COMMUNICATION

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

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Organocatalysis has provided new tools for making block copolymers, in particular active species able to polymerize monomers of different chemical nature such as cyclic esters, cyclic carbonates and epoxides. We report herein the first example of an organocatalytic active species able to polymerize sequentially a cyclic ester, ε-decalactone, and a vinyl monomer, methyl methacrylate. The resulting block copolymer shows the properties of thermoplastic elastomers.

Organocatalyzed polymerizations have attracted much interest in the two last decades.[1,2] A large variety of monomers can now be polymerized, including heterocycles such as cyclic esters, epoxides, cyclic carbonates, cyclic siloxanes, phospholanes, carboxyanhydrides, as well as acrylics and methacrylics.[3] This large scope affords new tools for macromolecular engineering and notably block copolymers synthesis.[4] The organocatalyzed sequential block copolymerization of monomers bearing the same chemical function is well documented in the literature,[4] involving cyclic esters, cyclic ethers, cyclic carbonates and (metha)acrylics.

The sequential copolymerization between monomers of different chemical nature is obviously more difficult to reach, and much less documented. Organocatalysts systems allowing such hetero block copolymerization have been reported in the frame of ring-opening polymerizations. Several catalytic systems were reported for the sequential block copolymerization of cyclic esters and cyclic carbonates, including the 1,8-diazabicyclo[5,4,0]undec-7-ene amidine (DBU),[5] Brönsted acids,[6-9] and H-bond catalytic systems[10-13] as *e.g* thiourea/sparteine[10] and base acid pairs.[11] A temperature dependant switch has also been reported using the 1,5,7-triazabicyclo[4.4.0]-dec-5-ene guanidine (TBD), allowing the formation of multiblock copolymers.[14] The sequential ring-opening copolymerization of a phospholane with lactide as a cyclic ester was reported using the DBU amidine.[15] Switching from epoxide to cyclic ester ring-opening polymerization has also been achieved using carbene[16] and phosphazene[17] based catalysts, while switching from an epoxide to a cyclic carbonate can be realized using an ammonium fluoride catalyst.[18]

The difficulties encountered while trying to make block copolymers from monomers of different chemical nature has led to the development of multistep strategies, where the active species is switched to a new form able to polymerize the second monomer.[19,20] For example, the base catalyzed ring-opening polymerization of a cyclic ether is quenched *in situ* by introduction of a weak Brönsted acid.[19] The resulting new active species can then catalyze the ring-opening polymerization of cyclic esters and carbonates, providing access to polyether-*block*-polyester and polyether-*block*-polycarbonate copolymers. Some variations were proposed where a second base can be introduced for the second block after the Brönsted acid neutralization,[21] providing access to block copolymers between low ring strained macrolactones and smaller lactones. These approaches allow the access to a wide scope of block copolymers. They are multistep and involve different catalytic/initiating systems.

A strategy based on multifunctional initiators has also been reported. The combination in a single molecule of a controlled radical polymerization initiator moieties with a hydroxyl group able to initiate an organocatalytic ring-opening polymerization allows the access to *e.g* poly(ε-caprolactone)-*block*-poly(methyl methacrylate) (PCL-*block*-PMMA) copolymers.[22,23] This approach involves additional synthetic steps of the initiator, and is not as versatile as a sequential processes, which should notably allow the access to triblock copolymers starting from a bifunctional co-initiator such as a diol for instance.

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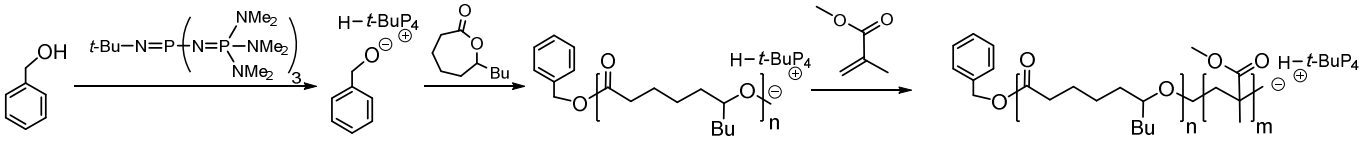
Table 1 ε-decalactone (ε-DL) polymerization mediated by the benzyl alcohol/*t*-BuP$_4$ catalytic system in THF at 25 °C

Entry[a]	*t*-BuP$_4$/benzyl alcohol [b]	Conversion [c] [%]	M_n^{RI} [d] [kg.mol^{-1}]	$Đ^{RI}$ [d]	M_n^{LS} [e] [kg.mol^{-1}]	$Đ^{LS}$ [e]	M_n^{theo} [f] [kg.mol^{-1}]
1	0.2	2	-	-	-	-	-
2	0.4	35	11.6	1.30	8.3	1.26	6.0
3	0.6	65	17.7	1.43	11.3	1.31	11.1
4	0.8	100	19.5	1.52	14.4	1.39	17.0
5[g]	1.0	100	19.8	1.66	12.1	1.54	17.0

[a][ε-DL]$_0$ = 2M, $n_{ε\text{-DL}}$ = 4 mmol, molar ratio of ε-DL/benzyl alcohol = 100/1, V_{total} = 2 ml, *t* = 1 h; [b]Molar ratio of *t*-BuP$_4$/benzyl alcohol; [c]Determined by ^{1}H NMR; [d]SEC-RI in THF at 40 °C calibrated with polystyrene standards; [e]SEC-MALLS in THF at 40 °C; [f]M_n^{theo} = ($n_{ε\text{-DL}}/n_{benzyl\ alcohol}$) · $M_{ε\text{-DL}}$ · conv$_{ε\text{-DL}}$; [g]*t* = 10 min

Scheme 1 *t*-BuP$_4$ phosphazene catalyzed ring-opening polymerization of ε-decalactone and sequential block copolymerization with methyl methacrylate



It should be noted that PCL-*block*-PMMA copolymers can also be synthesized sequentially using metallocene catalysts,[24,25] which can go with residual metal traces and eventually a related polymer coloration.

We report herein, for the first time, the sequential block copolymerization between a cyclic ester, and a vinyl monomer, using a single organocatalyst. The resulting new block copolymer self assembles in nanostructures that show mechanical properties typical of a thermoplastic elastomer.

Phosphazene bases seemed particularly suited to us for this purpose, as they allow the anionic polymerization of methacrylates such as methyl methacrylate (MMA)[26] as well as ring-opening polymerizations of various heterocycles.[27,28] The key lies in finding appropriate monomer/catalyst combinations regarding the basicity of phosphazenes. *t*-BuP$_4$, a very strong phosphazene base,[§] was reported for the anionic polymerization of MMA.[26] The polymerization of ε-caprolactone is however too fast and uncontrolled with this catalyst [19,29] to envision a block copolymerization. ε-Caprolactone is also barely polymerized by the less basic *t*-BuP$_1$[§] phosphazene[30] while the mild *t*-BuP$_2$[§] affords the polymerization.[17] We choose ε-decalactone (ε-DL) for our purpose, as this biobased lactone is known to be less reactive than ε-caprolactone in ring-opening polymerizations.[31,32]

The results of the polymerization of 100 eq. ε-DL *vs.* benzyl alcohol[§§] in the presence of the *t*-BuP$_4$ phosphazene (Scheme 1) are given in Table 1, and a typical NMR spectra is provided Fig. 1. A catalyst/initiator ratio of 0.4 is necessary to observe the formation of a polymer in THF at 25°C. Dispersities around 1.3/1.4 are obtained for values of 0.4 and 0.6 of this ratio, together with a reasonable agreement between calculated and measured number-average molecular weight. The conversion is increasing with the phosphazene loading, and a full conversion can be reached with 0.8 and 1.0 eq. of *t*-BuP$_4$ at room temperature (entries 4 and 5, Table 1). For these higher loadings, a slight broadening of the molecular weight distribution is observed (*Đ* ≈ 1.4/1.5, see also Fig. S1 in the ESI) together with a deviation between experimental and theoretical molar mass values.

Fig. 1 ^{1}H NMR spectra of PDL, PMMA and PDL-*block*-PMMA

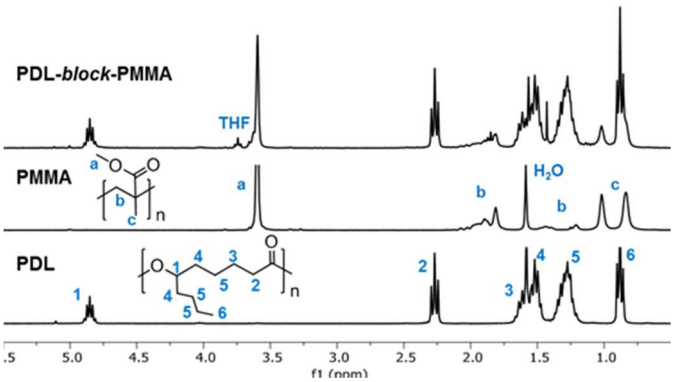
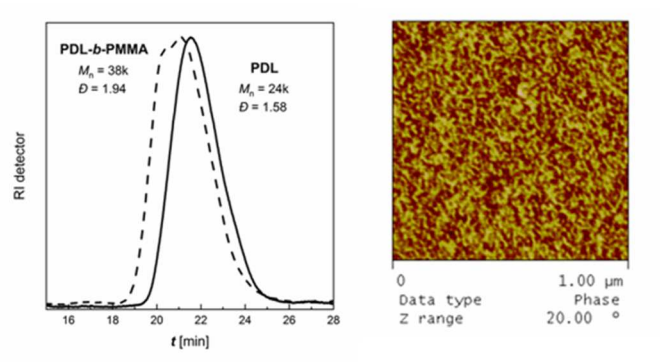


Fig. 2 SEC-RI chromatogram of poly(ε-decalactone)-*block*-poly(methyl methacrylate) (PDL-*block*-PMMA) copolymer synthesis initiated by *t*-BuP$_4$/benzyl alcohol ratio of 0.8 in THF at 25 °C together with the first PDL block (left side) and representative AFM (Atomic Force Microscopy) phase contrast image (Z range = 20°) of the block copolymer (right side)



Comparison of theoretical and absolute molar masses obtained by a light scattering detector together with low dispersity values ($Đ$ ≈ 1.3) indicates the controlled character of the polymerization with 0.4 and 0.6 eq. of *t*-BuP$_4$. Table 1 also shows a *ca.* 40% overestimation of the number-average molecular weight M_n measured using the refractive index detector (RI) and polystyrene standards.

The benzyl alcohol/*t*-BuP$_4$ catalytic system allows a full conversion in 10 minutes at room temperature (entry 5) and provides poly(ε-decalactone) (PDL) with a number-average molecular weight of 12.1 kg.mol^{-1} (LS) and a dispersity $Đ$ = 1.54 in these conditions. Regarding other catalysts reported in the literature, the reaction rate is faster than that catalysed by the TBD guanidine, as, for the latter, 24h reaction at 110°C are necessary to reach conversion higher than 80%.[32] Such a high reactivity prompted us to conduct a kinetic study that is provided in the ESI (Fig. S2). ε-DL polymerization catalyzed by 1.0 eq. of *t*-BuP$_4$ is extremely fast, reaching full monomer conversion in two minutes at 25°C (black plot, Fig. S2). Polymerization catalyzed by 0.8 eq. of *t*-BuP$_4$ is a bit slower and allows the full ε-DL conversion after eight minutes of polymerization, (red plot, Fig. S2).

A catalyst/initiator ratio of 0.8 seemed to us to be the best compromise to assess the ability of the active specie to switch to the polymerization of methyl methacrylate. The copolymerization was realized in the conditions of entry 4, with 100 eq. MMA added after letting ten minutes for the ring-opening polymerization of ε-DL, following the kinetic study. The reaction was then allowed to proceed for an additional 35 minutes. The conversion of both monomers was found to be quantitative in these conditions. The increase of molar mass after the addition of MMA is represented by the shift of SEC-RI curve (Fig. 2, left side) with a slight broadening of the molecular weight distribution from *ca.* 1.6 to 1.9. The bimodal character of the molecular weight distribution may be due to the very high viscosity of the reaction medium, that could hamper monomer diffusion to some growing centres. This is further accompanied by the exothermic character of the polymerization of MMA at the early stages. We try to add MMA with a higher dilution, but the reaction did not succeed. The NMR spectrum of the block copolymer is shown in Fig. 1.

Such a poly(ε-decalactone)-*block*-poly(methyl methacrylate) copolymer was never reported in the literature to the best of our knowledge. This prompted to study the microstructure and the mechanical properties of the material. The SAXS (Small Angle X-ray Scattering) profile provided in the SI section (Fig. S3) shows correlation lengths of 10 to 20 nm, highlighting a nanostructured material. The AFM picture (Fig. 1, right side) shows the presence of two distinct domains, *i.e.* soft and hard domains, confirming the nanostructured self-assembly of the copolymer. Tensile tests (which can be found in the ESI section as Fig. S4) led to a tensile modulus around 8.5 MPa, stress levels before breaking around 2 MPa and strain at break as high as 200%, which are characteristic of thermoplastic elastomers. Extension of the approach to other monomers together with thorough characterization of the so-formed materials are under course.

In conclusion, ε-decalactone can be polymerized in THF in the presence of the phosphazene base *t*-BuP$_4$ and benzyl alcohol in a controlled fashion. A full monomer conversion can be obtained in a few ~~two~~ minutes at room temperature, providing PDL of M_n^{LS} > 10 kg.mol^{-1} and dispersities around 1.4-1.5. The sequential addition of methyl methacrylate highlights the living character of the polymerization, and provide the first example of an organocatalytic active species able to polymerize sequentially a cyclic ester and a vinyl monomer.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

§ The name and structure of the *t*-BuP$_1$, *t*-BuP$_2$ and *t*-BuP$_4$ phosphazenes are provided in the SI section

§§ We also assessed an amine and an amide as co-initiator, but the results were less convincing than those obtained with benzyl alcohol. The experiments are provided in the SI section as Table S2

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Supporting Information

EXPERIMENTAL SECTION

General Considerations and Materials. All operations were performed under dry argon using standard Schlenk techniques and glove box. ε-decalactone (Aldrich, ≥99%) and methyl methacrylate (Fischer Chemical, ≥99.5%) were dried over 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 CaH_2, distilled under inert atmosphere and stored in the glove box. Phosphazene base *t*-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. ^1H NMR spectra were recorded on an AC 300 Bruker spectrometer at room temperature in $CDCl_3$. Approximately 5 mg of sample was directly dissolved into the NMR tube in 0.6 mL of $CDCl_3$. The chemical shifts were calibrated using the residual resonances of the solvent.

Size exclusion chromatography (SEC) was performed at 40°C in THF at an elution rate of 1 $ml.min^{-1}$ 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 $N.m^{-1}$ 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 $mg.ml^{-1}$. 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-Kα radiation (λ= 1.54 Å) and point collimation (beam size: 300*300 μm^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^3 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 ε-decalactone. In a typical polymerization procedure, initiator (40 µmol), ε-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 ε-decalactone with methyl methacrylate. The typical copolymerization procedure followed the same order as ε-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 ε-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

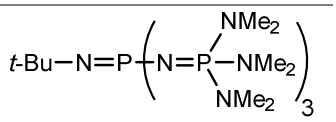
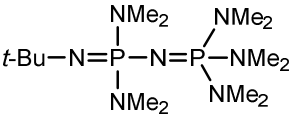
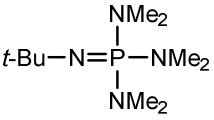
Acronym	Name	Structure
***t*-BuP$_4$**	1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene)	
***t*-BuP$_2$**	1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene)	
***t*-BuP$_1$**	*tert*-butylimino-tris(dimethylamino)phosphorane	

Table S2. ε-decalactone polymerization activated by different initiators and *t*-BuP$_4$ in THF at 25 [a]

Entry	INI	*t* [min]	Conversion [b] [mol %]	M_n^{RI} [c] [kg·mol^{-1}]	$Đ^{RI}$ [c] [-]
5	BnOH	10	100	19.8	1.66
S1	pentylamine	60	11	22.4	1.29
S2	benzamide	60	traces	-	-

[a][ε-DL]$_0$ = 2M, $n_{ε\text{-DL}}$ = 4 mmol, molar ratio of ε-DL/INI/*t*-BuP$_4$ = 100/1/1, V_{total} = 2 ml
[b]Determined by ^{1}H NMR
[c]SEC-RI in THF at 40 °C calibrated with polystyrene standards

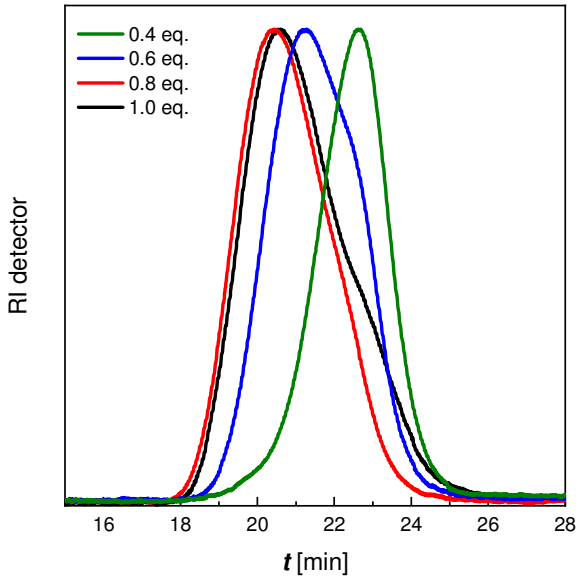


Fig. S1 SEC-RI chromatograms of poly(ε-decalactone)s obtained by BnOH and 0.4-1.0 eq. of *t*-BuP_4 in THF at 25 °C after 1h reaction (10 minutes for 1.0 eq.)

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 [1-2].

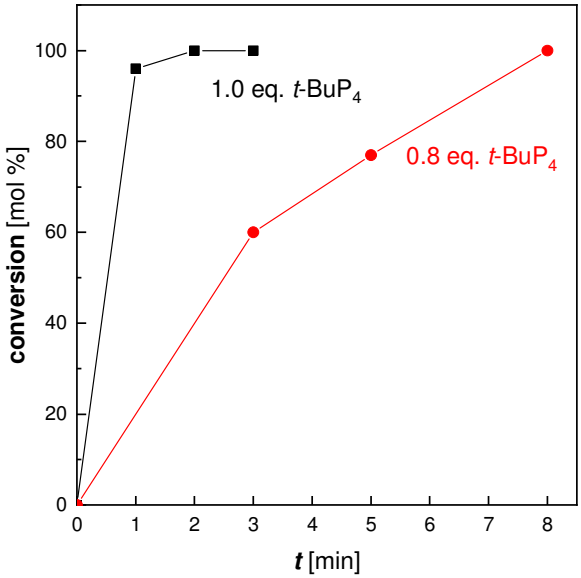


Fig. S2 Kinetics of ε-DL polymerization activated by BnOH and 0.8/1.0 eq. of *t*-BuP_4 in THF at 25 °C ([ε-DL]$_0$ = 2M, $n_{\varepsilon\text{-DL}}$ = 4 mmol, molar ratio of ε-DL/BnOH = 100/1, V_{total} = 2 ml)

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.

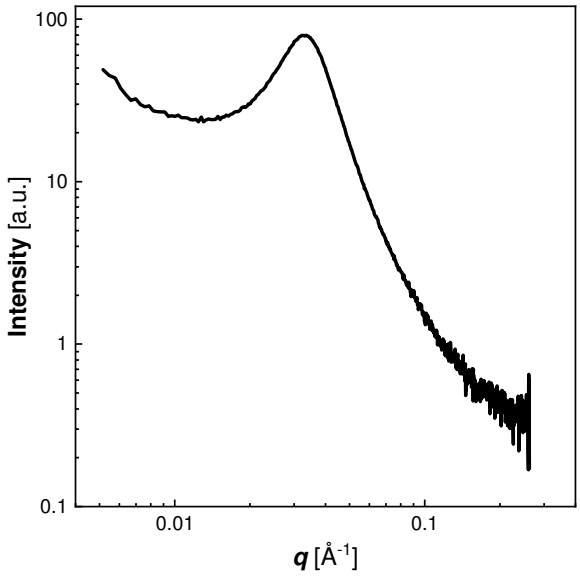


Fig. S3 SAXS analysis of PDL-*block*-PMMA copolymer synthesized by BnOH/0.8 e.q. *t*-BuP_4 in THF at 25 °C

The nanostructuration 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 ≈ 0.03-0.05 $Å^{-1}$ is observed, corresponding to typical correlation lengths of 10-20 nm. The fact that only one broad peak is observed indicates that a perfect nanostructuration 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.

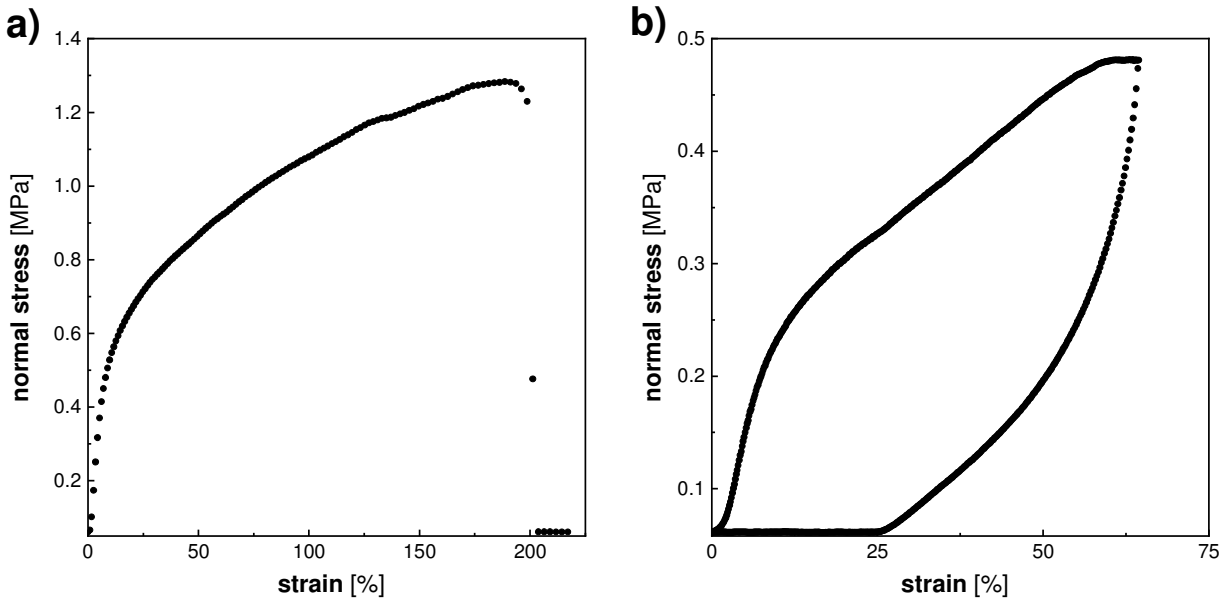


Fig. S4 Tensile testing (**a**) and recovery experiment (**b**) of the PDL-*block*-PMMA copolymer synthesized by BnOH/0.8 eq. *t*-BuP_4 in THF at 25 °C

References

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