

## Supporting Information

### **Organocatalytic sequential ring-opening polymerization of a cyclic ester and anionic polymerization of a vinyl monomer**

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## EXPERIMENTAL SECTION

**General Considerations and Materials.** All operations were performed under dry argon using standard Schlenk techniques and glove box.  $\epsilon$ -decalactone (Aldrich,  $\geq 99\%$ ) and methyl methacrylate (Fischer Chemical,  $\geq 99.5\%$ ) were dried over  $\text{CaH}_2$ , then distilled under inert atmosphere and stored in the glove box. Benzyl alcohol (Aldrich,  $+99\%$ ) was at first distilled under reduced pressure, then dried over  $\text{CaH}_2$ , distilled under inert atmosphere and stored in the glove box. Phosphazene base  $t\text{-BuP}_4$  (0.8 M in hexane) was purchased from Sigma Aldrich, stored in the glove box and used as received. THF was purified through the alumina column (MBraun SPS) and stored in the glove box. Benzamide (Aldrich, 95%) was recrystallized from hot ethanol, dried *in vacuo* and stored in the glove box. Pentylamine (Fluka,  $>98\%$ ) was dried with NaOH pellets and then distilled under an inert atmosphere.

**Characterization.**  $^1\text{H}$  NMR spectra were recorded on an AC 300 Bruker spectrometer at room temperature in  $\text{CDCl}_3$ . Approximately 5 mg of sample was directly dissolved into the NMR tube in 0.6 mL of  $\text{CDCl}_3$ . The chemical shifts were calibrated using the residual resonances of the solvent.

Size exclusion chromatography (SEC) was performed at  $40^\circ\text{C}$  in THF at an elution rate of  $1 \text{ ml}\cdot\text{min}^{-1}$  using an Alliance pump and passer system from Waters, a refractive index (RI) detector T-rEX from Wyatt and MALLS (LS) detector miniDAWN TREOS from Wyatt. The separation was carried out on 3 styragel columns in series from Waters (HR1, HR3, HR4) using polystyrene (PS) standards for calibration.

AFM analysis was performed on a Dimension 3100 apparatus from Digital Instruments operated in Tapping mode. The Nanoworld silicon SPM sensors (type NCL) have a tip radius of less than 10 nm, the nominal spring constant and a resonance frequency of the cantilever being, respectively,

48 N.m<sup>-1</sup> and 190 kHz. Observations were carried out on spin-coated samples. Samples were prepared by dissolving the copolymers in THF at a concentration of 2.0 wt % or 2 mg.ml<sup>-1</sup>. Thin films for AFM measurements were spin-coated from the solution onto silicon wafers at 2000 rpm during 30 s at room temperature. The samples were left overnight to remove solvent traces.

The SAXS measurements were performed on a SAXS Xeuss 2.0 apparatus (Xenocs) equipped with a micro source using Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) and point collimation (beam size: 300\*300  $\mu\text{m}^2$ ). The sample to detector distance, around 150 cm, is calibrated using silver behenate as standard. Bulk synthesized samples were analyzed in transmission. 2D-SAXS patterns were collected on a Pilatus200k detector (Dectris) in transmission mode. The integrated intensity profiles were computed using the Foxtrot software.

Mechanical tests were carried out on an RSA3 apparatus (TA Instruments). 5\*25\*0.1 mm<sup>3</sup> rectangular samples were used to determine the mechanical behavior of samples upon uniaxial stretching. Tests were performed at a constant stretching speed of 1%/s at room temperature. The recovery ability was also tested. The sample was stretched at room temperature up to 70% of deformation at a stretching speed of 1%/s. Then the sample was unloaded at the same speed until the applied stress reaches 0. Thin films suitable for mechanical tests were obtained by dissolving 0.4 g of the copolymer in THF, followed by the slow evaporation at room temperature.

**Polymerization of  $\epsilon$ -decalactone.** In a typical polymerization procedure, initiator (40  $\mu\text{mol}$ ),  $\epsilon$ -DL (0.7 ml, 4 mmol) and THF (1.3 ml) were transferred to a Schlenk flask equipped with a stirring bar in the glove box. The desired volume of phosphazene base was taken using a Hamilton syringe, then all the components were transferred from the glove box and polymerization was started by the addition of phosphazene base to the Schlenk flask via a rubber septum. The

reaction mixture was magnetically stirred at the desired reaction temperature for an allotted polymerization time. Polymerization was quenched with a solution of benzoic acid in chloroform and the resulting mixture was precipitated into cold methanol (300 ml). The precipitated polymer was separated (filtration or decantation) and dried *in vacuo* until constant weight.

**Block copolymerization of  $\epsilon$ -decalactone with methyl methacrylate.** The typical copolymerization procedure followed the same order as  $\epsilon$ -decalactone polymerization (*vide supra*). Equimolar amount (0.43 ml, 4 mmol) of methyl methacrylate was slowly added to the stirred reaction solution via rubber septum after the allotted time of  $\epsilon$ -DL polymerization. Polymerization was quenched with a solution of benzoic acid in chloroform and the resulting mixture was precipitated into cold methanol (300 ml). The obtained polymer was collected and dried *in vacuo* until constant weight.

Table S1. Names and structures of phosphazenes mentioned in this study

Acronym	Name	Structure
<b><i>t</i>-BuP<sub>4</sub></b>	1- <i>tert</i> -butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ <sup>5</sup> ,4λ <sup>5</sup> -catenadi(phosphazene)	
<b><i>t</i>-BuP<sub>2</sub></b>	1- <i>tert</i> -butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ <sup>5</sup> ,4λ <sup>5</sup> -catenadi(phosphazene)	
<b><i>t</i>-BuP<sub>1</sub></b>	<i>tert</i> -butylimino-tris(dimethylamino)phosphorane	

Table S2. ε-decalactone polymerization activated by different initiators and *t*-BuP<sub>4</sub> in THF at 25 °C<sup>a</sup>

Entry	INI	<i>t</i> [min]	Conversion <sup>b</sup> [mol %]	<i>M<sub>n</sub></i> <sup>RI c</sup> [kg·mol <sup>-1</sup> ]	<i>D</i> <sup>RI c</sup> [-]
<b>5</b>	BnOH	10	100	19.8	1.66
<b>S1</b>	pentylamine	60	11	22.4	1.29
<b>S2</b>	benzamide	60	traces	-	-

<sup>a</sup>[ε-DL]<sub>0</sub> = 2M, *n*<sub>ε-DL</sub> = 4 mmol, molar ratio of ε-DL/INI/*t*-BuP<sub>4</sub> = 100/1/1, *V*<sub>total</sub> = 2 ml

<sup>b</sup>Determined by <sup>1</sup>H NMR

<sup>c</sup>SEC-RI in THF at 40 °C calibrated with polystyrene standards

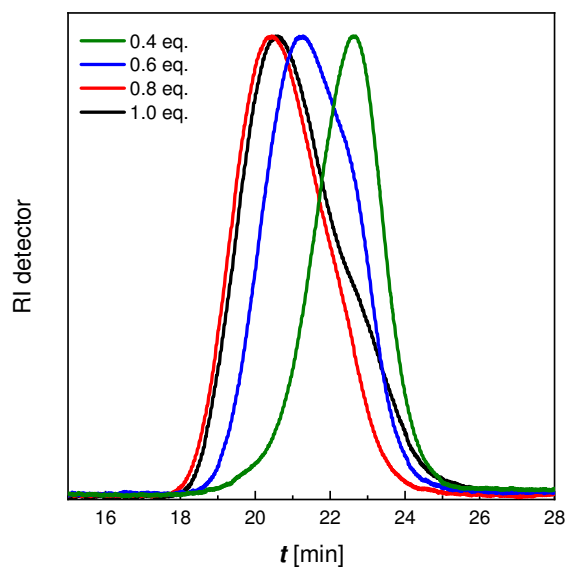


Fig. S1 SEC-RI chromatograms of poly( $\epsilon$ -decalactone)s obtained by BnOH and 0.4-1.0 eq. of *t*-BuP<sub>4</sub> in THF at 25 °C after 1h reaction (10 minutes for 1.0 eq.)

The shoulders observed on the chromatograms may be due to substantial intermolecular transesterification reactions. Transesterification reactions in the course of the ring-opening polymerization of lactones catalyzed by phosphazenes are indeed occurring, especially at high monomer conversion, see for example ref <sup>1-2</sup>.

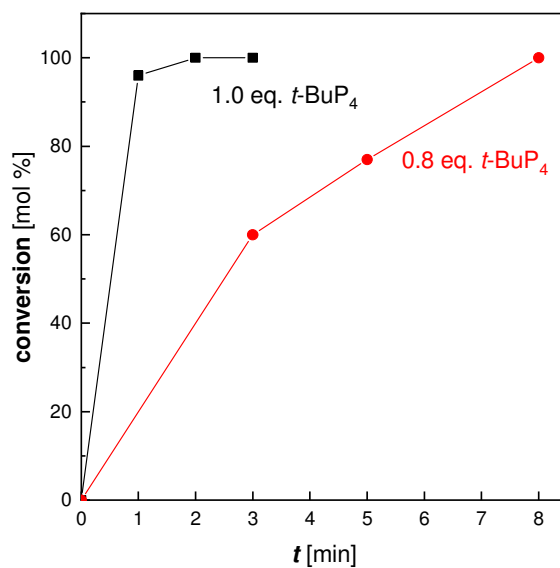


Fig. S2 Kinetics of  $\epsilon$ -DL polymerization activated by BnOH and 0.8/1.0 eq. of *t*-BuP<sub>4</sub> in THF at 25 °C ( $[\epsilon\text{-DL}]_0 = 2\text{M}$ ,  $n_{\epsilon\text{-DL}} = 4\text{ mmol}$ , molar ratio of  $\epsilon\text{-DL/BnOH} = 100/1$ ,  $V_{\text{total}} = 2\text{ ml}$ )

### SAXS analysis

The nanostructure of the materials was first investigated using SAXS. Integrated intensity profiles obtained on the as-synthesized samples are reported in Fig. S3.

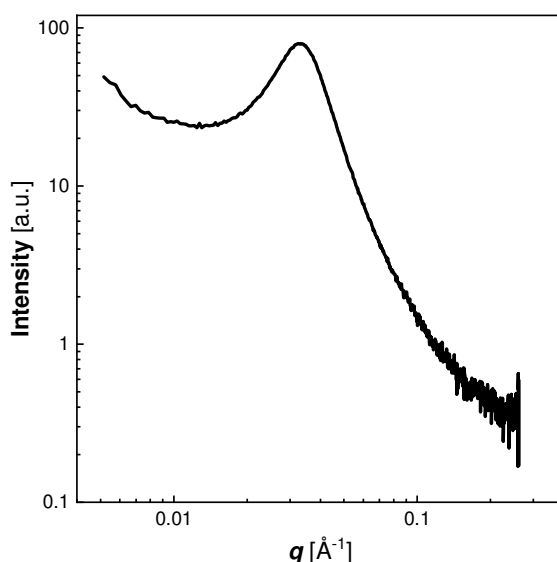


Fig. S3 SAXS analysis of PDL-*block*-PMMA copolymer synthesized by BnOH/0.8 e.q. *t*-BuP<sub>4</sub> in THF at 25 °C

The nanostructuring of the sample is clearly evidenced by this profile. Particularly a correlation peak indicating a regular alternation of the hard and soft domains, in the region  $q \approx 0.03\text{-}0.05 \text{ \AA}^{-1}$  is observed, corresponding to typical correlation lengths of 10-20 nm. The fact that only one broad peak is observed indicates that a perfect nanostructuring has been achieved. Consequently, the determination of the type of nanostructure was not possible from the SAXS data.



## Mechanical properties

The mechanical behavior of PDL-*block*-PMMA copolymer has been assessed. It is typical of a rubbery material with a tensile modulus around 8.5 MPa, strain at break as high as 200% and stress levels before breaking around 2 MPa. To complete the mechanical characterization, a recovery test was also conducted (Fig. S4 b). As can be seen, when stretched to a strain of 70%, the material depicts a “quasi” instantaneous recovery ratio of 50% which, for an un-vulcanized rubber, is a good value.

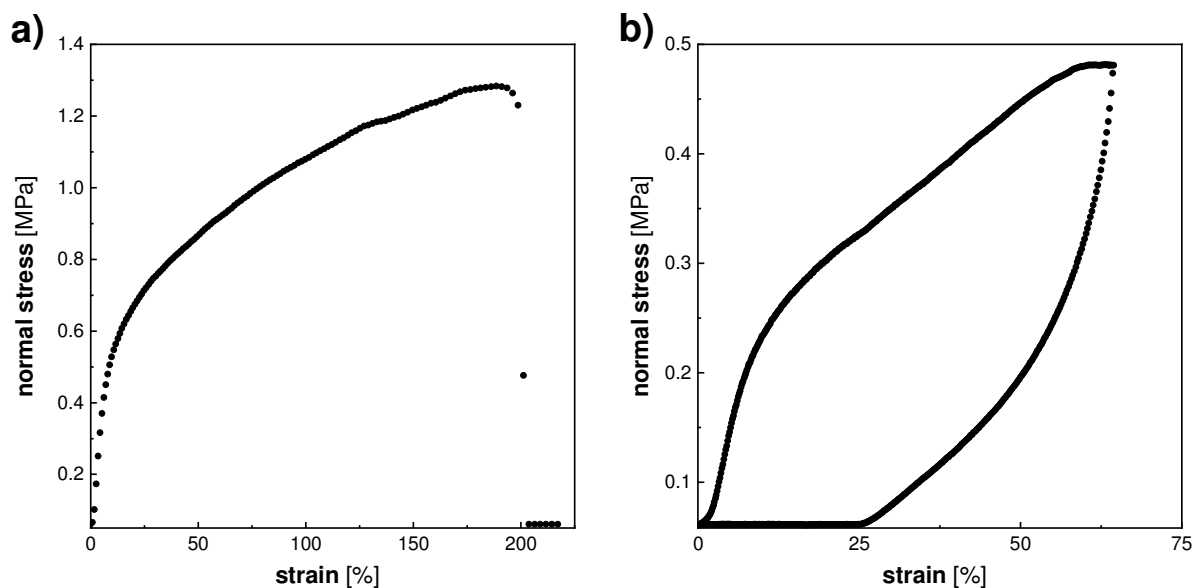


Fig. S4 Tensile testing (a) and recovery experiment (b) of the PDL-*block*-PMMA copolymer synthesized by BnOH/0.8 eq. *t*-BuP<sub>4</sub> in THF at 25 °C

## References

- 1 H. Alamri, J. Zhao, D. Pahovnik and N. Hadjichristidis, *Polym Chem*, 2014, **5**, 5471–5478.
- 2 N. Zhao, C. Ren, H. Li, Y. Li, S. Liu and Z. Li, *Angew. Chem. Int. Ed.*, 2017, **56**, 12987–12990.