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ARTICLE

Ring-Opening Polymerization of L-Lactide Catalyzed by an Organocatalytic System Combining Acidic and Basic Sites

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ABSTRACT: In this study, organocatalytic systems containing both basic and acidic sites, which can activate simultaneously the chain end and the monomer, were investigated in the ring-opening polymerization of L-lactide. To this end, equivalent amounts of (*N*,*N*-dimethylamino)pyridine (DMAP) and of its protonated form (DMAP·HX) were used as a dual catalytic system for L-lactide polymerization initiated by different alcohols. It is shown that the corresponding DMAP/DMAP·HX systems are significantly more active than DMAP alone, and yield well-controlled poly(L-lactide). Depending on the reaction conditions, the transesterification reaction can be prevented.

Introduction

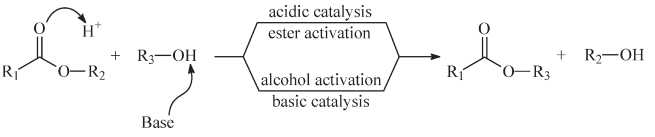
Over the past decades, great efforts have been made to develop new synthetic methods for polymer synthesis, such as single site catalysts for olefin polymerization,[1−7] metathesis polymerization,[8,9] or controlled free-radical polymerization (nitroxide-mediated, atom transfer, addition−fragmentation).[10−13] Most of them are based on transition metal catalysts, which appeared as undesirable impurities for some applications (biomedical and microelectronics, for example) and are very hard to remove from the polymer. Moreover, the presence of metallic residues in the polymers could lead to environmental problems. As a consequence, it is of high interest to develop new alternatives based on nonmetallic polymerization processes.

Enzyme-catalyzed polymerizations, which have been explored for quite a long time, constitute one alternative route to metal-free polymerization.[14−16] Thanks to various enzymes, several kinds of polymers (polysaccharides, polyphenol, polyaniline, polyesters, polycarbonate, ...) are now accessible by employing suitable enzymes as catalysts. Nevertheless, enzyme availability is still limited and polymerizations are often very slow and not well controlled.

Another alternative deals with the use of organic catalysts. Although organocatalysis is well developed in organic synthesis,[17,18] it is still relatively new in polymerization.[19−22] In 2001, (*N*,*N*-dimethylamino)pyridine was one of the first organocatalysts employed for the ring-opening polymerization of lactide.[23] More recently, other organic compounds (phosphine, carbenes, thioureas, guanidines, amidines, amido-indoles, ...) were also utilized for the ring-opening polymerization of different heterocyclic monomers.[20,24−34] Depending on the catalyst, the initiator (the chain-end) and/or the monomer can be activated.

In this paper, we report the ring-opening polymerization (ROP) of *L*-lactide via the activation of both the monomer and the initiator, respectively, by acidic and basic organic moieties through H-bonds. Indeed, catalysts for transesterification reactions are usually either acid-type or base-type (Scheme 1). On one hand, acidic catalysts activate ester groups via protonation or H-bond to increase the electrophilicity. On the other hand, basic catalysts activate alcohols through H-bonds interaction with the alcoholic proton, thus enhancing their nucleophilicity. Generally, acid-type and base-type catalysts cannot coexist, as they will neutralize each other immediately. However, if these two catalytic systems are able to operate together, the activity toward transesterification reactions should be strongly enhanced. Thus, it was envisioned to make compatible a base and an acid form. To this end, the use of equivalent amounts of *N*,*N*(-dimethylamino)-pyridine (DMAP, which has already revealed some catalytic activity for lactide polymerization) and protonated (*N*,*N*-dimethylamino)pyridine (DMAP·HX) was investigated as a dual catalyst for L-lactide polymerization (Scheme 2). The influence of the reaction conditions as well as the nature and the role of the counterion (X^-) were also studied. A proposed cooperative activation mechanism is also discussed.

Scheme 1. Brönsted Acid and Base Catalysis in Transesterification Reactions



Experimental Part

Materials. L-Lactide (98%, L-LA), *p*-phenylbenzyl alcohol (98%, *p*-PhBzOH), 1-Phenylethanol (98%, 1-PhEtOH), and (*N*,*N*-dimethylamino)pyridine (99%, DMAP) were purchased from Aldrich. Hydrochloric acid (37% in water solution) was purchased from Prochilab. Methanesulfonic acid (99.5%, Aldrich) and trifluoromethanesulfonic acid (98%, Acros organics) were used as received. Toluene, tetrahydrofuran, and dichloromethane (stabilized with amylene) were purchased from Atlantic Laboratories. CH_2Cl_2 and CD_2Cl_2 were distilled from CaH_2 prior to use. THF and toluene were dried over sodium/benzophenone. L-Lactide was recrystallized three times from toluene and stored under nitrogen. *p*-PhBzOH was recrystallized from dichloromethane and stored under nitrogen. DMAP was dried under vacuum before use.

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1-Phenylethanol was dried over 4 Å molecular sieves and distilled under reduced pressure.

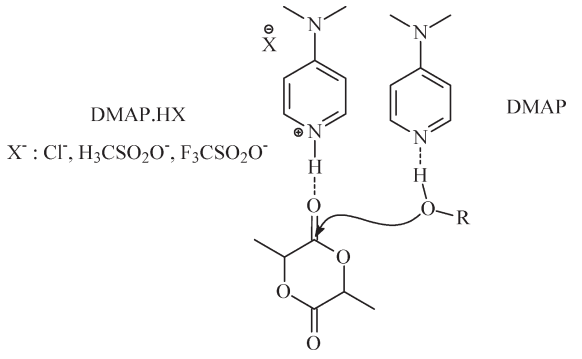
Products Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 apparatus at 400 and 100 MHz, respectively, at 25 °C. Polymer molar masses and dispersity were measured by size exclusion chromatography on a PL-GPC50 Plus apparatus equipped with RI and UV detectors and Tosoh G4000HXL, G3000HXL, and G2000HXL columns (eluent THF, flow rate 1.0 mL/min, temperature 40 °C), calibrated with polystyrene standards. Matrix-assisted laser desorption ionization time-of-flight (Maldi-TOF) mass spectrometry was performed using a Voyager-DE STR (Applied Biosystems) spectrometer equipped with a nitrogen laser (337 nm), a delay extraction, and a reflector. The Maldi-TOF mass spectra represent averages over 100 laser shots. This instrument operated at an accelerating potential of 20 kV. Polymer (2 μL) and matrix (20 μL, dithranol) solutions in CH_2Cl_2 (10 g·L^{-1}) were mixed with 2 μL of a sodium iodide solution (10 g·L^{-1} in methanol), which favors ionization. The final solution (1 μL) was deposited onto the sample target and dried in air at room temperature.

DMAP·HX Synthesis. DMAP·HCl, DMAP·$HOSO_2CH_3$, and DMAP·$HOSO_2CF_3$ were prepared from reaction of DMAP with the corresponding acid. The general procedure is as follows. DMAP (10 mmol, 1.22 g) is stirred with a stoichiometric amount of HX (HCl 37% in water solution, 1 mL; $HOSO_2CH_3$ 0.96 g; $HOSO_2CF_3$, 1.50 g) in THF (20 mL) at room temperature for 1 h to give a white precipitate. The salts were filtrated, washed, dried under vacuum, and stored under nitrogen.

DMAP·HCl (yield: 82%). ^{1}H NMR (400 MHz, in CD_2Cl_2, 25 °C, ppm): 3.19 (6H, s), 6.75 (2H, d), 8.09 (2H, d), 15.50 (1H, br).

DMAP·$HOSO_2CH_3$ (yield: 98%). ^{1}H NMR (400 MHz, in CD_2Cl_2, 25 °C, ppm): 2.69 (3H, s), 3.19 (6H, s), 6.77 (2H, d), 8.16 (2H, d), 14.33 (1H, br)

Scheme 2. Possible Activation Mechanism for the Ring-Opening Polymerization of L-Lactide with (*N*,*N*-Dimethylamino)pyridine and Its Protonated Form



DMAP·$HOSO_2CF_3$ (yield: 85%). ^{1}H NMR (400 MHz, in CD_2Cl_2, 25 °C, ppm): 3.22 (6H, s), 6.76 (2H, d), 8.07 (2H, d), 12.77 (1H, br).

Ring-Opening Polymerization (ROP) of L-Lactide in Solution. The general procedure is as follows. A 10 mL Schlenk flask was flame-dried under vacuum and initiator (*p*-phenylbenzyl alcohol, 6.35 mg, 0.0345 mmol or 1-phenylethanol, 4.21 mg, 0.0345 mmol), DMAP (4.21 mg, 0.0345 mmol), DMAP·$HOSO_2CF_3$ (9.39 mg, 0.0345 mmol), L-lactide (100 mg, 0.69 mmol), and dichloromethane (1 mL) were added successively. The solution was stirred under nitrogen at room temperature for 24 h. Dichloromethane was then evaporated under vacuum to give a white solid containing the polymer, the unreacted monomer, and the catalytic system. Monomer conversion was determined by ^{1}H NMR (integration of the methyl protons at 1.67 ppm for the monomer versus the methyl protons at 1.58 ppm for the polymer). Polylactide molar mass and dispersity were measured by size exclusion chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 1.58 (66H, m), 4.32 (1H, q), 5.15 (21H, m), 7.36−7.57 (9H, m).

Polymerization Kinetics. Kinetic studies of L-lactide polymerizations catalyzed by DMAP/DMAP·HX were performed by ^{1}H NMR. The general procedure is as follows. A 10 mL Schlenk flask was flame-dried under vacuum. Initiator (*p*-phenylbenzyl alcohol, 6.35 mg, 0.0345 mmol), DMAP (4.21 mg, 0.0345 mmol), DMAP·$HOSO_2CF_3$ (9.39 mg, 0.0345 mmol), L-lactide (100 mg, 0.69 mmol), and deuteriated dichloromethane-d_2 (0.5 mL) were then added successively. The reaction medium was stirred under nitrogen at room temperature for 10 min. The solution was transferred into a NMR tube via a syringe. NMR spectra were recorded up to 96 h.

Results and Discussion

Ring-Opening Polymerization (ROP) of L-Lactide Catalyzed by DMAP/DMAP·HX. The ring-opening polymerization of L-lactide was investigated under different reaction conditions (Scheme 3). *p*-Phenylbenzyl alcohol (*p*-PhBzOH) or 1-phenylethanol (PhEtOH) was used as the initiator. A first set of polymerizations was performed at room temperature in dichloromethane, using a ratio initiator/DMAP/DMAP·HX of 1/1/1. The results are summarized in Table 1.

As already mentioned in literature, DMAP alone is able to catalyze the ROP of L-lactide, but monomer conversion is fairly low (runs 1 and 6, less than 20% after 24 h). Besides, DMAP·HX (X = Cl, OSO_2CH_3, OSO_2CF_3) is unable to catalyze the ROP of L-lactide. In contrast, DMAP (5% mol) in combination with DMAP·HX (5% mol) was revealed to be more effective for ring-opening polymerization (runs 2−4 and 7−9).

Scheme 3. Ring-Opening Polymerization of L-Lactide Organocatalyzed by DMAP/DMAP·HX

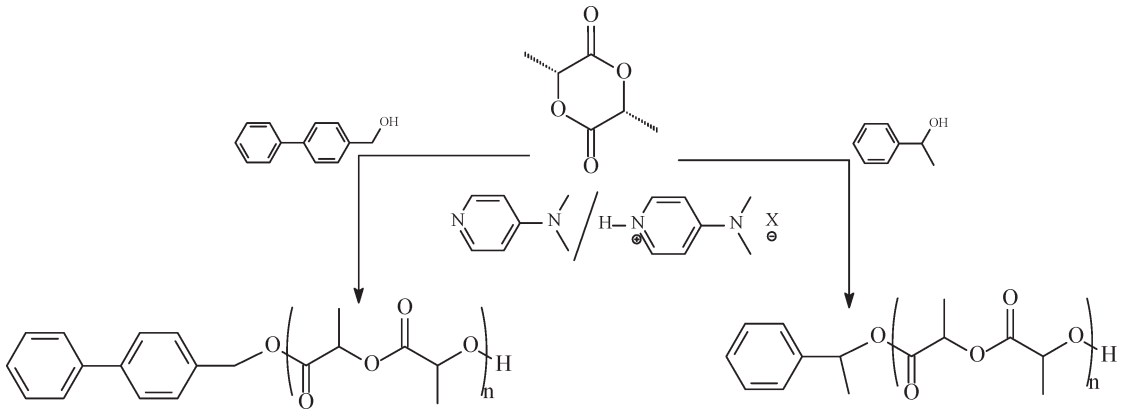


Table 1. L-Lactide ROP by DMAP/DMAP·HX in Dichloromethane at Room Temperature[a]

run	initiator	X	conv[b] (%)	$M_{n,th}$[c] (g/mol)	$M_{n,NMR}$[d] (g/mol)	$M_{n,SEC}$[e] (g/mol)	PDI[e]
1	*p*-PhBzOH	none	16	650	690	660	1.12
2	*p*-PhBzOH	Cl	35	1200	1200	1300	1.12
3	*p*-PhBzOH	OSO_2CH_3	38	1300	1300	1300	1.12
4	*p*-PhBzOH	OSO_2CF_3	54	1700	1800	2000	1.13
5[f]	*p*-PhBzOH	OSO_2CF_3	100	3100	3000	3500	1.06
6	PhEtOH	none	21	900	570	770	1.12
7	PhEtOH	Cl	29	950	910	850	1.17
8	PhEtOH	OSO_2CH_3	37	1170	1250	930	1.12
9	PhEtOH	OSO_2CF_3	62	1980	1400	930	1.13

[a] L-LA 100 mg; CH_2Cl_2 1 mL; initiator 5% mol; DMAP 5% mol; DMAP·HX 5% mol; temperature 25 °C; time 24 h. [b] Conversion of monomer determined by NMR (see Experimental Part). [c] Theoretical molar mass: $M_{n,th}$ = [L-LA]/[initiator] × $M_{L\text{-}LA}$ × yield + $M_{initiator}$. [d] Experimental molar mass determined by NMR (see Experimental Part). [e] Experimental molar mass and molar mass distribution determined by size exclusion chromatography in THF at 40 °C versus polystyrene standards. [f] Reaction time: 48 h.

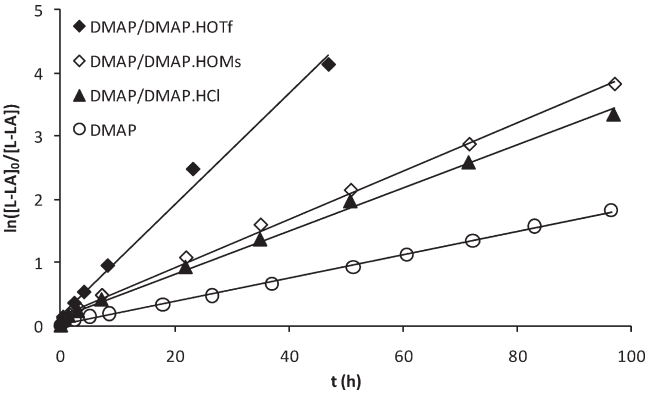


Figure 1. Kinetics of L-lactide polymerization catalyzed by DMAP/DMAP·HX at 25 °C in CD_2Cl_2.

The nature of the counteranion has also a significant effect, since under the same polymerization time, replacing Cl^- by $F_3CSO_3^-$ increased the yield from 35 to 54%. When the triflic acid salt of DMAP and DMAP are combined, quantitative polymerization of L-lactide was achieved in 48 h (run 5). Furthermore, the theoretical molar masses of poly(L-lactide)s are in good agreement with the experimental ones determined by ^{1}H NMR or SEC, those latter exhibiting low molar mass distribution, indicating that these catalytic systems yielded a controlled L-lactide polymerization. Finally, no effect of the nature of the alcohol used as initiator was observed, as both primary and secondary alcohols initiate the polymerization with similar yields.

When compared to cationic polymerization of lactide initiated by an alcohol and catalyzed by protic acids, our systems revealed less active but yield to more controlled polymerizations.[35,36] Indeed, with protic acids, quantitative yields could be obtained in 24 h but PDI are in the range 1.2−1.5. Kinetics of L-lactide polymerizations catalyzed by DMAP/DMAP·HX were investigated in more detail (Figure 1). The conversions (determined by ^{1}H NMR) versus time are plotted in Figure 1. Results confirm the reactivity order indicated in Table 1. DMAP/DMAP·HOTf was the most active catalytic system and activities decrease in the order DMAP/DMAP·HOTf > DMAP/DMAP·HOMs, DMAP/DMAP·HCl > DMAP alone. A linear variation of $\ln([M_0]/[M])$ versus time is observed in all cases, in agreement with a first kinetic order with respect to monomer.

To increase the polymerization rate, the ring-opening polymerization of L-lactide was performed at higher temperature, namely 40 °C (reflux of dichloromethane). Results are presented in Table 2. As expected, yields increased significantly compared to experiments achieved at room temperature. Again, DMAP·HX was unable to catalyze on its own the ring-opening polymerization of L-lactide, whatever the chemical nature of X. When DMAP was employed alone, the same results were observed for 10 or 5 mol % (runs 10 and 11, DMAP/initiator: 2/1 and 1/1 respectively). Theoretical and experimental molar masses of poly(L-lactide)s were found to be in very good agreement accompanied by low dispersity indexes. DMAP/DMAP·$HOSO_2CF_3$ revealed again to be the most active system.

To further check the controlled character of the polymerization, the influence of the L-lactide/initiator ratio on the polylactide molar mass and dispersity was studied. To this end, experiments were conducted using the most active catalytic system, varying its amount with respect to monomer and initiator (Table 3). As can be seen, in all cases, experimental molar masses were in good agreement with theoretical ones calculated assuming that one polylactide chain was formed per initiator molecule (Figure 2), with low dispersity. Besides, the decrease of either the acidic or basic form of the catalytic system leads to a rather similar decrease of the polymerization yield (runs 15, 16, 17 and 20, 22, 23). The polymerization yield increased with the catalyst/initiator ratio (runs 15, 18 and 20, 24). Using longer reaction time allowed an almost complete monomer conversion (runs 20 and 21).

Maldi-TOF Mass Spectrometry Measurements. A Maldi-TOF mass spectrum of a poly(L-lactide) initiated by *p*-PhBzOH is shown in Figure 3. One peak series was observed with molar masses corresponding to the equation: $M_n = 144.24 \times DP_n + 184.24 + 22.99(Na)$, in agreement with polylactide chains initiated by *p*-PhBzOH. No trace of chains resulting from side initiation was detected. Nevertheless, a second series shifted from 72 g/mol, corresponding to a half-lactide unit is also present. This latter resulted from a transesterification reaction.

A Maldi-TOF mass spectrum of a poly(L-lactide) initiated by 1-PhEtOH is shown in Figure 4. In this case, only one peak series is observed with molar masses corresponding to the equation: $M_n = 144.24 \times DP_n + 122.17 + 22.99(Na)$, in agreement with polylactide chains initiated by 1-PhEtOH. This has to be linked to the observation made by Hedrick in the case of the poly(L-lactide) depolymerization experiments, where DMAP was used as the catalyst. Indeed, it was shown that secondary alcohols are not able to depolymerize poly(L-lactide) in contrast to primary alcohols.[37]

It could be assumed from these results that in the presence of the primary alcohol, used as the initiator, transesterification reactions take place mainly during the initiation step, because after insertion of the first monomer unit, the alcoholic chain end formed is secondary and unable to react with the already formed polymer chain.

Interaction between the Initiator, the Monomer, and the Catalytic System: Mechanistic Insight. First, the catalysts

Table 2. L-Lactide ROP Catalyzed by DMAP/DMAP·HX in Dichloromethane at 40 °C (Reflux)[a]

run	DMAP (mol %)	X	DMAP·HX (mol %)	conv[b] (%)	$M_{n,th}$[c] (g/mol)	$M_{n,NMR}$[d] (g/mol)	$M_{n,SEC}$[e] (g/mol)	PDI[e]
10	10	none		39	1300	1400	1300	1.13
11	5	none		35	1200	1200	900	1.12
12	5	Cl	5	72	2300	2500	2600	1.10
13	5	OSO_2CH_3	5	77	2400	2800	2900	1.10
14	5	OSO_2CF_3	5	89	2700	2800	2800	1.13

[a] L-Lactide 100 mg; CH_2Cl_2 1 mL; *p*-PhBzOH 5 mol %; temperature 40 °C; time 24 h. [b] Conversion of monomer determined by NMR (see Experimental Part). [c] Theoretical molar mass: $M_{n,th}$ = [L-LA]/[initiator] × $M_{L\text{-}LA}$ × yield + $M_{initiator}$. [d] Experimental molar mass determined by NMR (see Experimental Part). [e] Experimental molar mass and molar mass distribution determined by size exclusion chromatography in THF at 40 °C versus polystyrene standards.

Table 3. L-Lactide ROP Catalyzed by DMAP/DMAP·$HOSO_2CF_3$ in CH_2CL_2 at 40 °C[a]

run	DMAP (mol %)	DMAP·HOTfl (mol %)	alcohol (mol %)	conv[b] (%)	$M_{n,th}$[c] (g/mol)	$M_{n,NMR}$[d] (g/mol)	$M_{n,SEC}$[e] (g/mol)	PDI[e]
15	5	5	2	89	6600	6700	7000	1.05
16	5	2	2	66	4900	5000	5500	1.05
17	2	5	2	60	4500	4200	5000	1.05
18	2	2	2	47	3600	3500	3900	1.06
19	5	0	1	7	1200	1300	800	1.17
20	5	5	1	57	8400	8300	8900	1.04
21[f]	5	5	1	95	13900	13100	14000	1.05
22	5	1	1	33	5000	4200	5100	1.06
23	1	5	1	27	4100	4200	4100	1.06
24	1	1	1	17	2600	2500	2400	1.04

[a] L-Lactide 100 mg; CH_2Cl_2 1 mL; *p*-PhBzOH 5% mol; temperature 40°C; time 24 h. [b] Conversion of monomer determined by NMR (see Experimental Part). [c] Theoretical molar mass: $M_{n,th}$ = [L-LA]/[initiator] × $M_{L\text{-}LA}$ × yield + $M_{initiator}$. [d] Experimental molar mass determined by NMR (see Experimental Part). [e] Experimental molar mass and molar mass distribution determined by size exclusion chromatography in THF at 40 °C versus polystyrene standards. [f] Time: 48 h.

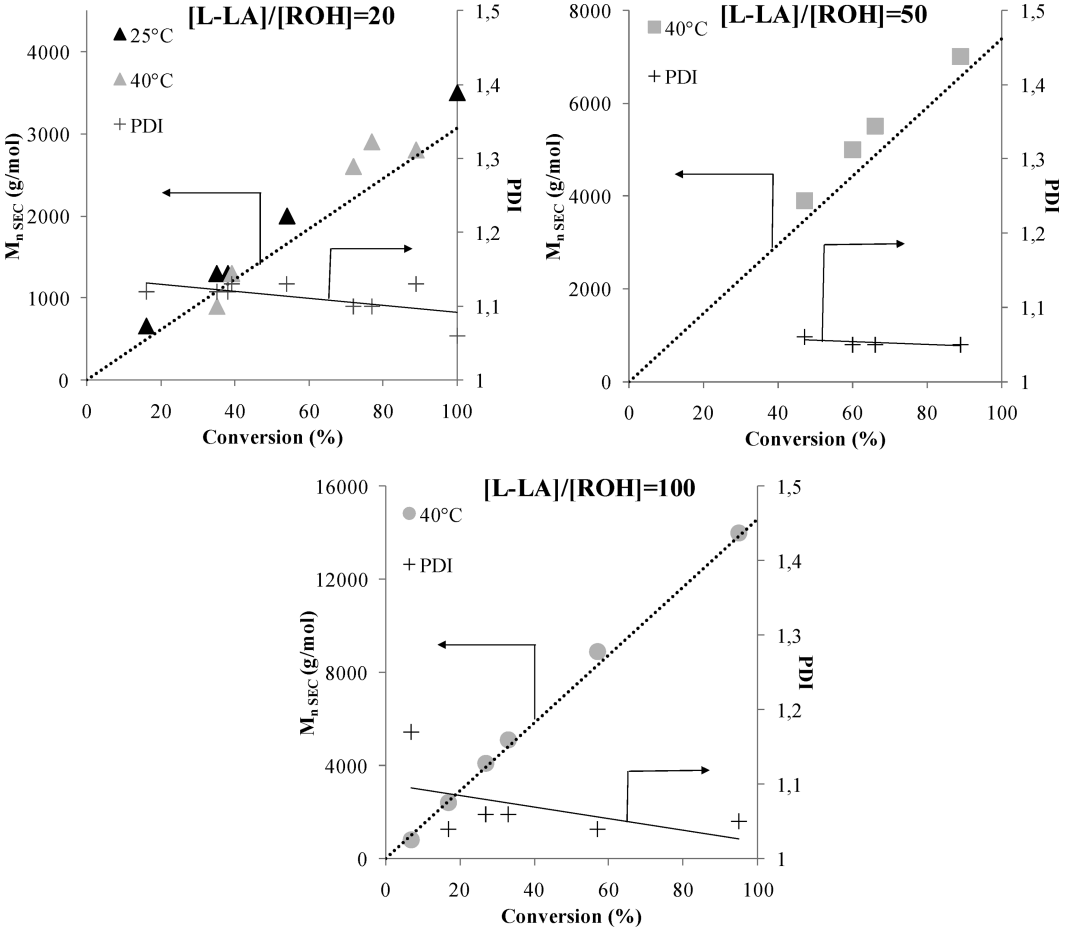


Figure 2. $M_{n,SEC}$ vs L-lactide conversion.

have been investigated by ^1H NMR. When equivalent amounts of DMAP and DMAP·HX are mixed together, only four kinds of protons are detected: $-CH_3$ (12H, s), H_o (4H, d), H_m (4H, d), and H_{acidic} (1H, s) (additional $-CH_3$ protons for counteranion $-OMs$ were observed). Observed chemical shifts are located between those of free DMAP and

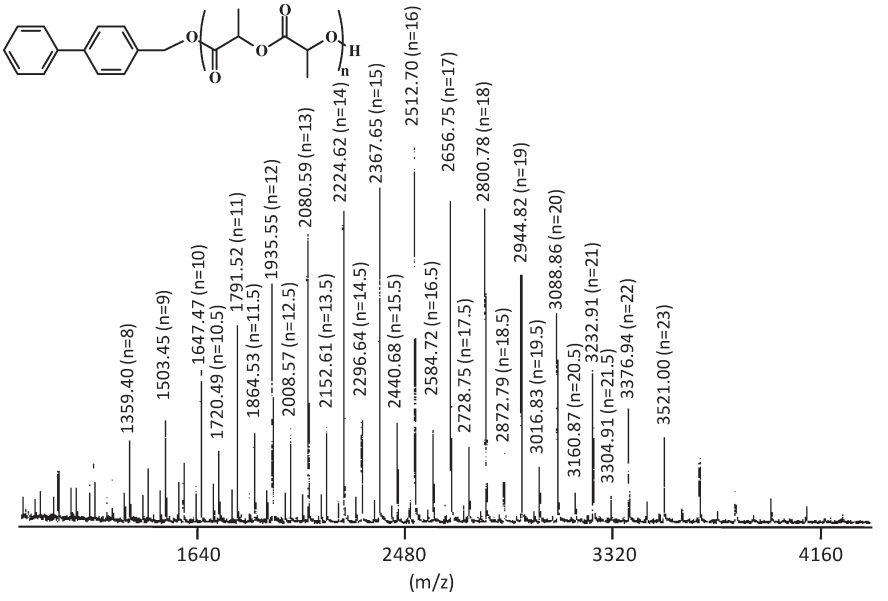


Figure 3. MALDI-TOF spectrum of poly(L-lactide) initiated by *p*-PhBzOH and catalyzed by DMAP/DMAP·HOTfl (run 5, Table 1).

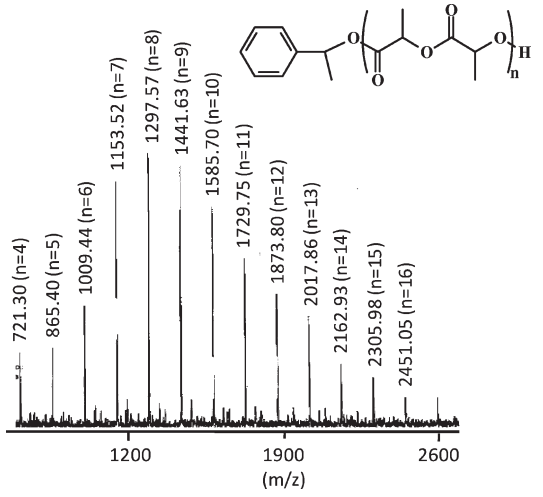
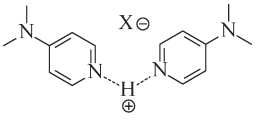


Figure 4. MALDI-TOF spectrum of poly(L-lactide) initiated by 1-PhEtOH and catalyzed by DMAP/DMAP·HOTfl (run 9, Table 1).

DMAP·HX, suggesting that in solution, DMAP and DMAP·HX protons are equivalent, allowing us to assume the structure drawn in Scheme 4. Nevertheless, a dissymmetric structure with fast exchange of the acidic proton at the NMR time scale is also conceivable. Besides, whatever the counterion, the chemical shifts are almost the same (see Supporting Information).

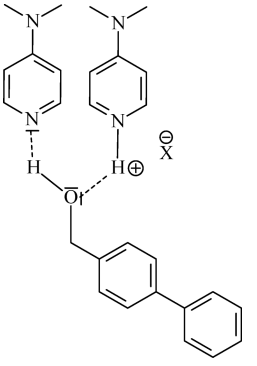
Interactions between the monomer (L-lactide), catalytic system (DMAP/DMAP·HX), and initiator (*p*-PhBzOH) were studied by ^{1}H NMR measurements. No interaction between the monomer and initiator was noticed. In contrast, strong interactions were observed between the catalytic system and the alcoholic proton of the initiator. In the presence of DMAP the alcoholic proton was located at 3.95 ppm, which corresponds to a chemical shift of +2.01 ppm compared to the alcohol alone. This means that the alcohol is activated by DMAP via a hydrogen bond, in agreement with theoretical calculations.[38] When DMAP and DMAP·HX were combined, a single peak was observed for both the alcoholic and the acidic protons of the initiator and DMAP·HX, respectively, indicating that they are

Scheme 4. Proposed Structure of the DMAP/DMAP·HX Catalyst



DMAP/DMAP.HX

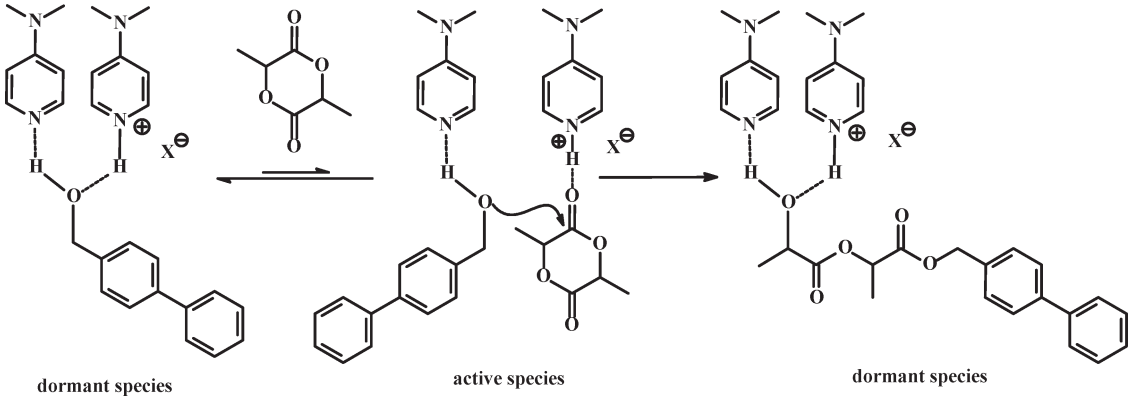
Scheme 5. Presumed Complex between DMAP/DMAP·HX and the Initiator



equivalent and suggesting the formation of a complex, as shown in Scheme 5. Concerning interaction between the lactide monomer and the catalytic system, a very small shift of the acidic proton signal of the DMAP/DMAP·HX was observed ($\delta_{ppm} < 0.5$ ppm). This is consistent with weaker interactions than those observed between the alcoholic function of the chain end and the catalytic system.

During polymerization kinetics followed by ^{1}H NMR, the complex shown in Scheme 5 was detected during the polymerization process (see Supporting Information). Indeed, the alcoholic proton and the acidic one were observed as a single peak all along the polymerization, indicating that they remained equivalent in the complex. One reaction pathway can be postulated to explain these observations (Scheme 6). The complex shown in Scheme 5 could correspond to dormant species that upon dissociation would yield the actual propagating species (initiator activated by DMAP

Scheme 6. Presumed L-Lactide Polymerization Mechanism with the DMAP/DMAP·HX Catalytic System



and monomer activated by DMAP·HX) that will ring-open L-lactide.

Conclusion

Fine controlled ring-opening polymerization of L-lactide by new organic catalysts based on a concept of acid−base cooperative functions was demonstrated. DMAP and DMAP·HX act as acidic and basic catalysts at the same time, and their combination is more active than DMAP alone, the enhancement depending on the nature of X (CF_3SO_3 > CH_3SO_3 > Cl). It is believed that activation of both chain end and the monomer simultaneously occurs, explaining the reactivity increase. Thus, well-controlled polymers up to 15000 g/mol were obtained in reasonable polymerization time. Finally, these organic catalysts are very simple and easily accessible.

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Supporting Information Available: Figures S1−S5 of NMR spectra and a GPC trace. This material is available free of charge via the Internet at http://pubs.acs.org.

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