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Review

Reversibility in Controlled Polymerization Systems: Recent Progress and New Opportunities

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Abstract: The field of controlled polymerization is growing and evolving at unprecedented rates, facilitating polymer scientists to engineer the structure and property of polymer materials for a variety of applications. However, the lack of degradability, particularly in vinyl polymers, is a general concern for not only environmental sustainability but also biomedical applications. In recent years, there has been a significant effort to develop reversible polymerization approaches in those well-established controlled polymerization systems. Reversible polymerization typically involves two steps including (i) forward polymerization which converts small monomers into macromolecules, and (ii) depolymerization capable of regenerating original monomers. Furthermore, recycled monomers can be repolymerized into new polymers. In this perspective, we highlight recent developments of reversible polymerization in those controlled polymerization systems and offer insight into the promise and utility of reversible polymerization systems. More importantly, the current challenges and future directions to solve those problems are discussed. We hope this perspective can serve as an "initiator" to promote continuing innovations in this fairly new area.

Keywords: Controlled Polymerization; Reversible Polymerization; Sustainable Polymers

1. Introduction

The fundamental concept of reversibility has been widely utilized to drive the development of new polymeric materials which can display distinct but reversible change in properties upon receiving a stimulus.[1,2] In light of this, a library of reversible materials based on polymers have been recently achieved, including self-healing materials bearing reversible-covalent linkages,[3-8] recyclable materials such as vitrimers,[9-11] polymer networks enabling reversible sol-gel transitions,[12-14] architecture-transformable polymers,[15] and covalent or metal organic frameworks harnessing reversible bonds.[16-21] Despite the tremendous success in the aforementioned polymer systems, little attention was paid to achieve reversible polymerizations. Compared with self-immolative polymers which can only undergo one-way depolymerization, a reversible polymerization typically features reversible transformations between polymers and original monomers.[22] Indeed, step-growth polymerizations relying on reversible-covalent chemistry, particularly Diels-Alder chemistry, has provided an approach to reversible polymers which favor forward polymerization at room temperature and tend to depolymerize at high temperatures (i.e., 120 °C).[23] However, those polymers prepared by step-growth polymerizations typically have very broad molecular weight distributions and small molecular weights, limiting their potentials in certain applications which requires precise polymer chain length, complicated architectures, and high molecular weights.[24,25]

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In the last two decades, the rapid advent of controlled and living polymerizations has offered polymer scientists a powerful synthetic toolbox for accessing polymers with predetermined molecular weights, well-defined architectures, and narrow distributions in molecular weights.[26-29] In addition, the excellent tolerance of functional groups in controlled polymerization systems has enabled us to achieve advanced polymer materials with desired functions and properties.[30-33] In general, controlled polymerization techniques can be categorized into two common classes. The first one involves ring-opening polymerization (ROP) of cyclized monomers (e.g., caprolactones, lactides, and *N*-carboxyanhydrides) in the presence of a nucleophilic initiator and a catalyst (metal- or organocatalysts).[34,35] The second class focuses on controlled radical polymerization (CRP) methodologies which are capable of polymerizing vinyl monomers such as acrylates, methacrylates, and styrene in a controlled manner.[36-38] To date, three mainstream CRP techniques including atom-transfer radical polymerization (ATRP),[39,40] reversible addition-fragmentation transfer (RAFT) polymerization,[41-43] and nitroxide-mediated polymerization have been developed.[44] Among them, ATRP and RAFT are receiving most attentions due to their unique advantages such as mild polymerization conditions, broad monomer scope, and ease of end-group functionalization.

These controlled polymerization systems are enjoying tremendous success in producing polymers accommodated for both industrial use and high-value added applications. However, the studies related to depolymerization was scarce because depolymerization was typically considered as a side reaction which would lessen the performance, e.g., mechanical properties of polymer materials.[45] While this is true in the pursuit of maximizing lifetime or long-term stability of polymer materials, serious pollution problems have yet arisen from the lack of degradability in commercial polymer plastics under common conditions.[46] Sustainable polymers such as degradable polyesters deriving from biomass resource represent a promising platform to environmental remedy. However, those polymers currently suffer from high manufacturing cost and low mechanical properties compared to vinyl polymer-based materials from petroleum resource. Moreover, the degradation of those polyesters is typically one-way, resulting in non-polymerizable fragments which are not useful for regeneration of new materials. To fully achieve sustainability in polymer materials, recent attentions have been shifted to the development of new methods to depolymerize polymers back into original monomers under accessible conditions.[45,47-56] On the other hand, those regenerated monomers can be recycled and further repolymerized to obtain new polymer materials. In this perspective, we aim to first critically assess the state-of-the-art toolbox for achieving reversible polymerization in controlled polymerization systems (Schemes 1 and 2). Recent examples on reversible polymerizations will be classified according to their controlled polymerization mechanisms, i.e., ROP and CRP (Table 1). In addition, we believe it is important to assess the current challenges of reversible polymerizations which can trigger polymer chemists to solve. Finally, potential applications deriving from this fairly new concept will be predicted and discussed.

Scheme 1. Reversibility in controlled polymerization systems: controlled polymerization and controlled depolymerization.

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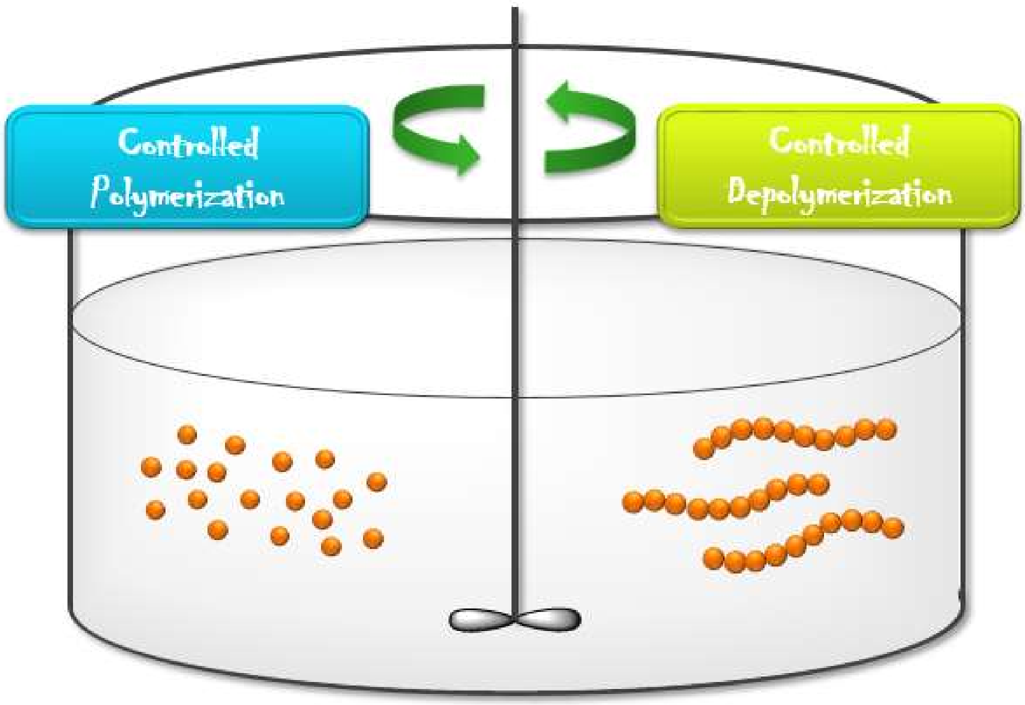

Scheme 2. Reversible polymerization approaches in controlled polymerization systems. (a) ROP; (b) ATRP; (c) RAFT.

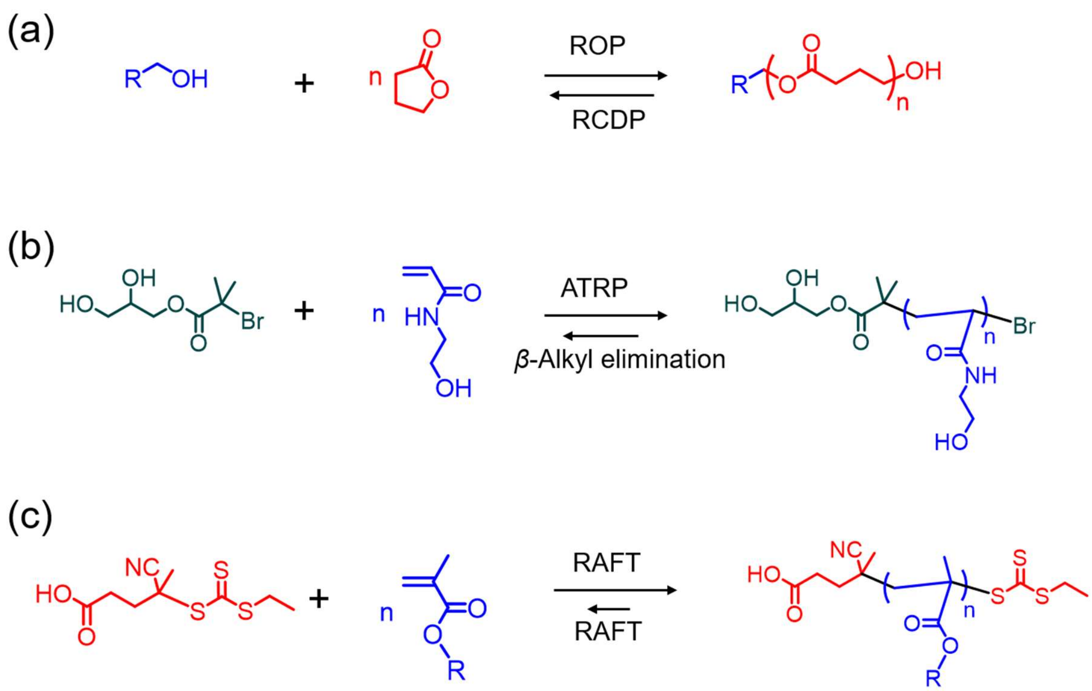

Table 1. Summary of reversible polymerization approaches in this perspective

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Type of polymers	Polymerization mechanism	Depolymerization mechanism	Depolymerization conversion	References
Polyester	ROP	RCDP	≥ 99%	Albertsson[49]
Polyester	ROP	RCDP	≥ 99%	Chen[53]
Polyester	ROP	RCDP	≥ 99%	Chen[56]
Polyester	ROP	RCDP	≥ 99%	Chen[54]
Polyester	ROP	RCDP	≥ 99%	Chen[55]
Polyester	ROP	RCDP	≥ 99%	Chen[52]
Polyester	ROP	RCDP	≥ 99%	Hoye[51]
Vinyl polymer	ATRP	β-alkyl elimination	24-34%	Zhu[47]
Vinyl polymer	ATRP	Not identified	43-71%	Haddleton[50]
Vinyl polymer	RAFT	RAFT	28%	Gramlich[45]

2. Reversible Polymerization in Ring-Opening Polymerization Systems

We begin our exploration of reversible polymerization approaches in ROP systems.[48,49,51-56] As one of the most popular controlled polymerization strategies, ROP of cyclic monomers has emerged as a useful synthetic route to prepare technologically interesting polymers with desirable architectures and specific properties. In particular, nucleophile-initiated ROP in the presence of metal- or organocatalyst allows the polymerization to proceed in a controlled manner, affording polymers with pre-determinable molecular weights and narrow molecular weight distributions. Applicable monomers include lactones, lactides, cyclic carbonates, *N*- or *O*-carboxyanhydrides, and cyclooligosiloxanes, among others.[35] To date, well-defined polymers produced from those monomers have attracted significant interest in both academic research and industry.[35,57,58]

Although many of the ROP polymers comprise hydrolysable ester linkages in their backbones, which can cause the polymers to degrade into oligomers or possibly small molecules, it is yet challenging to completely convert the polymers back to the original cyclized monomers. In 2014, Albertsson and coworkers demonstrated their pioneering work on ring-closing depolymerization to obtain functional six-membered cyclic carbonate monomer, 2-allyloxylmethyl-2-ethyltrimethlene carbonate (AOMEC) from its oligomeric form.[48] The synthesis of AOMEC was performed in a one-pot reaction, involving the oligomerization of trimethylolpropane allyl ether, diethyl carbonate, and NaH, followed by an in situ anionic depolymerization. It was observed that the depolymerization can occur beyond ceiling temperature of the polyester at a certain polymer/monomer concentration, suggesting the reversible nature of the polymerization of AOMEC. However, there was still room to

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improve since the oligomers were synthesized simply by condensation reaction rather than ROP and the degree of polymerization was only from 1 to 7.

Inspired by this pioneering work, Albertsson's team continued the study on AOMEC and first demonstrated the reversible ROP of this six-membered cyclic carbonate monomer in 2016.[49] It was concluded that the equilibrium between controlled ROP of AOMEC and controlled ring-closing depolymerization (RCDP) of poly(AOMEC) were dictated by various reaction parameters such as monomer concentration, reaction temperature, and even solvents. In their approach, AOMEC was polymerized by ROP in the presence of organocatalyst, that is, 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) in either bulk or different solvents (Figure 1a). Various temperatures were used to evaluate the equilibrium conversion for calculating the ceiling temperature at certain polymerization conditions. According to the thermodynamic principle, ROP of AOMEC was favored at a temperature lower than the ceiling temperature. As the reaction temperature was higher than the ceiling temperature, RCDP of poly(AOMEC) dominated. It is worth nothing that the molecular weights increased/decreased linearly as a function of monomer conversion in the cases of both ROP and RCDP (Figure 1b). Moreover, the molecular weight distribution of all the evolving polymers remained as low as 1.1, which further verified the exceptional control over both the course of polymerization and depolymerization.

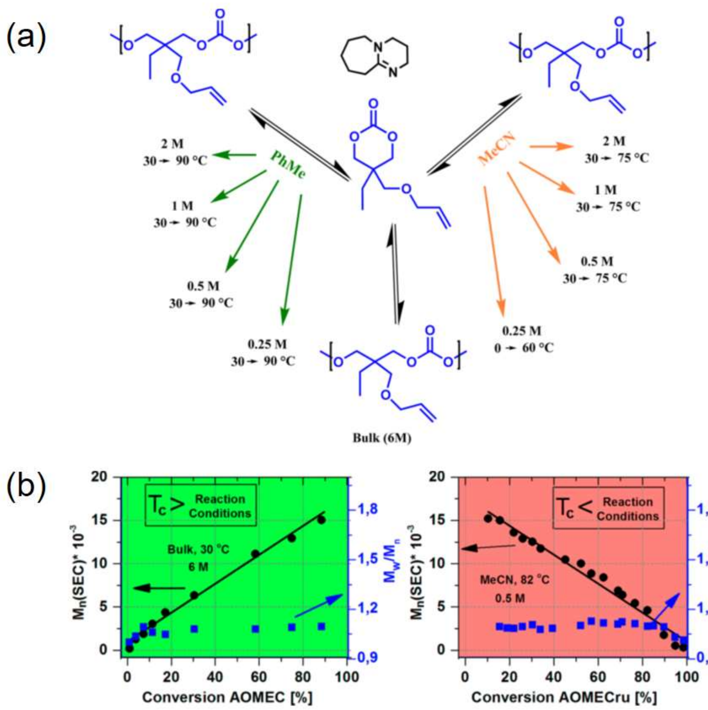

Figure 1. Reversible polymerization in ring-opening polymerization systems. (a) Reversible ROP of AOMEC at various reaction conditions; (b) Correlations of molecular weights, polydispersity index, and monomer conversions under two different polymerization conditions. Reproduced with permission from [49]

As one of the best suitable biomass-derived compounds to replace petroleum-derived chemicals, γ-butyrolactone (γ-BL) and its polymer PγBL are of great potential as sustainable materials.[53,55] However, γ-BL was commonly considered as "non-polymerizable" due to its low strain energy, which thereby rendered the ROP of γ-BL extremely challenging. Starting from 2016, Chen et al. has conducted extensive research on ROP of γ-BL, and have now developed several exciting synthetic methodologies to achieving PγBL by ROP. In agreement with Albertsson's viewpoint on the thermodynamic basis, Chen anticipated that reaction conditions should be modulated to achieve successful ROP, including a much lower reaction temperature than the ceiling temperature, a high initial monomer concentration, and most importantly, a robust catalyst. In their first work associated with γ-BL, the ROP of γ-BL was carried out at -40 °C in the presence of lanthanide (Ln)-based

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coordination polymerization catalyst.[53] The polymerization was capable of affording PγBL with M_n as high as 30,000 g mol^{-1} and up to 90% monomer conversion. In addition, the polymer topology (e.g., linear, cyclic) can be also controlled by varying the initiator structure and the feeding ratio of raw materials (Figure 2). From the sustainable perspective, a quantitative depolymerization of PγBL was realized by heating the purified polymers for 1 hour at higher temperatures (i.e., 220 or 300 °C) than the ceiling temperature. Interestingly, the PγBL that was dissolved in appropriate solvents depolymerized much more rapidly in the presence of organocatalyst (e.g., TBD) or metal catalyst (e.g., $La[N(SiMe_3)_2]_3$) even at room temperature.

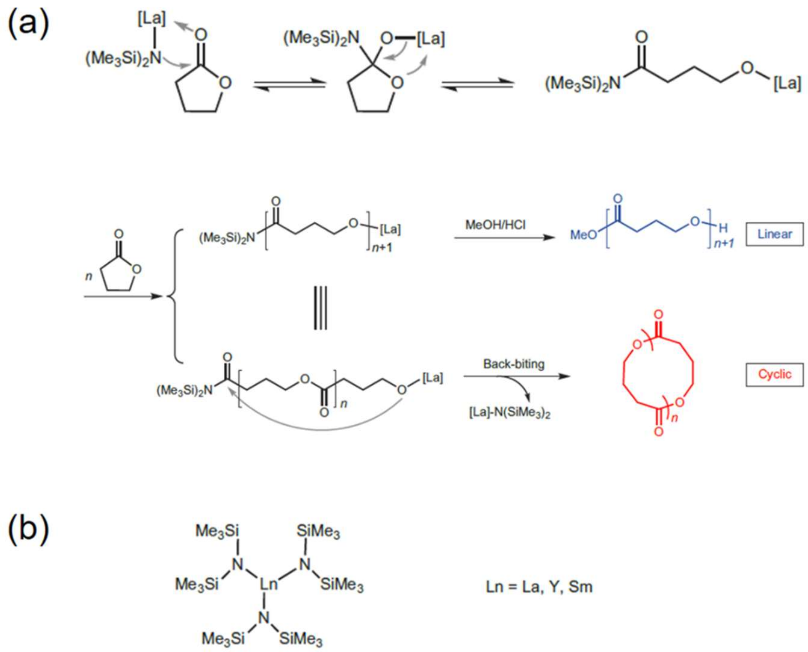

Figure 2. Reversible polymerization in ring-opening polymerization systems. (a) Proposed mechanism for lanthanide catalyzed ROP of γ-BL in the preparation of both linear and cyclic PγBL; (b) Chemical structure of lanthanide catalyst. Reproduced with permission from[53]

In parallel, Chen and coworkers also discovered a metal-free ROP strategy to produce PγBL using a superbasic organocatalyst with abbreviation: tert-Bu-P_4 (Figure 3a).[56] It should be noted that the catalyst itself was able to initiate the ROP of γ-BL at -40 °C by abstracting protons from γ-BL to form highly reactive enolate species (Figure 3b). However, the monomer conversion was limited up to 30.4% due to the possible interference of $[tert\text{-}Bu\text{-}P4H]^+$ and anionic dimer. Furthermore, the ROP performance was greatly enhanced when tert-Bu-P_4 was added along with a suitable alcohol serving as the initiator (e.g., BnOH). With the help of alcoholic initiator, the monomer conversion reached as high as ca. 90% and the corresponding PγBL possessed a molecular weight at 26,700 g mol^{-1}. Notably, the PγBL prepared by this organocatalyzed ROP was completely recyclable, which can depolymerize back to γ-BL upon heating at 260 °C for 1 hour.

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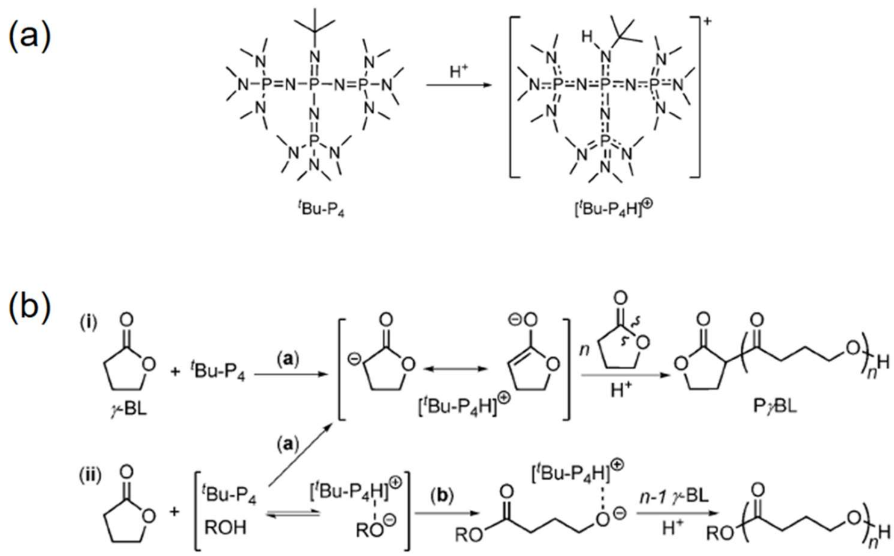

Figure 3. Reversible polymerization in ring-opening polymerization systems. (a) Structure and basicity of tert-Bu-P_4; (b) Proposed mechanism for tert-Bu-P_4 catalyzed ROP of γ-BL with (i) and without (ii) alcohol as initiator. Reproduced with permission from[56]

Encouraged by the success in preparing fully recyclable PγBL via ROP with either metal (La, Y) or organocatalyst, Chen's group proceeded to apply this unique polymerization process to an enriched variety of monomers. ROP of α-Methylene-γ-butyrolactone (MBL), a small molecule derived from biomass and regarded as a potential alternative to the petroleum-based MMA, was subsequently investigated (Figure 4)[54]. Since the monomer comprises a non-strained five-membered lactone and a highly reactive exocyclic C=C double bond, many knee-jerk studies were exclusively focused on the traditional vinyl addition polymerization (VAP).[59,60] In Chen's work, the lanthanide (Ln)-based coordination polymerization catalyst was utilized, leading to an unsaturated polyester P(MBL) with M_n up to 21,000 g mol^{-1} through ROP process. Remarkably, by adjusting the reaction conditions such as the catalyst (La)/initiator (ROH) ratio and temperature, three pathways of the MBL polymerization can be realized independently including conventional VAP, ROP, and crosslinking polymerization. As was foreseeable, only the polymers resulted from ROP pathway were fully recyclable.

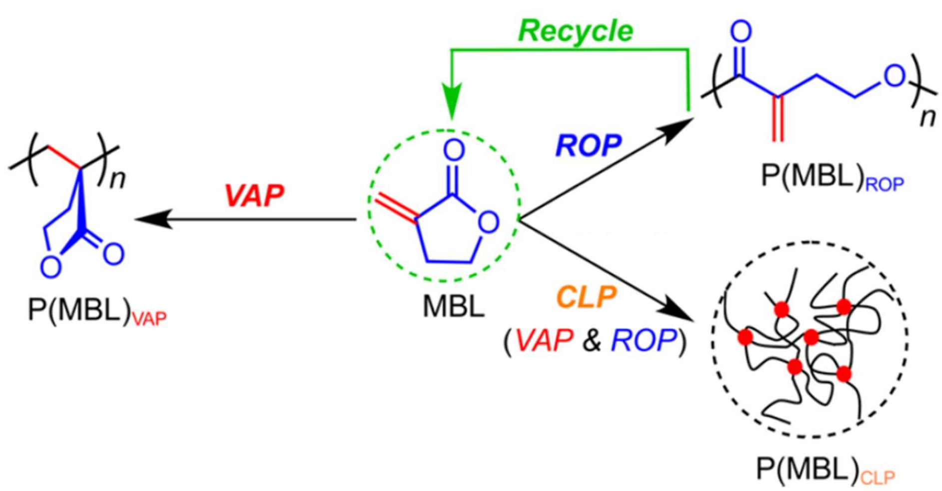

Figure 4. Reversible polymerization in ring-opening polymerization systems. Polymerization of MBL following three distinct mechanisms. Reproduced with permission from[54]

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Despite of the notable achievement in lanthanide (La, Y) or superbase (tert-Bu-P_4) catalyzed ROP of γ-BL and its derivatives, the undesirable low-temperature (i.e., -40 °C) to implement the process still remained as one of biggest hurdles for industry use. Moreover, the as-synthesized polymers suffered from limited thermostability and crystallinity. Hence, the exploration in new materials with both superior properties and energy economy are still demanding. Recently, Chen's group proposed a γ-BL derivative (abbreviated as 3,4-T6GBL), with a cyclohexyl ring trans-fused to the five-membered lactone at the α and β positions.[55] This monomer can be polymerized by using the coordinative insertion ROP catalysts, producing linear or cyclic polymers with high molecular weights at room temperature (Figure 5a). Following this finding, Chen et al. extended the scope of ROP of another γ-BL derivative (4,5-T6GBL), where the cyclohexyl ring was fused at β and γ (or 4,5) positions of the BL ring, giving rise to linear/cyclic polymers at room temperature (Figure 5b).[52] A controlled polymerization behavior was observed as the molecular weights of evolving polymers increased linearly with the monomer conversions. As expected, in both studies the resulting polymers possess enhanced thermostability and can be quantitatively recycled back to their original building monomers by either thermolysis or chemolysis.

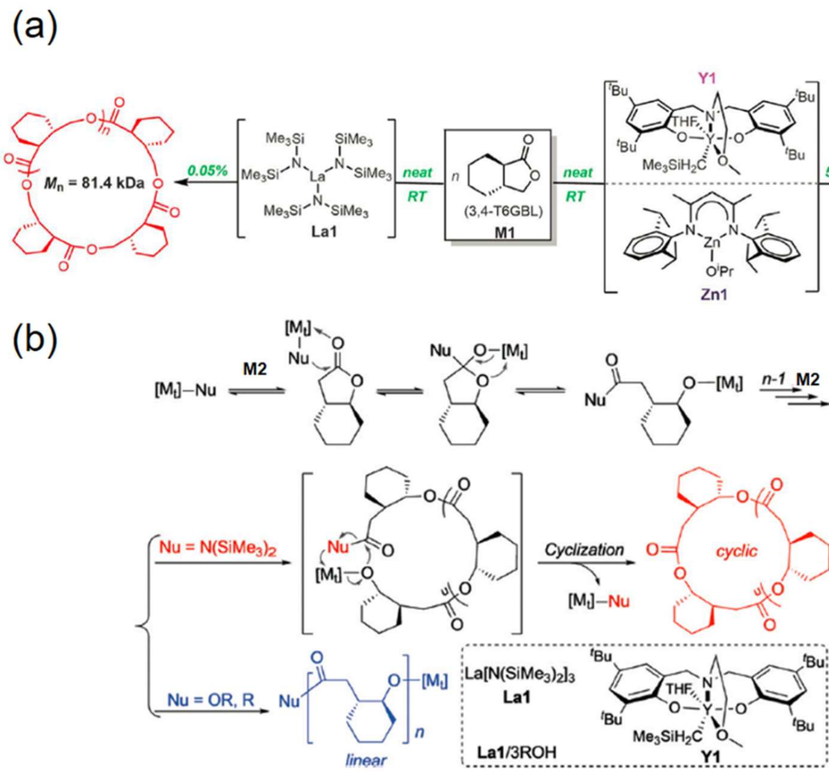

Figure 5. Reversible polymerization in ring-opening polymerization systems. (a) Metal catalyzed ROP of 3,4-T6GBL (M1) to linear and cyclic polymers; (b) Proposed pathways for metal catalyzed ROP of 4,5-T6GBL (M2) to linear and cyclic polymers. Reproduced with permission from[52,55]

Very recently, Hoye et al. described the synthesis of a novel substituted polyvalerolactone from a malic acid derived monomer, 4-carbomethoxyvalerolactone (CMVL).[51] In their work, this six-membered ring monomer was blended with a diol (1,4-benzenedimethanol) and an organic acid (diphenyl phosphate) at ambient temperature, finally affording a semicrystalline material with a molar mass up to 71,000 g mol^{-1}. Notably, the resulting polymers can be either depolymerized back into its original precursor monomer or degraded into acrylate-type analogues (Figure 6a). The former process was catalyzed by tin octanoate ($Sn(Oct)_2$), providing 87% monomer recovery; while the latter was promoted by DBU with a comparable yield. In particular, a substantial kinetics study showed that CMVL was polymerized smoothly and reached ca. 90% conversion after 15 hours (Figure 6b). It also revealed that nearly all the initiator was consumed within 20 minutes. This "fast initiation" can be regarded as one of the characteristic behaviors of controlled polymerization systems.

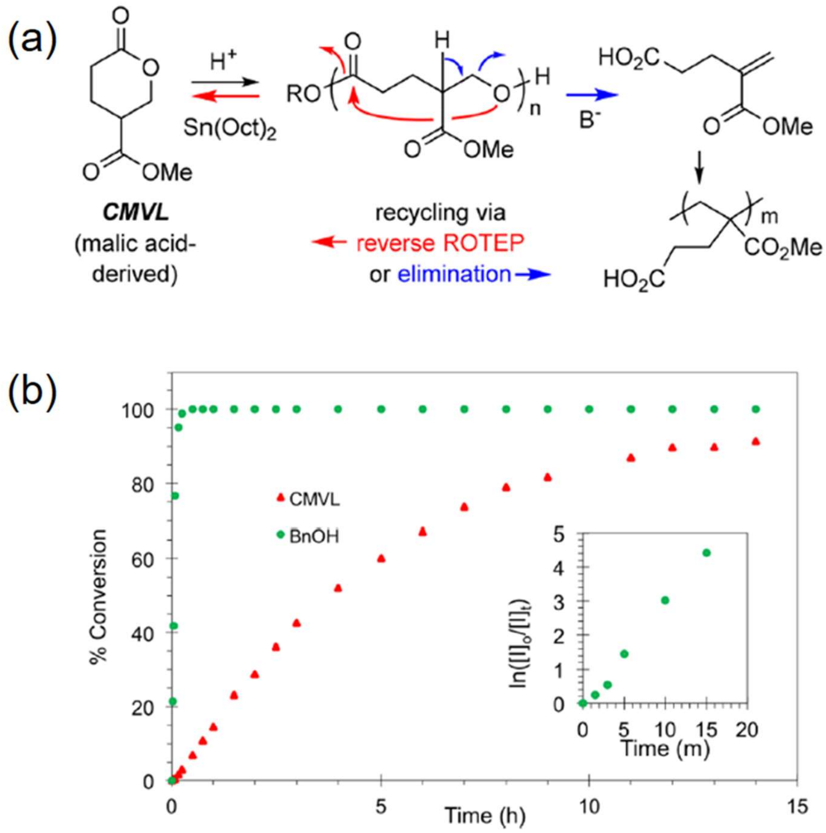

Figure 6. Reversible polymerization in ring-opening polymerization systems. (a) Acid-catalyzed ROP of CMVL and the divergent chemical recycling; (b) Kinetics of the ROP of CMVL in the presence of BnOH as an initiator. Reproduced with permission from[51]

3. Reversible Polymerization in Controlled Radical Polymerization Systems

Albeit reversible polymerizations in ROP systems have shown great promise in next generation sustainable polymer materials, the major market of commodity polymers are still occupied by vinyl polymers due to their low-cost in manufacturing. Vinyl polymers derive from petroleum, a non-renewable resource. Therefore, recycling of used vinyl polymer materials such as plastics has immense merits not only in global waste reduction but also petroleum sustainability.[61] In this section, recent examples in depolymerization of vinyl polymers derived from CRP systems will be discussed. We hope those timely developments will prompt more innovative thinking of plastic recycling via reversible polymerization approach.

In 2012, Zhu et al. reported the first example of reversible polymerizations in CRP system.[47] In their pioneering work, vinyl polymerizations of several acrylamide monomers including *N*-isopropylacrylamide (NIPAM) and *N*,*N*-dimethylacrylamide (DMA) were successfully achieved in the presence of CuCl and tris(2-dimethylaminoethyl)amine (Me6TREN) (Figure 7a). Very intriguing, they unexpectedly observed a phenomenon of depolymerization when radical inhibitors such as 2,2,6,6-tetramethylpiperidinooxy (TEMPO) or 1,4-benzoquinone (BQ) was added to the ongoing polymerization system with the initial purpose of terminating radical polymerizations. To further elucidate the role of copper catalyst in depolymerization process, a control experiment with regard to a conventional radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) as radical initiator was carried out in the absence of copper catalyst and ligands. TEMPO was added during the conventional radical polymerization, resulting in only termination of polymerization without any

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noticeable depolymerization. Those results unequivocally verified that copper catalyst is essential in depolymerization. Therefore, a depolymerization mechanism based on β-alkyl elimination from copper (II) coordination center was proposed (Figure 7b).

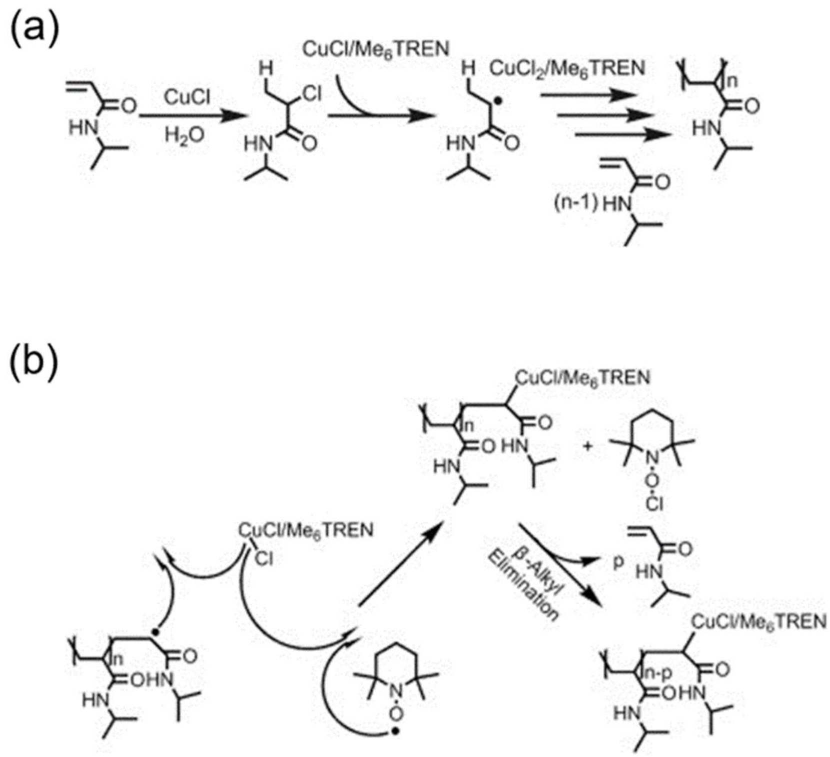

Figure 7. Reversible polymerization in copper-mediated polymerization systems. (a) Proposed mechanism of CuCl/Me6TREN based radical polymerization of NIPAM; (b) TEMPO-induced depolymerization mechanism via β-alkyl elimination. Reproduced with permission from[52]

In a similar demonstration of reversible polymerization mediated by copper catalyst, Haddleton and coworkers were able to prepare well-defined polyacrylamides and polyacrylates through aqueous copper-mediated radical polymerization in the presence of dissolved CO_2 (Figure 8a).[50] In the case of NIPAM monomer, the forward polymerization adopted a rapid reaction kinetics, achieving full monomer conversion within 10 min. Thereafter, a significant in situ depolymerization occurred to an extent of 52% and thereby led to regeneration of NIPAM monomer which was systemically confirmed by NMR, GPC, and EI-MASS. Importantly, those recycled NIPAM can be repolymerized upon deoxygenation of the resulting solutions, illustrating the reversibility of the polymerization (Figure 8b). Furthermore, the scope of reversible copper-mediated polymerization was extended to *N*-hydroxyethyl acrylamide (HEAm) and 2-hydroxyethyl acrylate (HEA), demonstrating the versatility of this system. However, it should be noted that the mechanism of depolymerization as well as the role of CO_2 in the depolymerization process was not identified in their study.

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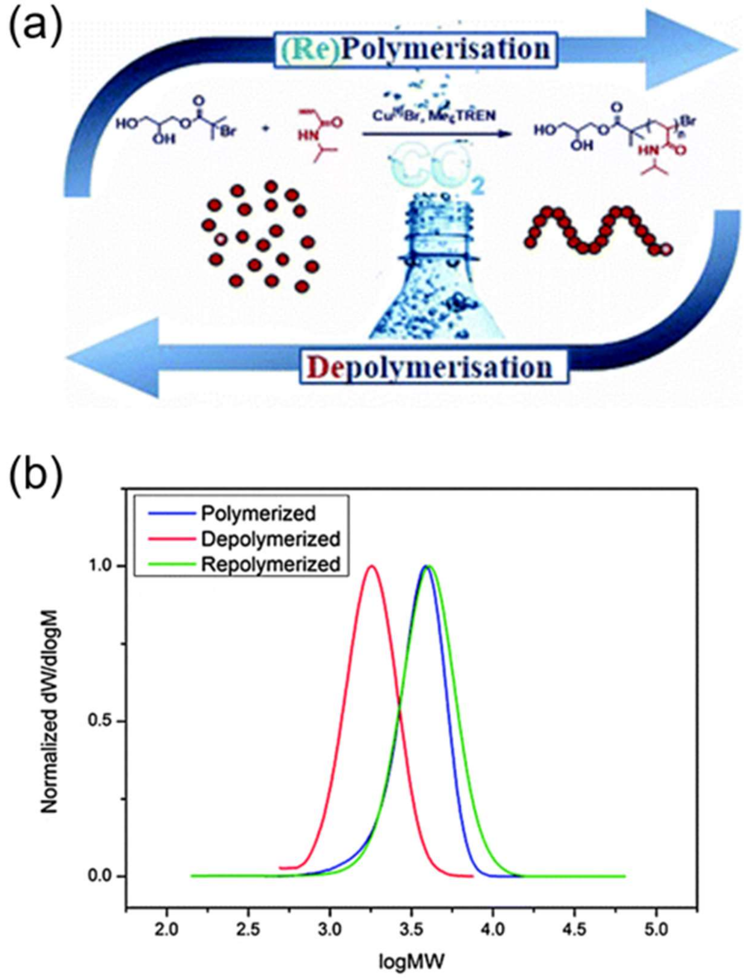

Figure 8. Reversible polymerization in copper-mediated controlled polymerization system. (a) schematic illustration of aqueous reversible polymerizations mediated by copper catalyst and CO_2; (b) GPC traces of original PNIPAM (blue), depolymerized PNIPAM (red), and repolymerized PNIPAM (green). Reproduced with permission from[50]

In the aforementioned CRP systems (Vide supra), depolymerization phenomenon was only observed during the course of the polymerization. However, it is arguably more interesting in the materials point of view if one can depolymerize a polymer post the synthesis or manufacturing process. In a very recent work described by Gramlich, a set of brush polymers consisting of oligo-ethylene glycol or oligo-dimethylsiloxane side chains were prepared by traditional RAFT polymerization in the presence of AIBN at 70 °C (Figure 9a).[45] After the polymerization, those polymers were thoroughly purified by repeatedly precipitations to ensure the removal of residual monomers and initiators. Upon purification, thermally induced depolymerization of the as-synthesized polymer was conducted in dilute dioxane solutions, leading to regeneration of vinyl monomers until reaching the monomer's inherent equilibrium monomer concentration. Importantly, the residual polymers exhibited high chain-end fidelity by retaining the trithiocarbonate moiety after depolymerization, allowing for further reinitiation and repolymerization via RAFT mechanism (Figure 9b and c).

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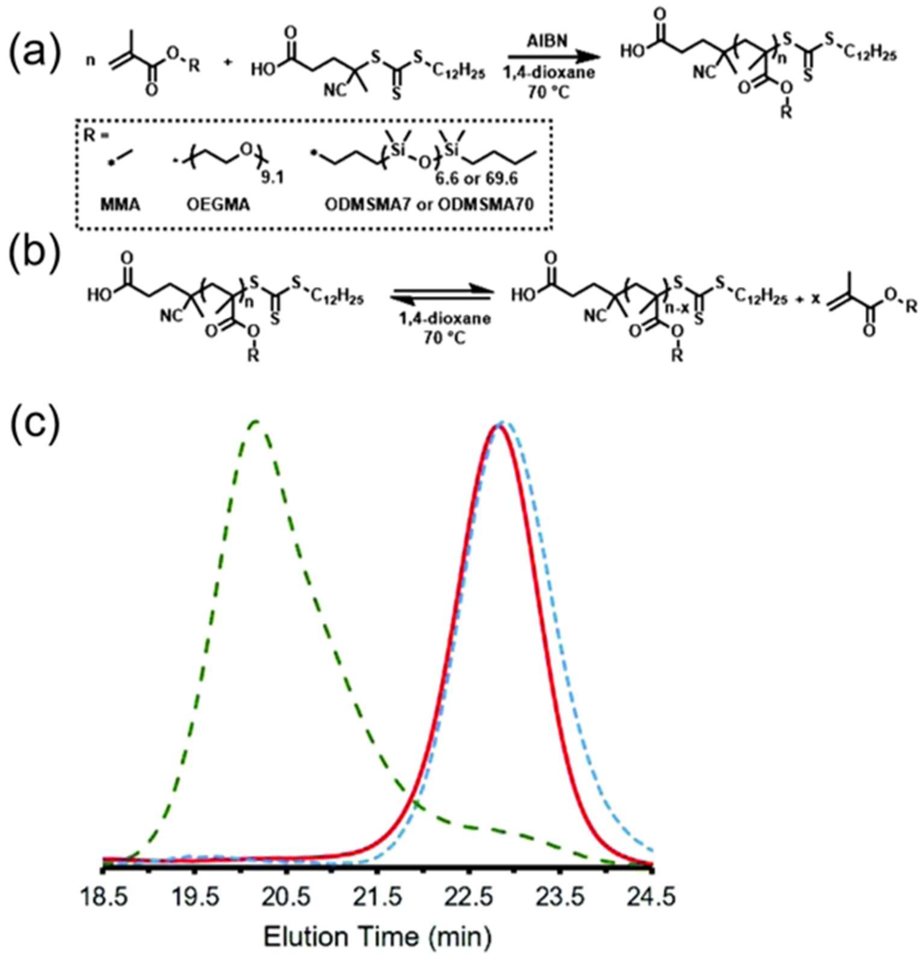

Figure 9. Reversible polymerization in RAFT system. (a) Preparation of brush-type polymers via RAFT polymerizations of methacrylate monomers; (b) Depolymerization and repolymerization of RAFT polymers; (c) GPC trance of original RAFT polymer (red solid), depolymerized polymer (blue dotted), and repolymerized polymer (green dotted). Reproduced with permission from[45]

4. Closing Remarks

The current success in reversible polymerizations has enabled us to think about many new possibilities in future polymer science. However, many challenges still remained to be addressed, hampering the further translation of this new concept into real world applications. One apparent hurdle is how to achieve good control over the depolymerization process. While all the examples covered in this perspective are related to controlled polymerizations allowing for predictable degree of forward polymerizations, little information was provided to reveal the kinetics of depolymerization process, especially those involved in controlled radical polymerization. Indeed, previous literatures placed much focus on the start and endpoint of depolymerization (in other word, the highest degree of depolymerization). Notwithstanding, it will shed more light on the fundamental mechanisms of reversible polymerizations if one can predetermine and control the degree of depolymerization by changing several reaction parameters such as time, temperature, catalyst/initiator loading, and polymer/monomer concentrations, among others. Moreover, the ability to tune the depolymerization rate under normal conditions is expected to open the door for many interesting applications (in addition to sustainable materials), for example, self-healable materials, and sustained release systems which require slow and controllable depolymerization.

Another challenge stems from the relatively low efficiency in depolymerizations, particularly those in CRP systems. In comparison with ROP based depolymerization systems which mainly rely on breaking weak polyester backbones, the energy input necessary for reversing vinyl polymer backbones (i.e., carbon-carbon single bonds) back to vinyl monomers is considerably higher. To our best knowledge, the highest reported depolymerization conversion in CRP systems was only 71% when *N*-hydroxyethyl acrylamide was involved in copper(0)-mediated reversible polymerizations.[50] In the RAFT mediated depolymerization approach, only 30% monomer can be regenerated after heating the dilute RAFT polymer solutions at 70 °C under vacuum for several days.[45] From the viewpoint of potential industrial applications, insufficient depolymerizzation could dramatically increase the cost deriving from separating regenerated monomers from residual polymers. Therefore, we envision that more attention will be paid to detailed mechanism study and rational design of depolymerization systems with the goal of achieving high depolymerization efficiency (such as effort to lowering equilibrium monomer concentration). While the concept of reversible polymerizations is still in its infant stage, it is anticipated that the future development in this area will not only deepen our understanding of fundamental depolymerization mechanisms but also promote many new opportunities and applications in polymer science and engineering.

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