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Organic Catalysis for Ring-Opening Polymerization

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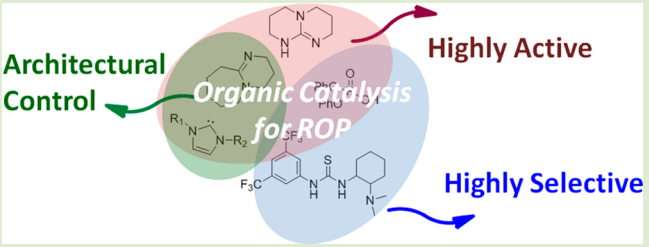
ABSTRACT: Organic catalysis in ring-opening polymerization (ROP) has become a powerful alternative to more traditional metal-based catalysts. The field has developed to a point at which there are not only excellent low cost and easy to use organocatalysts for day-to-day polymerizations, but the ability to precisely control the synthesis of advanced polymer architectures and ROP monomers that are extremely challenging to polymerize with other catalysts now exists. This viewpoint article will highlight the key advances in organocatalyst design with the aim of encouraging the wider application of organic catalysts in ROP.



Since the first report of the use of 4-dimethylaminopyridine (DMAP) for the ring-opening polymerization (ROP) of lactide in 2001,[1] the field of organic catalysis for ROP has grown to the point that it now provides a powerful alternative to the use of more traditional metallo-organic catalysts.[2−4] Indeed the field has progressed to the point that organic catalysts now provide many potential advantages to their metallo-organic counterparts that make them preferential to apply in such processes. Many organic catalysts are simple, commercially available molecules that are typically easily purified and, as a consequence of insensitivity to water and oxygen, have long shelf lives. Indeed, many organic catalysts only require drying to allow control over molecular weight and high levels of end-group fidelity to be obtained (water is able to act as an initiator in many cases and leads to altered end groups and lower molecular weights than are targeted; with some monomers, water initiation can also lead to additional distributions with higher molecular weight). Furthermore, organic catalysts are well suited to a range of reaction conditions, solvents, and monomers and, as a consequence of their acidic or basic nature, are typically very easy to remove from the resultant polymers by simple washing or trapping in resin beads.

The field of organic catalysis for ROP has expanded rapidly, and a wide range of choices from which to choose an appropriate catalyst now exist. Following the report of DMAP (Figure 1) as an ROP catalyst,[1] other nucleophilic bases were investigated for activity in ROP. Among the most successful and widely studied were the family of *N*-heterocyclic carbenes (NHCs, Figure 1).[5,6] NHCs have been applied to a wide range of monomers including other lactones,[7,8] epoxides,[9,10] cyclic carbonates,[11] and cyclic siloxanes,[12,13] among others, and are noted to display extremely high activities in the ROP of lactide (ROP of 200 equiv to initiator achieving 88% monomer conversion in less than 25 s at ambient temperature with 0.5 mol % catalyst, [LA] = 0.7 M).[14] These species, however, are highly air sensitive, with catalyst deactivation in the presence of water leading to lower reactivities and long-term storage

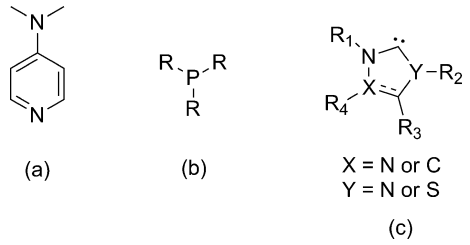


Figure 1. Nucleophilic catalysts applied in organocatalytic ring-opening polymerization: (a) 4-dimethylaminopyridine; (b) general structure of a phosphine; (c) general structure of a *N*-heterocyclic carbene.

problems. While several methods by which to generate NHCs in situ have been reported,[8,15−17] the shift to supramolecular, organic "super-base" and acid catalysts has made the application of organic catalysts significantly more accessible to a greater number of researchers. None-the-less, as a consequence of the proposed "activated-monomer" mechanism, NHCs provide unique opportunities to undertake complex macromolecular engineering. Notably, in the absence of added protic initiators, nucleophilic attack on the monomer by the NHC, followed by a zwitterionic polymerization and the subsequent elimination of the NHC by ring-closure leads to the isolation of cyclic poly(ester)s.[18] Extension of this principle to a bromine-functional lactide derivative has enabled the synthesis of jellyfish copolymers by ROP and atom-transfer radical polymerization (ATRP),[19] while reaction with β-lactone monomers results in a single insertion to form a spirocyclic compound that is able to be expanded to form cyclic polymers with a single functionalization point.[20] The lower polymerization activity of triazolium carbenes results in them behaving as thermally activated catalysts for ROP.[15] This has provided the opportunity to prepare a cyclic carbonate monomer with a

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triazolium carbene pendant to the polymerizable unit. Following ambient temperature ROP of the carbonate monomer, thermal activation of the NHC in the presence of β-butyrolactone (βBL) resulted in the facile synthesis of comb copolymers.[21]

In 2005, the report of the application of the bifunctional thiourea-amine catalyst (TU/A) for the ROP of lactide marked a paradigm for the field (Figure 2).[22] With this catalyst, ROP

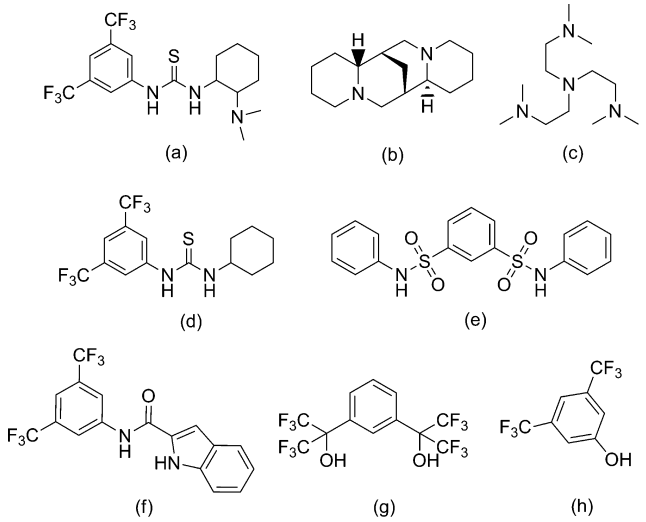
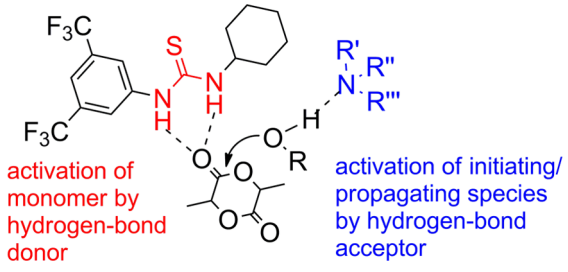


Figure 2. Examples of "supramolecular" catalysts commonly applied in organocatalytic ring-opening polymerization: (a) conjoined thiourea-amine (TU/A); (b) (−)-sparteine; (c) tris[2-(dimethylamino)ethyl]-amine (Me_6TREN); (d) thiourea cocatalyst (e) sulfonamide; (f) amide; (g) fluorinated alcohol; (h) phenol.

proceeded by concurrent activation of the monomer by the hydrogen-bond-donating thiourea and the initiating/propagating alcohol by the hydrogen bond-accepting tertiary amine (Scheme 1). Most notably, following consumption of

Scheme 1. Proposed Activation Pathway of "Supramolecular" Hydrogen-Bond Donor and Acceptor Species in Ring-Opening Polymerization



monomer, no transesterification side reactions were observed. The origin of the effect was later shown to be the result of supramolecular recognition between the thiourea moiety and cyclic ester in preference to the linear *s-trans* ester that would require activation for transesterification of the polymer backbone to occur.[23] While both H-bond donor (thiourea) and acceptor (amine) were demonstrated to be required for ROP to occur,[22] separating them into two independent molecules did not affect the polymerization and, in turn, enabled the study of a wider range of cocatalysts. To this end, (−)-sparteine was found to provide the ideal balance of reactivity and selectivity;[23] however, low commercial supplies have required the study of potential replacements. A recent report has shown tris[2-(dimethylamino)ethyl]amine (Me_6TREN) to be an adequate replacement for (−)-sparteine for the ROP of lactide.[24] Several other hydrogen-bond acceptors have been reported to be acceptable replacements in the intervening years, including (sulfon)amides and fluorinated alcohols.[25−28] Perhaps, most notably is the range of simple commercially available phenols[29] that, while slightly less active than the original thiourea, provide a commercially available method to produce polymers by ROP with high levels of control.

Polymerizations using TU/A-type systems are typically slow in comparison to the NHC and "superbase" systems.[22,23] However, largely as a consequence of the base alone showing no polymerization activity and the H-bond acceptor mediating the selective activation of cyclic over linear esters, these catalyst systems do offer very high selectivity in the ROP process. The very low levels of transesterification that are observed using these catalyst systems has enabled the selective polymerization of monomers with ester side chains without complications of branching, thus, giving rise to a wider range of potential functional monomer feedstocks. Most notably, the ROP of cyclic ester monomers derived from malic[30] and glutamic acid[31] as well as cyclic carbonate monomers derived from 2,2-bis(hydroxymethyl)propionic acid (bis-MPA)[32,33] that all display pendant esters has been shown to proceed in the absence of any significant transesterification side reactions or branching. Furthermore, the ROP of cyclic phosphate monomers, which can be further complicated by the presence of three linkages that are able to be scrambled by trans-esterification, has been shown to be well controlled using such supramolecular activation.[34]

The application of more strongly basic amines than (−)-sparteine resulted in ROP of lactide without the requirement for the additional H-bond donor cocatalyst.[35] Specifically, the commercially available base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) has proven to be a valuable ROP catalyst and has been applied by a wide range of researchers (Figure 3). DBU

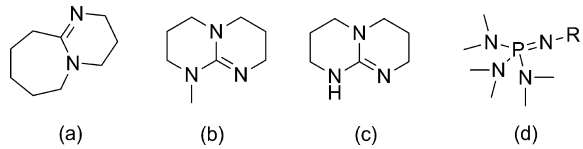


Figure 3. "Super base" catalysts commonly applied in organocatalytic ring-opening polymerization: (a) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); (b) 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD); (c) 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD); (d) general structure of a phosphazene base.

displays high catalytic activity with >98% monomer conversion being observed within 2 h for 500 equiv L-lactide (to initiator) with 1 mol % catalyst and [LA] = 0.7 M at ambient temperature and while transesterification side reactions can occur with this catalyst at greatly extended reaction times, quenching the reaction by addition of a (solid-supported) acid leads to its deactivitation. In the same study, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, Figure 3) was also shown to display a similar activity profile however the consumption of 500 equiv L-LA (to initiator) under comparable conditions but with only 0.5 mol % catalyst was complete within 0.5 h.[35] It is worthy of note, however, that the addition

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of only 1 equiv of benzoic acid to DBU leads to the formation of a bifunctional catalyst that is still capable of mediating ring-opening polymerization,[36] although no transesterification was observed when such systems were studied. While DBU is an excellent catalyst for the polymerization of lactide or six-membered cyclic carbonate monomers,[11,32] the addition of a cocatalyst is also required to polymerize lactone monomers such as δ-valerolactone (δVL) or ε-caprolactone (εCL) as well as phosphoesters.[34,35] DBU has also been recently reported to be capable of mediating the synthesis of cyclic PLA, in the absence of a protic initiator,[37] in a comparable manner to the NHC catalysts.[18]

Extension of these studies to examine other organic bases revealed 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Figure 3)[35,38] and the family of phosphazene bases[39] to be extremely active catalysts for ROP that, in turn, present other interesting observations and opportunities in ROP. Notably, ROP catalyzed by phosphazene bases has led to the ability to operate polymerizations at low temperatures which, along with NHCs,[40] has enabled the demonstration of highly stereoselective ROP of *rac*-lactide at −78 °C.[41] In common with other basic organocatalysts, phosphazenes show lower activity toward the ROP of lactones through O-acyl scission however in a recent report by Coulembier and co-workers, the ROP of βBL was demonstrated to be achieved to high molecular weights using a carboxylic acid initiator in the presence of a phosphazene base catalyst.[42] Phosphazene bases have also been demonstrated to offer unique methods for the synthesis of functional poly(ester)s by copolymerization of lactones with methacrylate monomers by a combination of ROP and group-transfer polymerization (GTP).[43] To this end, copolymerization of εCL and methyl methacrylate has demonstrated a potential alternative route to the synthesis of functional degradable polymers.

TBD has perhaps had one of the widest impacts of this family of basic organic catalysts. TBD has been demonstrated to be extremely active in the ROP of lactide, with the ROP of 500 eq. to initiator achieving 95% monomer conversion after only 1 min at ambient temperature (0.1 mol % catalyst, [LA] = 0.7 M). These high polymerization rates at ambient temperatures have enabled the ROP of monomers with low ring strain to proceed to higher monomer conversion. In this manner, the ROP of a norbornene-functional lactide monomer,[44,45] cyclic phosphoesters,[46,47] and ω-pentadecalactone,[48] as well as hindered δ-lactone monomers,[49,50] have been able to be polymerized to high monomer conversions. While the high activities have undoubtedly enabled a wider range of less-activated monomers to be studied, the high activity of the catalyst also leads to it being an excellent transesterification catalyst and, as such, loss of control of the molecular parameters can be observed at extended reaction times. Surprisingly, TBD has not been reported to be as highly active for the ROP of lactones as it is for lactide monomers. While the ROP of δVL proceeds to >90% monomer conversions within reasonable time periods, the ROP of εCL only proceeds to about 75% monomer conversion before the onset of transesterification and resultant broadening of the dispersity of the polymer is observed.[38] Furthermore, TBD was reported to not be active for the ROP of βBL,[38] however, is active for the ROP of cyclic carbonates.[11]

In contrast, acid catalysts (Figure 4) have been shown to be more active for the ROP of simple lactones such as δVL and εCL than for cyclic diester monomers such as lactide, offering

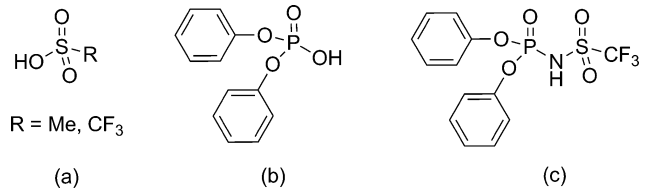

Figure 4. Acidic catalysts commonly applied in organocatalytic ring-opening polymerization: (a) methane- and trifluoromethane-sulfonic acid (MsOH and TfOH); (b) diphenyl phosphate (DPP); (c) phosphoramidic acid.

comparable rates of polymerization to the more active basic catalysts with excellent control of the molecular properties of the resultant polymers. A wide range of acidic compounds have been shown to mediate the ROP of lactones including amino acids[51] and citric acid.[52] Perhaps most notably, reports by Martin-Vaca, Bourissou, and co-workers, among others, have demonstrated that strong acids that are capable of acting as dual H-bond acceptors and donors, in a similar manner to the TU/A catalysts previously described, are highly active for the ROP of εCL and δVL.[53−56] Specifically, trifluorormethanesulfonic acid (HOTf) and methanesulfonic acid (MSA) have been shown to be highly efficient for the ROP of εCL, mediating well-controlled polymerizations.[53,54] HOTf was also noted to be active for LA ROP.[57] Diphenylphospate (DPP) was also shown to mediate ROP of δVL to high monomer conversions within short reaction times at ambient temperature, achieving polymers that displayed high levels of control (as indicated by the molecular parameters).[55,56] Furthermore, DPP was able to efficiently mediate the ROP of εCL to high (>95%) monomer conversions with high levels of control such that polymers with narrow dispersity (ca. 1.08) were obtained. A related study revealed that H-bond interactions were again responsible for the high activities observed and that extension to the related phosphoramidic acid resulted in lower reaction times and comparable levels of control.[56]

The field of organic catalysis for ROP has grown significantly in the past 10 years to the point that several catalysts provide viable and advantageous alternatives to metal-based catalyst species. On account of its high ROP activity for lactide under mild conditions, low cost, and excellent control over the polymerization process, DBU presents an excellent choice and is rapidly becoming the workhorse of the organic catalyst stable. For the ROP of small lactone monomers, acidic organocatalysts present an excellent option to produce polymers with high degrees of control in reasonable reaction times. The bifunctional catalyst family typified by the TU/A catalyst offer exciting opportunities to perform selective polymerizations, whereas the highly active NHC, TBD, and phosphazene bases present unique opportunities to access a wider range of polymers from less-activated monomers and with a broad range of macromolecular architectures. Despite these significant advances, exciting opportunities still exist to address challenges to design organic catalysts that can mediate stereocontrolled ROP of lactide at ambient temperature and above, that have higher thermal stability to enable ROP under industrially relevant melt processing conditions, and that are able to polymerize an even wider range of monomers with which to further diversify the range of materials available for further study and application.

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Notes

The authors declare no competing financial interest.

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