

Review

Organocatalytic Copolymerization of Mixed Type Monomers*

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Abstract Triggered by environmental concerns and the rising demands for metal-free polymers in *e.g.* bio-related and microelectronic applications, studies on organocatalytic polymerization have been launched and developed unprecedentedly during the last 15 years. A wide range of organic molecules are now available in polymer chemists' toolbox to choose from as catalysts for polymerization of (hetero)cyclic and polar vinyl monomers. Apart from the intrinsic merits such as lower toxicity and better solubility compared with (transition) metal catalysts/initiators, organocatalysts have also shown, in many cases, excellence to achieve high polymerization rates and/or good control (selectivity). In addition, particular natures and catalytic/activating mechanisms of organocatalysts have led to new opportunities for rational design and efficient synthesis of macromolecular architectures, *i.e.* chain structures, topological structures and functionalities. This mini-review is specially themed on pathways to construct copolymer chain structures by organocatalytic copolymerization of mixed type monomers (comonomers bearing different polymerizing moieties) and will be sectioned by different comonomer combinations, including cyclic monoesters of different sizes, cyclic monoesters and lactides, cyclic esters and cyclic carbonates or epoxides, heterocycles and vinyl monomers.

Keywords Chain structure; Copolymer; Organocatalytic polymerization

INTRODUCTION

In virtue of increasing environmental concerns and rapidly growing demands for polymeric materials free of metal residuals to meet the requirement of applications in biomedicine, microelectronics, food packaging, *etc.*, small-molecule organic catalysts (organocatalysts) were brought in the field of polymer synthesis, giving rise to the conceptualization of “organocatalytic polymerization” in early 21st century^[1, 2]. As compared to organometallic catalysts/initiators, except for being “metal-free”, organocatalysts are also desirably featuring good solubility in organic solvents or monomers (bulk condition), inexpensiveness, simpler or even effortless preparation (many are commercially available), lower air-sensitivity, easier handling, longer shelf lives, readily tunable chemical structures and catalytic activities. Such natural merits have stimulated constant growth of studies on this topic in the last 15 years (Fig. 1, black bars). A rich diversity of organocatalysts have shown to be effective for different types of polymer-related reactions, such as (quasi)ionic ring-opening polymerization (ROP) of heterocycles^[2–6], group-transfer polymerization (GTP) of (meth)acrylic monomers^[7–9], step-growth polymerization^[10], degradation/depolymerization of polyesters^[11–13]. Excellence in polymerization rate and control over macromolecular molar masses have been achieved, which provides good suitability between the monomer and organocatalyst/condition. Moreover, a majority of such efforts are accompanied or closely followed by attempts to use organocatalysts for design and synthesis of macromolecular architectures (Fig. 1,

* This work was financially supported by the National Natural Science Foundation of China (Nos. 21504024 and 21674038) and Fundamental Research Funds for Central Universities.

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Received December 15, 2016; Revised January 3, 2017; Accepted January 3, 2017

doi: 10.1007/s10118-017-1925-6

gray bars), including chain structures, topological structures, functionalities and their combinations^[14, 15]. Some convenient and efficient routes towards various macromolecular architectures have been developed taking advantage of the particularities of organocatalysts, further highlighting the strength and potential of organocatalysis for advancing polymer synthesis. Studies related to organocatalytic polymerization have been reviewed several times, either generally^[15, 16] or specifically on a certain type of polymerization/monomer^[4–7, 9, 10, 17, 18] or organocatalyst^[8, 19–26].

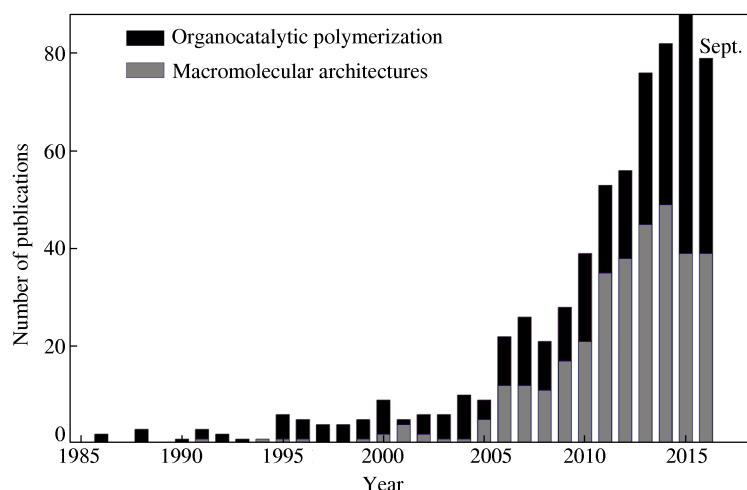


Fig. 1 Yearly number of publications in the last two decades on the topic of organocatalytic polymerization (black bar) and macromolecular architectures through organocatalysis (gray bar)
Data are obtained by searches in Web of Science using keywords as “organocatalytic polymerization”, “metal-free polymerization”, “organocatalyst, polymerization”, “organo-catalyzed polymerization”, and derivatives.

Macromolecular architecture (polymer structure) plays a crucial role in polymer science linking polymer synthesis and properties/applications. Expanding the diversity and advancing sophisticated synthesis of macromolecular architectures have always been guiding principles for the development and practice of synthetic polymer chemistry^[14, 27, 28]. In general, chain structure, topological structure and functionality represent three basic elements of macromolecular architectures, among which chain structure is the essential and basis as it is formed as soon as a polymerization process takes place^[29]. It then refers to the fashion that monomers transform into monomeric (repeat) units and connect covalently to form (linear) polymer chains, and includes sub-elements such as types, sequence, composition and chemo-, regio-, stereo-isomerism of the monomeric units.

Copolymerization has been the most frequently utilized strategic approach to construct or modify polymer chain structures. In most cases, monomers with the same polymerizing group are copolymerized to afford copolymers consisting of a homogeneous main chain and different pendent groups. Copolymerization of monomers carrying different polymerizing groups, termed herein as mixed type monomers, has also been often studied and used, though to a less extent, to generate copolymers with both a heterogeneous main chain and different pendent groups. Such copolymers are substantially distinguished from the corresponding homopolymers and copolymers of the first type in terms of structures and properties. Thus, copolymerization of mixed type monomers has acted as a unique and significant pathway to enlarge the variety of polymer chain structures and properties/functions. On the other hand, comonomers of this type are usually (quite) different in terms of polymerizability and suitable catalysts/polymerization conditions, which poses challenges and requires special efforts to explore for appropriate catalytic/initiating system for their copolymerization. In the progress of organocatalytic polymerization, copolymerization of mixed type monomers has been reported quite frequently. Special utilities and strengths of organocatalysis have been demonstrated for such a purpose. Therefore, in this mini-review, we intend to briefly depict some general mechanistic aspects of organocatalytic polymerization,

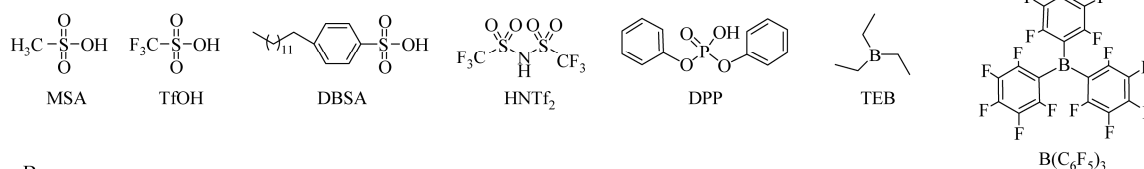
then specially summarize the studies and results on organocatalytic copolymerization of mixed type monomers by sectioning our discussion into different combinations of comonomers, in the hope that more attention will be attracted and paid to this important and promising research topic in polymer synthesis. Random, gradient/tapered and alternating comonomer sequence distributions will be involved. Block copolymers, although also regarded as a major class of chain structure, is excluded herein because of the uniqueness of the synthetic strategies associated with their blocky forms.

GENERAL ASPECTS OF ORGANOCATALYTIC POLYMERIZATION

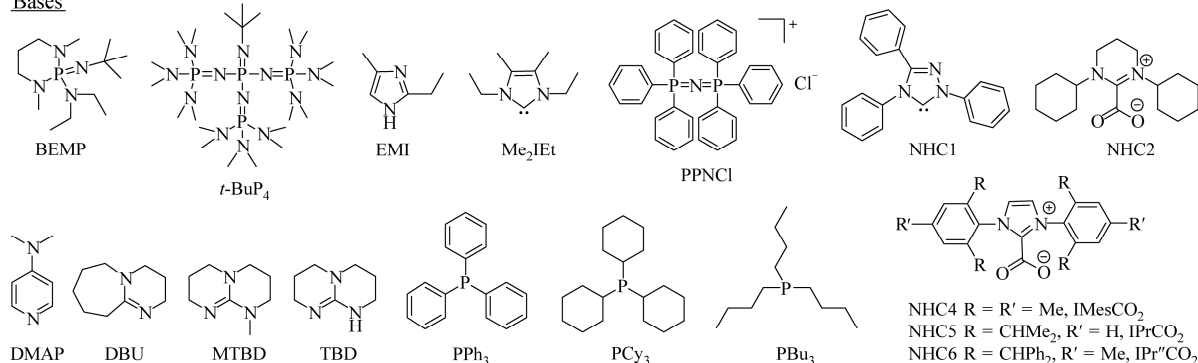
Organocatalysts

A variety of small-molecule organic compounds have been employed as catalysts or initiators in polymer synthesis^[15, 16], which can be generally classified as Brønsted acids (*e.g.*, sulfonic acid or phosphate derivatives), Lewis acids (*e.g.*, trialkylborane), non-nucleophilic bases (*e.g.*, phosphazene bases) and nucleophilic bases (*e.g.*, *N*-heterocyclic carbenes (NHCs), amidines, guanidines, phosphines). There are also organocatalysts that consist of both an acidic (or hydrogen donating) and a basic (or hydrogen accepting) component, which are either a bimolecular catalytic system or a bifunctional catalytic molecule. Figure 2 shows the structural formula of the representatives of each type of organocatalyst, especially those that have been employed for the copolymerization of mixed type monomers, and the abbreviation used herein for each one.

Acids



Bases



Acid-base pairs

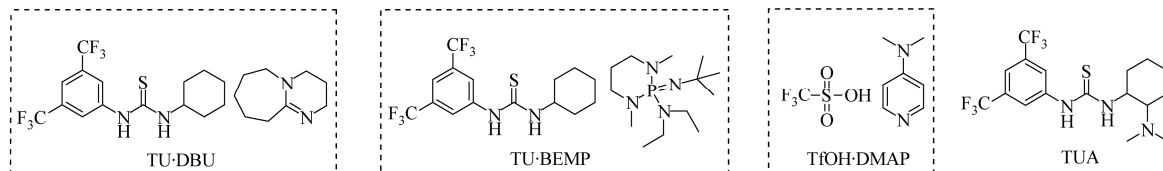
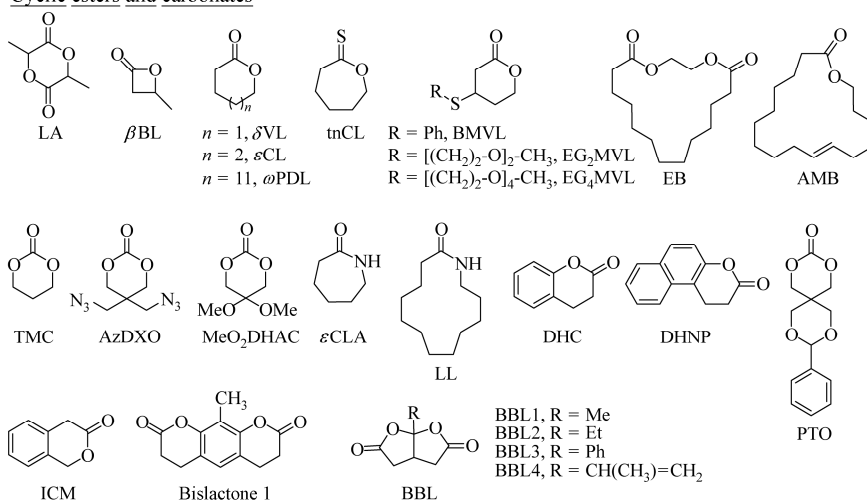


Fig. 2 Representative families of organic molecules used as catalysts or initiators for organocatalytic polymerization

Monomer Scope

Figure 3 lists representative monomers that have been subjected to organocatalytic (co)polymerization, classified by the polymerizing groups, among which carbonyl-containing heterocycles, such as cyclic esters and cyclic carbonates, have been studied most frequently because of their high accessibility, good polymerizability, and the importance of their (co)polymers for biomedical applications^[2–4, 16]. Different monomers are usually suited with

Cyclic esters and carbonates



 R = Me, MP
 R = *i*Pr, *i*PP
 R = *i*Bu, *i*BP
 R = 3-Butenyl, BP
 R = 3-Butynyl, BYP
 R = 2-Ethylbutyl, EBP

 R = Cyclohexyl, ^{cy}HexPPn
 R = *i*Pr, ^{Pr}PPn

The figure shows three chemical structures: TMOSC (top left), D3 (bottom left), and D4 (top right). TMOSC is a five-membered ring with three silicon atoms and two oxygen atoms. D3 is a six-membered ring with three silicon atoms and three oxygen atoms. D4 is an eight-membered ring with four silicon atoms and four oxygen atoms. Each silicon atom in the rings has two additional bonds extending outwards, representing the polymer backbone.

			$R^1 = R^2 = \text{Bn, DBGA}$ $R^1 = \text{Bn, } R^2 = \text{Me, BMGA}$
$R = \text{Ph, GPE}$ $R = n\text{Bu, } n\text{BuGE}$ $R = t\text{Bu, } t\text{BuGE}$ $R = \text{Allyl, AGE}$ $R = \text{Bn, BGE}$ $R = 2\text{-Ethylhexyl, EHG}$	$R = \text{H, EO}$ $R = \text{Me, PO}$ $R = \text{Et, BO}$ $R = \text{Ph, SO}$ $R = t\text{Bu, DMBO}$		$R^1 = R^2 = \text{Me, IBO}$ $R^1 = \text{Vinyl, } R^2 = \text{H, BDO}$ $R^1 = \text{Vinyl, } R^2 = \text{Me, ISPO}$

 R = *i*Pr, IPVE
 R = Et, EVE
 R = *i*Bu, IBVE

 R = Me, MMA
 R = *t*Bu, BMA
 R = Allyl, AMA
 R = Glycidyl, GMA
 R = 2-(*N,N*-dimethylamino)ethyl, DMAEMA

THF CHO MEK

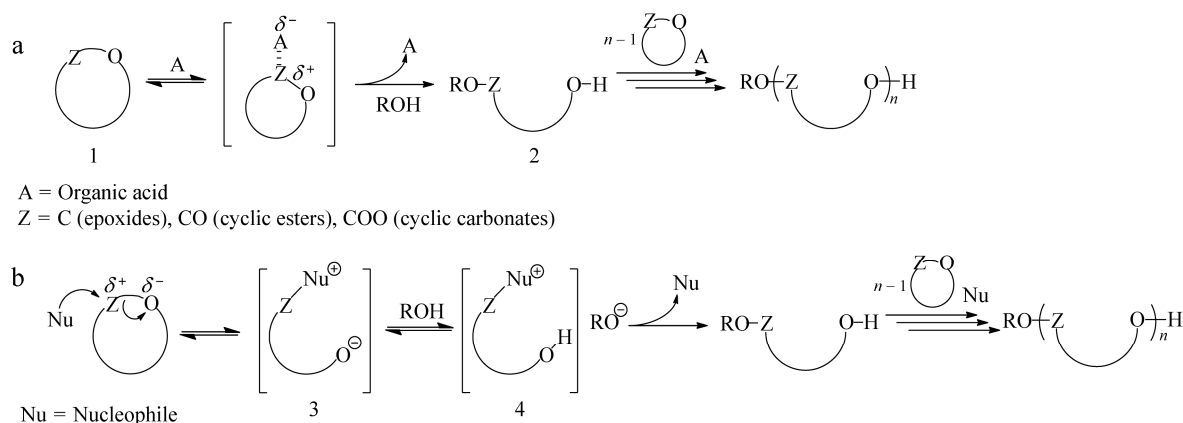
Fig. 3 Representatives of different types of monomers that have been subjected to organocatalytic polymerization

Based on the mode of activation, the mechanism of organocatalytic polymerization can be generally classified into three types, (1) activation of the monomer, following either an electrophilic or a nucleophilic pathway, or the “activated monomer mechanism” (AMM); (2) activation of the initiator or polymer chain end (the propagating species), usually referred to as the “activated chain end mechanism” (ACEM); (3) cooperative dual activation of both the monomer and the initiator/chain end (AMM+ACEM). Acidic organocatalysts (Fig. 2)

usually catalyze the polymerization by electrophilic AMM, while there are also reports demonstrating a dual activation mechanism for some of the acids (bifunctional catalytic molecule, *e.g.*, TfOH and DPP)^[39–41], which is similar to that of the acid-base pairs. It is believed that non-nucleophilic organic bases (*e.g.*, phosphazene bases) catalyze/promote the polymerization exclusively by ACEM^[23–25] and the nucleophilic ones (*e.g.*, phosphines, *N*-heterocycles, NHCs) follow a nucleophilic AMM, or a mixed nucleophilic AMM and general base type ACEM^[2, 8, 15, 16]. Organocatalytic ROP of heterocycles will be used as follows to exemplify such activating/mechanistic pathways.

Activated monomer mechanism (AMM)

Electrophilic AMM is usually induced by a Brønsted/Lewis acid (A in Scheme 1a), which activates the cyclic monomer by protonating or withdrawing ion pair from the basic moieties, *e.g.* the oxygen atom on the carbonyl group (C=O) of a lactone or a cyclic carbonate, or the oxygen atom of an epoxide, so as to enhance the electrophilicity of the monomer (1 in Scheme 1a). As a consequence, nucleophilic attack of the initiator/chain end (*e.g.*, hydroxy species) on the activated monomer becomes feasible, leading to the ring-opening of the monomer and regeneration of the acid catalyst. The monoadduct (2 in Scheme 1a) then acts as a new hydroxy species and the process repeats to finally afford the formation of a polymer chain.

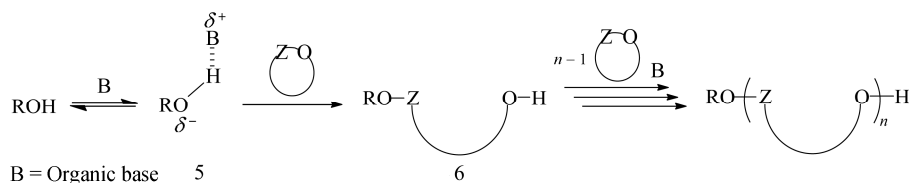


Scheme 1 Polymerization pathways by AMM via electrophilic (a) or nucleophilic (b) monomer activation

In a nucleophilic AMM pathway, a direct attack of the nucleophile (Nu in Scheme 1b) on the electrophilic moiety of the monomer occurs, leading to the formation of a zwitterionic intermediate (3 in Scheme 1b). Protonation of 3 by the hydroxy species (ROH) results in the formation of 4 and an alkoxide species (RO[−]), and subsequently Nu in the α -position of 4 is replaced by RO[−]. The generated monoadduct 2 then acts as a new hydroxy species and the propagation proceeds likewise.

Activated chain end mechanism (ACEM)

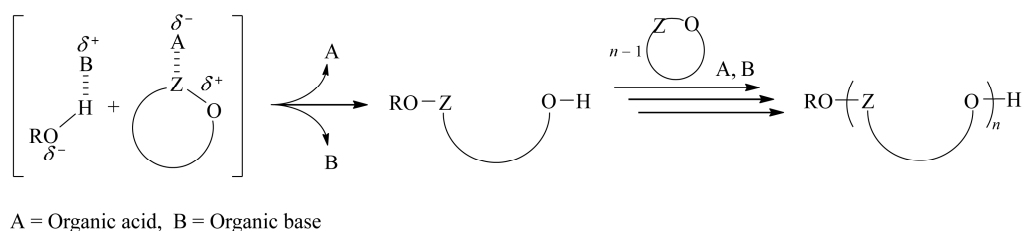
With organocatalysts, activation of the initiator/chain end (hydroxy species) can be done under milder conditions as compared with traditional metal-based procedures^[42]. Generally, the basic catalyst (or hydrogen acceptor) activates (improves the nucleophilicity of) the initiator or polymer chain end through deprotonation or formation of hydrogen bond, generating the activated initiating/chain-propagating species (5 and 6 in Scheme 2), which favors the attack on the electrophilic moiety of the monomer thus leads to the formation of the polymer chain.



Scheme 2 Polymerization pathway by activated initiator/chain-end mechanism (ACEM) using general base catalyst

Dual activation mechanism

Cooperative dual activation of both the monomer and the initiator/chain end can be carried out through bifunctional organocatalytic systems, including bimolecular catalysts like TU with tertiary amine derivatives and bifunctional unimolecular catalysts like the cyclic guanidine TBD. Such bifunctional dual activation is the result of the combination of an electrophile (*e.g.*, a weak Brønsted acid) activating the monomer and a general base activating the initiator/chain end (Scheme 3), which provides an effective means to trigger/promote the ROP and, more importantly, enhance selectivity of polymerization over side reactions.



Scheme 3 Acid-base bifunctional activation mechanism (AMM+ACEM)

As mentioned above, for different types of monomers, considerable differences may exist in the activities of their polymerizing moieties and propagating species (electrophilicity or nucleophilicity, ring strain, *etc.*), polarities and steric hindrances of the substituents, stabilities of corresponding polymer chains, and/or potential side reactions, which lead to diversities of the suitability between monomer and catalyst types, activation modes or polymerization conditions. Therefore, (concurrent) copolymerization of mixed type monomers, forming heterogeneous copolymer chains, has been an interesting and, in many cases, challenging research topic. Endeavors recently made with organocatalysis will be summarized and illustrated below, sectioned by the different combination of monomers.

ORGANOCATALYTIC COPOLYMERIZATION OF MIXED TYPE MONOMERS

Copolymerization of Cyclic Monoesters of Different Sizes

Organocatalytic ROP of cyclic esters is usually based on repeated nucleophilic ring-opening transesterification reactions between the initiators/chain ends and the monomers^[2], but the differences in the numbers of ester groups, size, strain and substituents of the monomeric rings often result in remarkably dissimilar polymerizability and suitable catalytic systems. Therefore, some of the synthetic approaches toward copolyesters are involved herein in our discussion as copolymerization of mixed type monomers.

Copolymerization of δ -valerolactone (δ VL) and ϵ -caprolactone (ϵ CL) has been performed in toluene at room temperature by the catalysis of 1,3-diethyl-4,5-dimethylimidazol-2-ylidene (Me_2IET in Fig. 2) *via* a zwitterionic ROP mechanism^[43]. Due to the substantially higher ring strain associated with the 6-membered cyclic monoester, δ VL polymerizes much faster than the 7-membered ϵ CL, leading to gradient copolymers with macrocyclic structures and total number-average molar masses (M_n) in the range of 46–77 kg/mol and high dispersities ($D_M = 1.9$ –2.4). The formation of macrocyclic structures has been a special and greatly desirable feature of zwitterionic ROP mediated by NHC and some other *N*-heterocycle type nucleophilic organocatalysts^[5], and has been demonstrated in these cases by the fact that the product shows lower intrinsic viscosity compared with the corresponding linear copolymers. The gradient sequence distribution of poly(ϵ CL-*co*- δ VL)s is confirmed by the variation of cumulative and instantaneous fraction of δ VL in the copolymer as a function of conversion. Interestingly, the gradient copolymer has exhibited different properties from the corresponding random and block copolymers. For instance, the melting point (T_m) of the gradient copolymer is higher than the random one but lower than the blocky analogue.

Copolymers of ϵ CL with δ VL derivative carrying a 2-(2-methoxyethoxy)ethylthio group at the β -position (EG_2MVL in Fig. 3) have been synthesized in toluene at room temperature using TBD as a catalyst^[44]. It is

observed that copolymerization of a 1:1 (mol/mol) mixture proceeds faster with higher conversions as compared to the homopolymerization of the substituted δ VLs, and leads to the formation of random copolymers ($M_n = 5.8\text{--}6.9$ kg/mol, $D_M = 1.21\text{--}1.47$) with compositions fitting well with the initial feed ratios. Functional ϵ CL and δ VL carrying, respectively, a propargyl and an allyl group at the α -positions have been copolymerized in a 1:1 molar ratio by the catalysis of TBD^[45], giving rise to the formation of a gradient copolymer as indicated by the appearance of multiple carbonyl peaks in the ^{13}C -NMR spectrum. This is considered to be the result of the higher polymerization rate and more preferential incorporation of the substituted δ VL at the early stage of the copolymerization as compared with the substituted ϵ CL. The generated copolyesters with pendent alkene and alkyne groups readily undergo orthogonal azide-alkyne and thiol-ene coupling reactions for postpolymerization modification and cross-linking. Based on the results presented above, it can be inferred that the polymerizability roughly follows the order of δ VL > ϵ CL > substituted δ VL > substituted ϵ CL, though which may vary upon numbers, positions and sizes of the substituents.

Copolymerization of ϵ CL and its 6-membered structural isomer, bio-renewable δ -hexalactone (5-methyl- δ -valerolactone, δ HL), has been performed in bulk at 100 °C using diphenyl phosphate (DPP) as the catalyst^[46]. Due to lower polymerizability and/or polymerization-depolymerization equilibrium of substituted δ VL^[47], incomplete conversion of δ HL (*ca.* 65%) has been obtained regardless of the feed ratio of ϵ CL to δ HL. The incorporation of δ HL units with pendent methyl groups, as compared with a more traditionally used comonomer (TMC, see section *Copolymerization of Cyclic Esters and Cyclic Carbonates*), has shown to be a quite effective way to reduce the crystallinity of P ϵ CL and enhance its enzymatic degradability as revealed by the investigation using quartz crystal microbalance with dissipation.

The release of ring strain is usually the main driving force for the ring-opening of small- and medium-sized heterocycles, while the ROP of macrocycles is mainly entropically driven^[48]. Metallic and enzymatic transesterification catalysts have been traditionally employed for the ROP of macrolactones and their copolymerization with smaller-sized lactones^[49–52]. Recently, organocatalysis have provided alternative and efficient pathways for such tasks. For example, copolymerization of ϵ CL and ω -pentadecalactone (ω PDL) has been conducted in bulk at 100 °C in presence of TBD. Instead of gradient copolymers that would have originated from different reactivity ratios associated with distinct ring strains of the two monomer, random copolymers are formed upon concurrent copolymerization of the two monomers due to the rapid and competitive intra- and intermolecular transesterification reactions^[53]. Moreover, random copolymers are obtained even by sequential monomer addition which originally aims at block copolymers. A dependence of T_m on comonomer composition has been demonstrated.

Ethylene brassylate (EB in Fig. 3), a macrolactone which is available in large quantities for the fragrance industry, has also been copolymerized with ϵ CL in bulk at 80 °C using TBD as a catalyst (Fig. 4b)^[54]. According to the results of computational study, the most favourable mechanism for ROP of EB is the dual activation of the monomer and initiator. Compared to the homopolymerization of ϵ CL or EB, copolymerization presents relatively lower rates and affords a series of random copolymers with slightly lower dispersities ($M_n = 8.0\text{--}9.7$ kg/mol, $D_M = 1.6\text{--}1.7$). T_m of the copolymer shows a gradual decrease (from 69 °C to 39 °C) with increasing ϵ CL content, which is considered as a result of the breakage of the structural order and the sequences average length.

Besides, organocatalytic copolymerization of macrolactones of different ring sizes/structures has also been investigated. For example, ω PDL and ambrettolide (AMB in Fig. 3) have been copolymerized under miniemulsion conditions at 80 °C by the catalysis of dodecylbenzenesulfonic acid (DBSA in Fig. 2)^[55]. Following a hydrolysis-polycondensation mechanism, a copolyester latex of a low molar mass ($M_n = 1.5$ kg/mol) is obtained, which can be subsequently used for preparation of cross-linked polyester films through free-radical cross-linking reaction in a thermal treatment process. The cross-linking is confirmed by FTIR analysis based on the decrease of the C=C stretching band at 1650 cm^{-1} compared with the uncross-linked ones. Thus, the feasibility of utilizing such a miniemulsion route to synthesize unsaturated polyester latexes which can be subsequently transformed into stable thermoset films has been demonstrated.

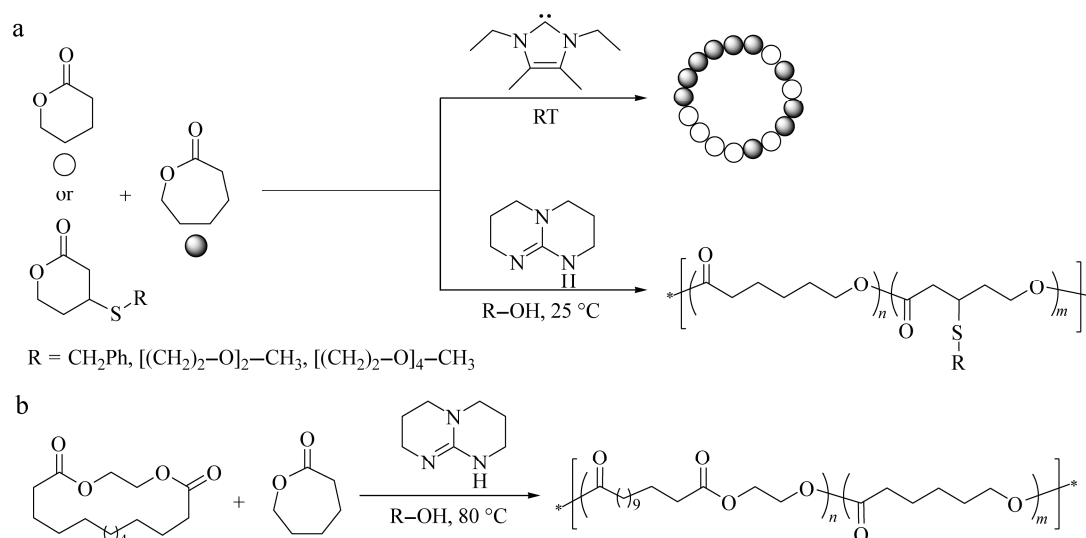


Fig. 4 Examples of organocatalytic copolymerization of cyclic monoesters of different sizes: (a) 6- and 7-membered cyclic monoesters^[43, 44]; (b) εCL and a macrolactone^[54]

Copolymerization of Cyclic Monoesters and Lactides

Traditionally, lactides and cyclic monoesters (*e.g.* εCL and δVL) have been copolymerized, usually in a random manner, in the presence of organometallic catalysts at high temperatures (100–150 °C) as a means of *e.g.* tuning the glass transition temperature (*T_g*) and hydrolysis rate of polyesters^[56, 57]. Interestingly, attempts to copolymerize LA with εCL or δVL in the presence of an organocatalyst, TBD, turn out to be unsuccessful (Fig. 5a)^[58], even though homopolymerization of LA, εCL or δVL proceeds well under the same catalytic condition. Only PLA homopolymers have been obtained with the absence of cyclic monoesters incorporated in the polymer chain even after full consumption of LA when transesterification on the PLA chain occurs. This indicates that the terminal secondary hydroxyl of PLA is incapable of inducing ring-opening of εCL/δVL under such a mildly basic organocatalytic condition.

On the other hand, the use of highly acidic trifluoromethanesulfonic acid (TfOH in Fig. 2) has led to copolymerization of L-lactide (LLA) and εCL (Fig. 5b)^[59–61], which proceeds in dichloromethane at 35 °C with either isopropanol or ethylene glycol as the initiator *via* an AMM pathway (Fig. 5b) and results in poly(εCL-*co*-LLA)s with *M_n* of 3–10 kg/mol. It is observed that LLA is consumed faster in the early stage of the copolymerization than εCL, but random copolymers are still formed because the occurrence of transesterification reaction rearranges the sequence distribution of monomeric units. NMR analysis shows that the end groups of the copolymers are mostly derived from εCL other than LLA, indicating that transesterification reaction more preferably occurs on less hindered end primary hydroxyls derived from ROP of εCL. Molar mass distributions of the copolyesters are intermediate (*D_M* = 1.2–1.3) between those of the corresponding homopolymers obtained under the same conditions (*i.e.* *D_M* = 1.05 for PεCL and 1.40 for PLLA) and increases as the feed ratio of [LLA]₀/[εCL]₀ increases. This is also considered to be associated with the transesterification scrambling reaction which is significant in the case of LLA homopolymerization while negligible for εCL homopolymerization, as has been confirmed by matrix assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analysis of the homopolymers. *T_g* and thermal stability of the copolyesters are intermediate between those of corresponding homopolyesters as well.

A limited number of studies have been reported on the copolymerization of LA and β-butyrolactone (βBL) including ones using organometallic catalysts^[62–64]. Recently, LA and βBL have been copolymerized at 60 °C by the catalysis of NHC carboxylates (*e.g.*, NHC4 in Fig. 2) in different solvents, *e.g.*, toluene or mixture of toluene and tetrahydrofuran (THF)^[61]. Racemic lactide (*rac*LA) and βBL with a molar ratio of 1:1 are simultaneously introduced into the reaction mixture, resulting in poly(*rac*LA-*co*-βBL) (*M_n* = 5.9–9.5 kg/mol, *D_M* = 1.21–1.24)

with the targeted comonomer compositions regardless of solvent used (Fig. 5c). On the other hand, when LLA is used instead of *rac*LA, the compositional ratio of LLA to β BL in the obtained poly(LLA-*co*- β BL) is 1/2 (mol/mol) due to a lower conversion of LLA (28%) in THF, which increases to 45% in a mixture of toluene and THF. The explanation of such a solvent effect has not been given.

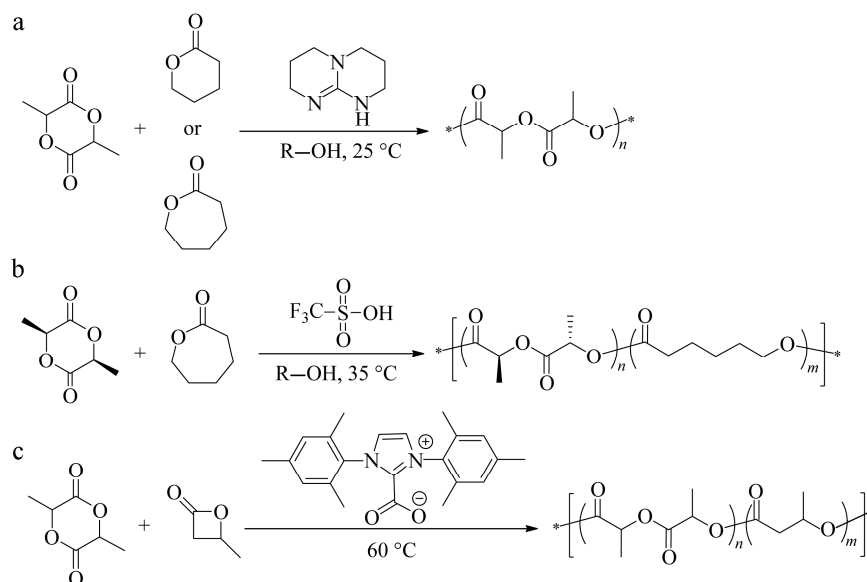


Fig. 5 Examples of organocatalytic copolymerization of LA and lactones^[58–61]

Copolymerization of Cyclic Esters and Cyclic Carbonates

The most frequently studied and used cyclic carbonate monomers for organocatalytic polymerization are 6-membered TMC and its derivatives^[6]. Being similar with aliphatic polyesters, poly(trimethylene carbonate) (PTMC) and derivatives are also (bio)degradable. Unlike the bulk degradation/erosion process of polyesters, the degradation of polycarbonates takes place hydrolytically in a surface erosion mode^[57]. Therefore, copolymerization of cyclic esters and cyclic carbonates has been used as an effective method for tuning their degradability^[46, 65, 66].

TBD-catalyzed copolymerization of trimethylene carbonate (TMC) and δ VL has been reported with the latter serving as a reactive solvent^[65]. The concurrent ROP of both monomers is conducted at ambient temperature with complete monomer conversions reached in 2 h, resulting in random poly(TMC-*co*-P δ VL) copolymers with comonomer composition being identical to the targeted value (feed ratio). Only one T_g (−43 °C) of the fully amorphous copolymers is presented, further identifying the successful (random) copolymerization of the two monomers.

Copolymerization of TMC and ϵ CL has been conducted by the catalysis of Brønsted acids such as methanesulfonic acid (MSA)^[66] and diphenyl phosphate (DPP)^[46]. In the case of MSA, copolymerization of the two monomers has been performed in toluene at 30 °C with a total comonomer concentration of 1.65 mol/L, yielding gradient copolymers with ϵ CL units enriched initially in the polymer chains, which is proven by more rapid consumption of the corresponding monomer. This is explained by the different reactivity ratios of ϵ CL and TMC ($r_{\text{CL}} = 3.4$, $r_{\text{TMC}} = 1.2$) as well as the absence of transesterification type scrambling reactions under such conditions. A series of gradient copolymers ($M_n = 14.5\text{--}18.3$ kg/mol, $D_M = 1.1\text{--}1.2$) with comonomer compositions agreeing well with the feed ratios are obtained in this way. In contrast with the two T_g s exhibited by block copolymers, only one T_g is observed for the gradient copolymers of comparable molar masses and compositions, which lies between those of the corresponding homopolymers ($T_g(\text{P}\epsilon\text{CL}) = -65$ °C, $T_g(\text{PTMC}) = -15$ °C) and varies from −55 °C to −15 °C as the molar ratio of [ϵ CL]/[TMC] in the feed varies from 80/20 to

20/80. Interestingly, for the gradient copolymers with a comonomer ratio of 50/50 ($[\epsilon\text{CL}]/[\text{TMC}]$) or below, the absence of T_m is observed. This phenomenon can be attributed to the insertion of TMC units in the P ϵCL enriched segments, which makes the P ϵCL blocks too short to crystallize^[66] (Fig. 6). On the other hand, crystallinity is exhibited by copolymers with higher $[\epsilon\text{CL}]/[\text{TMC}]$ ratios.

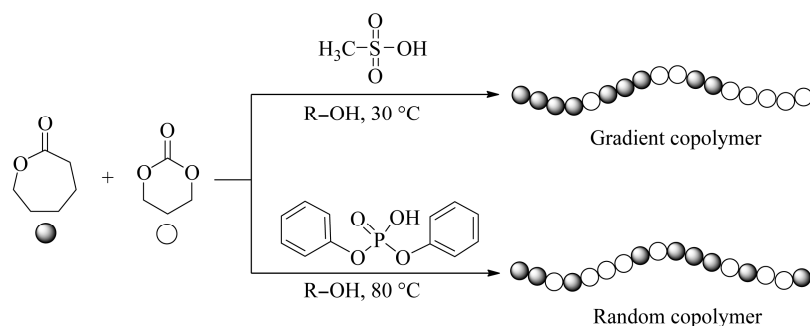


Fig. 6 Copolymerization of ϵCL and TMC using acidic organocatalysts^[46, 66]

DPP-catalyzed copolymerization of ϵCL and TMC has been carried out at a higher total comonomer concentration (5 mol/L) and reaction temperature (80 °C)^[46]. Random copolymers ($M_n = 37.5\text{--}40.3$ kg/mol) are formed under such conditions despite different reactivity ratios of the two monomers with DPP catalysis^[32, 67, 68]. The random sequence distribution of the comonomers is evidenced by NMR analysis. This is considered as the consequence of transesterification scrambling reactions occurring simultaneously with or at the end of the copolymerization process, which randomized the distribution of the two monomeric units along the copolymer chains. Another sign for the transesterification scrambling reaction is the relatively higher dispersities of the copolymers ($\bar{D}_M = 1.32\text{--}1.50$). Complete conversion of ϵCL is obtained in all cases in 4–36 h, while incomplete conversion of TMC is observed at a relatively high initial molar feed ratio of $[\text{TMC}]_0/[\epsilon\text{CL}]_0$ (50/50) due to lower polymerizability of TMC under acidic conditions. As compared with P ϵCL , poly($\epsilon\text{CL-co-TMC}$) copolymers have shown lower crystallinity and, consequently, enhanced enzymatic degradability in lipase *Pseudomonas* (lipase PS) solution.

Copolymerization of ϵCL and dimethylacetal dihydroxyacetone carbonate (MeO_2DHAC in Fig. 3), a glycerol-derived six-membered cyclic carbonate, has been conducted in bulk at 90 °C or 100 °C using TBD as a catalyst^[69]. The random distribution of the two monomeric units ($\text{MeO}_2\text{DHAC/CL}$) along the copolymer chains is confirmed by ^{13}C -NMR analysis. The molar mass distributions of the resulting copolymers are broad ($M_n = 9.7\text{--}16.4$ kg/mol, $\bar{D}_M = 1.80\text{--}2.17$), which is believed to be owing to the extensive occurrence of transesterification scrambling reactions at such high reaction temperatures. Deprotection (removal of the ketal groups) affords ketone groups in the carbonate units of the copolymers which exhibit semicrystalline behaviours (cocrystallization of the two monomers) with T_m varying with comonomer composition.

While TBD brings about rapid ROP of 6-membered cyclic carbonate, less basic DBU allows for a better control over molar mass and dispersity of the polycarbonates^[65]. 5,5-Bis(azidomethyl)-1,3-dioxan-2-one (AzDXO in Fig. 3), a diazido-functionalized TMC derivate, has been copolymerized with LLA in the presence of DBU^[70]. Random poly(ester-carbonate) copolymers with pendent azido groups, varying molar masses ($M_n = 18.7\text{--}22.6$ kg/mol) and low dispersities ($\bar{D}_M = 1.10\text{--}1.12$) have been achieved. Interestingly, it is observed that the existence of AzDXO can accelerate the consumption rate of LLA, which has been confirmed by a higher rate constant observed for LLA ($k = 0.171\text{ min}^{-1}$) during its copolymerization with AzDXO than that in its homopolymerization ($k = 0.116\text{ min}^{-1}$). This is considered due to the fact that the former generates alternating primary alcohol (higher reactivity) and second alcohol (lower reactivity) chain ends whereas the latter only produces second alcohol chain ends. The copolymers show altered crystallinity and thermal stability by the comonomer composition, and are subjected to postpolymerization modification by azido-alkyne cycloaddition.

TU·DBU bimolecular organocatalytic system (Fig. 2) has been utilized for the copolymerization of *rac*LA with a 6-membered cyclic carbonate bearing protected 2,2-bis(hydroxymethyl) groups, 9-phenyl-2,4,8,10-tetraoxaspiro[5,5]undecan-3-one (PTO in Fig. 3)^[71]. Because of the higher activity of *rac*LA than PTO, a faster consumption rate of the cyclic ester than the cyclic carbonate is observed. Therefore, a tapered comonomer sequence distribution along the copolymer chain is more likely to be formed, *i.e.* enrichment of ester groups at the initiating end and carbonate groups at the terminal. A low dispersity ($D_M < 1.07$) of the copolymer is preserved throughout the copolymerization. Interestingly, the apparent reaction rate constant for PTO in the initial stage of its copolymerization with *rac*LA ($k = 0.32 \text{ h}^{-1}$) is higher than that of its homopolymerization ($k = 0.16 \text{ h}^{-1}$). As the secondary alcohol chain ends derived from *rac*LA is supposed to be less reactive than the primary alcohol ones from PTO, the acceleration of PTO consumption is considered to be more likely owing to the decrease of overall steric hindrance in the polymer chain by the incorporation of lactide units which facilitates the incorporation of the bulky cyclic carbonate. It is considered that such an accelerative effect can be extended to enhance the ROP reactivity of other bulk derivatives of TMC. 1,3-Diol-functionalized poly(ester-carbonate)s, generated from postpolymerization deprotection of benzylidene acetal groups of PTO units, show a change in their degradation mechanism, *i.e.* from bulk (characteristic of polyesters) to surface erosion (polycarbonates).

Copolymerization of Cyclic Esters and Epoxides

Strongly basic organocatalysts, such as phosphazene superbases^[23, 24] and highly active NHCs (without bulky/electron-withdrawing substituents)^[8], have so far appeared to be the most ideal choices for organocatalytic (anionic) ROP of epoxides. However, such catalysts are usually unsuitable for the ROP of cyclic esters because of the inter- and intramolecular transesterification reactions which would occur extensively under strongly basic conditions, causing loss of control over molar masses and structures of the polyesters. Moderately basic and strongly acidic catalysts have shown to be better choices for cyclic esters, frequently giving rise to controlled synthesis of polyesters with well-defined molar masses and low dispersities^[16]. Such facts have posed challenges in finding catalytic systems for efficient and controlled copolymerization of epoxides and cyclic esters to afford poly(ester-ether)s with well-defined structures and low dispersities. However, due to the abundance and high accessibility of epoxides, copolymerization of cyclic esters and epoxides has been regarded as an efficient pathway to tune the properties and functionalities of polyesters; such efforts have also been made through organocatalysis.

Anionic copolymerization of ϵ CL and *tert*-butyl glycidyl ether (*t*BuGE in Fig. 3) has been performed in bulk at 80 °C through the catalysis of *t*-BuP₄^[72], generating statistical copolymers ($M_n = 12.0\text{--}49.2 \text{ kg/mol}$, $D_M = 1.28\text{--}1.43$) as confirmed by the analysis of ¹³C-NMR spectrum (Fig. 7a). Hydrolysis of the copolymers yields amphiphilic poly(ϵ CL-*co*-glycidol) copolymers ($M_n = 10.2\text{--}46.3 \text{ kg/mol}$, $D_M = 1.36\text{--}1.46$) which exhibit low cytotoxicity, tunable thermal properties and enzymatic degradation rates. 3-Isochromanone (ICM), which lacks the ability to undergo homopolymerization, has been shown to undergo cationic copolymerization at 100 °C with epoxides such as *n*-butyl glycidyl ether (*n*BuGE) using TfOH as the catalyst/initiator, resulting in copolymers with random distributions of ICM-derived monomeric units ($M_n = 6.3 \text{ kg/mol}$, $D_M = 2.1$)^[73].

Except from traditional copolymerization of the two types of monomers, an alternative “noncopolymerization” approach has been recently developed for the synthesis of poly(ester-ether)s^[74]. Hydroxyl-terminated P ϵ CLs have been used as macroinitiators for *t*-BuP₄-catalyzed anionic ROP of epoxides. Instead of polyester-polyether block copolymers, poly(ester-ether) random copolymers are formed because of the concurrence of ring-opening reaction of epoxides and transesterification reaction on the (co)polymer chains. When the reaction is performed with a large initial ratio of epoxide to P ϵ CL (*e.g.*, $m_{\text{epoxide}}/m_{\text{P}\epsilon\text{CL}} = 10$), all ϵ CL units in the original P ϵ CL are separated eventually by polyether segments and the obtained copolymers are regarded as multiblock-like polyethers with ester junctions (Fig. 7b). Thus, it is preliminarily demonstrated that transesterification type side reactions which are usually considered detrimental for the achievement of well-defined polymer structures can actually be utilized for the modification and/or functionalization of the chemical

composition and properties of an existing polymer (Fig. 7b). On the other hand, the nonselective feature (unspecific reaction sites) of the transesterification reaction has caused difficulties in precisely controlling the molar masses of the copolymer, which requires further endeavors to find more proper catalytic systems and/or reaction conditions.

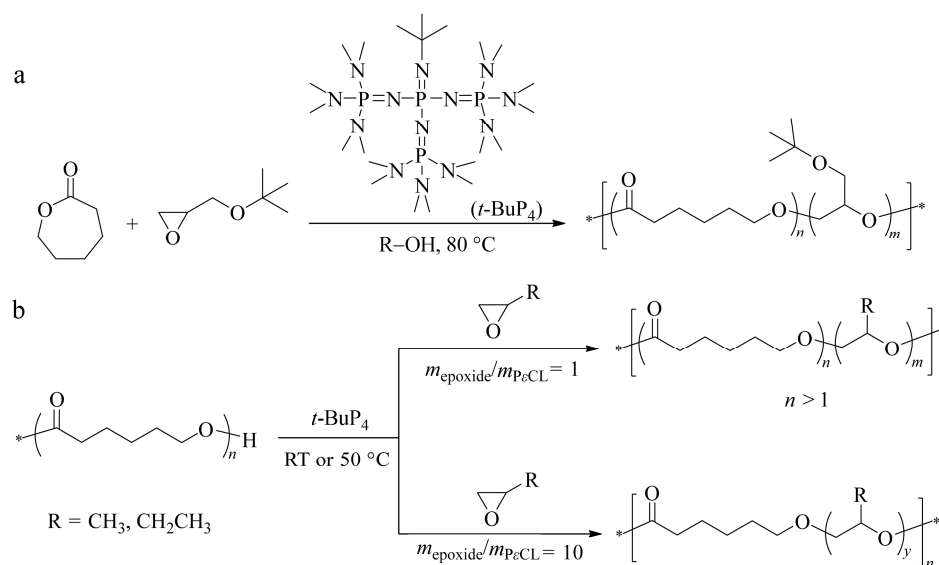


Fig. 7 Synthesis of poly(ester-ether) copolymers via *t*-BuP₄-catalyzed (a) copolymerization of ϵ CL and BGE^[72] and (b) ROP of epoxides from polyester macroinitiators^[74]

In addition to random or statistical copolymers, poly(ester-ether) type alternating copolymers have also been synthesized under organocatalytic conditions^[75–81]. Alternating copolymers have been of great interests in all aspects of polymer sciences because of the uniform comonomer sequence distributions and substantially different properties from the corresponding homo-, random, gradient/tapered, or block copolymers^[82]. Copolymerization in a precisely alternating way has allowed achievement of new polymer chain structures utilizing compounds that lack the ability to undergo homopolymerization, which has served as a significant strategy to enrich the catalog of monomers and polymers. Alternating copolymerization of epoxides and non-homopolymerizable compounds such as carbon dioxide (CO₂) and derivatives^[83–85], cyclic anhydrides^[86–88], and aromatic lactones^[76–78, 80, 81, 87] has been extensively studied, mostly with organometallic catalysts, and employed to constitute heterochain polymers. Recently, organocatalysis has also shown potentials and new strengths in this aspect.

To achieve alternating anionic or nucleophilic type copolymerization with epoxides, the following general mechanistic pathway needs to be followed for a certain compound (monomer A). A should be extremely active toward nucleophilic attack by the initiator to form the active species A*, which cannot react with A because of *e.g.* low nucleophilicity of A*, steric hindrance, and/or low stability of the potential product. But A* can react with the epoxide, usually in a slower manner, to produce an alkoxide species, which preferably reacts with A due to its much higher electrophilicity so that self-propagation of the epoxide cannot take place, generating a new A*. Such a process occurs repeatedly until an alternating copolymer sequence structure forms. It is obvious that normal aliphatic lactones (*e.g.*, ϵ CL, δ VL, LAs) cannot undergo alternating copolymerization with epoxides due to their self-polymerizability. On the other hand, phenolic lactones such as 3,4-dihydrocumarin (DHC) and derivatives, have shown to possess the appropriate natures for such a purpose.

The alternating copolymerization of DHC with epoxides such as glycidyl phenyl ether (GPE in Fig. 3) has been conducted with 2-ethyl-4-methylimidazole (EMI in Fig. 2) as an initiator at 120 °C (Fig. 8a)^[75, 76]. The formation of alternating comonomer sequence distribution has been confirmed by ¹H-NMR spectroscopic

analysis and examination of reductive cleavage products of the copolymers. It is observed that the consumption rate of GPE in the copolymerization is faster than that in the homopolymerization. The resultant copolymers have low molar masses (M_n up to 2 kg/mol) and relatively high dispersities ($D_M = 1.3$ – 1.5) with the molar feed ratio ($[GPE]_0:[DHC]_0$) varying from 85:15 to 30:70. The increase of DHC content in the feed is found to suppress the formation of GPE–GPE (polyether) sequence, thus enhance the formation of alternating sequence^[75, 76].

The scope of this alternating copolymerization system can be expanded by the employment of diverse epoxides, including *n*BuGE, *t*BuGE and allyl glycidyl ether (AGE in Fig. 3)^[77]. All the obtained copolymers ($M_n = 1.4$ – 2.6 kg/mol, $D_M = 1.2$ – 1.3) show a strictly alternating monomeric sequence distribution. Other aromatic lactones such as 10-methyl-2*H*,8*H*-benzo-[1,2-*b*:5,4-*b'*]bipyran-2,8-dione (Bislactone 1 in Fig. 3)^[78, 79], a bifunctional DHC analogue, and 1,2-dihydro-3*H*-naphtho[2,1-*b*]pyran-3-one (DHNP in Fig. 3)^[80], an aromatic lactone bearing a naphthyl moiety (Fig. 8a), have also been subjected to alternating copolymerization with glycidyl ethers. In the former case^[78, 79], the most striking feature is that only one lactone moiety of Bislactone 1 participates in the copolymerization, giving rise to the copolymers bearing alternating lactone and allyl pendent groups (AGE as the epoxide monomer) in the side chains. Therefore, two types of postpolymerization reactions can be operated with these alternating copolymers, *i.e.* ring-opening reaction of the lactone with amines and the platinum-catalyzed hydrosilylation of the allyl group. Interestingly, conversion of the two monomers reaches up to *ca.* 60% after 1 h, and prolonging the polymerization time leads to no further increase of the conversion. In the latter case^[80], networked copolymers are obtained from copolymerization of bisphenol A diglycidyl and DHNP, showing a higher T_g than that obtained similarly with DHC.

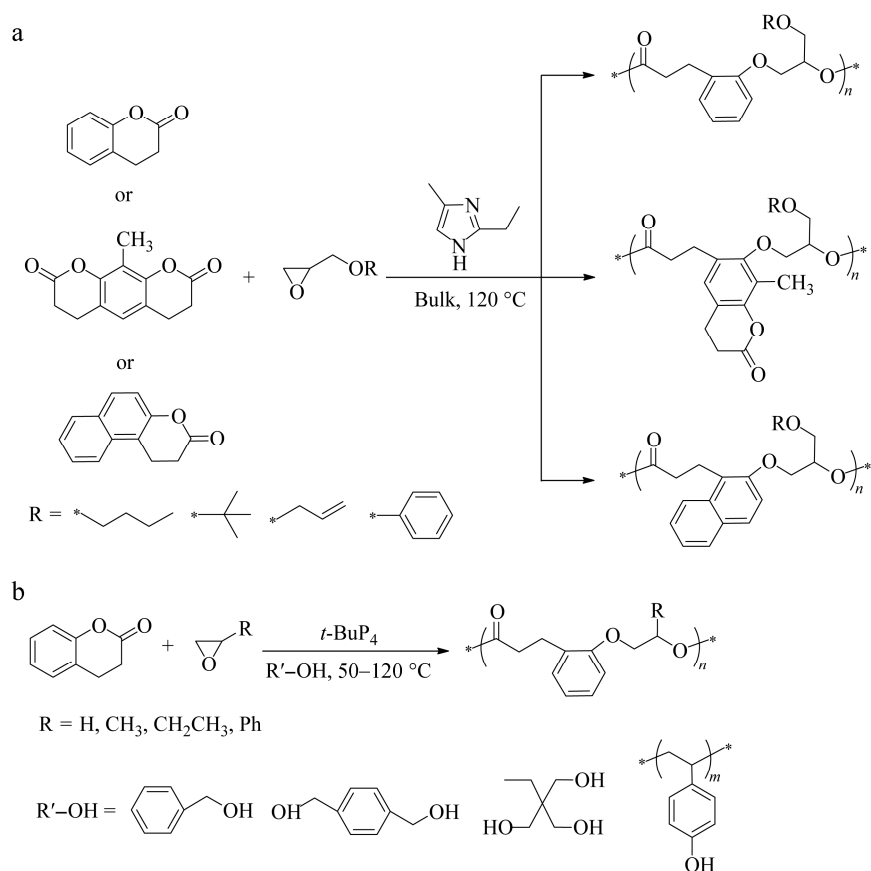


Fig. 8 Alternating copolymerization of DHC or its derivatives with epoxides (a) initiated by EMI^[75–80] or (b) promoted by *t*-BuP₄^[81]

Recently, alternating copolymerization of DHC with several commonly used epoxides, *i.e.* ethylene oxide (EO), propylene oxide (PO), 1,2-butylene oxide (BO) and styrene oxide (SO), has been triggered by alcoholic initiators in the presence of *t*-BuP₄ (Fig. 8b)^[81]. Relatively milder reaction temperature (50 °C or 80 °C) is used, and the copolymers are demonstrated to be mixtures of linear and cyclic alternating copolymers ($M_n = 2.4\text{--}4.4$ kg/mol, $D_M = 1.05\text{--}1.29$, bimodal molar mass distributions). The formation of macrocyclic byproducts is considered as a consequence of intramolecular transesterification (backbiting) reactions, which limits the achievable molar mass. It is interesting and still puzzling that such alternating copolymer structures seem to favor backbiting over intermolecular transesterification reactions. The alternating copolymers have shown good thermal stabilities and higher T_g s as compared with the homopolymers of the corresponding epoxides. Very importantly, the *in situ* initiator-activation and chain-growth mechanism of phosphazene-catalyzed ROP have allowed for facile synthesis of nonlinear (*e.g.*, graft, star-shaped) macromolecular architectures with alternating copolymer branches using multifunctional initiators.

Anionic copolymerization of bicyclobis(γ -butyrolactone) derivatives (BBL in Fig. 3) and epoxides has been conducted in THF at 120 °C with phosphines including triphenylphosphine, tri-*n*-butylphosphine and tricyclohexylphosphine (PPh₃, PBu₃ and PCy₃, respectively, in Fig. 2) as initiators, which generates polyesters with alternating sequence structures^[89, 90]. For the BBL derivative bearing a methyl group (BBL1 in Fig. 3)^[89], phosphine-initiated copolymerizations with GPE show higher rates than the *t*-BuOK-initiated ones and suppressed backbiting reactions which usually accompanies the latter, leading to the linear polyesters with M_n of 5.2–6.5 kg/mol and D_M of 1.32–1.41. The use of 2,8-dioxo-1-isopropenylbicyclo[3.3.0]octane-3,7-dione (BBL4 in Fig. 2) leads to the formation of alternating copolyesters ($M_n = 6.5$ kg/mol, $D_M = 2.1$) bearing α,β -unsaturated ketone pendent groups which can be further used to functionalize the copolymer by Michael addition of thiol compounds^[90].

Copolymerization of Heterocycles and Vinyl Monomers

Combination of vinyl-addition and ring-opening polymerizations, namely, copolymerization of heterocyclic and vinyl compounds, the two major families of monomers, is of great interest and potential for developing new types of (co)polymer chain structures with undiscovered properties. However, such attempts are usually encountered with difficulties owing to the inherently different polymerization mechanisms and widely disparate monomer reactivity ratios. Nevertheless, efforts have still been made achieving successful copolymerization of *e.g.* electrophilic *N*-phenyl-maleimides with several nucleophilic heterocycles^[91–94]. Recently, some organocatalytic copolymerization systems have been developed for anionic copolymerization of lactones with methacrylates catalyzed by an organic superbases^[95–98], and cationic copolymerization of epoxides with vinyl ethers catalyzed by a highly active organic Lewis acid^[99–102].

Copolymerization of ϵ CL and methyl methacrylate (MMA) in the presence of *t*-BuP₄ has been conducted in toluene at room temperature with alcohols or ethyl acetate as initiators (Fig. 9a)^[95]. NMR analysis demonstrates random distribution of the two monomeric units. It is found that solvent and reaction temperature have little effect on the result of copolymerization ($M_n = 1.8\text{--}47.3$ kg/mol). Broad and bimodal molar mass distributions ($D_M = 1.44\text{--}2.87$) are observed for all of the products by the size exclusion chromatography (SEC) analysis, which is attributed to the nucleophile attack on the carbonyl group of MMA. It indicates the complicated mechanisms of initiation, chain growth, chain transfer, cross-propagation and termination. In comparison with the corresponding homopolymers (PMMA, $T_g = 115$ °C; P ϵ CL, $T_g = -60$ °C), the poly(ϵ CL-*co*-MMA) random copolymers exhibit intermediate T_g s ($-42\text{--}35$ °C) and higher decomposition temperature. Although the copolymerization mechanism awaits further clarification, the discovery of such an anionic “hybrid copolymerization” system has paved a pathway toward a diversity of new copolymer chain structures, functionalized polyesters and, more importantly, (bio)degradable polymers derived from vinyl monomers.

The hybrid copolymerization approach has allowed for facile synthesis of (bio)degradable polyesters bearing various functional pendent groups taking advantages of the inexpensiveness, diversity and high accessibility of methacrylates^[96–98]. For example, copolymerization of ϵ CL and *tert*-butyl methacrylate (BMA in Fig. 3) in the presence of *t*-BuP₄ followed by hydrolysis of the pendent *tert*-butyl ester groups leads to poly(ϵ CL-

co-methacrylic acid)s (Fig. 9a)^[96]. Such copolymers exhibit slightly higher T_g s than the poly(ϵ CL-*co*-BMA) precursors, which is explained by the formation of intermolecular hydrogen bonding among the pendent carboxyl groups. Both poly(ϵ CL-*co*-BMA) and the hydrolysis product are biodegradable in the presence of lipase PS solution, and the former degrades somewhat faster than the latter, which is presumably because the pendent carboxyls bind with lipase PS *via* electrostatic interaction preventing lipase PS from contacting with the P ϵ CL segments. Allyl methacrylate (AMA in Fig. 3) has shown to undergo copolymerization with ϵ CL selectively through the methacrylic double bond^[97], yielding the random copolymers with pendent allylic double bonds in the side chain ($M_n = 21.3$ – 23.8 kg/mol, $D_M = 1.91$ – 2.18) which can be used for postpolymerization modification by thiol-ene radical addition reaction. Hybrid copolymerization of ϵ CL and 2-(*N,N*-dimethylamino) ethyl methacrylate (DMAEMA) has led to copolymers with tertiary amino groups, which are subjected to betainization by 1,3-propane sulfone to afford zwitterionic pendants^[98]. Both the cationic poly(ϵ CL-*co*-DMAEMA) precursors (in aqueous solution, pH = 7.4) and zwitterionic copolymers are found to form stable and uniform micelles with hydrodynamic radius of *ca.* 100 nm, and the zwitterionic copolymers show improved protein resistance in comparison with the cationic ones as the protein shifts from negatively charged (bovine serum albumin) to positively charged (lysozyme).

In addition to linear ϵ CL-based functional copolymers, hybrid copolymerization has also been used to synthesize hyperbranched P ϵ CL (*h*-P ϵ CL) using glycidyl methacrylate (GMA in Fig. 3) as a bifunctional comonomer^[103]. The reaction is carried out in toluene at 80 °C, resulting in hyperbranched copolymer structures ($M_n = 252$ – 882 kg/mol, $D_M = 3.18$ – 5.25 , SEC results) owing to the simultaneous occurrence of ROP and anionic vinyl addition reactions on GMA. The formation of highly branched structure is demonstrated by NMR and FTIR spectroscopic analysis, as well as comparison with the corresponding linear P ϵ CL on molar mass dependence of intrinsic viscosity, elution volume (SEC analysis) and average radius of gyration (light scattering study).

There have also been some successful attempts recently on organocatalytic cationic copolymerization through concurrent vinyl-addition and ring-opening reactions, *i.e.* copolymerization of vinyl ethers (VEs) and epoxides catalyzed by a strong organic Lewis acid, tris(pentafluorophenyl)borane (B(C₆F₅)₃ in Fig. 2)^[99–102]. The copolymerization reaction is conducted in dichloromethane at –78 °C. More specifically, isopropyl vinyl ether (IPVE) has been copolymerized with several epoxides such as isobutylene oxide, butadiene monoxide, isoprene monoxide and 3,3-dimethyl-1,2-butylene oxide (IBO, BDO, ISPO and DMBO, respectively, in Fig. 3)^[100]. The key to concurrence of ring-opening and vinyl-addition reactions on the same growing chain is the frequent conversion of the propagating species between carbocation and oxonium ion. It is found that the frequency of such crossover reactions is mainly affected by the ease of (stabilized) carbocation generation at the epoxide-derived living chain end. For instance, epoxides that generate resonance-stabilized or tertiary carbocation structures upon ring-opening (*e.g.*, ISPO and IBO) can be copolymerized with IPVE through frequent crossover reactions to yield corresponding copolymers with variable comonomer sequence distributions, including random or alternating-rich copolymers with short IPVE and ISPO blocks ($M_n = 0.8$ – 3.8 kg/mol, $D_M = 2.38$ – 2.89) and multiblock-like copolymers with long IPVE and IBO blocks ($M_n = 6.9$ – 16.9 kg/mol, $D_M = 1.87$ – 2.00). In contrast, epoxides such as DMBO and BO, which generate less stable secondary carbocations, are not efficiently copolymerized with IPVE (Fig. 9b) as the frequency of crossover reactions is significantly lower. The influence of additives has also been shown, *e.g.* weak Lewis bases such as ethyl acetate can promote crossover reactions, which is owing to facilitated ring-opening reactions of IBO-derived propagating ends by the nucleophilic attack of the ester on the oxonium ion and stabilization of the generated carbocation by interaction with the carbonyl. On the other hand, solvent polarity shows little influence on the crossover from the IBO-derived propagating end to VE but increases the frequency of crossover from the VE-derived ones to IBO^[101].

Recently, a very interesting B(C₆F₅)₃-catalyzed cationic terpolymerization system of IPVE, cyclohexene oxide and methyl ethyl ketone (CHO and MEK, respectively, in Fig. 3) has been developed and investigated (Fig. 9c)^[102]. Terpolymers with alternating-like (IPVE-₂-epoxide-₂-ketone)_{*n*} chain structures are obtained through concurrent vinyl-addition, ring-opening, and carbonyl-addition reactions in dichloromethane at –78 °C ($M_n =$

2.1–12.7 kg/mol, $\bar{D}_M = 1.96$ –2.25). The formation of this particular comonomer sequence distributions along the polymer main chain has been explained by an exclusive one-way reaction cycle, namely, the reaction proceeds only in the IPVE→CHO, CHO→MEK, and MEK→IPVE manner. Therefore, it is considered as an efficient method to synthesize sequence-regulated polymers by precisely designing crossover reactions among various types of monomers.

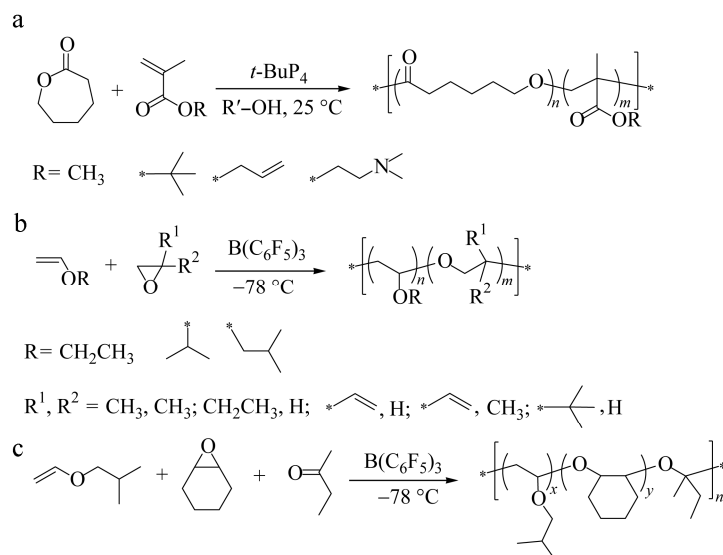


Fig. 9 Copolymerization of heterocycles and vinyl monomers: (a) $t\text{-BuP}_4$ -promoted copolymerization of ϵ -CL and methacrylates^[95–98]; (b) $\text{B}(\text{C}_6\text{F}_5)_3$ -initiated copolymerization of vinyl ether and epoxides^[99, 100]; (c) synthesis of sequence-regulated terpolymers using $\text{B}(\text{C}_6\text{F}_5)_3$ ^[102]

Copolymerization of Other Mixed Type Monomers

Anionic bulk copolymerization of 13-membered laurolactam and 7-membered ϵ -caprolactam (LL and CLA, respectively, in Fig. 3) catalyzed by the latent (CO_2 -protected) NHCs (e.g. NHC2 in Fig. 2) at 180°C has been investigated^[104]. It is believed that gradient copolymers are formed in the early stage of reaction ($t = 140$ s, $M_n = 13.2$ kg/mol, $\bar{D}_M = 2.4$) because faster consumption (preferential incorporation) of smaller-sized CLA is observed in the beginning, and LL is incorporated largely only at high CLA conversion. However, with prolonged reaction time, M_n decreases from 13.2 kg/mol (140 s) to 9.4 kg/mol (400 s) until becoming undetectable in 45 min. Also the gradient comonomer sequence distribution of the initially formed polyamide is scrambled after extended reaction time.

Zwitterionic ring-opening copolymerization of THF (5-membered cyclic ether) and GPE (3-membered cyclic ether with an substituent) has been conducted in bulk at room temperature with $\text{B}(\text{C}_6\text{F}_5)_3$ as an catalyst/initiator (Fig. 10a)^[105]. A faster consumption of THF than GPE has been confirmed by quantitative ^{13}C -NMR analysis from a reaction with a 50:50 molar ratio of THF and GPE. Copolymers with M_n of 15–330 kg/mol and $\bar{D}_M$ of 1.6–1.9 are obtained, and the macromolecular architecture is found to be dependent on the reaction conditions. Namely, cyclic copolyethers together with cyclic homopolymer of GPE is preferentially formed at low THF fractions (e.g., 20 mol%), whereas linear copolymers are mainly generated at high THF fractions (e.g., 78 mol%). This has been explained by the formation of zwitterionic species with different reactivities toward propagation and termination (cyclization). More specifically, in the presence of excess GPE, (co)polymeric macrozwitterions terminated by a GPE-derived unit are preferentially formed, which is prone to termination by cyclization. On the other hand, in the presence of excess THF, the preferentially formed macrozwitterions terminated by a THF-derived unit tend to propagate by addition of a new THF molecule, which eventually leads to an increase in the fraction of linear chains. T_g of the copolyethers can be tuned from -84°C to -4°C by variation of the initial comonomer feed ratio.

As an important alternative approach, in addition to traditional polycondensation of *e.g.* diacids–diols and ROP of cyclic esters^[86–88], alternating copolymerization of epoxides and cyclic anhydrides has also been involved in the field of organocatalytic polymerization. For example, copolymerization of CHO and norbornene anhydride (NA) stereoisomers has been conducted in toluene at 110 °C in the presence of quaternary onium salts such as tetrabutylammonium chloride and bis(triphenylphosphine)iminium chloride (PPNCl in Fig. 2) (Fig. 10b)^[106]. The resulting alternating copolymers ($M_n = 3.0\text{--}9.3$ kg/mol, $\bar{D}_M = 1.2\text{--}2.7$) exhibit high stereoregularity and geometrical structures readily tuned by varying the conformation of NA (*endo*-, or *exo*-NA), monomer feed ratio and reaction temperature. Specifically, *cis*-polyesters comprising 2,3-(*exo*, *exo*) ester repeat units are achieved at a 1:1 molar feed ratio of [CHO]/[*exo*-NA] at 110 °C, whereas copolymerization of CHO and *endo*-NA at the same feed ratio and temperature results in *trans*-polyesters. It is also found that *trans*-polyesters are formed in the presence of excess CHO (*e.g.*, [CHO]/[*exo*-NA] = 1.5 or 2.0, 110 °C), while an excess of NA isomers (*e.g.*, [CHO]/[*exo*-NA] = 0.5, 110 °C) plays a negative role in achieving high stereoregularity. In addition, *trans*-polyesters are formed preferably at a high reaction temperature (110 °C) for *endo*-NA, but low temperature (60 °C) leads to polyesters with mixed conformation. T_g of the copolymers is dependent on the geometrical structures, *i.e.* *cis*- and *trans*-polyesters exhibit T_g s of 129.8 and 115.9 °C, respectively, while thermal decomposition temperatures (T_d) are similar (*ca.* 320 °C) for both.

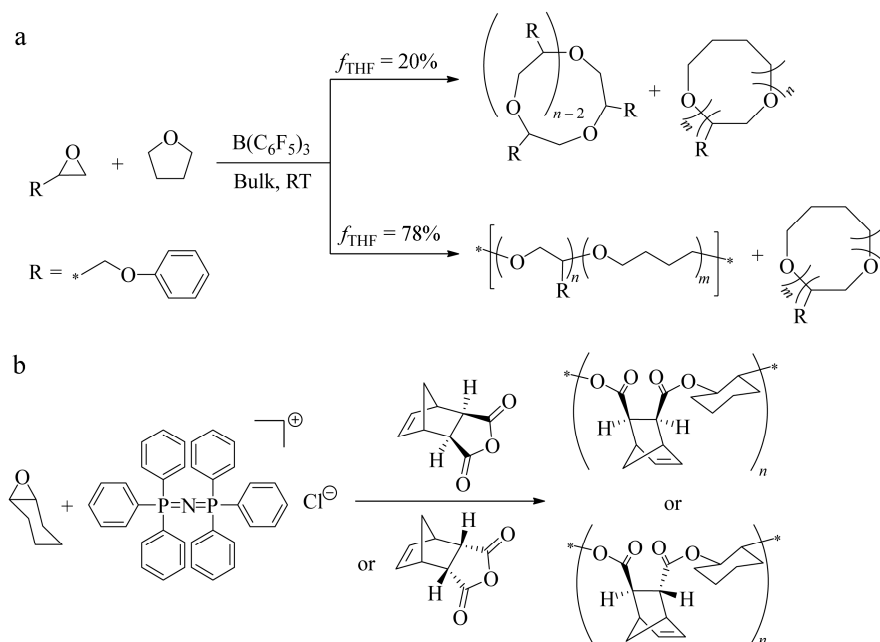


Fig. 10 (a) Zwitterionic ROP of THF and GPE^[105]; (b) Alternating copolymerization of CHO and NA isomers^[106]

Metal-free alternating copolymers of carbon dioxide (CO_2) and epoxides such as PO and CHO have been synthesized by use of binary organocatalytic systems composed of triethylborane (TEB) and basic organic salts (*e.g.*, onium halides or onium alkoxides)^[107]. It has been demonstrated that both TEB and onium salts, activating the epoxide and CO_2 respectively, are necessary for the formation of polycarbonates. The copolymers of CO_2 and PO obtained at 60 °C have M_n of 1.6–50 kg/mol and low dispersities ($\bar{D}_M < 1.2$). Copolymerization of CO_2 and CHO conducted at 80 °C targeting at lower molar masses leads to similar results ($M_n = 10.2\text{--}67.4$ kg/mol, $\bar{D}_M < 1.2$), whereas high dispersities ($\bar{D}_M > 1.7$) are obtained with high molar masses targeted at (theoretical $M_n = 131\text{--}511$ kg/mol, while the obtained apparent M_n is 19.3–76.4 kg/mol). The latter is considered to be caused by the presence of water acting as transfer agent. Moreover, such a metal-free system shows a good selectivity for linear polycarbonate over macrocycles.

Copolymerization of ϵ -thionocaprolactone (tnCL) and δ VL has been reported recently which is performed at room temperature with a bimolecular organocatalytic system consisting of TU and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (TU·BEMP in Fig. 2)^[108]. Differing from ϵ CL, tnCL is found to have similar ring strain and ROP thermodynamics with δ VL. Therefore, random or gradient copolymers can be obtained ($M_n = 19.6$ – 29.8 kg/mol, $D_M = 1.02$ – 1.25) simply by variation of comonomer feed ratios. Copolymers with increasing tnCL content show reduced T_m and T_d . The hydrolytic stability of copolymers is found to be reduced under basic conditions and increased under acidic conditions, which are associated with the stability of C=S type thioester.

CONCLUSIONS

Development of approaches for copolymerization of mixed type monomers has greatly enriched the variety of chain structures and inherent properties of polymers. Also, in some cases, copolymerization of mixed type monomers allows for production of polymers from compounds that lack the ability to homopolymerize and has served as a significant means to enrich the catalogue of monomers (raw materials for polymer synthesis). Therefore, we believe that copolymerization of mixed type monomers holds an important position for the development of synthetic polymer chemistry, even general polymer science. Present achievements, as summarized in this mini-review, have already manifested the strengths and promising perspectives of organocatalysis for such purpose. On the other hand, challenges still remain such as further clarifying the copolymerization mechanisms, increasing the selectivity of polymerization over side reactions, more precisely controlling the molar masses and tuning (controlling) the comonomer sequence distribution or other microstructures. It is our expectation to motivate more attentions to be paid and efforts to be made for such a research topic in the future development of organocatalytic polymerization methods.

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