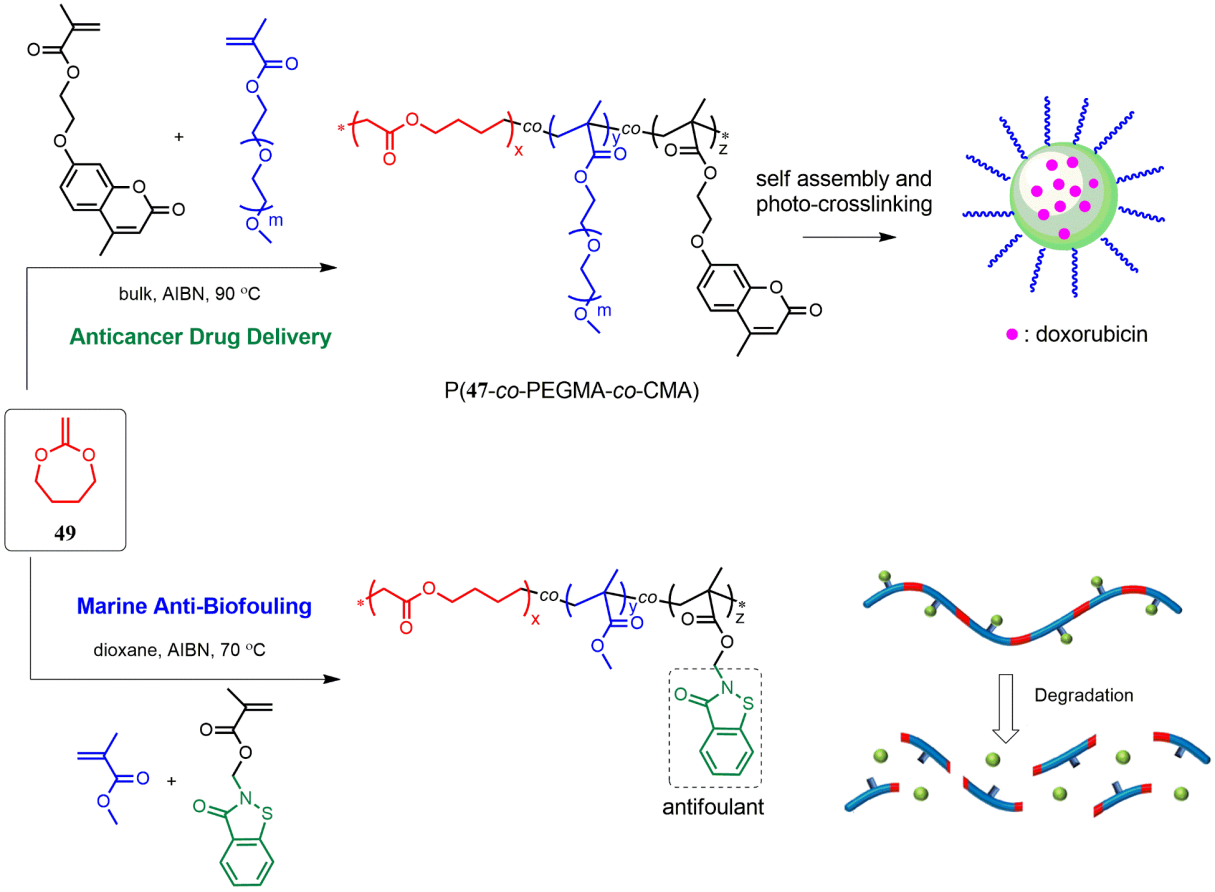

Figure 36: Typical applications of CKA-based copolymers in drug delivery[172] and anti-biofouling fields. [175]

Recently, cyclic ketene hemiacetal esters (CKHEs) have been considered as alternative to CKAs for the preparation of degradable polymers (**Figure 37**).[176,177] Compared to CKAs, CKHEs bears a carbonyl group and mainly polymerizes via rRRP. For example, **53** derived from aspirin was homopolymerized and copolymerized with VAc exclusively via rRRP leading to the corresponding (co)polymers.[177] The cyclic ketene hemiacetal ester units of the resulting (co)polymers could be degraded to salicylic acid and acetic acid by acid hydrolysis. Similarly, **54a** generated the corresponding homopolymers via rRRP and, **54a** and **54b** were copolymerized radically with various vinyl monomers (acrylate, methacrylate, styrene, etc).[176] (Co)polymers derived from **54a** degraded in the presence of hydroxyde and amine at mild temperatures into 2-hydroxyisobutyric acid, which can be reused as precursor for the CKHE monomer synthesis.

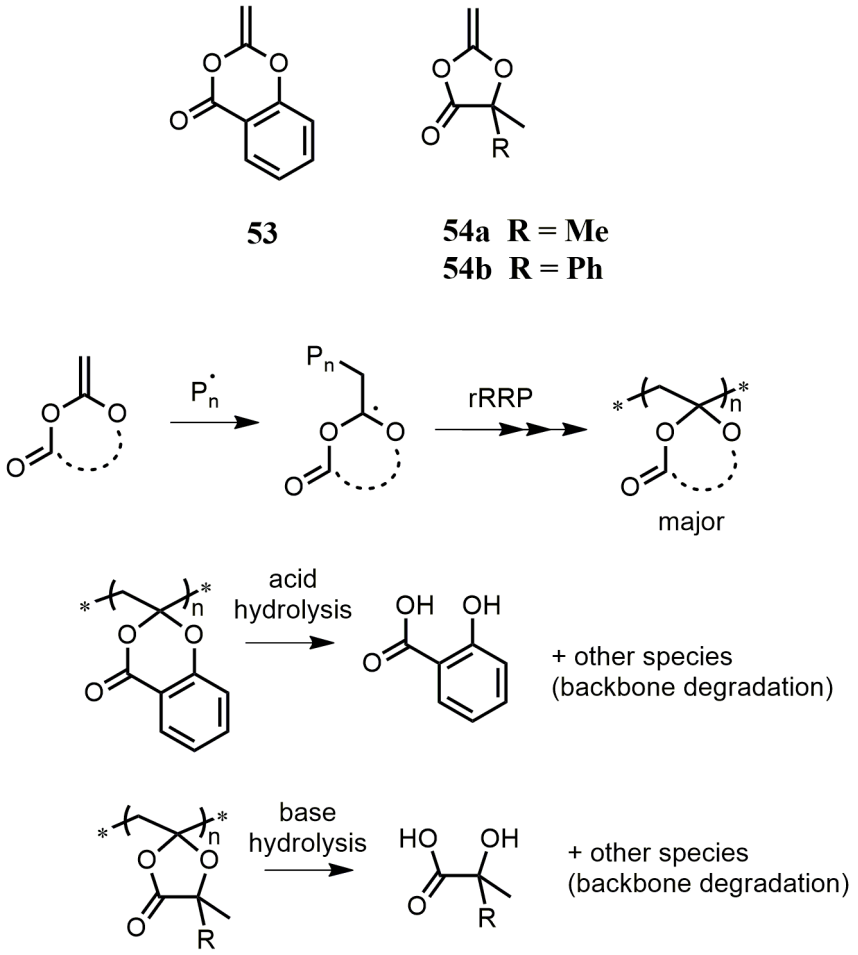

Figure 37: Cyclic ketene hemiacetal ester (CKHE) monomer polymerization and degradation.

The radical polymerization of nitrogen or sulfur analogs of CKA monomers was also considered (**Figure 38**). The replacement of the oxygen atoms by other heteroatoms in the MHCs not only changed the nature of the groups incorporated in the polymer but also it influenced their polymerization pathway. Monomer **55**, a 5 membered ring nitrogen analog of **47**, underwent essentially 100% ring opening polymerization.[98,162] Degradable poly(**55**-*co*-St) was obtained through copolymerization of **55** with styrene and its hydrolysis yielded oligomers capped with a methylamino group on one end and a carboxylic acid group on the other.[162] Instead, sulfur containing CKA analogs showed less propensity for rROP. Indeed, only 45% of **56**[162] and **57**[98] underwent rROP even at 120 °C whereas the 6-membered ring

58 exclusively polymerized by rRRP at 80 °C.[178] Surprisingly, no polymerization occurred in the case of the 7-membered ring **59**.[179]

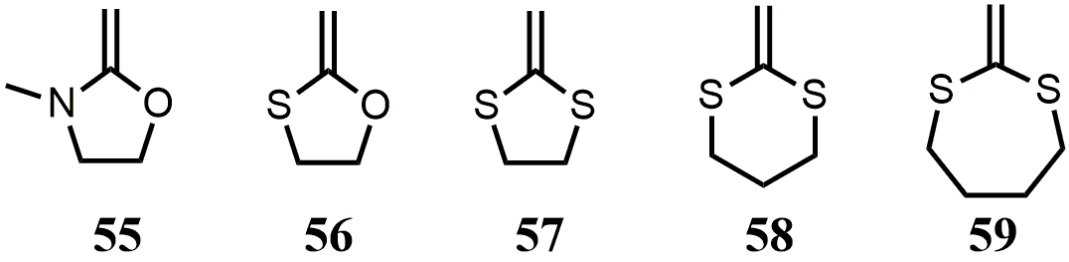

Figure 38: Typical nitrogen or sulfur analogs of CKA monomers.

3. Conclusions and perspectives.

Free radical polymerization is one of the most widespread process in polymer production due to its robustness, tolerance to moisture and functional groups. Besides the common acyclic monomers, including several industrially important polymer precursors, the radical polymerization of methylene heterocyclic monomers (MHC) is gaining more and more interest in recent years. While the first examples of MHC polymerization date back several decades, as highlighted in the present review, this research field is still vivid. The variety of MHCs differing by their ring size, substituents, nature and position of hetero atoms and functional groups, affords a great diversity of polymer structures. As key characteristic, the radical polymerization of MHC can undergo two types of polymerization pathways, namely rRRP and rROP, depending on the monomer structure and polymerization conditions. In rRRP, the cyclic group is preserved and incorporated in the polymer as side group. These lateral cyclic groups not only improve the thermal properties and stability of the polymers but can also undergo numerous ring opening post-polymerization modifications. The hydrolysis of some of them, like pendant lactones or cyclic carbonates, notably releases two functional groups per repeating units imparting peculiar solution behaviors to the modified polymers. In this case, the MHC behaves as monomer bearing a cyclic protective group. In rROP, however, the heteroatoms and functional groups are incorporated within the backbone of linear polymers and confer them some degradability, a characteristic valued in

biomedical and environmental applications. Importantly, the RDRP of several MHCs, either through rRRP and rROP, has been demonstrated paving the way to the precision design of complex MHC-based architectures which broaden the scope of their application.

Future prospects of radical polymerization of MHCs are vast and promising. First, a wide range of MHC candidates could be considered in radical polymerization in order to enlarge the scope of functional polymers. In line with the recent developments in the radical (co)polymerization of non-conjugated MHCs, such as α-alkylidene cyclic carbonates or γ-methylene-γ-butyrolactone, further efforts should be dedicated this category of monomers at the benefit of the functionalization of industrially important polymers derived from non-conjugated monomers such as VAc, ethylene, N-vinyl amides or VC. Obviously, the competition between rRRP and rROP will remain a particular point of attention and will need to be examined on a case-by-case basis. Nevertheless, proper control of the balance between these pathways, notably via adjustment of the polymerization conditions, constitutes an opportunity to tune simultaneously the degradability and other polymer properties. As suggested by few examples on chiral MHCs, the steric hindrance of the ring and proximity with the polymerizable double bond in MHCs allow to envision some control of the polymer tacticity, which certainly deserves further investigations. With only a few exceptions, the MHCs used as monomers in radical polymerization are largely petroleum-based compounds, which contravenes to sustainable development. Indeed, apart from α-MBL compounds notably derived from tulipalin A and from the CO_2-sourced α-alkylidene cyclic carbonates and 4,4-dimethyl-5-methyleneoxazolidin-2-one, examples of bio-sourced MHCs remain scarce. Therefore, besides optimizing the MHCs polymerization conditions and making the later environmentally friendlier (lower temperature polymerization, use of benign solvents, etc…), there is still a lot of work ahead to extend the scope of the radical polymerization of MHCs to renewable and bio-based monomers. Overall, there is still a huge field of exploration for the radical polymerization of MHCs and the preparation of functional polymers which should benefit to many applications in the coming years.

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