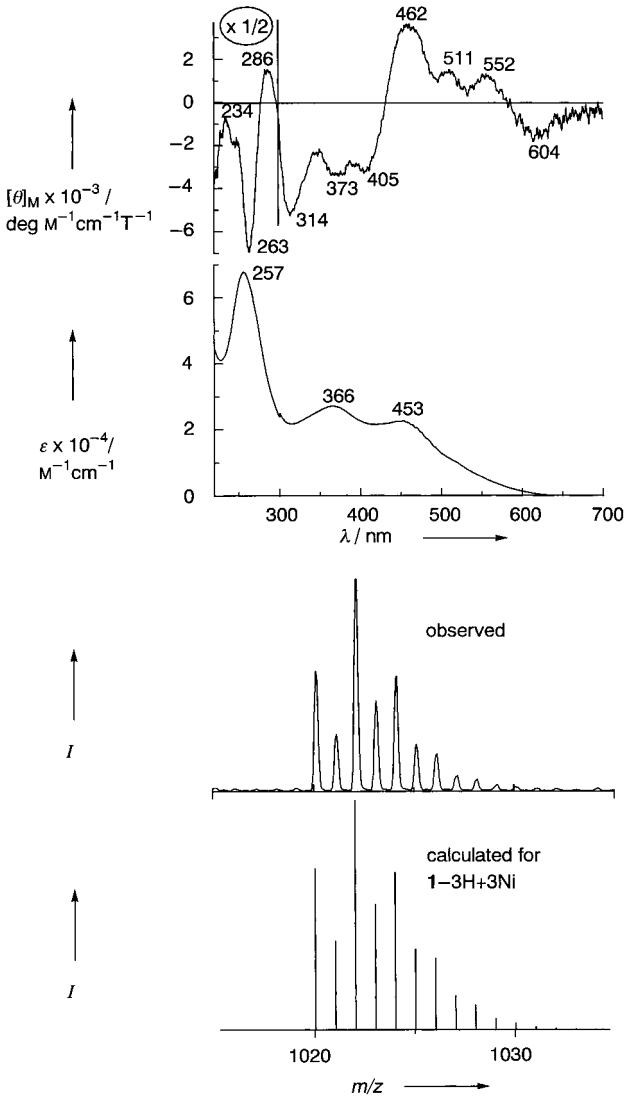


Figure 2. MCD (top) and electronic absorption (2nd from the top) spectra in THF and experimental (2nd from the bottom) and theoretical (bottom) ESI-MS spectra of $Ni_3 \cdot \mathbf{1}$.


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[6] Selected data for new macrocycles: **1**: elemental analysis (%) calcd for $C_{42}H_{39}N_{15}S_3$: C 59.36, H 4.59, N 24.73, S 11.31; found: C 59.07, H 4.83, N 24.60, S 11.07; FAB-MS (*m*-nitrobenzyl alcohol): *m*/*z*: 850 [$M^+$+H]; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 12.47$ (s, 3H, NH), 8.01 (m, 3H, ArH), 7.84 (m, 3H, arom), 7.67 (m, 3H, ArH), 1.45–1.47 (m, 27H, *t*Bu); IR (KBr): $\tilde{\nu} = 3225$ (NH), 2961 (CH, *t*Bu), 1645, 1616, 1489, 1406, 1366, 1317, 1223, 1132, 1089, 1032, 837 cm$^{-1}$; UV/Vis (THF): $\lambda_{max}$ ($\varepsilon \times 10^{-4}$) = 499 (1.2), 471 (1.7), 412 (8.7), 391 (8.5), 281 (3.1), 239 nm (3.7). $Ni_3 \cdot \mathbf{1}$: elemental analysis (%) calcd for $C_{42}H_{36}N_{15}Ni_3S_3 \cdot 3H_2O$: C 46.83, H 3.93, N 19.51; found: C 46.00, H 4.04, N 17.20; ESI-TOF MS: *m*/*z*: 1020 [$M^+$]; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.81–7.24$ (m, 9H, ArH), 1.45–1.42 (m, 27H, *t*Bu); UV/Vis (THF): $\lambda_{max}$ ($\varepsilon \times 10^{-4}$) = 453 (2.3), 366 (2.7), 257 nm (6.8). **2**: Elemental analysis (%) calcd for $C_{78}H_{81}N_{15}S_3$: C 70.72, H 6.16, N 15.86, S 7.26; found: C 71.05, H 6.93, N 15.04, S 7.03; ESI-TOF MS: *m*/*z*: 1324.5 [$M^+$+H]; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 12.32$ (s, 3H, NH), 7.51 (d, $J = 8.4$ Hz, 12H, ArH), 7.41 (d, $J = 8.4$ Hz, 12H, ArH), 1.37 (s, 54H, *t*Bu); UV/Vis (THF): $\lambda_{max}$ ($\varepsilon \times 10^{-4}$) = 551 (1.2), 510 (1.9), 449 (8.1), 426 (8.0), 328 (2.9), 265 nm (4.2).

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## New Paradigms for Organic Catalysts: The First Organocatalytic Living Polymerization**

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In the last three decades, a significant effort has gone into the development of biodegradable polymers with the object of designing resorbable biomaterials and, more recently, for designing commodity thermoplastics from renewable resources. Aliphatic polyesters, particularly poly(lactide), combine biocompatibility and biodegradability with remarkable physical properties and possess the requisite thermal stability at the processing temperatures. Advances in organometallic chemistry in the design and synthesis of single-site metal catalysts for olefin,[1] ring opening metathesis,[2] and ring opening polymerization techniques[3] have enabled the preparation of well-defined functional polymeric materials with predictable molecular weights and narrow polydispersities. The ring-opening polymerization (ROP) of lactide has been accomplished with a variety of metal catalysts including aluminum, tin, zinc, and yttrium through a coordination–insertion mechanism.[4] Currently, considerable research is directed towards the preparation of organometallic compounds with tailored ligands that produced poly(lactides) with controlled stereochemistry and microstructure.[3, 5] However, there are few reports on the ROPs of lactides which do not use organometallic promoters.[6] Alternative strategies using only

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organic compounds as reaction catalysts have led to new and versatile organocatalysts amenable to a number of asymmetric transformations.[7] The extension of organic catalysis to controlled polymerizations would be a highly desirable alternative to traditional organometallic approaches.

Here we detail the first organocatalytic approach to the living ROP of lactide using strongly basic amines as transesterification catalysts. 4-(Dimethylamino)pyridine (DMAP) and related bases such as 4-pyrrolidinopyridine (PPY) are widely used and prove to be extremely efficient reagents for acylation, alkylation, silation, phosphorylation, condensation, and transesterification reactions.[8] Taber and co-workers[9] discovered the effectiveness of DMAP as a transesterification catalyst for $\beta$-keto esters. Others[10] showed that the removal of the alcohol coproduct in the transesterification reaction biased the equilibrium towards product. In another example, Menger and McCann[11] demonstrated quantitative transesterification of methyl *p*-nitrobenzoate to methyl acetate using DMAP immobilized on cross-linked polystyrene. Morken and Taylor[12a] combined solid-phase synthesis and combinatorial chemistry to rapidly produce a large number of organic transesterification catalysts to survey acylation reactions. A variety of other transesterification procedures using DMAP have been reported.[12, 13] The strategy employed for the ROP of lactide using an organic transesterification catalyst is as follows: First, a nucleophile such as an alcohol must be used to initiate the polymerization of lactide in the presence of the organic catalyst, providing a means of contolling molecular weight and end group functionality. Polymerization proceeds when a terminal $\omega$-hydroxyl group acts as the nucleophile and reacts with additional lactide/DMAP. Second, the ring-opening reaction does not evolve a coproduct and since the ring opening is enthalpically driven, the equilibrium is prejudiced towards polymerization. When this general approach is considered, it is apparent that a proliferation of variables must be well thought-out. For example, the type and concentration of amine, solution or bulk-reaction conditions, polymerization temperature, undesirable transesterification side reactions, and the general classes of initiators all influence the polymerization. To survey these variables, a parallel approach to polymer synthesis, designed to enable rapid screening of optimal catalyst/initiator systems and associated polymerization conditions, was employed. The Quest 210 robotic reactor proved to be an excellent platform for performing up to 20 polymerizations in parallel, providing the necessary environment, temperature control, and agitation to accomplish the ROP.[14]

The catalytic behavior of DMAP and PPY in the polymerization of lactide was studied in dichloromethane at 35 °C using ethanol as the initiator with 0.1 to 4.0 equivalents of amine relative to initiating alcohol (see Table 1). Although a number of polymerization media were evaluated, most of the polymerizations were conducted in dichloromethane, since it is a good solvent for both the lactide and poly(lactide). Under anhydrous conditions, no detectable polymerization of lactide was observed in this solvent in the presence of these amines without the addition of a nucleophile. Amine concentrations of 0.1 equiv relative to initiator (ethanol) produced only modest conversions after prolonged reaction times. Conversely, higher amine concentrations proved to be active and highly selective for the ROP of lactide in 100 % yields with no adverse side reactions, as evidenced by the retention of the narrow polydispersities. A targeted degree of polymerization (DP) of 30 was calculated from the monomer-to-initiator ratio, and a value of 29 was obtained by $^1$H NMR analysis of the end groups (36 h).[15] The polydispersity was 1.13. A plot of molecular weight versus monomer conversion for the ROP of lactide initiated from ethanol in the presence of DMAP is shown in Figure 1. The correlation between molecular weight

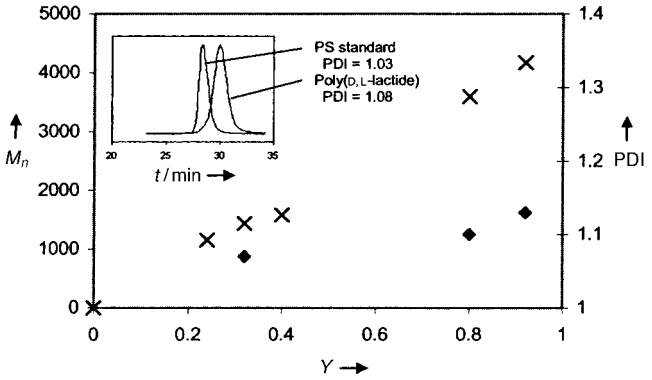


Figure 1. Plot of molecular weight ($M_n$, ×) versus monomer conversion ($Y$) for the ROP of lactide initiated from ethanol in the presence of DMAP. The polydispersities (PDI, ◆) are also shown. Inset: The GPC traces for a polystyrene calibration standard together with poly(D,L-lactide) are also shown to facilitate comparison and demonstrate the narrow polydispersity.

and conversion is consistent with a living polymerization. The polydispersities are extremely low and, unlike for most organometallic-promoted polymerizations,[16] remained invariant to high monomer conversions (100 % conversion, 36 h). To investigate possible undesirable transesterification reactions, the polymerization was allowed to continue; the polydispersity after 72 and 96 h reaction time was 1.08 and 1.10, respectively, without a detectable change in molecular weight. In another experiment, two polylactides having different molecular weights were stirred in dichloromethane for 24 h (35 °C) in the presence of DMAP and closely followed by gel permeation chromatography (GPC).[17] No transesterification reactions were detected by GPC, as each of the polymers retained their initial elution volumes. Importantly, once quantitative monomer conversion is achieved no undesirable transesterification side reactions were evident, and these combined data point to a living polymerization process.

The versatility of the organocatalyzed ROP of lactide is demonstrated by the data in Table 1, which contains selected results of the poly(lactide) polymerization initiated from assorted alcohols in the presence of several amines for different targeted molecular weights in either dichloromethane or in bulk. The amines DMAP and PPY showed comparable catalytic activity, producing polymers with molecular weights that closely tracked the monomer-to-initiator ratio (M/I) with extremely narrow polydispersities (entries 5 – 16). Moreover, $^{13}$C NMR spectroscopy and calorimetry studies on the polymerization of the enantiomerically pure L-lactide (entry 19) clearly show that racemization does

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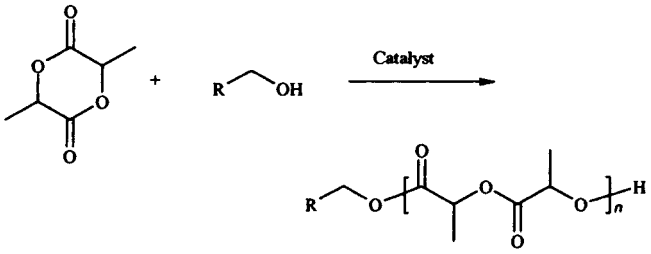
Table 1. Characteristics of poly(lactides) prepared by reactions catalyzed by organic compounds.

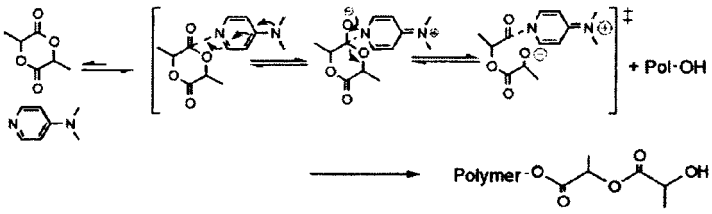



| Entry | Catalyst[a] | Initiator | $T$ [°C] | $t$ | M/I[b] | DP[c] | PDI[d] |
|---|---|---|---|---|---|---|---|
| 1 | DMAP (0.1 equiv) | EtOH | 35 | 96 h | 30 | 5 | / |
| 2 | DMAP (1 equiv) | EtOH | 35 | 60 h | 30 | 29 | 1.13 |
| 3 | DMAP (2 equiv) | EtOH | 35 | 36 h | 30 | 29 | 1.13 |
| 4 | DMAP (4 equiv) | EtOH | 35 | 24 h | 30 | 29 | 1.08 |
| 5 | DMAP (2 equiv) | EtOH | 35 | 24 h | 15 | 17 | 1.12 |
| 6 | DMAP (2 equiv) | EtOH | 35 | 36 h | 30 | 29 | 1.13 |
| 7 | DMAP (2 equiv) | EtOH | 35 | 50 h | 60 | 62 | 1.10 |
| 8 | DMAP (4 equiv) | EtOH | 35 | 64 h | 100 | 78 | 1.10 |
| 9 | DMAP (2 equiv) | $PhCH_2OH$ | 35 | 30 h | 30 | 43 | 1.08 |
| 10 | DMAP (2 equiv) | $PhCH_2OH$ | 135 | 5 min | 30 | 29 | 1.10 |
| 11 | DMAP (2 equiv) | $PhCH_2OH$ | 135 | 10 min | 60 | 42 | 1.09 |
| 12 | DMAP (4 equiv) | $PhCH_2OH$ | 135 | 20 min | 100 | 77 | 1.19 |
| 13 | DMAP (2 equiv) | $PhCH_2OH$ | 135 | 20 min | 140 | 120 | 1.14 |
| 14 | PPY (2 equiv) | EtOH | 35 | 20 h | 30 | 31 | 1.10 |
| 15 | PPY (2 equiv) | $PhCH_2OH$ | 35 | 20 h | 30 | 27 | 1.08 |
| 16 | PPY (2 equiv) | $PhCH_2OH$ | 135 | 10 min | 30 | 32 | 1.16 |
| 17 | DMAP (2 equiv) | $(CH_3)_2CHOH$ | 35 | 48 h | 30 | 35 | 1.12 |
| 18 | DMAP on PS | EtOH | 35 | 70 h | 30 | 25 | 1.08 |
| 19 | DMAP (2 equiv)/L-lactide | EtOH | 35 | 30 | 30 | 29 | 1.06 |
| 20 | DMAP (2 equiv)/L-lactide | $PhCH_2OH$ | 185 | 6 min | 30 | 30 | 1.18 |
| 21 | DMAP (2 equiv)/L-lactide | $PhCH_2OH$ | 185 | 8 min | 60 | 50 | 1.14 |

[a] The equivalents of amine relative to initiating alcohol are given in parentheses. [b] Monomer-to-initiator ratio. [c] Degree of polymerization. [d] Polydispersity index.

not occur.[18] In addition, secondary alcohols effectively initiated the polymerization, which proceeded in quantitative yields (entry 17). Bulk polymerizations of D,L- and L-lactide were also investigated at 135 and 185 °C, respectively, using benzyl alcohol as the initiator. Narrowly dispersed poly(lactides) were obtained in about 5 to 20 minutes, depending on the targeted molecular weight (entries 10–13, 15, 20, 21). Poly(L-lactide) required a higher polymerization temperature since it is semicrystalline with a melting point around 180 °C. The molecular weights correlate closely to the monomer-to-initiator ratio, and even at these polymerization temperatures, the polydispersities remained narrow. In each case, the organic catalyst could be recovered in excess of 85 % yield. DMAP immobilized onto polystyrene particles also proved to be an effective media for catalyzing the ROP of lactide (entry 18). The molecular weights, polydispersities, and polymerization kinetics achieved from the solid-supported catalyst were comparable to those from previous experiments. In these experiments using the solid supported catalyst, the base was easily removed by filtration.

One plausible polymerization pathway is through a monomer-activated mechanism. Initiation occurs when a nucleophile such as an alcohol reacts with a lactide–DMAP complex to form the mono adduct, and the $\alpha$-chain end of the poly(lactide) bears an ester functionality derived from the alcohol, as in related acylation reactions (Scheme 1).[12a]




Scheme 1. A plausible polymerization pathway.

Polymerization proceeds when the terminal $\omega$-hydroxyl group acts as a nucleophile to facilitate further chain growth. Consistent with this mechanism, the $^1$H NMR spectrum of poly(lactide) initiated with ethanol using DMAP as the catalyst shows resonances associated with the ethoxy ester and the hydroxyl chain ends (Figure 2). To further substantiate the initiation step, the reaction of excess benzyl alcohol with one equivalent of DMAP (based on lactide) was investigated. The lactide was ring opened with formation of the benzyl ester; however, due to the large excess of the benzyl alcohol and DMAP catalyst, transesterification with the diester product afforded the monoester.[19] This product was isolated, characterized, and subsequently used to initiate the controlled polymerization of lactide using the same polymerization techniques as for the reactions in Table 1 (DP target 30, measured 29, PDI 1.09). These data support an initiation and polymerization mechanism which proceeds

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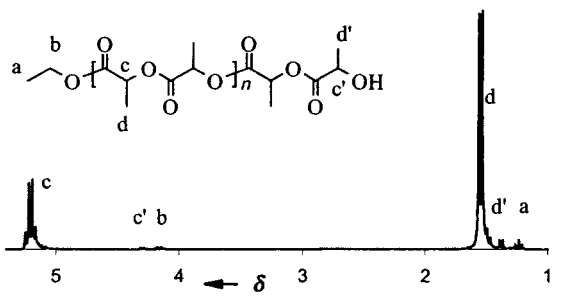


Figure 2. $^1$H NMR spectrum of polylactide initiated from ethanol in the presence of DMAP.

through a monomer-activation intermediate. This polymerization mechanism is similar, in many aspects, to that of modern controlled radical polymerization techniques, where the predominate species are dormant polymer chains with minimally active radical species. In this way, termination and side reactions are minimized, producing narrow polydispersities. By analogy, the narrow polydispersities realized in the amine-catalyzed lactide polymerization is a manifestation of the presence of predominately dormant chains with minimal active species.

The synthetic utility of selected amines as transesterification catalysts for "living" ring-opening polymerization of lactide was demonstrated. Mild and highly selective polymerization conditions produced poly(lactides) with predictable molecular weights and extremely narrow polydispersities (ca. 1.1), characteristic of a living polymerization with a specific reaction site. New strategies for organocatalysis that enable the formation of highly enantioselective polylactide from racemic mixtures will be forthcoming.

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[14] Initial screening of different organic catalysts, solvents, and a variety of polymerization conditions was performed on a Quest 210 reactor (Argonaut Technologies). This robotic reactor allowed up to 20 polymerizations to be performed in parallel under the appropriate environment. Polymers with targeted DPs of 30 were prepared and assayed by size-exclusion chromatography (SEC) and $^1$H NMR spectroscopy to optimize the polydispersity and the molecular weight control. For a general discription of ROP in Quest, see *Argonaut Application Note* **33**.

[15] General procedure for D,L-lactide polymerization: A round-bottom flask equipped with a stirbar and sealed with a septum was flame-dried under vacuum and purged with nitrogen. The D,L-lactide (1.0 g, 6.94 mmol) and DMAP (0.56 g, 0.46 mmol, for DP = 30) was added in a glove box. Dichloromethane (≈5 mL) and ethanol (14 μL, 0.23 mmol) were added, and the flask was heated to 35 °C. The polymer was isolated in cold methanol and dried to a constant weight, 100% yield. $^1$H NMR ([D$_6$]acetone): $\delta$ = 1.46–1.56 (d, 3H, CH$_3$), 5.05–5.25 (q, H, CH); $^{13}$C NMR ([D$_6$]acetone): $\delta$ = 17.0 (CH$_3$), 69.8 (CH), 169.8 (CO).

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[17] Poly(D,L-lactide) (0.5 g) with a molecular weight of about 11000 was dissolved in $CH_2Cl_2$ (5 mL) together with a poly(D,L-lactide) with a molecular weight of about 4000. DMAP (0.056 g, 0.46 mmol) was heated at 35 °C for 24 h; the reaction was followed by GPC.

[18] Catalyzed with DMAP: $^1$H NMR ([D$_6$]acetone): $\delta$ = 1.46–1.56 (d, 3H, CH$_3$), 5.05–5.25 (q, H, CH); $^{13}$C-NMR: $\delta$ = 17.0 (CH$_3$), 69.8 (CH), 169.8 (CO). Catalyzed with Sn(OTf)$_2$: $^1$H NMR ([D$_6$]acetone): $\delta$ = 1.46–1.56 (d, 3H, CH$_3$), 5.05–5.25 (q, H, CH); $^{13}$C NMR ([D$_6$]acetone): $\delta$ = 17.0 (CH$_3$), 69.8 (CH), 169.8 (CO).

[19] In a glove box, D,L-lactide (1.0 g, 6.94 mmol) and DMAP (1 equiv based on D,L-lactide, 0.848 g, 6.94 mmol) was added to a round-bottom flask. An excess of benzyl alcohol (10 equiv based on D,L-lactide (7.18 mL, 0.069 mmol) was charged together with $CH_2Cl_2$, and the reaction flask was slowly heated to 35 °C (5 h). The product was isolated by flash chromatography ($CH_2Cl_2$/ethyl acetate 90/10). $^1$H NMR ([D$_6$]acetone): $\delta$ = 1.34 (d, 3H, CH$_3$), 2.05 (s, H, OH), 4.30 (q, H, CH), 5.16 (s, 2H, CH$_2$), 7.40–7.30 (m, 5H, C$_6$H$_5$); $^{13}$C NMR ([D$_6$]acetone): $\delta$ = 175.4, 137.3, 129.3, 128.9, 128.8, 67.6, 66.8, 20.8.