# An Activated Equivalent of Lactide towards Organocatalytic RingOpening Polymerization 

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## SUPPLEMENTARY INFORMATION

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## Computational Studies

Computational Methods. All the calculations reported were performed in the gas phase within Density Functional Theory, ${ }^{1}$ using the hybrid three-parameter functional customarily denoted as B3LYP. ${ }^{2}$ The standard $6-31 G^{*}$ basis set $^{3}$ as implemented in the GAUSSIAN $03^{4}$ suite of programs has been used in all cases.



Table S1. Total energies ${ }^{\text {a,b }}$ in atomic units of stationary points associated with eqs. (1) and (2).

| Structure | E | $\mathrm{H}_{298}$ | $\mathrm{G}_{298}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{1 a}$ | -534.219521 | -534.209128 | -534.254153 |
| $\mathbf{2 a}$ | -649.907658 | -649.892817 | -649.949498 |
| $\mathbf{1 b}$ | -455.664465 | -455.656770 | -455.695793 |
| $\mathbf{2 b}$ | -382.788891 | -382.779657 | -382.821946 |
| $\mathrm{CH}_{3} \mathrm{OH}$ | -115.662941 | -115.658706 | -115.685664 |
| $\mathrm{CO}_{2}$ | -188.570806 | -188.566881 | -188.586719 |

${ }^{\mathrm{a}}$ Computed at the B3LYP/6-31G(g)+ZPVE level. ${ }^{\mathrm{b}} \mathrm{H}$ and G computed at 298 K .

## Cartesian coordinates of fully optimized compounds 1a,b and 2a,b.

## 1a

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | X | Y | Z |
| 1 | 8 | 0 | 0.257670 | -1.353787 | -0.108155 |
| 2 | 6 | 0 | 1.264898 | -0.465214 | 0.436634 |
| 3 | 6 | 0 | 1.038579 | 0.965259 | -0.055690 |
| 4 | 8 | 0 | -0.257668 | 1.353797 | -0.108094 |
| 5 | 6 | 0 | -1.264896 | 0.465215 | 0.436673 |
| 6 | 6 | 0 | -1.038584 | -0.965300 | -0.055548 |
| 7 | 8 | 0 | 1.924120 | 1.716213 | -0.375687 |
| 8 | 8 | 0 | -1.924128 | -1.716175 | -0.375721 |
| 9 | 6 | 0 | -2.622726 | 1.012378 | 0.038565 |
| 10 | 6 | 0 | 2.622738 | -1.012396 | 0.038598 |
| 11 | 1 | 0 | 1.162677 | -0.466042 | 1.532690 |
| 12 | 1 | 0 | -1.162737 | 0.466068 | 1.532735 |
| 13 | 1 | 0 | -3.410443 | 0.378694 | 0.452012 |
| 14 | 1 | 0 | -2.723813 | 1.022428 | -1.049833 |
| 15 | 1 | 0 | -2.738154 | 2.031086 | 0.417962 |
| 16 | 1 | 0 | 3.410443 | -0.378708 | 0.452063 |
| 17 | 1 | 0 | 2.723873 | -1.022471 | -1.049795 |
| 18 | 1 | 0 | 2.738142 | -2.031094 | 0.418027 |

## 2a

| Center | Atomic | Atomic | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Number | Number | Type | X | Y | Z |
| 1 | 8 | 0 | 3.558674 | $-0.567865$ | -0.733786 |
| 2 | 6 | 0 | 2.684409 | 0.112240 | 0.141292 |
| 3 | 6 | 0 | 1.301519 | 0.186651 | -0.492698 |
| 4 | 8 | 0 | 0.489558 | 1.058068 | 0.136119 |
| 5 | 8 | 0 | 0.973840 | -0.487910 | -1.448468 |
| 6 | 6 | 0 | 2.599111 | -0.577093 | 1.512700 |
| 7 | 6 | 0 | -0.877905 | 1.080296 | -0.303449 |
| 8 | 6 | 0 | -1.572689 | -0.201543 | 0.166452 |
| 9 | 6 | 0 | -1.522066 | 2.328905 | 0.291719 |
| 10 | 8 | 0 | -1.122850 | -0.988465 | 0.965409 |
| 11 | 8 | 0 | -2.777727 | -0.308643 | -0.423388 |
| 12 | 6 | 0 | -3.545937 | -1.469382 | -0.053529 |
| 13 | 1 | 0 | 2.988010 | -1.058925 | -1.353298 |
| 14 | 1 | 0 | 3.055469 | 1.137109 | 0.275375 |
| 15 | 1 | 0 | 1.969165 | -0.008298 | 2.203150 |
| 16 | 1 | 0 | 3.607321 | -0.660940 | 1.928478 |
| 17 | 1 | 0 | 2.180221 | -1.582919 | 1.406687 |
| 18 | 1 | 0 | -0.906986 | 1.103378 | -1.396259 |
| 19 | 1 | 0 | -2.567502 | 2.393281 | -0.021235 |
| 20 | 1 | 0 | -0.992687 | 3.221099 | -0.054653 |
| 21 | 1 | 0 | -1.478617 | 2.299711 | 1.384892 |
| 22 | 1 | 0 | -4.474986 | -1.395725 | -0.618687 |
| 23 | 1 | 0 | -3.745849 | -1.468823 | 1.020989 |
| 24 | 1 | 0 | -3.004167 | -2.380857 | -0.317439 |


| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | X | Y | Z |
| 1 | 6 | 0 | 0.790865 | -0.607575 | 0.462239 |
| 2 | 6 | 0 | 0.679802 | 0.863402 | 0.090926 |
| 3 | 6 | 0 | 1.734023 | -1.388752 | -0.442960 |
| 4 | 8 | 0 | 1.536956 | 1.692241 | 0.016976 |
| 5 | 8 | 0 | -0.651573 | 1.105013 | -0.176697 |
| 6 | 6 | 0 | -1.385604 | -0.066303 | -0.021253 |
| 7 | 8 | 0 | -2.559386 | -0.142618 | -0.194902 |
| 8 | 8 | 0 | -0.565675 | -1.076246 | 0.347365 |
| 9 | 1 | 0 | 1.092494 | -0.695835 | 1.512323 |
| 10 | 1 | 0 | 1.749107 | -2.441615 | -0.149375 |
| 11 | 1 | 0 | 2.743284 | -0.976876 | -0.350533 |
| 12 | 1 | 0 | 1.418026 | -1.317429 | -1.488063 |

## 2b

| Center | Atomic | Atomic | Coordinates (Angstroms) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Number | Number | Type | X | Y | Z |
| 1 | 8 | 0 | 2.025024 | -0.899834 | -0.231996 |
| 2 | 6 | 0 | 1.123085 | 0.170398 | -0.408613 |
| 3 | 6 | 0 | -0.283658 | -0.298095 | -0.046338 |
| 4 | 8 | 0 | -1.224377 | 0.614117 | -0.326438 |
| 5 | 6 | 0 | -2.575333 | 0.241264 | 0.008091 |
| 6 | 8 | 0 | -0.507635 | -1.384165 | 0.453380 |
| 7 | 6 | 0 | 1.536852 | 1.384591 | 0.435156 |
| 8 | 1 | 0 | 1.514364 | -1.612265 | 0.196261 |
| 9 | 1 | 0 | 1.109684 | 0.461980 | -1.469447 |
| 10 | 1 | 0 | -3.192644 | 1.088799 | -0.289313 |
| 11 | 1 | 0 | -2.664644 | 0.055884 | 1.081381 |
| 12 | 1 | 0 | -2.867167 | -0.659676 | -0.537224 |
| 13 | 1 | 0 | 0.878451 | 2.239124 | 0.250906 |
| 14 | 1 | 0 | 2.562683 | 1.662763 | 0.177113 |
| 15 | 1 | 0 | 1.509498 | 1.133499 | 1.500985 |

## Synthetic procedures and Spectroscopic data

Materials. All reactions were performed under an inert atmosphere of argon, using standard Schlenk techniques. Solvents were dried and distilled prior to use: toluene ( $>99.9 \%$ ), THF ( $>99.9 \%$ ) and diethyl ether ( $>99.9 \%$ ) over sodium, pentane ( $>99 \%$ ) over calcium dihydride and dichloromethane ( $>99.95 \%$ ) over phosphorus pentoxide. Dimethylaminopyridine (DMAP) (99\%, ALDRICH) was purified by recrystallization in toluene and stored under argon. n-Pentanol (99+\%), neo-Pentanol ( $99 \%$ ) and $i$-Propanol ( $99+\%$ ) were dried over sodium and distilled before use.

Characterizations. ${ }^{1} \mathrm{H}$ NMR measurements were used to determine the monomer conversion and the chain end groups. Spectra were recorded in $\mathrm{CDCl}_{3}$ on BRUKER Avance 300,400 and 500 MHz spectrometers at room temperature. ${ }^{1} \mathrm{H}$ chemical shifts are reported in ppm relative to $\mathrm{Me}_{4} \mathrm{Si}$ as an external standard. Monomer conversion was determined from the relative intensities of the methyl signals for the monomer (doublet at $\delta 1.72 \mathrm{ppm}$ ) and polymer (doublet at $\delta 1.54 \mathrm{ppm}$ ). The degree of polymerization DP was determined from the relative integration of the signals for the lactate units and chain ends.

The number-average and weight-average molar masses ( $M_{\mathrm{n}}$ and $M_{\mathrm{w}}$, respectively) and polydispersity indexes $\left(M_{\mathrm{w}} / M_{\mathrm{n}}\right)$ of the polyester samples were determined by size exclusion chromatography (SEC) at $35^{\circ} \mathrm{C}$ with a Waters 600 liquid chromatograph equipped with a Waters 2410 Refractive Index Detector. Tetrahydrofuran (THF) was used as the eluent and the flow rate was set up at $1.0 \mathrm{~mL} / \mathrm{min}$. A Waters pre-column and a Waters STYRAGEL column (HR 4E, 50-100,000 g/mol) were used. Calibrations were performed using polystyrene standards (400-100,000 g/mol).

Electrospray-ionization mass spectra (ESI-MS) were performed on a Perkin Elmer Sciex API-365 spectrometer operating in positive ion mode. Samples were dissolved in acetonitrile, doped with traces of ammonium hydroxide and infused with a syringe pump at $5 \mathrm{~mL} / \mathrm{min}$.

## Control experiment for Lactide Polymerization.

$L$-Lactide ( $89 \mathrm{mg}, 0.65 \mathrm{mmol}$, 10 equiv) was dissolved in dichloromethane ( 0.2 mL ) and a DCM solution of neo-Pentanol and DMAP ( $0.63 \mathrm{~mL}, 0.10 \mathrm{~mol} . \mathrm{L}^{-1}, 1$ equiv) was added. The reaction mixture was stirred at $35^{\circ} \mathrm{C}$ and monitored by ${ }^{1} \mathrm{H}$ NMR. The reaction was stopped after $96 \mathrm{~h}\left(93 \%\right.$ conversion showed by ${ }^{1} \mathrm{H}$ NMR).
$\mathrm{DP}_{\mathrm{NMR}}=19$
SEC (THF): $M_{n}=2980, M_{w} / M_{n}=1.24$

## Procedure for the preparation of(-) 5-methyl-1,3-dioxolane-2,4-dione (L-lacOCA).

*** CAUTION: phosgene is volatile and highly toxic ${ }^{* * *}$
A solution of diphosgene ( $40 \mathrm{mmol}, 2.82 \mathrm{~mL}$ ) in 10 mL of anhydrous THF was added dropwise ( 20 min ) at $0^{\circ} \mathrm{C}$ over a stirred suspension of L-lactic acid lithium salt ( $40 \mathrm{mmol}, 3.90 \mathrm{~g}$ ) in 60 mL of anhydrous THF under dry atmosphere. The homogeneous reaction mixture was stirred at room temperature for 2.5 h . THF was removed under reduced pressure and trapped with liquid nitrogen. ${ }^{* * *}$ CAUTION: The latter solution was carefully neutralized at $0^{\circ} \mathrm{C}$ with aqueous ammoniac diluted in ethanol. ${ }^{* * *}$ Dry diethyl ether $(30+20$ mL ) was added to the residue and the lithium salts were removed by filtration. Recristallisation from diethyl ether afforded colourless crystals ( $2.18 \mathrm{~g}, 47 \%$ ).
${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 200 \mathrm{MHz}\right): 5.15\left(\mathrm{q}, \mathrm{CHCH}_{3}, 7.2 \mathrm{~Hz}\right) ; 1,73\left(\mathrm{~d}, \mathrm{CHCH}_{3}, 7.2 \mathrm{~Hz}\right)$
${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): 170.5(\mathrm{CHCOO}) ; 147.7(\mathrm{OCOO}) ; 85.0\left(\mathrm{CHCH}_{3}\right) ; 23.4\left(\boldsymbol{C H}_{3}\right)$
$\mathrm{mp}: 65-67^{\circ} \mathrm{C}, \quad[\alpha]_{\mathrm{D}}=-17,4\left(1 \mathrm{~g} / \mathrm{L}, \mathrm{CHCl}_{3}\right)$
This procedure differs from that reported by Kricheldorf ${ }^{5}$ in that:
i) 1 equivalent of diphosgene can be used instead 3 eq of phosgene
ii) the addition of a base ( N -methylmorpholine) is not necessary
iii) diethyl ether is a good recristallisation solvent (instead of the mixture of ethyl acetate and carbon tetrachloride)

## General Procedure for L-lacOCA Polymerization.

$L$-lacOCA ( $157 \mathrm{mg}, 1.35 \mathrm{mmol}, 50$ equiv) was dissolved in dichloromethane ( 1.6 mL ) and a DCM solution of neo-Pentanol and DMAP ( $0.14 \mathrm{~mL}, 0.19 \mathrm{~mol} . \mathrm{L}^{-1}, 1$ equiv) was added. The reaction mixture was stirred at room temperature until $\mathrm{CO}_{2}$ no longer evolved. The complete monomer consumption was confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The reaction mixture was diluted with $\mathrm{DCM}(4 \mathrm{~mL})$ and washed with cold $2 \mathrm{~N} \mathrm{HCl}(2 \mathrm{x}$ 5 mL ), brine ( 5 mL ) and dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$. The solvent was removed by evaporation to give the polymer as a white solid ( $100 \mathrm{mg}, 99 \%$ ).
${ }^{1} \mathrm{H}^{\mathrm{NMR}}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta 0.93\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.60-1.40\left(\mathrm{~m}, 148 \mathrm{H}, \mathrm{OCHCH}_{3}\right), 3.80(\mathrm{~d}, \mathrm{~J}=10.5$ $\left.\mathrm{Hz}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 3.88\left(\mathrm{~d}, \mathrm{~J}=10.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 4.30\left(\mathrm{q}, \mathrm{J}=7.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HOCHCH}_{3}\right), 5.16(\mathrm{q}$, $\mathrm{J}=6.9 \mathrm{~Hz}, 49 \mathrm{H}, \mathrm{OCHCH} 3$ ).
$\mathrm{DP}_{\mathrm{NMR}}=50$
SEC (THF): $M_{n}=5930, M_{w} / M_{n}=1.13$

## Procedure for the determination of the relationship between DP and monomer conversion

Polymerization was carried out in an NMR tube $\left(\mathrm{CDCl}_{3}\right.$ solution, 29 mg of $L$-lacOCA, 100 equiv) and monitored by ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz})$ at $25^{\circ} \mathrm{C}$. At $\mathrm{t}=0$, a DCM solution of neo-Pentanol and DMAP ( $12 \mu \mathrm{~L}, 1$ equiv) was added. NMR spectra were recorded ( $\mathrm{NS}=1$ ) every 2 minutes during the first 30 minutes then every 5 minutes until completion.

## Influence of the reaction time on the polymer

A PLA with $M_{\mathrm{n}}=9130$ and $M_{\mathrm{w}} / M_{\mathrm{n}}=1.14$ just after complete monomer consumption was kept under the polymerization conditions (dichloromethane, $25^{\circ} \mathrm{C}, \mathrm{DMAP}$ ) for 3 days. No significant changes could be detected by $\operatorname{SEC}\left(M_{\mathrm{n}}=9100\right.$ and $\left.M_{\mathrm{w}} / M_{\mathrm{n}}=1.16\right)$.

Table S2. L-lacOCA polymerization with the initiator/DMAP system. ${ }^{a}$

| Entry | Initiator | $[\mathbf{M}]_{0} /[\mathbf{I}]_{0}$ | $\mathbf{T i m e}^{\boldsymbol{b}}$ | $\mathbf{D P}_{(\mathbf{N M R})}{ }^{\boldsymbol{c}}$ | $\boldsymbol{M}_{\mathrm{n}}{ }^{\boldsymbol{d}}$ | $\boldsymbol{M}_{\mathrm{w}} / \boldsymbol{M}_{\mathrm{n}}{ }^{\boldsymbol{d}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | neo-Pentanol | 11 | $<5$ | 12 | 1220 | 1.22 |
| 2 | neo-Pentanol | 20 | 5 | 20 | 2110 | 1.20 |
| 3 | neo-Pentanol | 50 | 20 | 50 | 5810 | 1.15 |
| 4 | neo-Pentanol | 100 | 90 | 97 | 11980 | 1.16 |
| 5 | neo-Pentanol | 200 | 120 | 197 | 24460 | 1.21 |
| 6 | neo-Pentanol | 400 | 480 | 386 | 39510 | 1.27 |
| 7 | neo-Pentanol | 600 | 1140 | 592 | 62290 | 1.18 |
| 8 | n-Pentanol | 20 | 5 | 20 | 2620 | 1.19 |
| 9 | i-Propanol | 20 | 5 | 21 | 2510 | 1.34 |
| 10 | Cholesterol | 20 | 5 | 21 | 2610 | 1.21 |
| 11 | 2-Bromoethanol | 20 | 5 | 18 | 1870 | 1.17 |

${ }^{a}$ Polymerizations of $L$-lacOCA in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ were carried out at $25^{\circ} \mathrm{C}$ with an initiator to catalyst ratio of 1 . In all experiments conversion were higher than $96 \%$. ${ }^{b}$ In minutes. ${ }^{c}$ Calculated by relative integration of the methyl signals (polymer and ester chain end) in ${ }^{1} \mathrm{H}$ NMR experiments. ${ }^{d}$ Obtained from Size Exclusion Chromatography (in tetrahydrofuran, THF) using polystyrene standards.

Figure S1. ${ }^{1} \mathrm{H}$ NMR spectrum $\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right)$ of a polylactide sample obtained by polymerization of $L$ lactic O-carboxyanhydride (L-lacOCA) with neo-PentOH as initiator $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 25^{\circ} \mathrm{C}\right.$, $[L \text {-lacOCA }]_{0} /[$ neoPentOH $\left.]_{0} /[\mathrm{DMAP}]_{0} 10 / 1 / 1,[\mathrm{LA}]_{0}=0.9 \mathrm{M}\right)$.


Figure S2. Electrospray-ionization mass spectrum (Region $\mathrm{m} / \mathrm{z} 150$ to 1700) of polyester prepared by polymerization of $L$-lacOCA with neo-Pentanol $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 25^{\circ} \mathrm{C}\right.$, $\left.[\mathrm{OCA}]_{0} /[\mathrm{ROH}]_{0} /[\mathrm{DMAP}]_{0} 10 / 1 / 1\right)$


Figure S3. GPC profile of a polylactide sample obtained by polymerization of $L$-lactic O-carboxyanhydride (L-lacOCA) with neo-PentOH as initiator $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 25^{\circ} \mathrm{C}\right.$, $[L \text {-lacOCA }]_{0} /[\text { neo-PentOH }]_{0} /[\mathrm{DMAP}]_{0} 50 / 1 / 1$, $\left.[\mathrm{LA}]_{0}=0.9 \mathrm{M}\right)$.


GPC Sample Results

|  | Retention <br> Time | $\mathbf{M n}$ | $\mathbf{M w}$ | $\mathbf{M P}$ | Polydispersity |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.184 | 5806 | 6691 | 6670 | 1.15 |

Second-feed experiment: 50 equiv. of L-lacOCA were polymerized with neo-Pentanol/DMAP (1/1) in dichloromethane at $25^{\circ} \mathrm{C}$. After 45 minutes, $\mathrm{CO}_{2}$ no longer evolved and SEC analysis indicated the formation of a PLA with $M_{\mathrm{n}}=5120 \mathrm{~g} / \mathrm{mol}$ and $M_{\mathrm{w}} / M_{\mathrm{n}}=1.13$. Polymerization was then restarted with 50 equiv. of $L$ lacOCA to afford, after additional 60 minutes, a PLA with $M_{\mathrm{n}}=10400 \mathrm{~g} / \mathrm{mol}$ and $M_{\mathrm{w}} / M_{\mathrm{n}}=1.14$.

Figure S4. GPC traces of the PLAs obtained after the first (a) and second (b) feeds of $L$-lacOCA.


Figure S5. Normal (a) and homonuclear decoupled (b) ${ }^{1} \mathrm{H}$ NMR spectra $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right)$ of a polymer sample prepared by polymerization of $L$-lacOCA initiated with $n$-Pentanol $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 25^{\circ} \mathrm{C}\right.$, [ $L$ lacOCA $]_{0} /[\mathrm{ROH}]_{0} /[\mathrm{DMAP}]_{0}=100 / 1 / 1$


## Procedure for Lactide Polymerization initiated with 2-bromoethanol.

Lactide ( $483 \mathrm{mg}, 3.35 \mathrm{mmol}, 10$ equiv) was dissolved in dichloromethane ( 5 mL ). The initiator ( $24 \mu \mathrm{~L}$ of 2bromoethanol, 1 equiv) and the catalyst ( 40 mg of DMAP, 1 equiv) were added successively. The reaction mixture was stirred at $35^{\circ} \mathrm{C}$ and monitored by ${ }^{1} \mathrm{H}$ NMR. The reaction was stopped after 5 days ( $93 \%$ conversion showed by ${ }^{1} \mathrm{H}$ NMR). The ${ }^{1} \mathrm{H}$ NMR spectrum revealed the alkylation of about $30 \%$ of the DMAP leading to a mixture of brominated and pyridinium chain ends.

Figure S6. ${ }^{1} \mathrm{H}$ NMR spectra $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right)$ of polymer samples prepared by polymerization of a) $L$ lacOCA initiated with 2-bromoethanol $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 25^{\circ} \mathrm{C}\right.$, $\left.[L-\mathrm{lacOCA}]_{0} /[\mathrm{ROH}]_{0} /[\mathrm{DMAP}]_{0}=20 / 1 / 1\right)$ and b) $L$ lactide initiated with 2-bromoethanol $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 35^{\circ} \mathrm{C}\right.$, $\left.[\text { lactide }]_{0} /[\mathrm{ROH}]_{0} /[\mathrm{DMAP}]_{0}=10 / 1 / 1\right)$.


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