**Supplementary Information**

**Lactide-valerolactone copolymers for packaging applications**

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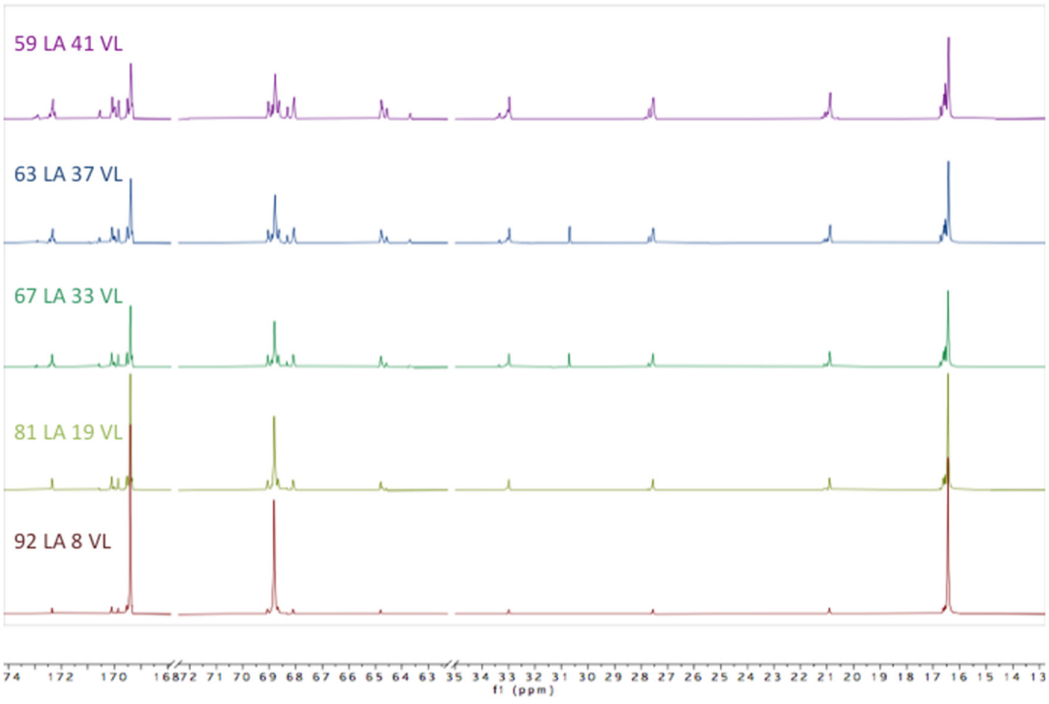



**Figure S1. $^{13}$C NMR of lactide-valerolactone copolymers.**

**Note S1. Estimation of the Monomer Reactivity Ratios**

The reactivity ratios were estimated employing the evolution of the individual comonomer conversion over overall conversion employing the nonlinear method developed by de la Cal et al. [1].

The model is briefly described below, where lactide is denoted as LA and valerolactone as VL. The equations corresponding to LA conversion ($x_{LA}$) and overall conversion ($X_T$) are, in a batch reaction:

$$x_{LA} = \frac{[LA]_0 - [LA]}{[LA]_0} \quad \text{(S1)}$$

$$X_T = \frac{([LA]_0-[LA])+([VL]_0-[VL])}{[LA]_0+[VL]_0} \quad \text{(S2)}$$

where $[LA]_0$ and $[VL]_0$ are the initial concentration of LA and VL, respectively. Therefore;

$$dx_{LA} = -\frac{d[LA]}{[LA]_0} \quad \text{(S3)}$$

$$dX_T = \frac{-d[LA]-d[VL]}{[LA]_0+[VL]_0} \quad \text{(S4)}$$

$$\frac{dx_{LA}}{dX_T} = \frac{[LA]_0+[VL]_0}{[LA]_0}\frac{d[LA]}{d[LA]+d[VL]} \quad \text{(S5)}$$

Ring opening copolymerization of LA and VL is a chain polymerization thus, the *copolymer composition equation* [2,3] holds for this system:

$$\frac{d[LA]}{d[LA]+d[VL]} = \left(\frac{1+r_{LA}\frac{[LA]}{[VL]}}{2+r_{LA}\frac{[LA]}{[VL]}+r_{VL}\frac{[VL]}{[LA]}}\right) \quad \text{(S6)}$$

where $r_{LA}$ and $r_{VL}$ are the reactivity ratios of LA and VL that are defined as,

$$r_{LA} = \frac{k_{pLALA}}{k_{pLAVL}} \quad \text{(S7)}$$

$$r_{VL} = \frac{k_{pVLVL}}{k_{pVLLA}} \quad \text{(S8)}$$

If Eq. S6 is replaced in Eq. S5 it gives:

$$\frac{dx_{LA}}{dX_T} = \frac{[LA]_0+[CL]_0}{[LA]_0}\left(\frac{1+r_{LA}\frac{[LA]}{[CL]}}{2+r_{LA}\frac{[LA]}{[CL]}+r_{CL}\frac{[CL]}{[LA]}}\right) \quad \text{(S9)}$$

Employing Equations S1 and S2, the ratio of monomer concentrations can be defined as a function of $x_{LA}$ and $X_T$:

$$\frac{[LA]}{[VL]} = \frac{[LA]_0(1-X_{LA})}{[B]_0-X_T([LA]_0+[VL]_0)+[LA]_0x_{LA}} \quad \text{(S10)}$$

If Equation S10 is replaced in Equarion S9, lactide conversion can be integrated over the overall conversion. On the other hand, the cumulative composition can be described as a function of the individual conversion of LA, $x_{LA}$, and the overall conversion:

$$Y_{LA} = \frac{[LA]_0x_{LA}}{([LA]_0+[VL]_0)X_T} \quad \text{(S11)}$$

In order to calculate the reactivity ratios $r_{LA}$ and $r_{VL}$ a parameter estimation algorithm is employed that minimizes the objective function of Equation S12, $H$, where $Y_{LAexp}$ is the cumulative composition refereed to LA determined by $^1$H NMR experimentally and $Y_{LAcal}$ is the cumulative composition calculated theoretically employing Equations S9-S11 and the initial monomer concentration. Subscripts $i$ and $j$ refer to the experiment and to the sample number of each experiments used in the estimation procedure. The only parameters of the model are the reactivity ratios.

$$H = \left[\sum_{i=1}^{N}\sum_{j=1}^{Pi}\left(Y_{LAexp} - Y_{LAcal}\right)^2\right] \quad \text{(S12)}$$

The model algorithm was coded in Matlab using ODE45 solver to solve ordinary differential equations and LSQNONLIN for nonlinear data fitting.

**Table S1.** Microstructure parameter of lactide-valerolactone copolymers.

| VL % in the copolymer | $l_{LA}$ | $l_{VL}$ | $R$ |
|---|---|---|---|
| 8 | 12.27 | 1.12 | 0.97 |
| 19 | 4.81 | 1.15 | 1.07 |
| 33 | 2.44 | 1.21 | 1.24 |
| 37 | 2.10 | 1.24 | 1.28 |
| 41 | 1.82 | 1.27 | 1.34 |

**Table S2**. Thermal degradation of lactide-valerolactone copolymers: $T_{5\%}$, temperature at which 5 % of weight is lost, and $T_{50\%}$, temperature at which 50 % of weight is lost.

| VL % in the copolymer | $T_{5\%}$ (ºC) | $T_{50\%}$ (ºC) |
|---|---|---|
| 8 | 214.3 | 267.1 |
| 19 | 218.2 | 330.0 |
| 33 | 214.4 | 324.5 |
| 37 | 213.4 | 323.0 |
| 41 | 224.6 | 345.4 |

**Table S3**. Mechanical properties of lactide-valerolactone copolymers.

| Sample | Tensile strength (MPa) | Young modulus (MPa) | Elongation at break (%) |
|---|---|---|---|
| PLLA | 54.2 ± 4.0* | 3390 ± 470 | 3.8 ± 0.8 |
| 8 VL | 6.9 ± 2.5* | 2050 ± 400 | 1.1 ± 0.4 |
| 19 VL | 10.3 ± 1.4* | 3020 ± 340 | 23.4 ± 4.8 |
| | 48.5 ± 6.2** | | |
| 33 VL | 19.4 ± 3.9* | 1150 ± 200 | 85.4 ± 13.2 |
| | 18.8 ± 4.1** | | |
| 37 VL | 10.9 ± 1.5* | 310 ± 60 | 210 ± 36 |
| 41 VL | 0.73 ± 0.1* | 4.3 ± 0.8 | 1800 ± 40 |

* Corresponds to ultimate stress

** Corresponds to yield stress

**Table S4**. Water vapour transmission rate and oxygen permeability of lactide-valerolactone copolymers.

| Sample | *WVTR* (g mm $m^{-2}$ $day^{-1}$) | *P* $O_2$ (Barrer) |
|---|---|---|
| 8 VL | 6.80 ± 0.85 | 0.26 ± 0.02 |
| 19 VL | 5.39 ± 0.67 | 0.19 ± 0.01 |
| 33 VL | 7.89 ± 0.93 | 0.22 ± 0.02 |
| 37 VL | 9.80 ± 0.64 | 0.28 ± 0.02 |
| 41 VL | 11.54 ± 0.65 | 0.43 ± 0.06 |