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Supporting Information

Catalytic Cracking of Lactide and Poly(Lactic Acid) to Acrylic Acid at Low Temperatures

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General remarks concerning the experiments and the analysis

Unless otherwise stated, all reaction mixtures were prepared in water free conditions, either in a glovebox or using Schenk techniques in order to minimize the exposure of hygroscopic compounds to air moisture. The reactions were done in autoclaves (inside volume of 9 mL). All liquids were degased using at least three freeze-pump-thaw cycles and dried on molecular sieves when applicable. Commercial sulfolane and acetic acid were distilled. Unless otherwise stated, hygroscopic solids were dried overnight in a vacuum oven in the presence of phosphorus pentoxide 10 °C below their melting point (up to 100 °C) and stored in a glovebox.
The reaction temperatures reported correspond to the temperature of the heating mantles (the temperature of the reaction mixture is about 125 °C when the heating mantle is at 130 °C and about 190 °C when the heating mantle is at 200 °C).
The composition of the reaction mixtures (quantity in mmol) were determined by NMR of the crude reaction mixture in deuterated DMSO using the CH_3 group of the sulfonic acid as an internal standard. From these values, a yield was calculated (compounds were not isolated). Because of the stoichiometry of the reaction, the percent yield of **AA**, **2BrPA**, **3BrPA** and **LA** corresponds to:

$$yield = \frac{n_{(species)}}{n_{i(lactide)} \times 2} \times 100 \quad (\mathbf{1})$$

Indeed, 1 equivalent of lactide is susceptible to give 2 equivalents of **AA** or 2 equivalents of **2BrPA** or 2 equivalents of **3BrPA** or 2 equivalents of **LA.**

The percent yield of **2** corresponds to:

$$yield = \frac{n_{(\mathbf{2})} \times 2}{n_{i(lactide)} \times 2} \times 100 \quad (\mathbf{2})$$

Therefore, 2 equivalents of lactide are susceptible to give 2 equivalents of **2**.
The percent yield of **3** corresponds to:

$$yield = \frac{n_{(\mathbf{3})} \times 3}{n_{i(lactide)} \times 2} \times 100 \quad (\mathbf{3})$$

Indeed, 3 equivalents of lactide are susceptible to give 2 equivalents of **3**.
The selectivity of all species corresponds to:

$$selectivity = \frac{yield_{(species)}}{conversion} \times 100 \quad (\mathbf{4})$$

When no sulfonic acid catalyst was added in the beginning of the reaction, it was added after the reaction at or below room temperature (external standard). Commercial HOTS•H_2O, HOMs, **AA**, **2BrPA** and **3BrPA** and samples of **LA** and (*meso*)- and (*S*,*S*)-lactide given by the company Corbion were used to assign the NMR peaks. The alpha protons of **AA**, **2**, **3**, **2BrPA**, **LA** and **3BrPA** were used for the integration. "Oligomers" designates the sum of the lactate and 2-bromopropionate units involved in oligo(lactic acids) and co-oligomers of lactic acid and 2-bromopropionic acid and of lactic acid and acrylic acid; their NMR shift range (4.6 ppm to 5.2 ppm and 4.15 ppm) correspond to what has been reported for oligo(lactic acid).[1] The yield of oligomer has for only purpose the calculation of the mass balance (m.b.). In the tables S1 to S11, "esters" corresponds to the sum of the lactate and 2-bromopropionate units involved in oligo(lactic acids) and co-oligomers of lactic acid and 2-bromopropionic acid and of lactic acid and acrylic acid expect **2** ($n_{esters} = n_{oligomers} - n_{\mathbf{2}}$) The mass balance is calculated using formula **(5)**

$$m.b. = \frac{n_{(lactides)} \times 2 + n_{(\boldsymbol{AA})} + n_{(\mathbf{2})} + n_{(\mathbf{3})} + n_{(\boldsymbol{2BrPA})} + n_{(\boldsymbol{3BrPA})} + n_{(\boldsymbol{LA})} + n_{(oligomers)}}{n_{i(lactide)} \times 2} \times 100 \qquad (\mathbf{5})$$

Table S0. Proton NMR signals in dmso-d6 used to calculate the yields.

	acrylate units	**AA**	**2**	**3**	rac lactide	meso lactide	oligomers	**2BrPA**	oligomers	**LA**	**3BrPA**	HOMs
ppm	5.8 – 6.5	5.86	6.35	6.37	5.44	5.35	4.6 – 5.2	4.53	4.15	4.05	3.60	2.31
number of H	3	1	1		2	2	1	1	1	1	2	3

Identification of compounds **2** and **3**

Compounds **2** and **3** are not reported in the literature and could not be isolated. However, the excellent quality of the proton NMR of the crude reaction mixtures allows peak assignment (see figure S1 and S2).

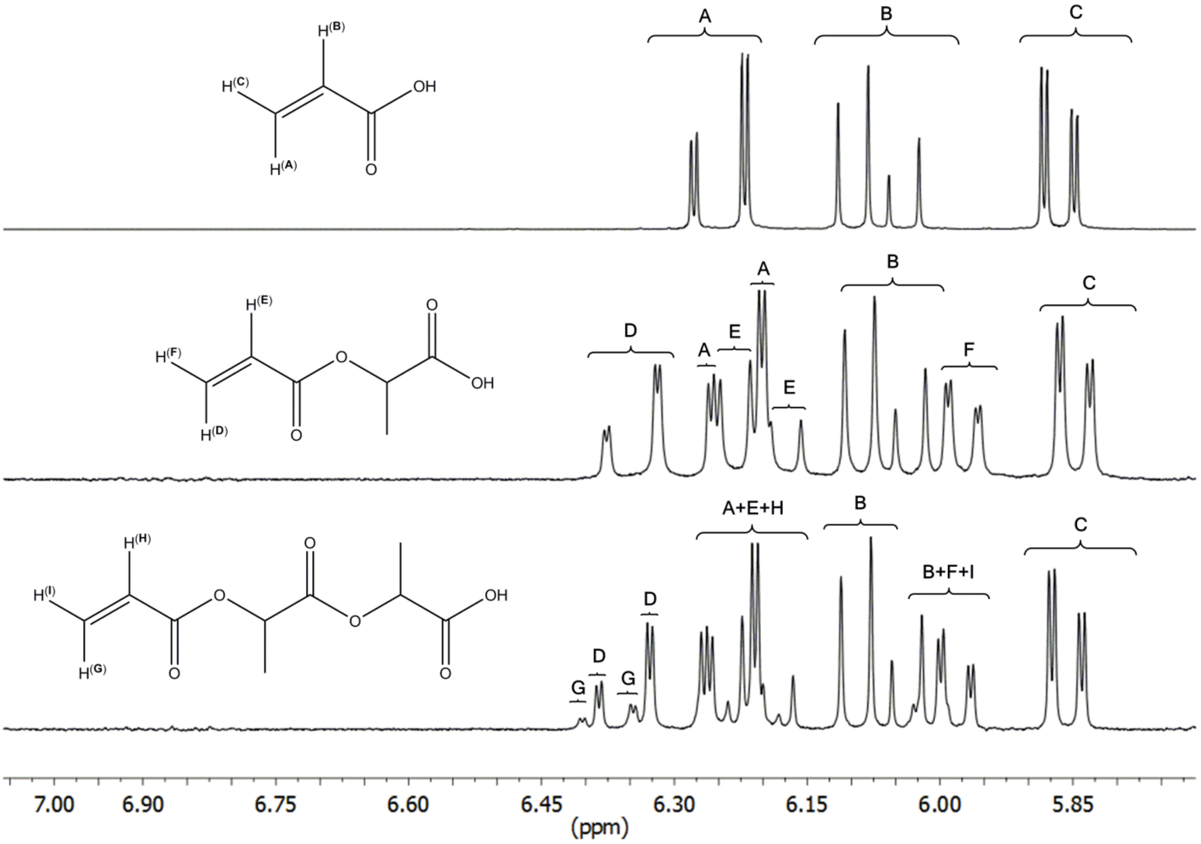


Figure S1. Proton NMR and peak assignment of (a) commercial acrylic acid, (b) the reaction mixture corresponding to the entry 5 in table 1, (c) the reaction mixture corresponding to the entry 8 in table 1.

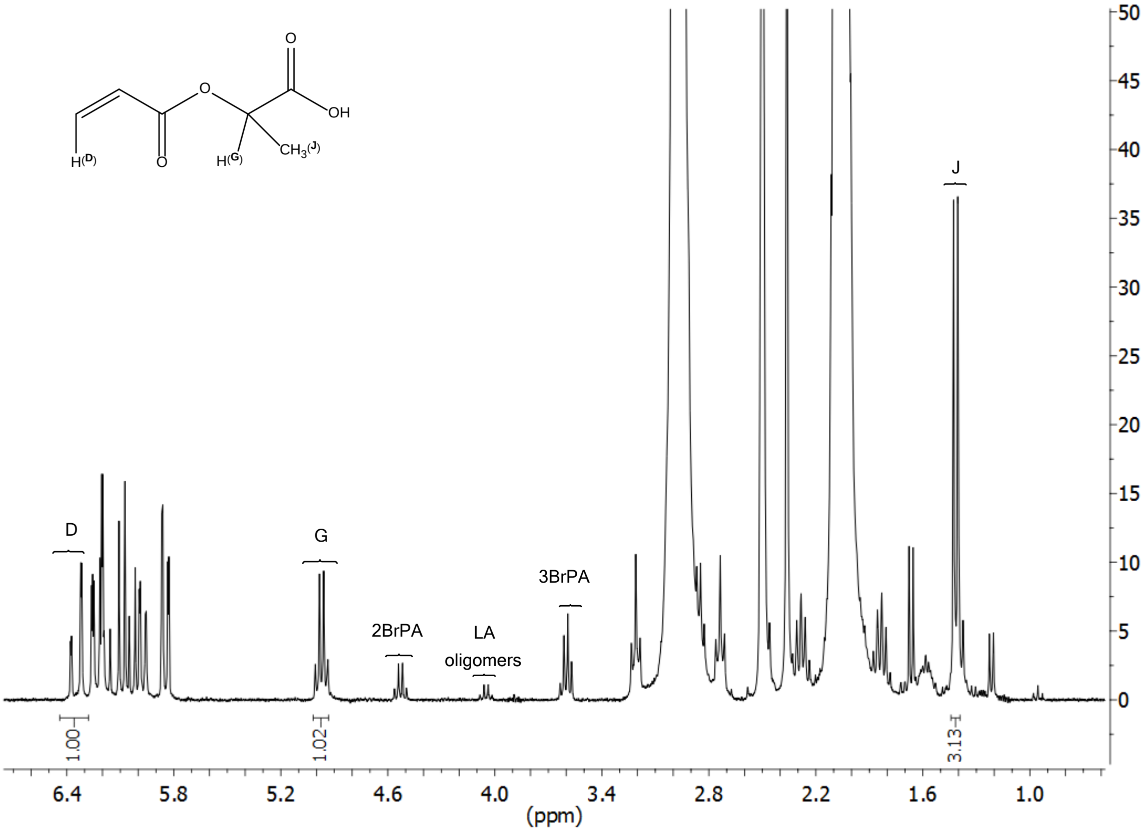


Figure S2. Proton NMR and peak assignment of the reaction mixture corresponding to the entry 5 in table 1.

2: 1H NMR (300 MHz, DMSO-d6): δ = 6.35 (proton (D), dd, 1H, $J_{D\text{-}E}$ = 17.2 Hz, $J_{D\text{-}F}$ = 1.6 Hz), 6.20 (proton (E), dd, $J_{E\text{-}D}$ = 17.2 Hz, $J_{E\text{-}F}$ = 10.2 Hz), 5.97 (proton (F), dd, 1H, $J_{F\text{-}E}$ = 10.2 Hz, $J_{F\text{-}D}$ = 1.6 Hz), 4.97 (proton (G), q, 1H, $J_{G\text{-}J}$ = 7.1 Hz), 1.42 (proton (J) d, 3H, $J_{J\text{-}G}$ = 7.1 Hz).

1) Dehydration of Lactic Acid

360 mg of **LA** (4.0 mmol), 2 g of TBAB (6.2 mmol, 1.6 eq) and optionally 152 mg of HOTs•H_2O (0.8 mmol, 0.2 eq) were introduced in the glass insert of an autoclave equipped with a stirring bar. The autoclave was closed and pressurized with 50 bars of N_2 and then heated to 130 °C (temperature of the heating mantle) for 18 h under magnetic stirring (400 rpm). Then the autoclave was placed in an ice bath for 30 min before being vented and opened.

Table S1. Dehydration of Lactic Acid in TBAB

entry	Conversion (%)	Selectivity (%)	
		AA	**2BrPA**
S1-1	24	4	25
S1-2(a)	0	0	0
S1-3(b)	19	< 1	21

(a) No TsOH•H_2O added. (b) 1 eq of water added (4 mmol, 72 µl).

2) Rearrangement of lactide: study of the influence of the acid to lactide ratio

2 mmol of (*S*,*S*)-lactide, the indicated amount of p-toluene sulfonic acid monohydrate or methanesulfonic acid and 6.2 mmol of tetrabutylammonium bromide TBAB (3.1 eq) are placed in a glass insert equipped with a stirring bar which is introduced in an autoclave. When p-toluene sulfonic acid monohydrate was used, TBAB was not dried prior to use. The autoclave is closed and pressurized with 50 bars of N_2 and then heated to 130°C (temperature of the heating mantle) for 16h under magnetic stirring (400 rpm). The autoclave was placed in an ice bath for 10 to 30 min before being vented and opened.

Table S2. Rearrangement of lactide in the presence of various amounts of HOTs

entry	n_i (mmol) / **(equivalents)**			conv.(%)	n_{final} (mmol) / **yield (%)** / *selectivity (%)*							m.b.(a)
	TBAB	HOTs	lactide		lactide	**AA**	**2**	**LA**	esters(b)	**2BrPA**	**3BrPA**	
S2-1	6.2	0.2	2.00	25	1.50	0.00	0.00	0.18	0.56	0.00	0.00	93
	(3.1)	**(0.1)**	**(1)**			**0**	**0**	**4**	**14**	**0**	**0**	
						0	*0*	*18*	*55*	*0*	*0*	
S2-2	6.2	1	2.00	93	0.14	0.08	0.26	0.38	1.85	0.21	0.04	84
	(3.1)	**(0.5)**	**(1)**			**2**	**13**	**10**	**46**	**5**	**1**	
						2	*14*	*10*	*50*	*6*	*1*	
S2-3	6.2	2	2.00	99	0.02	0.10	0.03	1.47	1.05	0.63	0.13	87
	(3.1)	**(1)**	**(1)**			**2**	**2**	**37**	**26**	**16**	**3**	
						2	*2*	*37*	*27*	*16*	*3*	
S2-4	6.2	3	2.00	100	0.00	0.05	0.00	1.84	0.39	0.85	0.12	81
	(3.1)	**(1.5)**	**(1)**			**1**	**0**	**46**	**10**	**21**	**3**	
						1	*0*	*46*	*10*	*21*	*3*	

The temperature is 130 °C, the reaction time is 16h. No special precautions were taken to exclude water as TsOH contained water (not dried prior to use) and TBAB was not dried prior to use. (a) m.b. = mass balance in %. (b) esters excluding ***2****.*

Table S3. Rearrangement of lactide in the presence of various amounts of HOMs

entry	n_i (mmol) / **(equivalents)**			conv.(%)	n_{final} (mmol) / **yield (%)** / *selectivity (%)*							m.b.(a)
	TBAB	HOMs	lactide		lactide	**AA**	**2**	**LA**	esters(b)	**2BrPA**	**3BrPA**	
S3-1	6.2	0.2	2.00	<5	2.07	0.00	0.00	0.00	0.18	0.00	0.00	108
	(3.1)	**(0.1)**	**(1)**			**0**	**0**	**0**	**5**	**0**	**0**	
						0	*0*	*0*	*100*	*0*	*0*	
S3-2	6.2	0.5	2.00	31	1.38	0.05	0.26	0.00	0.64	0.07	0.00	101
	(3.1)	**(0.25)**	**(1)**			**1**	**13**	**0**	**16**	**2**	**0**	
						4	*42*	*0*	*52*	*5*	*0*	
S3-3	6.2	1	2.00	63	0.75	0.12	0.54	0.00	0.99	0.17	0.00	96
	(3.1)	**(0.5)**	**(1)**			**3**	**27**	**0**	**25**	**4**	**0**	
						5	*43*	*0*	*39*	*7*	*0*	
S3-4	6.2	2	2.00	82	0.36	0.10	0.61	0.00	1.53	0.29	0.03	97
	(3.1)	**(1)**	**(1)**			**3**	**30**	**0**	**38**	**7**	**1**	
						3	*37*	*0*	*46*	*9*	*1*	
S3-5	6.2	3	2.00	86	0.28	0.05	0.40	0.00	1.95	0.25	0.03	92
	(3.1)	**(1.5)**	**(1)**			**1**	**20**	**0**	**49**	**6**	**1**	
						1	*24*	*0*	*57*	*7*	*1*	

*The temperature is 130°C, the reaction time is 16 h. (a) m.b. = mass balance in %. (b) esters excluding **2**.*

3) Rearrangement of lactide: study of the influence of the bromide to lactide ratio

Various amounts of of (*S*,*S*)-lactide, 1 mmol of methanesulfonic acid and 6.2 mmol of tetrabutylammonium bromide are placed in a glass insert equipped with a stirring bar which is introduced in an autoclave. The autoclave is closed and pressurized with 50 bars of N_2 and then heated to 130°C (temperature of the heating mantle) for 16h under magnetic stirring (400 rpm). The autoclave was placed in an ice bath for 10 to 30 min before being vented and opened.

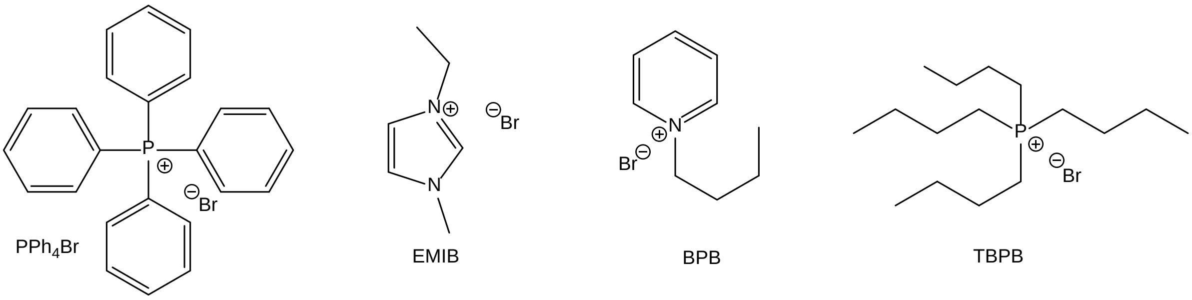
Table S4. Rearrangement of lactide with various bromide to lactide ratio

entry	n_i (mmol) / **(equivalents)**			conv.(%)	n_{final} (mmol) / **yield (%)** / *selectivity (%)*							m.b.(a)
	TBAB	HOMs	lactide		lactide	**AA**	**2**	**LA**	esters(b)	**2BrPA**	**3BrPA**	
S4-1	6.2	1.0	2.00	59	0.81	0.10	0.48	0.00	1.21	0.15	0.00	101
	(3.1)	**(0.5)**	**(1)**			**2**	**24**	**0**	**30**	**4**	**0**	
						4	*40*	*0*	*51*	*6*	*0*	
S4-2	6.2	1.0	1.24	76	0.30	0.10	0.44	0.00	0.80	0.15	0.00	102
	(5)	**(0.8)**	**(1)**			**4**	**36**	**0**	**32**	**6**	**0**	
						5	*47*	*0*	*43*	*8*	*0*	
S4-3	6.2	1.0	0.62	91	0.06	0.05	0.25	0.00	0.45	0.09	0.00	97
	(10)	**(1.6)**	**(1)**			**4**	**41**	**0**	**36**	**7**	**0**	
						4	*45*	*0*	*40*	*8*	*0*	
S4-4	6.2	1.0	0.41	93	0.03	0.04	0.17	0.00	0.32	0.07	0.00	101
	(15)	**(2.4)**	**(1)**			**5**	**42**	**0**	**39**	**8**	**0**	
						5	*45*	*0*	*41*	*9*	*0*	

*The reaction time is 16h, the temperature is 130°C, TBAB/MsOH = 6.2. (a) m.b. = mass balance in %. (b) esters excluding **2**.*

4) Rearrangement of lactide: use of various bromide sources

100 mg of (*S*,*S*)-lactide, various amount of methanesulfonic acid and various amount of bromide sources (tetraphenylphosphonium bromide (PPh_4Br), 1-ethyl-3-methylimidazolium bromide (EMIB), 1-butylpyridinium bromide (BPB), lithium bromide or tetrabutylphosphonium bromide (TBPB)) are placed in a glass insert equipped with a stirring bar which is introduced in an autoclave. Since the melting point of PPh_4Br is 295 °C, sulfolane was used as a solvent (for 1 g of PPh_4Br, 1 mL of solvent was used) when this bromide salt was employed. The autoclave is closed and pressurized with 50 bars of N_2 and then heated to 130°C (temperature of the heating mantle) for 16h under magnetic stirring (400 rpm). The autoclave was placed in an ice bath for 10 to 30 min before being vented and opened.



PPh_4Br EMIB BPB TBPB

Figure S3. Bromide sources used in this study

Table S5. Rearrangement of lactide with various bromide sources

entry	n_i (mmol) / **(equivalents)**			conv.(%)	n_{final} (mmol) / **yield (%)** / *selectivity (%)*							m.b.$^{(a)}$
	Br$^-$ source	HOMs	lactide		lactide	**AA**	**2**	**LA**	esters$^{(b)}$	**2BrPA**	**3BrPA**	
S5-01	0.69	0.23	0.69	64	0.25	0.01	0.04	0.01	0.57	0.03	0.00	87
	(1)	**(0.33)**$^{(c)}$	**(1)**			**0**	**6**	**1**	**41**	**2**	**0**	
	PPh$_4$Br					*1*	*10*	*1*	*64*	*4*	*0*	
S5-02	0.69	0.12	0.69	56	0.31	0.01	0.04	0.01	0.50	0.02	0.00	89
	(1)	**(0.17)**$^{(d)}$	**(1)**			**0**	**6**	**1**	**36**	**2**	**0**	
	PPh$_4$Br					*1*	*10*	*1*	*65*	*3*	*0*	
S5-03	3.47	1.15	0.69	91	0.06	0.03	0.15	0.15	0.67	0.13	0.03	103
	(5)	**(1.66)**$^{(c)}$	**(1)**			**2**	**21**	**11**	**48**	**9**	**2**	
	PPh$_4$Br					*2*	*23*	*12*	*53*	*10*	*2*	
S5-04	3.47	0.58	0.69	85	0.10	0.03	0.12	0.10	0.63	0.10	0.01	95
	(5)	**(0.83)**$^{(d)}$	**(1)**			**2**	**18**	**7**	**45**	**7**	**1**	
	PPh$_4$Br					*3*	*21*	*8*	*53*	*8*	*1*	
S5-05	3.47	1.17	0.35	95	0.02	0.01	0.03	0.13	0.32	0.07	0.02	92
	(10)	**(3.36)**$^{(c)}$	**(1)**			**2**	**8**	**19**	**46**	**10**	**2**	
	PPh$_4$Br					*2*	*8*	*20*	*48*	*11*	*2*	
S5-06	3.47	0.58	0.35	94	0.02	0.02	0.04	0.13	0.35	0.05	0.01	98
	(10)	**(1.68)**$^{(d)}$	**(1)**			**2**	**11**	**19**	**51**	**7**	**1**	
	PPh$_4$Br					*2*	*12*	*21*	*54*	*8*	*1*	
S5-07	1.39	0.46	1.39	60	0.55	0.01	0.09	0.00	1.30	0.05	0.00	95
	(1)	**(0.33)**$^{(c)}$	**(1)**			**0**	**7**	**0**	**47**	**2**	**0**	
	EMIB					*1*	*11*	*0*	*77*	*3*	*0*	
S5-08	1.39	0.23	1.39	43	0.79	0.01	0.08	0.00	1.01	0.02	0.00	100
	(1)	**(0.17)**$^{(d)}$	**(1)**			**0**	**6**	**0**	**36**	**1**	**0**	
	EMIB					*1*	*13*	*0*	*85*	*2*	*0*	
S5-09	6.94	2.31	1.39	100	0.01	0.13	0.21	0.00	1.18	0.36	0.10	80
	(5)	**(1.66)**$^{(c)}$	**(1)**			**5**	**15**	**0**	**43**	**13**	**4**	
	EMIB					*5*	*15*	*0*	*43*	*13*	*4*	
S5-10	6.94	1.16	1.39	98	0.02	0.16	0.32	0.00	1.15	0.24	0.03	82
	(5)	**(0.83)**$^{(d)}$	**(1)**			**6**	**23**	**0**	**41**	**8**	**1**	
	EMIB					*6*	*24*	*0*	*42*	*9*	*1*	
S5-11	13.88	4.63	1.39	100	0.00	0.11	0.08	0.00	0.96	0.63	0.26	76
	(10)	**(3.36)**$^{(c)}$	**(1)**			**4**	**6**	**0**	**35**	**23**	**9**	
	EMIB					*4*	*6*	*0*	*35*	*23*	*9*	
S5-12	13.88	2.31	1.39	98	0.02	0.16	0.21	0.00	1.06	0.32	0.11	76
	(10)	**(1.68)**$^{(d)}$	**(1)**			**6**	**15**	**0**	**38**	**12**	**4**	
	EMIB					*6*	*16*	*0*	*39*	*12*	*4*	
S5-13	0.69	0.12	0.69	41	0.41	0.01	0.05	0.00	0.48	0.00	0.00	101
	(1)	**(0.17)**$^{(d)}$	**(1)**			**1**	**7**	**0**	**35**	**0**	**0**	
	BPB					*2*	*17*	*0*	*85*	*0*	*0*	
S5-14	3.45	0.58	0.69	93	0.05	0.11	0.21	0.00	0.30	0.00	0.00	68
	(5)	**(0.83)**$^{(d)}$	**(1)**			**8**	**31**	**0**	**22**	**0**	**0**	
	BPB					*8*	*33*	*0*	*24*	*0*	*0*	
S5-15	3.5	0.58	0.69	95	0.03	0.07	0.16	0.00	0.51	0.00	0.00	70
	(10)	**(1.68)**$^{(d)}$	**(1)**			**5**	**23**	**0**	**37**	**0**	**0**	
	BPB					*6*	*24*	*0*	*39*	*0*	*0*	
S5-16	0.69	0.12	0.69	45	0.38	0.00	0.02	0.00	0.41	0.01	0.00	88
	(1)	**(0.17)**$^{(d)}$	**(1)**			**0**	**2**	**0**	**30**	**1**	**0**	
	TBPB					*0*	*6*	*0*	*67*	*2*	*0*	
S5-17	3.45	0.58	0.69	79	0.15	0.02	0.16	0.00	0.55	0.11	0.01	95
	(5)	**(0.83)**$^{(d)}$	**(1)**			**2**	**24**	**0**	**40**	**8**	**1**	
	TBPB					*2*	*30*	*0*	*51*	*10*	*1*	
S5-18	3.5	0.58	0.69	92	0.06	0.02	0.18	0.00	0.38	0.16	0.03	76
	(10)	**(1.68)**$^{(d)}$	**(1)**			**1**	**25**	**0**	**27**	**12**	**2**	
	TBPB					*1*	*28*	*0*	*30*	*13*	*2*	

The reaction time is 16h, the temperature is 130°C. When PPh$_4$ is the bromide source, sulfolane is used as a solvent (1 mL of sulfolane per g of PPh$_4$Br). (a) m.b. = mass balance in %. (b) esters excluding ***2****. (c) bromide source/HOMs = 0.6. (d) bromide source / HOMs = 0.3*

5) <u>Rearrangement of lactide: use of various acid catalysts</u>

0.69 mmol of (*S*,*S*)-lactide, the indicated acid in the indicated amount, 3.47 mmol of tetrabutylphosphonium bromide (5 eq) and 1.5 mL of sulfolane are placed in a glass insert equipped with a stirring bar which is introduced in an autoclave. The autoclave is closed and pressurized with 50 bars of N_2 and then heated to 150°C (temperature of the heating mantle) for 16h under magnetic stirring (400 rpm). The autoclave was placed in an ice bath for 10 to 30 min before being vented and opened. Then 0.58 mmol of methanesulfonic acid was added as an NMR internal standard.

Table S6. Rearrangement of lactide: use of various acid catalysts

entry	n_i (mmol) / **(equivalents)**			conv.(%)	n_{final} (mmol) / **yield (%)** / *selectivity (%)*							m.b.[(a)]
	PPh_4Br	acid	lactide		lactide	**AA**	**2**	**LA**	esters[(b)]	**2BrPA**	**3BrPA**	
S5-03	3.47	1.15	0.69	91	0.06	0.03	0.15	0.15	0.67	0.13	0.03	103
	(5)	**(1.66)**	**(1)**			**2**	**21**	**11**	**48**	**9**	**2**	
		HOMs				*2*	*23*	*12*	*53*	*10*	*2*	
S5-04	3.47	0.58	0.69	85	0.10	0.03	0.12	0.10	0.63	0.10	0.01	95
	(5)	**(0.83)**	**(1)**			**2**	**18**	**7**	**45**	**7**	**1**	
		HOMs				*3*	*21*	*8*	*53*	*8*	*1*	
S6-1	3.47	0.07	0.69	18	0.57	0.00	0.00	0.00	0.00	0.00	0.00	82
	(5)	**(0.1)**	**(1)**			**0**	**0**	**0**	**0**	**0**	**0**	
		TFA				*0*	*0*	*0*	*0*	*0*	*0*	
S6-2	3.47	0.35	0.69	54	0.32	0.08	0.11	0.00	0.12	0.00	0.00	75
	(5)	**(0.5)**	**(1)**			**5**	**16**	**0**	**8**	**0**	**0**	
		TFA				*10*	*29*	*0*	*15*	*0*	*0*	
S6-3	3.47	0.69	0.69	78	0.15	0.14	0.20	0.00	0.24	0.04	0.00	80
	(5)	**(1)**	**(1)**			**10**	**29**	**0**	**17**	**3**	**0**	
		TFA				*13*	*37*	*0*	*22*	*4*	*0*	
S6-4	3.47	0.35	0.69	61	0.27	0.00	0.00	0.14	0.51	0.00	0.00	85
	(5)	**(0.5)**	**(1)**			**0**	**0**	**10**	**37**	**0**	**0**	
		oxalic				*0*	*0*	*16*	*60*	*0*	*0*	
S6-5	3.45	0.69	0.69	76	0.17	0.00	0.00	0.29	0.57	0.00	0.00	86
	(5)	**(1)**	**(1)**			**0**	**0**	**21**	**41**	**0**	**0**	
		oxalic				*0*	*0*	*28*	*54*	*0*	*0*	
S6-6	3.47	0.35	0.69	66	0.23	0.15	0.23	0.00	0.10	0.11	0.00	93
	(5)	**(0.5)**	**(1)**			**11**	**33**	**0**	**7**	**8**	**0**	
		HPO3				*16*	*50*	*0*	*11*	*12*	*0*	
S6-7	3.47	0.69	0.69	97	0.02	0.32	0.34	0.00	0.02	0.10	0.03	85
	(5)	**(1)**	**(1)**			**23**	**49**	**0**	**1**	**7**	**2**	
		HPO3				*24*	*50*	*0*	*1*	*7*	*2*	
S6-8	3.47	0.35	0.69	32	0.47	0.00	0.00	0.04	0.14	0.00	0.00	81
	(5)	**(0.5)**	**(1)**			**0**	**0**	**3**	**10**	**0**	**0**	
		acetic				*0*	*0*	*9*	*31*	*0*	*0*	
S6-9	3.47	0.69	0.69	32	0.47	0.00	0.00	0.03	0.14	0.00	0.00	80
	(5)	**(1)**	**(1)**			**0**	**0**	**2**	**10**	**0**	**0**	
		acetic				*0*	*0*	*7*	*31*	*0*	*0*	

*The temperature is 150°C, the reaction time is 16h, bromide source/lactide = 5, PPh_4Br is the bromide source, sulfolane is used as solvent (1 mL of sulfolane per g of PPh_4Br). (a) m.b. = mass balance in %. (b) esters excluding **2**.*

6) Rearrangement of lactide at various temperatures

0.69 mmol of (*S,S*)-lactide, 0.58 mmol of methanesulfonic acid (0.83 eq), 3.47 mmol of tetraphenylphosphonium bromide (5 eq) and 1.5 mL of sulfolane are introduced in the glass insert of an autoclave equipped with a stirring bar. The autoclave is closed and pressurized with 50 bars of N_2 and then heated to the indicated temperature for 16h under magnetic stirring (400 rpm). Then the autoclave was placed in an ice bath for 30 min before being vented and opened.

Table S7. Rearrangement of lactide at various temperatures

entry	T (°C)	n_i (mmol) / **(equivalents)**			conv. (%)	n_{final} (mmol) / **yield (%)** / *selectivity (%)*							m.b.[a]
		bromide source	HOMs	lactide		lactide	**AA**	**2**	**LA**	esters [b]	**2Br PA**	**3Br PA**	
S5-4	130	3.47	0.58	0.69	85	0.10	0.03	0.12	0.10	0.63	0.10	0.01	95
		(5)	**(0.83)**	**(1)**			**2**	**18**	**7**	**45**	**7**	**1**	
		PPh_4Br					*3*	*21*	*8*	*53*	*8*	*1*	
S7-1	150	3.47	0.58	0.69	100	0.00	0.44	0.31	0.00	0.06	0.08	0.09	93
		(5)	**(0.83)**	**(1)**			**32**	**44**	**0**	**4**	**6**	**7**	
		PPh_4Br					*32*	*44*	*0*	*4*	*6*	*7*	
S7-2	175	3.47	0.58	0.69	100	0.00	0.72	0.02	0.00	0.00	0.00	0.06	59
		(5)	**(0.83)**	**(1)**			**52**	**3**	**0**	**0**	**0**	**4**	
		PPh_4Br					*52*	*3*	*0*	*0*	*0*	*4*	
S7-3	200	3.47	0.58	0.69	100	0.00	0.03	0.00	0.00	0.00	0.00	0.00	2
		(5)	**(0.83)**	**(1)**			**2**	**0**	**0**	**0**	**0**	**0**	
		PPh_4Br					*2*	*0*	*0*	*0*	*0*	*0*	
S7-4	150	6.90	1.15	1.39	100	0.00	0.50	0.61	0.00	0.61	0.22	0.02	92
		(5)	**(0.83)**	**(1)**			**18**	**44**	**0**	**22**	**8**	**1**	
		TBAB					*18*	*44*	*0*	*22*	*8*	*1*	
S7-5	175	6.90	1.15	1.39	100	0.00	0.87	0.20	0.00	0.13	0.07	0.15	58
		(5)	**(0.83)**	**(1)**			**31**	**14**	**0**	**5**	**2**	**5**	
		TBAB					*31*	*14*	*0*	*5*	*2*	*5*	
S7-6	200	6.90	1.15	1.39	100	0.00	0.78	0.00	0.00	0.00	0.00	0.12	32
		(5)	**(0.83)**	**(1)**			**28**	**0**	**0**	**0**	**0**	**4**	
		TBAB					*28*	*0*	*0*	*0*	*0*	*4*	

*The reaction time is 16h, bromide source/lactide = 5. When PPh_4Br is the bromide source, sulfolane is used as solvent (1 mL of sulfolane per g of PPh_4). (a) m.b. = mass balance in %. (b) esters excluding **2**.*

7) Rearrangement of lactide at 175 °C for various reaction times

0.69 mmol of (*S,S*)-lactide, 0.58 mmol of methanesulfonic acid (0.83 eq), 3.47 mmol of tetraphenylphosphonium bromide (5 eq) and 1.5 mL of sulfolane are introduced in the glass insert of an autoclave equipped with a stirring bar. The autoclave is closed and pressurized with 50 bars of N_2 and then heated at 175°C for the indicated time under magnetic stirring (400 rpm). Then the autoclave was placed in an ice bath for 30 min before being vented and opened.

Table S8. Rearrangement of lactide at 175 °C for various reaction times

entry	t (h)	n_i (mmol) / **(equivalents)**			conv. (%)	n_{final} (mmol) / **yield (%)** / *selectivity (%)*(e)						m.b.(a)
		PPh_4Br	HOMs	lactide		lactide	**AA**	**2**	esters(b)	**2BrPA**	**3BrPA**	
S8-1	1	3.47	0.58	0.69	83	0.12	0.13	0.28	0.28	0.16	0.02	100
		(5)	**(0.83)**	**(1)**			**10**	**40**	**20**	**11**	**1**	
							12	*49*	*24*	*14*	*2*	
S8-2	2	3.47	0.58	0.69	94	0.04	0.24	0.32	0.20	0.14	0.03	97
		(5)	**(0.83)**	**(1)**			**17**	**47**	**15**	**10**	**2**	
							18	*50*	*16*	*10*	*3*	
S8-3	4	3.47	0.58	0.69	100	0.00	0.59	0.28	0.03	0.08	0.08	96
		(5)	**(0.83)**	**(1)**			**42**	**40**	**2**	**6**	**6**	
							42	*40*	*2*	*6*	*6*	
S8-4	6	3.47	0.58	0.69	100	0.00	0.64	0.24	0.03	0.05	0.09	93
		(5)	**(0.83)**	**(1)**			**46**	**35**	**2**	**4**	**7**	
							46	*35*	*2*	*4*	*7*	
S8-5	8	3.45	0.58	0.69	100	0.00	0.75	0.10	0.00	0.03	0.08	76
		(5)	**(0.83)**	**(1)**			**54**	**15**	**0**	**2**	**6**	
							54	*15*	*0*	*2*	*6*	
S8-6	10	3.47	0.58	0.69	100	0.00	0.80	0.08	0.03	0.00	0.07	76
		(5)	**(0.83)**	**(1)**			**58**	**12**	**2**	**0**	**5**	
							58	*12*	*2*	*0*	*5*	
S7-2	16	3.47	0.58	0.69	100	0.00	0.72	0.02	0.00	0.00	0.00	59
		(5)	**(0.83)**	**(1)**			**52**	**3**	**0**	**0**	**0**	
							52	*3*	*0*	*0*	*0*	

The reaction temperature is 175°C, $PPh_4Br/MsOH$ = 6, PPh_4Br/lactide = 5. Sulfolane is used as solvent (1 mL of sulfolane per g of PPh_4). (a) m.b. = mass balance in %. (b) esters excluding ***2*** *(e) No lactic acid was detected in the products.*

8) Rearrangement of lactide in the presence of tetraphenylphosphonium chloride

The reaction corresponding to table S7 (150 °C) was repeated with tetraphenylphosphonium chloride (PPh_4Cl) and mixtures of PPh_4Cl and PPh_4Br instead of pure PPh_4Br. The ratio halide / lactide was kept at 5.

Table S9. Rearrangement of lactide in the presence of tetraphenylphosphonium chloride and mixtures of tetraphenylphosphonium chloride and bromide

		n_i (mmol) / **(equivalents)**					n_{final} (mmol) / **yield (%)** / *selectivity (%)*								
entry	Cl:Br	PPh_4Cl	PPh_4Br	HOMs	lactide	conv.(%)	lactide	**AA**	**2**	**LA**	esters(b)	**2BrPA**	**2ClPA**	**3BrPA**	m.b.(a)
S9-1	1:99	0.03	3.44	0.58	0.69	100	0.00	0.42	0.30	0.00	0.06	0.08	0.00	0.06	88
		(0.05)	**(4.95)**	**(0.83)**	**(1)**			**30**	**43**	**0**	**5**	**6**	**0**	**5**	
								30	*43*	*0*	*5*	*6*	*0*	*5*	
S9-2	5:95	0.17	3.30	0.58	0.69	98	0.02	0.30	0.26	0.00	0.20	0.07	0.07	0.02	83
		(0.25)	**(4.75)**	**(0.83)**	**(1)**			**21**	**38**	**0**	**14**	**5**	**5**	**2**	
								22	*39*	*0*	*15*	*5*	*5*	*2*	
S9-3	10:90	0.35	3.13	0.58	0.69	96	0.02	0.28	0.26	0.00	0.13	0.05	0.12	0.03	77
		(0.5)	**(4.5)**	**(0.83)**	**(1)**			**20**	**38**	**0**	**10**	**4**	**8**	**2**	
								21	*40*	*0*	*10*	*4*	*9*	*2*	
S9-4	25:75	0.87	2.60	0.58	0.69	93	0.05	0.22	0.18	0.00	0.23	0.00	0.26	0.02	66
		(1.25)	**(3.75)**	**(0.83)**	**(1)**			**16**	**26**	**0**	**16**	**0**	**19**	**1**	
								17	*28*	*0*	*18*	*0*	*21*	*1*	
S9-5	50:50	1.74	1.74	0.58	0.69	90	0.07	0.13	0.13	0.00	0.25	0.00	0.30	0.00	55
		(2.5)	**(2.5)**	**(0.83)**	**(1)**			**9**	**18**	**0**	**18**	**0**	**22**	**0**	
								10	*20*	*0*	*20*	*0*	*24*	*0*	
S9-6	100:0	3.47	0	0.58	0.69	86	0.09	0.13	0.17	0.00	0.36	0.00	0.32	0.00	74
		(5)	**(0)**	**(0.83)**	**(1)**			**9**	**25**	**0**	**26**	**0**	**23**	**0**	
								11	*29*	*0*	*30*	*0*	*26*	*0*	

*The reaction time is 16h, the temperature is 150°C, (chloride + bromide)/MsOH = 6, (chloride + bromide)/lactide = 5, 1.5 mL of sulfolane was used as a solvent for every reaction. (a) m.b. = mass balance in %. (b) esters excluding **2**.*

9) Use 2-Bromopropionic Acid or 3-Bromopropionic Acid as HBr source

0.69 mmol of (*S*,*S*)-lactide, the indicated acid in the indicated amount, 3.47 mmol of tetrabutylphosphonium bromide (5 eq) and 1.5 mL of sulfolane are placed in a glass insert equipped with a stirring bar which is introduced in an autoclave. The autoclave is closed and pressurized with 50 bars of N_2 and then heated to 150°C (temperature of the heating mantle) for 16h under magnetic stirring (400 rpm). The autoclave was placed in an ice bath for 10 to 30 min before being vented and opened. Then 0.58 mmol of methanesulfonic acid was added as an NMR internal standard.

Table S10. Rearrangement of lactide in the presence of tetraphenylphosphonium bromide and bromopropionic acid (without sulfonic acid added).

entry	n_i (mmol) / **(equivalents)**			conv. (%)	n_{final} (mmol) / **yield (%)** / *selectivity (%)*						m.b.[(a)]
	PPh_4Br	BrPA	lactide		lactide	**AA**	**2**	esters[(b)]	**2BrPA**	**3BrPA**	
S10-1	3.47	0.07	0.69	61	0.28	0.15	0.17	0.22	0.04	0.00	91
	(5)	**(0.1)**	**(1)**			**10**	**24**	**15**	**3**	**0**	
		2BrPA				*16*	*39*	*25*	*4*	*1*	
S10-2	3.47	0.35	0.69	100	0.00	0.54	0.31	0.13	0.10	0.18	90
	(5)	**(0.5)**	**(1)**			**31**	**35**	**7**	**6**	**10**	
		2BrPA				*31*	*35*	*7*	*6*	*10*	
S10-3	3.47	0.69	0.69	100	0.00	0.56	0.29	0.19	0.21	0.39	93
	(5)	**(1)**	**(1)**			**27**	**28**	**9**	**10**	**19**	
		2BrPA				*27*	*28*	*9*	*10*	*19*	
S10-4	3.47	0.35	0.69	100	0.00	0.62	0.31	0.11	0.11	0.18	94
	(5)	**(0.5)**	**(1)**			**35**	**35**	**6**	**6**	**10**	
		3BrPA				*35*	*35*	*6*	*6*	*10*	
S10-5	3.47	0.69	0.69	100	0.00	0.81	0.22	0.15	0.12	0.43	94
	(5)	**(1)**	**(1)**			**39**	**21**	**7**	**6**	**21**	
		3BrPA				*39*	*21*	*7*	*6*	*21*	

*The temperature is 150°C, the reaction time is 16h, $BrPPh_4$ source/lactide = 5. (a) m.b. = mass balance in %. (b) esters excluding **2**.*

For this particular experiment, the yield was calculated according to equations **(6)** and **(7)**:

For compound **2**:

$$yield = \frac{n_{(2)} \times 2}{\left(n_{i(lactide)} \times 2\right) + n_{i(\boldsymbol{BrPA})}} \times 100 \quad (\mathbf{6})$$

For the other compounds:

$$yield = \frac{n_{(species)}}{\left(n_{i(lactide)} \times 2\right) + n_{i(\boldsymbol{BrPA})}} \times 100 \quad (\mathbf{7})$$

$$m.b. = \frac{n_{(lactides)} \times 2 + n_{(\boldsymbol{AA})} + n_{(\mathbf{2})} + n_{(3)} + n_{(\boldsymbol{2BrPA})} + n_{(\boldsymbol{3BrPA})} + n_{(\boldsymbol{LA})} + n_{(oligomers)}}{\left(n_{i(lactide)} \times 2\right) + n_{i(\boldsymbol{BrPA})}} \times 100 \quad (\mathbf{8})$$

With $n_{i(BrPA)}$ the quantity of **2BrPA** or **3BrPA** introduced in the beginning of the reaction.

The conversion corresponds to the conversion of lactide only.

10) <u>Poly(lactic acid) (PLA) and oligo(lactic acid) as substrates</u>

The various substrates were processed as follows: 100 mg of substrate, 0.58 mmol of methane sulfonic acid, 3.47 mmol of tetraphenylphosphonium bromide and 1.5 ml of sulfolane were placed in a glass jar inset equipped with a stirring bar which was introduced in an autoclave. The autoclave was closed and pressurized with 50 bar N2, and heated using a heating mantle under stirring to a temperature of 150ºC for 16 hours reaction time. When the reaction was completed, the autoclave was placed in an ice bath for 30 minutes, before being vented and opened.

Table S11. Rearrangement of oligo and poly(lactic acid) in the presence of tetraphenylphosphonium bromide and methyl sulfonic acid. For clarity, the yield is given in mg.

entry	n_i (mmol) / **mass (mg)**			n_{final} (mmol) / **yield (mg)** / *selectivity (%)*							m.b.(a)(h)
	PPh_4Br	HOMs	substrate	**AA**	**2**	**3**	**LA**	esters(b)	**2BrPA**	**3BrPA**	
S11-1	3.47	0.58	0.68(f)	0.31	0.18	0.05	0.10	0.08	0.10	0.06	87
			100	**23**	**27**	**11**					
			Oligo(lactic acid)	*23*	*27*	*11*	*7*	*6*	*7*	*4*	
S11-2	3.47	0.58	0.69(f)	0.33	0.18	0.07	0.07	0.11	0.11	0.06	93
			100	**24**	**26**	**16**					
			Bulk PLA	*24*	*27*	*16*	*5*	*8*	*8*	*5*	
S11-3	3.47	0.58	0.46(f)	0.22	0.12	0.05	0.02	0.06	0.06	0.04	86
			67	**16**	**17**	**10**					
			Recycled PLA(g)	*25*	*13*	*5*	*3*	*6*	*6*	*5*	

The temperature is 150°C, the reaction time is 16h, (a) m.b. = mass balance in %. (b) Esters excluding ***2****. (f) Amount of lactide corresponding to the given amount of PLA or oligo(lactic acid) (g) 100 mg of a piece of cutlery containing 67% PLA and 33% of an inert filler was used. The composition of the material was estimated by NMR after hydrolysis in basic conditions.(h) Unconverted starting material cannot be detected by NMR (insolubly of* ***PLA*** *of high molecular mass): a conversion cannot be given and the remaining starting material (if any) cannot be included in the mass balance (explaining the relatively low mass balance for S11-1 and S11-3). PLA and oligo(lactic acid) used in this experiment were not dried prior to use; this explains the formation of* ***LA*** *and can partially explain the relatively low mass balance.*

1. Espartero, J. L.; Rashkov, I.; Li, S. M.; Manolova, N.; Vert, M., NMR Analysis of Low Molecular Weight Poly(lactic acid)s. *Macromolecules* **1996,** *29* (10), 3535-3539.