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Polymerizing Base Sensitive Cyclic Carbonates Using Acid Catalysis

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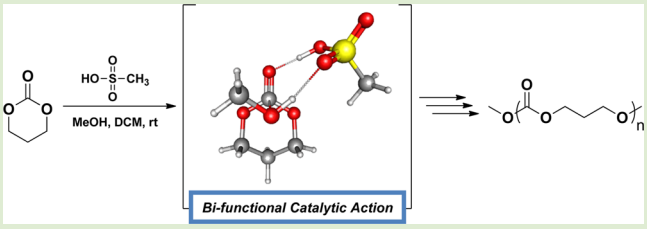
Supporting Information

ABSTRACT: Organic acids were explored as a means to expand the library of cyclic carbonate monomers capable of undergoing controlled ring-opening polymerization. Various nitrogenous bases have proven incredibly adept at polymerizing cyclic carbonates; however, their use has largely precluded monomers with an acidic proton. Molecular modeling of acid catalysis provided new mechanistic insight, wherein a bifunctional activation pathway was calculated. Depending on acid structure, modeling experiments showed both monomer carbonyls and propagating hydroxyl groups undergo hydrogen bonding activation. The dual activation mechanism suggests acid strength, as well as conjugate base effects, play vital roles in catalyzing cyclic carbonate polymerizations. Moreover, the use of acid catalysis was shown to be compatible with amide-containing monomers while promoting controlled polymerizations.



Organocatalytic ring-opening polymerization (ROP) of cyclic esters and carbonates has proven a versatile strategy for synthesizing well-defined polymers.[1,2] Examples of organocatalyst innovations have included alkyl phosphines,[3] *N*-heterocyclic carbenes,[4−7] bifunctional cocatalysts,[8−12] superbases,[13−15] phosphazenes,[16,17] and even acid/base conjugates,[18] wherein each provided a unique profile of advantages and limitations. Some improvements garnered through continual organocatalyst development have included increased accessibility, faster kinetics, convenience, functionality tolerance, and of course, enhanced polymerization control.[19,20]

A key reason for transitioning to organocatalysts is their ability to be effectively removed from resultant polymers. Transition metal catalysts are often extremely oxophilic, making their removal from oxygen-rich polyesters and polycarbonates exceedingly difficult. Residual metal catalyst has been linked to adverse effects within dielectric materials, unwanted toxicities, and deleterious side reactions such as transesterifications.[18] Despite these limitations, many metallic species have proven very reliable and efficacious polymerization catalysts.[21,22] Therefore, in order to supplant reliance on transition metals in ROP, suitable organic replacements must demonstrate comparable if not improved catalytic properties. Arguably, the most important of these properties is polymerization control. The ability to target specific molecular weights while maintaining narrow polydispersities allows block copolymer formation, providing access to higher order architectures and self-assembly potential. Functional group tolerance is also extremely desirable as it permits improved polymer variability and utility. The previously mentioned organic catalysts have all utilized basic functionalities. This has made polymerization of acidic monomers considerably more difficult if not impossible. Consequently, monomers incorporating carboxylic acid, amide, or other acidic functionalities have largely been outside the scope of basic organocatalysts.

With the exception of *N*-heterocyclic carbenes,[4] the aforementioned organocatalysts are believed to function through coordinated hydrogen bonding mechanisms as determined by molecular modeling experiments.[23−25] These calculations defined two distinct forms of catalytic hydrogen bonding: electrophilic activation of monomer carbonyls and nucleophilic activation of propagating hydroxyls. The combination of these two effects is readily demonstrated by the proposed catalytic mechanism of bifunctional cocatalysts (−)-sparteine and thiourea.[10] Individually, neither compound can polymerize cyclic esters/carbonates with reasonable reaction kinetics. However, in combination, they create an effective yet mild catalyst system capable of excellent functional group tolerance and polymerization control (Scheme 1a). Increasing the basicity of nucleophilic activators was found to dramatically enhance polymerization rates and inspired several subsequent organocatalyst discoveries. Unfortunately, attempts

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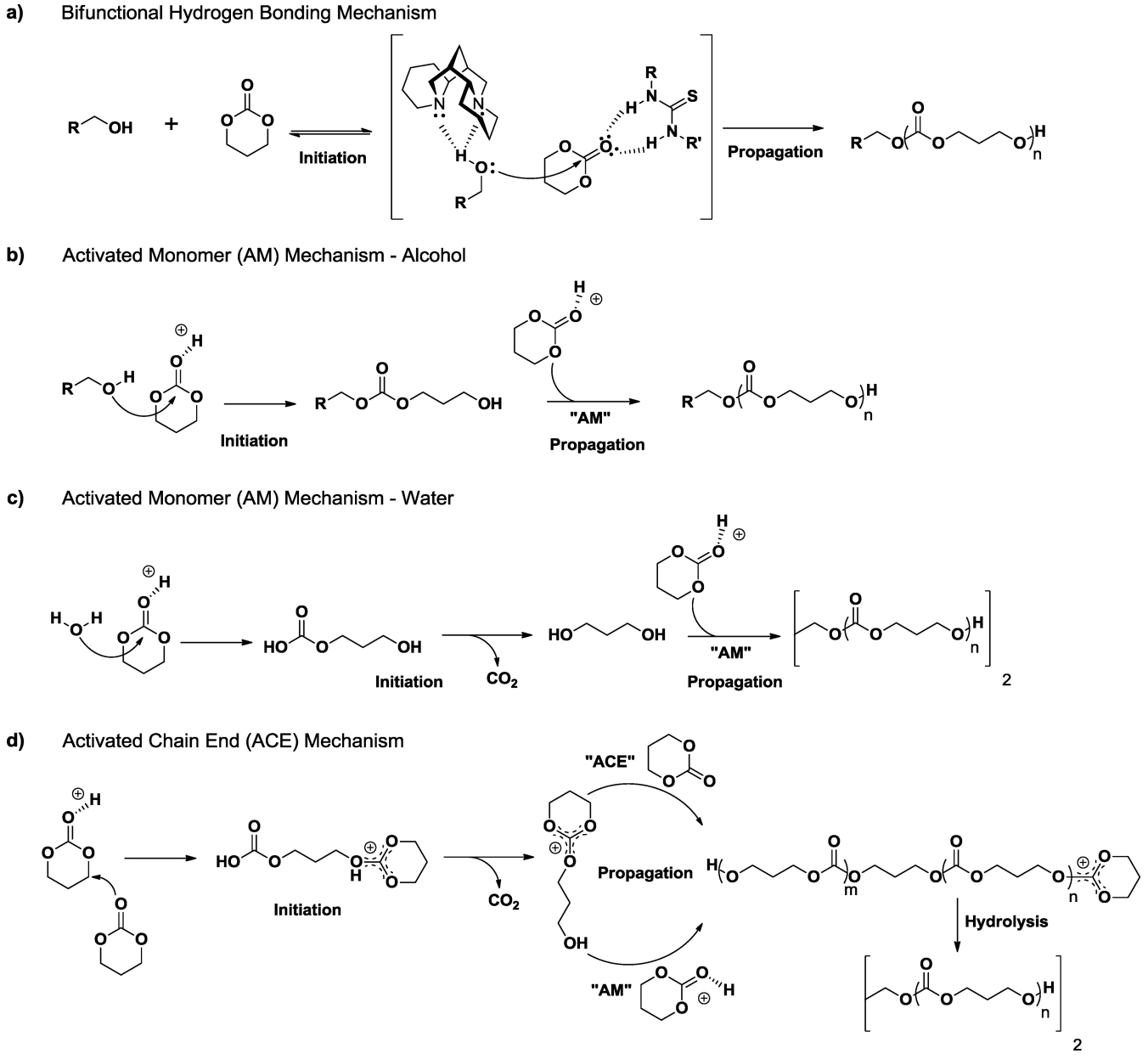
Scheme 1. Proposed TMC Polymerization Pathways for (a) (−)-Sparteine/Thiourea, (b) Alcohol-Initiated Activated Monomer (AM) Mechanism, (c) Water-Initiated Activated Monomer (AM) Mechanism, and (d) Active Chain End (ACE) Mechanism



at increasing electrophilic activation within the bifunctional paradigm led to acid/base reactions and decreased catalytic activity.[18,26] In an attempt to polymerize acidic monomers, namely, those containing an amide, our efforts focused on using only electrophilic activation. Herein, findings for acid-catalyzed ROP of cyclic carbonates is presented.

A previous report by Bourissou et al. showed sulfonic acids as effective polymerization catalysts for trimethylene carbonate (TMC).[27] However, they reported control issues arising from competing reaction mechanisms which caused formation of two distinct polymer populations. The activated monomer (AM) mechanism[27] was operative when either water or an alcohol was used to initiate the polymerization (Scheme 1b and c, respectively). The only mechanistic difference between the initiation sources was that water formed a bifunctional initiator (1,3-propanediol) following decarboxylation. As a bis-initiator, it effectively polymerized from both hydroxyl groups forming a symmetrical telechelic polymer. When *n*-pentanol was used no decarboxylation was observed resulting in an asymmetric polymer. Alternatively, an activated chain end (ACE) mechanism was proposed where an acid activated TMC was ring opened by another TMC monomer (Scheme 1d). This produced a carbonic acid derivative and an oxonium species. As in the AM mechanism, the carbonic acid derivative rapidly decomposed into an active hydroxyl group capable of AM polymer propagation. The opposing oxonium species was reported to undergo propagation via continual nucleophilic attack by neutral TMC monomers allowing continual regeneration of the active oxonium. Upon oxonium hydrolysis, the ACE mechanism was postulated to produce an analogous polymer to that of AM mechanism initiated by water.

The ability of sulfonic[28−32] and phosphate[33,34] acids to catalyze ROP has been well established; our objective was to explore their reaction mechanisms and its application to

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functional carbonates. Catalyst evaluation was done using TMC because of its similarity to functionalized carbonates,[35] commercial availability, and previous success with acid catalysis. Survey polymerizations were initiated using 1-pyrenebutanol permitting gel permeation chromatography (GPC) characterization with both refractive index (RI) and UV detection. Standardized polymerization conditions were employed using an initiator/catalyst/monomer ratio of 1/10/100 unless otherwise noted. Catalyst evaluation results are listed in Table 1.

Table 1. Organic Acids Screened for Catalytic Activity in TMC Polymerizations in DCM at 25 °C

organic acid	pK_a	conv. (%)	time (h)	M_n (kDa)	PDI
triflic acid	−13	>99	6	7.6	1.26
PTSA	−2.8	>99	17	9.7	1.08
MSA	−2	>82	24	6.8	1.09
DPP	1.1	>99	22	11	1.06
TFA	0	0	24	n/a	n/a
benzoic acid	4.2	0	24	n/a	n/a
acetic acid	4.8	0	24	n/a	n/a

After screening various organic acids (triflic acid, *p*-toluene sulfonic acid (PTSA), methanesulfonic acid (MSA), diphenylphosphate (DPP), trifluoroacetic acid (TFA), benzoic acid, and acetic acid) a weak correlation was observed between pK_a and catalytic activity. Despite this relationship, the observation provided little if any mechanistic insight. In order to better understand how acidity affected catalytic activity, molecular modeling was used for calculating reaction mechanism energetics. Similar modeling experiments on polymerizations catalyzed by 1,5,7-triazabicyclododecene (TBD) produced a radical paradigm shift from a conventional acyl-transfer mechanism to the currently accepted bifunctional hydrogen bonding activation mechanism.[23,36]

To gain better understanding of the acid-catalyzed ROP process, we conducted a comprehensive computational study of possible mechanistic pathways comparing different acids while focusing on the initial monomer enchainment. Computation suggested a counterintuitive mechanism for sulfonic acid catalyzed ROP. Instead of full carbonyl protonation (as shown in Scheme 1b), a pathway utilizing bifunctional activation was instead found. This is an important distinction because catalytic activity was calculated to have arisen from the close proximity of monomer carbonyl and propagating hydroxyl group brought about by catalyst/initiator/monomer hydrogen bonding. A similar mechanism was previously reported by Bourissou and co-workers during a computational study on the ROP of ε-caprolactone catalyzed by MSA and triflic acid.[37]

In the following examples, three separate methanol-initiated TMC polymerizations were modeled using MSA, TFA, or triflic acid as the catalyst. All calculations were performed with GAMESS-US[38,39] using M11 density functional theory and report lowest energy pathway.[40] Geometry optimizations were performed with the 6-311+G(2d,p) basis set[41−44] followed by single point energy calculations with the aug-cc-pVTZ basis set.[45,46] Reaction conditions were represented by a continuum dielectric representation of dichloromethane (DCM) with the SMD (IEF-cPCM) method.[47−49] Only vibrational free energy corrections to the electronic energy at the experimental temperature (298 K) were used in accordance with recommendations for molecules optimized in an implicit solvent.[50,51] Normal modes of all structures were examined to verify that their ground states possessed no imaginary frequencies and that transition structures possessed only one imaginary frequency corresponding to bond formation or bond breaking.

When catalyst type is disregarded, it is apparent that all acid catalyzed ROP mechanisms possess very similar reaction profiles. For the purpose of summarizing salient features of these mechanisms, we show an idealized representation of key ROP stationary points (Figure 1). The identity of the cyclic carbonate, alcohol initiator, catalyst, and any associated energies were removed for discussion generality. It should be noted that the catalyst in Figure 1 consists of an acidic group capable of hydrogen bond donation (H-A) and a Lewis basic atom capable of accepting a hydrogen-bond (B); these groups interchange roles during the mechanism allowing proton transfer to occur between the organocatalyst and the alcohol or carbonate.

The initial reaction step involves formation of a reactant complex (**RC**) wherein the organocatalyst, initiating/propagating alcohol and cyclic carbonate are all bound together by hydrogen bonding and dispersion forces. The catalyst holds the reactants in an ideal conformation during the first transition state (**TS1**) to promote nucleophilic attack on the monomer carbonyl. Upon carbonyl addition, the catalyst proton is transferred to the monomer while simultaneously accepting a proton from the initiating alcohol forming the first intermediate (**INT1**). The organocatalyst then becomes complexed to a ring

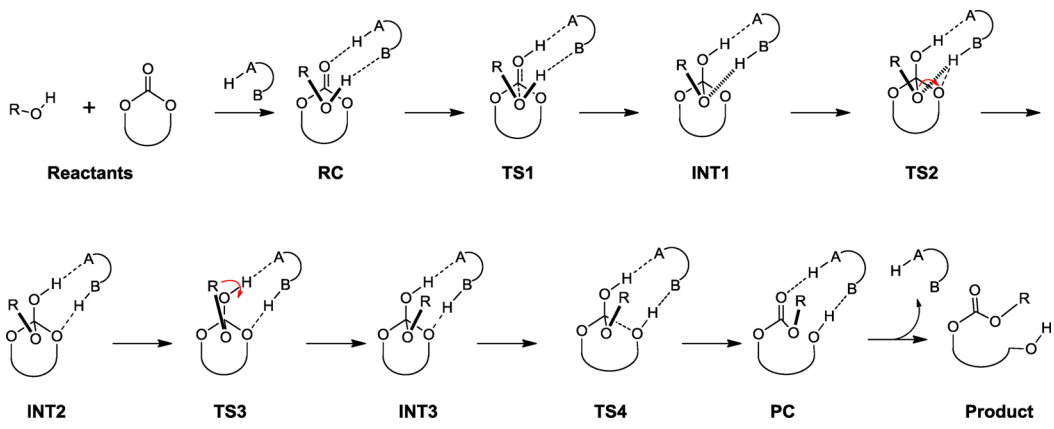

Figure 1. Proposed acid-catalyzed mechanism for the ROP of cyclic carbonates.

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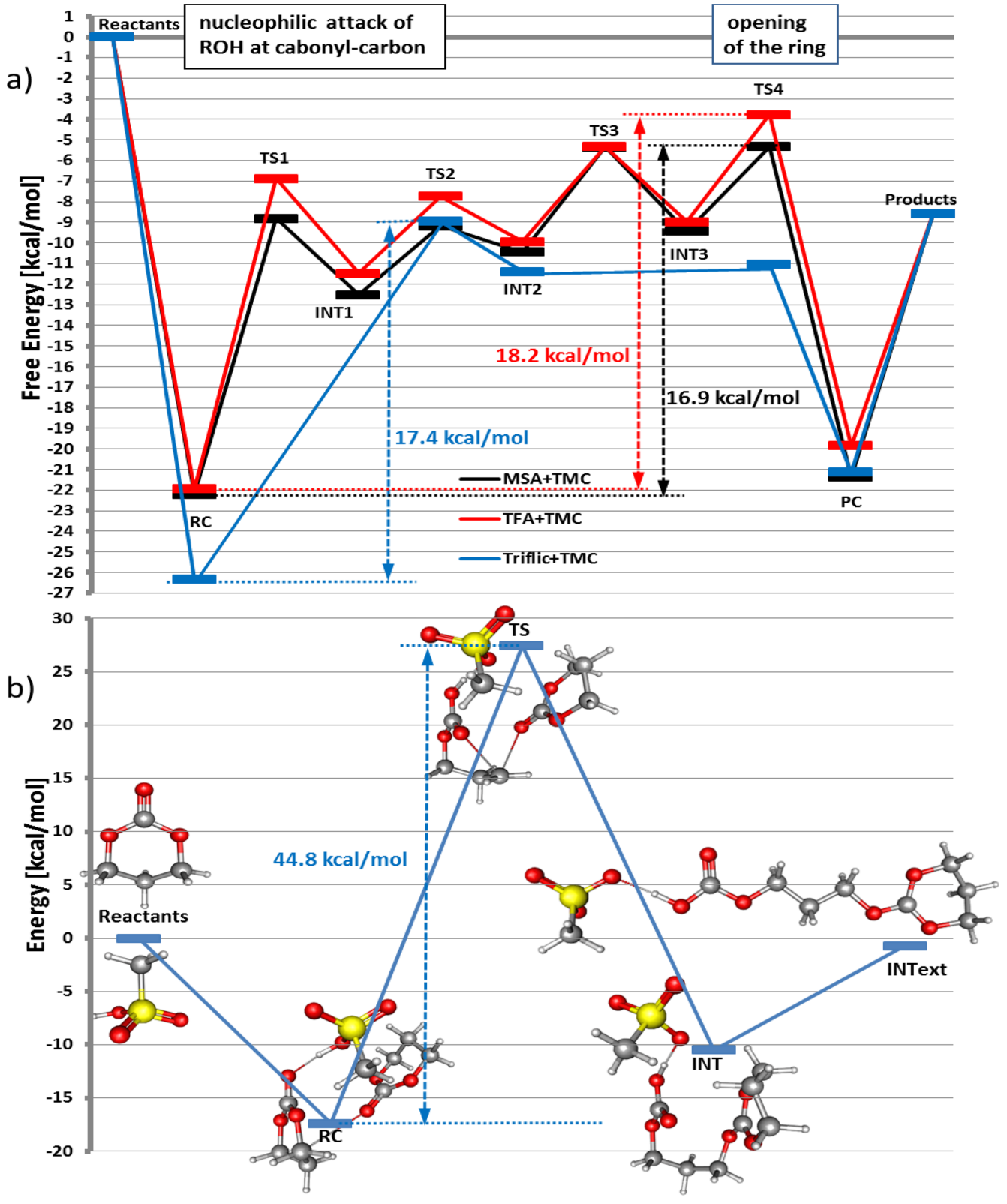

Figure 2. Reaction energy profiles for (a) ROP of TMC initiated by methanol and catalyzed by MSA, TFA, or triflic acid and (b) ACE mechanism.

oxygen (**TS2**) and results in **INT2**. The alcohol R-group undergoes a torsional rotation in **TS3**, forming **INT3** and placing the R-group in close proximity to the catalyst. Ring-opening occurs in **TS4**, followed by product complex (**PC**) formation and catalyst release. It is also possible for ring-opening to occur after **INT2**, but this was found to have a slightly higher energy barrier. Monomer ring-opening was predicted to be the rate-determining step in all reaction profiles.

The calculations showed catalysis was dependent on both acid strength (pK_a) and ability of its conjugate base to act as a hydrogen-bond acceptor. In order to better understand the effect of hydrogen bond acceptance, as it pertains to ROP

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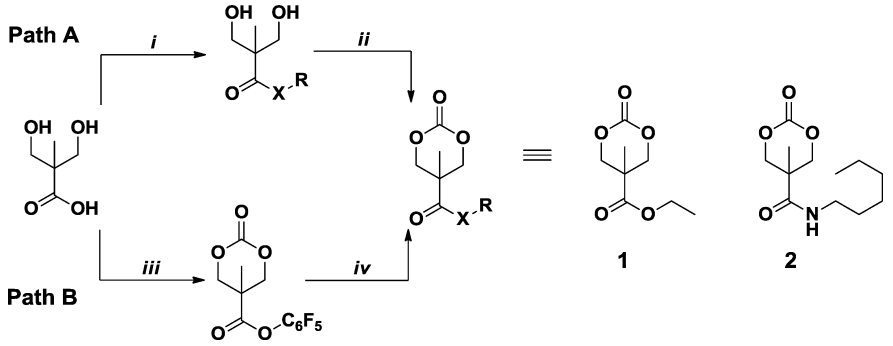
Scheme 2. Two Pathways for the Synthesis of Functional Carbonate Monomers[a]



[a](*i*) Carboxylic acid esterification, (*ii*) phosgene cyclization, (*iii*) two step reaction using pentafluorophenyl carbonate for both cyclization and formation of activated ester, and (*iv*) transesterification of activated ester.

catalytic activity, various acids were modeled for their strength as a conjugate base. The results from this study yielded the relative order: phosphate > sulfonate > carboxylate (see Supporting Information for details). A comparison of modeled reaction profiles for MSA- and TFA-catalyzed polymerizations showed very similar transition state energies despite TFA having no experimental catalytic activity (Figure 2a). This was originally attributed to MSA being a stronger acid. However, when DPP and TFA were compared, the same pK_a argument failed to support experimental results (Table 1). A better explanation was provided by the combination of acidity and conjugate base strength arguments. Using the cooperative trends, it was clearly seen that DPP more effectively acted as a hydrogen bond acceptor (**TS4**), thereby lowering the activation energy during the rate-limiting step and allowing the reaction to proceed. On the other hand, despite TFA being a slightly stronger acid it was unable to adequately stabilize the rate-determining step disallowing polymerization. In the case of triflic acid, proton transfer was already complete prior to **RC** formation. As a consequence, we were unable to locate a transition state for nucleophilic attack (i.e., **TS1**), and only optimized structures for **TS2**, **TS4**, along with their associated intermediates were found (Figure 2a).[52] Although MSA has a higher pK_a than triflic acid, the calculations predicted comparable catalytic activities. This again was not in agreement with experimental results which showed much faster kinetics for triflic acid. This disparity presumably stems from a propensity of sulfonic acids to dimerize. Because MSA forms a much more stable dimer, one can assume noncatalytic hydrogen bonding suppressed MSA catalytic activity relative to triflic acid (see Supporting Information for details). To support this supposition, HCl in dioxane was tested as a polymerization catalyst. The strong acidity of HCl (pK_a −7) coupled with its weakly coordinating conjugate base was assumed to predispose the catalyst for poor activity. Experimentally, HCl was able to promote polymerizations, albeit much more slowly (38% conversion after 24 h) than sulfonic acids and DPP.[53]

Computational study of the ACE versus AM mechanism: The new mechanistic insights allowed us to investigate previously postulated reaction pathways.[27] Computational investigations of the ACE mechanism energetics (Figure 2b) showed that the initial mechanism step involved formation of a reactant complex (**RC**) in which the MSA catalyst forms a hydrogen bond with a carbonyl group belonging to a TMC monomer, while a second TMC molecule was loosely associated by dispersion forces. During the transition state (**TS**), the acidic proton was fully transferred to the first monomer along with simultaneous ring-opening; this process produced an energy barrier of ≈45 kcal/mol, approximately 28 kcal/mol higher than the AM mechanism, and generally considered too high for a viable mechanistic alternative. Consequently, rather than two distinct mechanisms, we believe that only the AM mechanism is operative during this reaction.

The presence of adventitious water is most likely the cause of two polymer populations because its presence facilitates the formation of 1,3-propanediol initiators (Scheme 1c). During the course of this investigation various drying techniques were attempted to effect complete water removal. As they became more efficient, the fraction of high molecular weight polymer decreased and ultimately disappeared. DPP was readily dried and consistently remained anhydrous upon storage. However, in our hands, sulfonic acids were difficult to dry and, upon storage, continually took on water manifesting in the reoccurrence of two polymer populations. For this reason, we attempted the use of PTSA monohydrate as both a catalyst and initiator. Through controlling catalyst-loading, targeted molecular weights and narrow polydispersities were possible using the monohydrate catalyst.

One of the main driving forces for catalyst discovery is the continual expansion of monomer variety. Scheme 2 shows two published routes for synthesizing functionalized cyclic carbonates.[35] Unfortunately, base catalysis has shown limited utility when X is generated from primary amines because poor polymerization control resulted from amide deprotonation. Through the use of electrophilic activation, any deprotonation can be eliminated greatly expanding potential monomers. Polymerizations of both pendent ester (**1**) and amide (**2**) monomers were attempted using organic acid catalysis. Both **1** and **2** were found to polymerize but with considerably slower reaction kinetics as compared to TMC (days rather than hours). Considering acid catalysts nonselectively associate with monomer carbonyls, additional ester or amide functionalities was reasoned to effectively reduce catalyst concentration and depress polymerization rate. This was further supported by relative reaction rates of **1** and **2**, wherein the more electron-rich amide was found to have increased reaction times.[54] Polymerization of **1** was catalyzed by MSA, DPP, and PTSA and took 4, 3, and 2 days, respectively, to obtain a DP = 100 while maintaining molecular weight distributions under 1.1. Alternatively, only PTSA effectively polymerized **2** and still required 6 days to reach 82% conversion, however, excellent polymerization control was maintained. Despite these relatively

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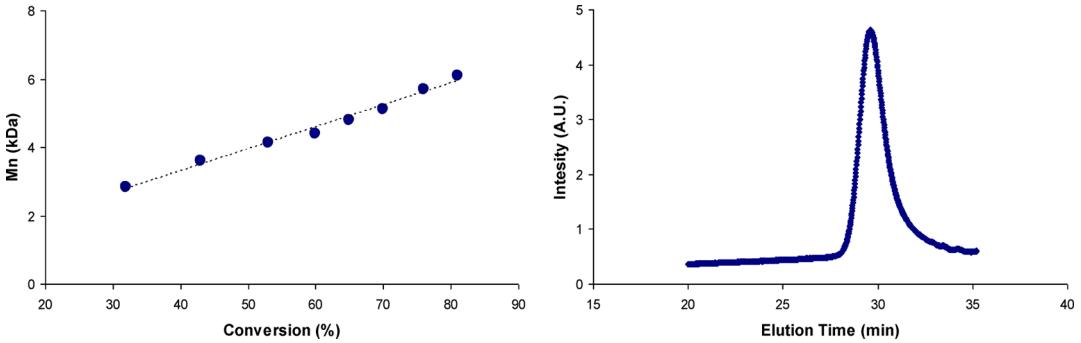

Figure 3. (a) Linear correlation between monomer conversion and molecular weight and (b) GPC curve for a polymerization of **2** (81% conversion; M_n, 6.1 kDa; PDI, 1.07).

long reaction times, no deleterious chain transfer or degradation was observed during polymerization (evidenced by narrow polydispersities) and was further verified experimentally by substituting poly(TMC) (M_n, 19 kDa; PDI, 1.08) for carbonate monomer under analogous polymerization conditions. This experiment resulted in no discernible change in M_n or PDI after 48 h. Furthermore, polymerization of **2** demonstrated a linear correlation between M_n and conversion while also having a near Gaussian GPC curve (Figure 3).

A hallmark of controlled polymerizations is their ability to uniformly synthesize block copolymers. To demonstrate control and fidelity, acid catalysis was used to synthesize both diblock and triblock copolymers. The diblock polymer (A-B motif) was formed via initiation from 1-pyrenebutanol using DPP catalyst. Upon full conversion of **1** (DP = 100), TMC (DP = 100) was added providing monomer for the second block. Using GPC with UV and RI detection, a single monomodal peak was observed with M_n 10.9 kDa and PDI 1.13 for the first block, and M_n 17.8 kDa and PDI 1.10 for the second block. Similarly, a triblock polymer (A-B-A motif) was synthesized by initiating from a PEG diol (8 kDa, PDI - 1.02) using TMC monomer and DPP catalyst. The resulting p(TMC-PEG-TMC) triblock copolymer exhibited a narrow molecular weight distribution (M_n = 17.6 kDa, M_w/M_n = 1.06), again demonstrating excellent control and fidelity.

In conclusion, the ability to polymerize cyclic carbonates has been demonstrated using various acids. Organic acids were found to be of particular interest because of their ability to undergo bifunctional activation. Insight into potential activation mechanisms was provided using molecular modeling. These calculations demonstrated lowest energy pathways involving point structures with the organic acid bound to both monomer carbonyl and propagating hydroxyl group. The use of acid catalysis is expected to greatly expand the range of polymerizable monomers to include amide and other acidic functionalities. Furthermore, utility of acid catalyzed ROP was demonstrated by synthesizing homo and block polymers having targeted molecular weights and narrow polydispersities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, computational results, and analytical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(51) A note on accuracy of calculated free energies and comparisons with experimental data (e.g., rates). In fact, the authors of the DFT functional we used (M11, ref 41) assess an error (MUE) of 1.84 kcal/mol (within M11's training set), which is likely to be compounded by the use of an implicit solvent model (SMD, ref 42). Unfortunately, at room temperature, an error of this magnitude is bigger than the thermal energy (kT ≈ 0.6 kcal/mol). With this in mind, we shall refrain from making any quantitative rate comparisons with the experiment.
(52) Note that the RC ion pair could not have been found through the common practice of estimating solvent effects by applying single-point PCM corrections to the energies of vacuum-optimized structures.
(53) The catalyst loading used for HCl in dioxane was 50 mol % instead of 10 mol % used for the other acids.
(54) Conversions above 80% were generally not achieved with amide-functionalized monomers due to prolonged reaction times, despite exhibiting excellent polymerization fidelity.

NOTE ADDED AFTER ASAP PUBLICATION

This letter posted ASAP on March 26, 2013. The table of contents graphic and abstract graphic have been revised. The correct version posted on March 28, 2013.