Nanoporous thermosets with percolating pores from block polymers chemically fixed above the order-disorder transition

Supporting information

Thomas Vidil, Nicholas Hampu, Marc A. Hillmyer*

*To whom correspondence should be addressed: hillmyer@umn.edu

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1- Materials and methods

Note: no unexpected or unusually high safety hazards were encountered with the reported work.

a- Materials

Unless specifically noted, all chemicals were purchased from Sigma-Aldrich. 1,8-dizabicycloundec-7-ene (DBU) was used without further purification. Azobisisobutyronitrile (AIBN) (98%) was recrystallized from methanol and dried under reduced pressure overnight. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanol was dried under reduced pressure overnight prior to use. Styrene (S) (≥99%, stabilized) and glycidyl methacrylate (GMA) (97%, stabilized) were passed through a basic alumina column prior to use. 4- lactide (99%) was kindly provided by Altasorb, recrystallized from toluene and stored under a N₂ atmosphere. All bulk solvents were purchased from Fisher and used as received unless otherwise specified. Dichloromethane (DCM) was purified using a solvent system composed of columns of activated alumina and molecular sieves.

b- Methods

NMR. 1H NMR spectroscopy experiments were performed on a Bruker Avance III HD 500 spectrometer equipped with a 5mm Prodigy TCI cryoprobe. Spectra of the polymers were acquired in CDCl₃ using tetramethylsilane as a reference. Acetone-d₆ was used for the kinetics study of the RAFT copolymerization of styrene and glycidyl methacrylate.

SEC. SEC analysis was performed in tetrahydrofuran at 25 °C using an Agilent 1260 Infinity liquid chromatograph system equipped with three Waters Styragel columns in series, as well as a Wyatt DAWN Heleos II 18-angle laser light scattering detector S4 and a Wyatt OPTILAB T-rEX refractive index detector.

FTIR. FTIR spectra were obtained on a Bruker Alpha Platinum ATR spectrometer.

DSC. DSC analyses were performed on a TA Instruments Discovery DSC using standard aluminum T-zero pans with hermetic lids. Scans were conducted under an inert (N₂) atmosphere at a rate of 10 °C min⁻¹. Glass transition temperatures, Tgs’s, were determined using the final heating ramp within the temperature range of 0 °C to 230 °C.

TGA. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ with typical sample size of 10–15 mg.

Dynamic Mechanical Analysis. The low-frequency rheological response of the block polymers was evaluated on a Rheometrics ARES mechanical spectrometer equipped with a 25 mm parallel plates geometry. The plates and the sample were preheated in the environmental chamber of the rheometer for approximately 10 min at the set temperature before starting the measurement procedure. The oven was maintained under nitrogen atmosphere to prevent thermal degradation.
of the sample. Order-disorder transition temperatures (T\text{ODT}'s) of the block polymers were determined from linear dynamic temperature sweeps acquired using a heating rate of 1 °C min\(^{-1}\) with an angular frequency \(\omega = 1\) rad s\(^{-1}\) and a shear strain \(\varepsilon = 1\%\). A precipitous drop in \(G'\) indicates the transition of the ordered microstructure to a disordered state. Gel point measurements (gel time, \(t_{gel}\)) were determined from isothermal time sweep experiments using \(T = T_{curing}\), an angular frequency \(\omega = 1\) rad s\(^{-1}\) and a shear strain \(\varepsilon = 1\%\). \(t_{gel}\) was estimated as the point of crossover of the storage modulus \(G'\) and the loss modulus \(G''\) (further details provided below).

**SAXS.** SAXS profiles were collected at the Advanced Photon Source (APS) at Argonne National Laboratories using the Sector 5-ID-D beamline, which is maintained by the DuPont-Northwestern-Dow Collaborative Access Team. Scattering experiments were performed using X-rays of wavelength 0.76 Å and the scattering intensity was collected on a 2D Mar CCD detector. Sample-to-detector distances were calibrated using a silver behenate standard. Intensity as a function of the wave vector, \(q\), where \(q = (4\pi/\lambda) \sin(\theta/2)\) (\(\theta\) is the scattering angle and \(\lambda\) is the X-ray wavelength), was obtained by azimuthally integrating the 2D patterns. For the crosslinked samples, SAXS profiles were collected at room temperature by directly using a monolith of the materials. For the measurement of the T\text{ODT}, samples were hermetically sealed in T-zero DSC pans (TA Instruments). DSC pans were mounted in a Linkam heating stage for variable temperature measurements. Samples were equilibrated 2 min at each temperature prior to data collection (further details provided below).

**SEM.** SEM micrographs were obtained on a Hitachi S-4700 cold FEG-SEM with an accelerating voltage of 3 kV and an upper secondary electron detector. Before imaging, monoliths were cryo-fractured and coated with ca. 2 nm of Pt via sputtering using a VCR ion beam coater.

**TEM.** Prior to electron imaging, samples were microsectioned at \(T = –120\) °C using a LEICA UC6 microtome with a Diatome diamond knife. Samples were collected on carbon-coated grids. The specimens were examined using a Tecnai TF30 300 kV FEG (FEI-Company, Hillsboro, OR, and Eindhoven, The Netherlands) at 78,000x and 93,000x nominal magnification (further details below).

**Gas sorption.** Nitrogen adsorption isotherms were obtained on a Quantachrome Autosorb iQ (Boynton Beach, FL) at the temperature of liquid nitrogen (77.3 K). Samples were loaded in 6 mm stems and degassed for 20–24 h at room temperature before measurement using a turbomolecular pump. BET specific surface areas were obtained from the adsorption branch from \(P/P_0 = 0.05-0.35\). Mesopore size distributions were estimated using a quenched solid density functional theory (QSDFT) kernel for the adsorption branch of nitrogen on carbon using a cylindrical pore model.
2- Synthesis and characterization

a- Macro-chain transfer agents, PLA-CTAs

i. Synthesis

The trithiocarbonate terminated PLAs (PLA-CTA) were prepared by using 4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanol as an initiator and DBU as a catalyst. The procedure was adapted from PLA syntheses reported in the literature.\textsuperscript{1} The typical procedure for a 10K PLA-CTA is as follow: in a glovebox under N\textsubscript{2} atmosphere, L-lactide (10 g, 0.069 mol, 69 eq.) was dissolved with DCM (120 mL) in a pressure vessel containing a stir bar. In a separate vial, 4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanol (0.390 g, 0.001 mol, 1 eq.) was dissolved in DCM (20 mL). The resulting solution was added to the pressure vessel using a Pasteur pipette. The mixture was stirred for a few minutes and DBU (0.152 g, 150 \(\mu\)L, 0.001 mol, 1 eq.) was then added dropwise to the stirring solution using a microsyringe. The pressure vessel was hermetically sealed, taken out of the glovebox and stirred at room temperature for 20 min. The mixture was quenched through acidification with benzoic acid (0.3 g, 0.0025 mol, 2.5 eq.), and precipitated in 20-fold volume excess of methanol. The precipitated polymer was dried under reduced pressure at 60 °C for 24 h to give 8.2 g of a yellow and glassy polymer (yield = 82%)

\[\text{HO-NC-S-S-C_{12}H_{25}} + \text{n L-lactide} \xrightarrow{\text{Room temperature}} \text{HO-} \text{O-} \text{C-O-} \text{O-} \text{C}_{2n-1} \text{NC-S-S-C_{12}H_{25}} + \text{DBU}\]

\textbf{Figure S1:} Synthesis of the macro chain transfer agent PLA-CTA

ii. NMR characterization

NMR spectra were recorded using the aforementioned method (see 1. Materials and methods). The number average molar mass of the polymers, \(M_n\), were determined by using end-group analysis: the methine protons (Figure S2, a) of the backbone were integrated with respect to the methylene protons (Figure S2, b) adjacent to the trithiocarbonate moiety of the CTA. Figure S2 represents the typical NMR spectrum for a PLA-CTA with a targeted mass of 10K. The end-group analysis assuming exactly one CTA-derived end group per chain gives \(M_n = 8.5K\) (this is in good accordance with the yield of the reaction, 82%). The various PLA synthesized and used in this study are noted PLA-x where x is the molecular weight of the polymer as measured by NMR. They are all reported in Table S1.
iii. SEC characterization

SEC traces and the $M_n$ value derived from these traces were obtained by using the aforementioned method (see materials and methods). Mass-average molar masses were determined using the asymptotic value of $dn/dc$ at high molar mass$^2$ for PLA in THF at 25 °C, $dn/dc = 0.049$ mL g$^{-1}$. Figure S3 represents the SEC traces for PLA-8.5, PLA-17.4 and PLA-27.6. The number-average molar mass and the molar mass dispersity obtained from SEC are reported in Table S1 for all the PLA used in this study. There was generally good agreement between the SEC-LS and NMR estimates of molar mass.
Figure S3: Representative SEC traces of PLA-CTAs used in this study.

Table S1: Characterization of the PLA-CTAs used in this study. The polymers are noted PLA-x where x is the molar mass of the polymer as determined by NMR spectroscopy. aNumber-average molar mass calculated from 1H-NMR spectroscopy. bNumber-average molar mass obtained from THF SEC. cMolar mass dispersity determined using LS-SEC.

| PLA-x  | $M_n$ (kg mol$^{-1}$) | $M_n$ (kg mol$^{-1}$) | $M_w/M_n$ |
|--------|----------------------|----------------------|-----------|
| PLA-7.7| 7.7                  | 10.3                 | 1.07      |
| PLA-8.5| 8.5                  | 7.9                  | 1.02      |
| PLA-10.5| 10.5                 | 11.2                 | 1.19      |
| PLA-13.2| 13.2                 | 14.0                 | 1.06      |
| PLA-14.1| 14.1                 | 14.2                 | 1.09      |
| PLA-19.7| 19.7                 | 19.2                 | 1.13      |
| PLA-17.4| 17.4                 | 20.9                 | 1.08      |
| PLA-27.6| 27.6                 | 28.2                 | 1.01      |
| PLA-32.0| 32.0                 | 29.1                 | 1.01      |

b- PLA-P(S-s-GMA)

i. Synthesis

The crosslinkable block, poly(styrene-s-glycidyl methacrylate) (P(S-s-GMA)), was obtained by RAFT copolymerization of styrene (S) and glycidyl methacrylate (GMA) using the PLA-CTA as
a macro-CTA. The procedure was adapted from a protocol described in the literature for the RAFT copolymerization of styrene and hydroxyethylmethacrylate. The typical procedure for the synthesis of a nearly symmetrical diblock with a GMA content of 30 mol% in the P(S-s-GMA) block and starting from a 17.4K PLA-CTA is as follow: PLA-CTA (4 g, 0.23 mmol, 1 eq.), styrene (6 g, 57.7 mmol, 251 eq.) and GMA (2.61 g, 18.4 mmol, 80 eq.) are introduced in a round bottom flask containing a stir bar. The mixture is stirred until full dissolution of the PLA-CTA. For high PLA-CTA molecular weight (typically Mn > 15K), the mixture is slightly heated to ~ 50 °C to accelerate the dissolution process. AIBN (9.4 mg, 57.5 µmL, 0.25 eq., 218 µL, (as a 5 wt % solution in toluene), use of a microsyringe) is then added to the yellow homogeneous solution (cooled down to room temperature beforehand when necessary) and the resulting system was stirred and sparged with argon for 20 min. The flask was then placed in a preset oil bath at 70 °C under static argon atmosphere and aliquots were taken from the system at different intervals of time (under dynamic argon flow). The NMR analysis of the aliquot (solvent: acetone-d₆) gives access to styrene and GMA conversions by using the aliquot taken at t = 0 min as a reference (details regarding the kinetics studies are provided below). The reaction was cooled to room temperature and exposed to air once the styrene conversion reached 40%, i.e. the estimated conversion to obtain a symmetrical diblock. The polymer was isolated by precipitation into MeOH and dried under reduced pressure at 100 °C overnight to give a yellow solid.

**Figure S4:** Synthesis of the crosslinkable diblock PLA-b-P(S-s-GMA) starting form the PLA-CTA precursor.

## ii. NMR characterization

**Estimation of Mn and X_{GMA}**

The composition of the diblock polymers was analyzed by ¹H-NMR spectroscopy. Figure S5 represents a typical ¹H-NMR spectrum of a PLA-b-P(S-s-GMA). The peaks corresponding to the glycidyl protons of GMA (2.1-4.2 ppm, 5H per repeating unit) were assigned according to the literature. The peak corresponding to the methine protons of PLA (5.5-5.4 ppm, 1H per repeating unit) can be used to define a reference integral, I_{Ref}, as follows:

\[
I_{Ref} = \frac{I_{PLA} \times M(LA)}{M_n(PLA)} \quad \text{eq. (1)}
\]

where \(I_{PLA}\) is the integral of the methine protons, \(M_n(PLA)\) is the molecular weight of the PLA block calculated by NMR (using the NMR spectrum of the corresponding PLA-CTA), and \(M(LA)\) is the molar mass of one repeating unit of PLA (72.07 g mol⁻¹).
By using the integral of the aromatic protons of styrene, $I_S$ (6.3–7.2 ppm, 5H per repeating unit), and the integral of the glycidyl protons of GMA, $I_{GMA}$ (2.1–4.2 ppm, 5H per repeating unit), it is possible to calculate the molecular weight of P(S-s-GMA), $M_n(P(S-s-GMA))$, as well as the molar content of GMA, $X_{GMA}$, according to the following equations:

$$M_n(P(S-s-GMA)) = \frac{[M(S) \times I_S + M(GMA) \times I_{GMA}]}{5 \times I_{Ref}}$$  \hspace{1cm} \text{eq. (2)}$$

$$X_{GMA} = \frac{I_{GMA}}{(I_{GMA} + I_S)}$$  \hspace{1cm} \text{eq. (3)}$$

where $M(S)$ and $M(GMA)$ are the molar masses of styrene and GMA, respectively.

The values of $M_n(P(S-s-GMA))$ and $X_{GMA}$ are reported in Table S2 for all the polymers synthesized in this study. In the following, the diblock polymers are noted PLA-$\alpha$-P(S-s-GMA)-$\beta$-$X_{GMA}$-$\gamma$ where $\alpha$ is the molar mass of the PLA block (in kg mol$^{-1}$, determined from NMR), $\beta$ is the molecular weight of the P(S-s-GMA) block (in kg mol$^{-1}$, determined from NMR) and $\gamma$ is the molar fraction of GMA in the P(S-s-GMA) block, $X_{GMA}$ (mol%).

**Figure S5:** $^1$H-NMR spectrum of PLA-$b$-P(S-s-GMA) with indication of the signals of the aromatic protons of styrene, the glycidyl protons of GMA and the methine proton of PLA. These signals are used to estimate the molecular weight as well as the composition of the diblock.
Estimation of dn/dc

The composition of P(S-s-GMA) is also used to estimate dn/dc for the copolymer. dn/dc(P(S-s-GMA)) is obtained by a weighted average of homopolymer’s dn/dc values:\(^5,\,6\)
\[
dn/dc(P(S-s-GMA)) = w_S \times dn/dc(PS) + w_{GMA} \times dn/dc(PGMA) \quad \text{eq. (4)}
\]
where \(w_S\) and \(w_{GMA}\) are the weight fraction of styrene and GMA, respectively, in P(S-s-GMA) as determined by NMR. dn/dc(PS) and dn/dc(PGMA) are the asymptotic dn/dc value for PS and PGMA, respectively, in THF at 25 °C.

Note: dn/dc(PGMA) was estimated to be \(\sim\) dn/dc(PMMA) the asymptotic dn/dc value for PMMA.

The diblock polymers’ dn/dc, dn/dc(PLA-b-P(S-s-GMA)) values, can then be estimated by a weighted average of dn/dc(PLA) and dn/dc(P(S-s-GMA)). The estimated values are reported in Table S2 for all the polymers synthesized in this study. They were used to determine the average molar masses of the polymers from the SEC traces. These values were generally in good agreement with the NMR estimated values in the lower molar mass regime (see Table S2 below).

Estimation of the volume fraction of the blocks

The volume fractions of the blocks were estimated by using the molecular weight of the block as determined by NMR and room temperature density values for PLA, PS and PGMA: \(d_{PLA} = 1.25, \, d_{PS}=1.1, \, d_{PGMA}=0.8\).

The density of the crosslinkable block, P(S-s-GMA), was estimated using a simple formula for ideal mixtures:
\[
1/ d_{P(S-s-GMA)} = w_S/ d_{PS} + w_{GMA}/ d_{PGMA} \quad \text{eq. (5)}
\]

The volume fractions were calculated as follow:
\[
f_{PLA} = \frac{M_n(PLA)}{M_n(PLA) + M_n(P(S-co-GMA))} \quad \text{eq. (6)} \quad f_{P(S-s-GMA)} = \frac{M_n(P(S-co-GMA))}{M_n(PLA) + M_n(P(S-co-GMA))} \quad \text{eq. (7)}
\]
The values of \(f_{P(S-s-GMA)}\) are reported in Table S2 for all the polymers synthesized in this study.

iii. SEC characterization

The number-average molar mass and the molar mass dispersity were obtained using THF SEC (see materials and methods) with the dn/dc values estimated from \(^1\)H-NMR analysis of the molecular composition of the diblocks. Figure S6 illustrates the SEC traces for two representative
diblocks synthesized in this study. The number-average molar mass and the molar mass dispersity are reported in Table S2 for all the diblocks used in this study.

**Figure S6:** SEC traces for PLA-17.4-P(S-s-GMA)-11.3-X_{GMA}-29.2 and PLA-10.5-P(S-s-GMA)-9.7-X_{GMA}-14.4 (solid lines). They are compared to the SEC traces of their PLA precursors (dashed lines).
| PLA  | P(S-s-GMA)-PLA-XGMA | Mn (P(S-s-GMA)) (kg mol⁻¹)ᵃ | Mn (diblock) (kg mol⁻¹)b | Mn (diblock) (kg mol⁻¹)c | D⁴ | FRGMA (mol%)e | XGMA (mol%)f | f⁰ | dn/dc (mL g⁻¹)h |
|------|---------------------|-----------------------------|--------------------------|--------------------------|-----|--------------|-------------|-----|----------------|
| PLA-7.7 | P(S-s-GMA)-7.4-XGMA-7.7 | 7.4 | 15.1 | 14.9 | 1.04 | 3.8 | 7.7 | 0.54 | 0.1107 |
| PLA-8.5 | P(S-s-GMA)-6.7-XGMA-8.2 | 6.7 | 15.2 | 15.5 | 1.03 | 3.9 | 8.2 | 0.50 | 0.1042 |
| PLA-10.5 | P(S-s-GMA)-9.7-XGMA-14.4 | 9.7 | 20.2 | 17.0 | 1.05 | 8.0 | 14.4 | 0.54 | 0.1054 |
| PLA-13.2 | P(S-s-GMA)-11.5-XGMA-14.3 | 11.5 | 22.0 | 18.9 | 1.04 | 8.0 | 14.3 | 0.58 | 0.1105 |
| PLA-14.1 | P(S-s-GMA)-8.7-XGMA-8.7 | 8.7 | 22.8 | 23.7 | 1.09 | 8.2 | 8.7 | 0.44 | 0.0965 |
| PLA-17.4 | P(S-s-GMA)-13.0-XGMA-20.4 | 13.0 | 27.1 | 20.1 | 1.06 | 10.8 | 20.4 | 0.54 | 0.1019 |
| PLA-19.7 | P(S-s-GMA)-14.6-XGMA-18.9 | 14.6 | 34.3 | 27.9 | 1.04 | 10.6 | 18.9 | 0.49 | 0.0967 |
| PLA-27.6 | P(S-s-GMA)-25.5-XGMA-40.2 | 25.5 | 53.1 | 46.5 | 1.07 | 26.2 | 40.2 | 0.55 | 0.0916 |
| PLA-32.0 | P(S-s-GMA)-19.8-XGMA-38.0 | 29.8 | 61.8 | 47.2 | 1.04 | 26.3 | 38.0 | 0.55 | 0.0928 |

Table S2: Characterization of the PLA-b-P(S-s-GMA) used in this study. The polymers are noted PLA-α-P(S-s-GMA)-β-XGMA-γ where α is the molecular weight of the PLA block (in kg mol⁻¹, determined from NMR), β is the molecular weight of the P(S-s-GMA) block (in kg mol⁻¹, determined from NMR) and γ is the molar fraction of GMA in the P(S-s-GMA) block, XGMA. ᵃNumber-average molar mass of the P(S-s-GMA) block calculated from ¹H-NMR spectroscopy. ᵇNumber-average molar mass of the diblock obtained from ¹H-NMR. ᶜNumber-average molar mass of the diblock obtained from THF SEC with LS. ᵈMolar mass dispersity of the diblock determined using LS-SEC. ᵉFeed ratio of GMA in the initial reactive mixture. ᶠMolar percentage of GMA in the P(S-s-GMA) block after purification of the polymer. ⁰Volume fraction of the P(S-s-GMA) block. ʰEstimated value of dn/dc for the diblock polymer.
iv. Kinetics of the polymerization

The kinetics of the copolymerization were monitored to ensure that symmetric diblocks were obtained.

Using the $^1$H NMR spectra of the aliquots, the normalized integrals of the vinylic protons of styrene and GMA can be determined as a function of time. Figure S7 represents the signals of the vinylic protons at $t = 0$ for the synthesis of PLA-14.1-P(S-s-GMA)-8.8-XGMA-14.2. It is noteworthy that the signal of the b$_2$ proton of styrene are overlapping with the signal of the methine proton c of PLA. The PLA protons are not involved in the RAFT polymerization and thus can be used as an internal reference. To do so, the integral of the protons c, $I_c$, can be calculated according to eq. 8:

$$I_c = I_{c+b_2} - I_{b_1} \quad \text{eq. (8)}$$

where $I_{b_1}$ and $I_{b_2}$ are the integrals of the vinylic protons b1 and b2 of styrene ($I_{b_1} = I_{b_2}$) and $I_{c+b_2}$ is the integral of the signal corresponding to the superimposition of the b2 protons of styrene and the methine protons c of PLA. Once $I_c$ is calculated, the normalized integrals of the vinylic protons of styrene, $I_{b_2}$, and GMA, $I_{a_2}$ ($=I_{a_1}$), can be obtained according to eq. (9) and eq. (10) respectively:

$$I_{b_2} = \frac{I_{b_2}}{I_c} \quad \text{eq. (9)}$$

$$I_{a_2} = \frac{I_{a_2}}{I_c} = \frac{I_{a_1}}{I_c} \quad \text{eq. (10)}$$

The styrene conversion, $x_S$, and the GMA conversion, $x_{GMA}$, are then obtained according to eq. (11) and eq. (12) respectively:

$$x_S = 1 - \frac{I_{b_2}}{I_{b_2}} \quad \text{eq. (11)}$$

$$x_{GMA} = 1 - \frac{I_{a_2}}{I_{a_2}} = 1 - \frac{I_{a_1}}{I_{a_1}} \quad \text{eq. (12)}$$

where $I_{a_1}, I_{a_2}$ and $I_{b_2}$ are the normalized integral of the vinylic protons obtained from the NMR spectrum of the aliquots taken after the reaction time $t$, where $t > 0$, and $I_{a_1}, I_{a_2}$ and $I_{b_2}$ are the normalized integral of the vinylic protons obtained from the NMR spectrum of the aliquots taken at the beginning of the reaction for $t=0$. 
Figure S7: $^1$H-NMR signals for the vinylic protons of styrene and GMA and the methine protons of PLA for the reactive mixture at $t = 0$ for the synthesis of PLA-14.1-P(S-s-GMA)-8.8-X$_{GMA}$-14.2.

Figure S8 represents the superposition of the NMR spectra obtained at different intervals of time for the synthesis of PLA-14.1-P(S-s-GMA)-8.8-X$_{GMA}$-14.2. The spectra have been normalized with the signal of the PLA protons. The intensities of the vinylic protons decrease over time as expected.

Figure S8: $^1$H-NMR signals of the vinylic protons of styrene and GMA and the methine protons of PLA obtained at different interval of time for the synthesis of PLA-14.1-P(S-s-GMA)-8.8-X$_{GMA}$-14.2. The spectra have been manually normalized by the signal of the PLA protons.
Figure S9 represents the conversions of styrene and GMA plotted as a function of time for three different syntheses. GMA reacts slightly faster than styrene. This was confirmed for all the syntheses.

This result makes sense in light of the reactivity ratios reported in the literature for the radical copolymerization of styrene and GMA. For the bulk ATRP copolymerization of styrene and GMA, Brar et al. reported $r_{GMA} = 0.73$ and $r_S = 0.42$.\(^7\) The free radical copolymerization of the two monomers in chlorobenzene gives $r_{GMA} = 0.53$ and $r_S = 0.45$.\(^8\)

This preference for GMA over styrene was also confirmed by the incorporation degree of GMA in the final polymer. Indeed, the molar content of GMA in the P(S-s-GMA) block, $X_{GMA}$, is systematically higher than the GMA feed ratio, $FR_{GMA}$, used during the copolymerization. The values of $X_{GMA}$ and $FR_{GMA}$ are reported in Table S2 for all the polymer synthesized in this study. Overall at the point when the polymerizations were terminated, $FR_{GMA}/X_{GMA} \approx 0.63$.

This result was used to adjust the feed ratio of GMA to the targeted content of GMA in the final copolymer.

**Figure S9:** Styrene and GMA conversion plotted as a function of time for three representative syntheses of PLA-$b$-P(S-s-GMA): (a) PLA-8.5-P(S-s-GMA)-6.7-$X_{GMA}$-8.2 (b) PLA-13.2-P(S-s-GMA)-11.3-$X_{GMA}$-21.5 (c) PLA-14.1-P(S-s-GMA)-8.8-$X_{GMA}$-14.2.
3- Thermal properties of the diblock polymers

The DSC and TGA analyses of the polymers were performed according to the protocol described in the materials and methods section (1- Materials and methods). Figure S10 illustrates a representative DSC thermogram obtained on the second heating at 10 °C min$^{-1}$ for PLA-17.4-P(S-s-GMA)-11.9-XGMA-32.1. As expected, two transitions can be observed. The first one corresponds to the PLA block, $T_g \approx 55$ °C. This value correlates well with the $T_g$ of PLA blocks previously reported in the literature.$^3$ The second transition corresponds to the P(S-s-GMA) block. Overall, $T_g \approx 75$ °C. We used the Flory-Fox equation and $T_g$ values reported in the literature for homo-PGMA and homo-PS to estimate the $T_g$ expected for a random copolymer of styrene and GMA. With $T_g$(PGMA) $\sim$ 60 °C$^9$ and $T_g$(PS) $\sim$ 90 °C (approximated value for low molecular weight PS)$^{10}$, $T_g$(P(S-s-GMA)) are expected to vary from 74 °C to 82 °C for the compositions of the blocks we used in this study. This is consistent with the values we measured (Table S3).

![DSC thermogram](image)

**Figure S10:** Representative DSC thermogram obtained on the second heating at 10 °C min$^{-1}$ for PLA-17.4-P(S-s-GMA)-11.9-XGMA-32.1. The inset represents the TGA thermogram for the same polymer heated under nitrogen at a ramp rate of 10 °C min$^{-1}$. The decomposition temperature, $T_d$, is defined as 5% weight loss of the sample.
then loaded in the rheometer at a temperature as well. Prior to measurement, the samples were annealed for one hour in a vacuum oven at 130 °C. The samples were then loaded in the rheometer at a temperature between 110 °C and 130 °C (i.e., higher than the highest \( T_g \) in the samples).

The typical experimental procedure starts with a strain sweep (1% ≤ \( \varepsilon \) ≤ 10%) to identify the linear viscoelastic regime of the block polymer at the temperature used to load the sample. A frequency sweep is then performed at the same temperature. Usually, \( \omega \) (the angular frequency, \( \omega = 2\pi f \) where \( f \) is the frequency) was varied from 100 rad s\(^{-1}\) to 0.01 rad s\(^{-1}\). The strain was chosen according to the results from the strain sweep to ensure that the sample remained in the linear viscoelastic regime (typically \( \varepsilon = 1\% \)). The plot of the loss and the storage moduli as a function of \( \omega \) was used to estimate the exponent, \( b \), of the power law that relates the moduli to the angular frequency, \( G' \sim G'' \sim \omega^b \), during the low frequency viscoelastic response of the block polymer. To

| PLA-8.5  | P(S-s-GMA)-6.7-X\(_{GMA}\)-8.2  | 0.50 | 8.2  | 56  | 75  | 80  | 286 |
| PLA-10.5 | P(S-s-GMA)-6.9-X\(_{GMA}\)-27.8 | 0.51 | 27.8 | 55  | -   | -   | 288 |
| PLA-13.2 | P(S-s-GMA)-9.7-X\(_{GMA}\)-14.4 | 0.54 | 14.4 | 55  | 76  | 79  | 319 |
| PLA-14.1 | P(S-s-GMA)-11.5-X\(_{GMA}\)-14.3 | 0.58 | 14.3 | 53  | 78  | 79  | 317 |
| PLA-17.4 | P(S-s-GMA)-13.8-X\(_{GMA}\)-14.1 | 0.62 | 14.1 | 52  | 79  | 79  | 293 |
| PLA-27.6 | P(S-s-GMA)-25.5-X\(_{GMA}\)-40.2 | 0.55 | 40.2 | 56  | 76  | 76  | 317 |

Table S3: Thermal properties of the PLA-b-P(S-s-GMA) block polymers obtained from DSC and TGA measurements. The polymers are noted PLA-\( \alpha \)-P(S-s-GMA)-\( \beta \)-X\(_{GMA}\)-\( \gamma \) where \( \alpha \) is the molecular weight of the PLA block (in kg mol\(^{-1}\), determined from NMR spectroscopy), \( \beta \) is the molecular weight of the P(S-s-GMA) block (in kg mol\(^{-1}\), determined from NMR) and \( \gamma \) is the molar fraction of GMA in the P(S-s-GMA) block, X\(_{GMA}\).

Volume fraction of the P(S-s-GMA) block. Molar percentage of GMA in the P(S-s-GMA) block. \( T_g \) of the blocks as measured by DSC. \( T_g \) of the P(S-s-GMA) block estimated by using the Flory-Fox equation. The decomposition temperature, \( T_d \), defined as 5% weight loss of the sample in TGA.

4- Study of the structure and the ODT of the diblock polymers

a- Dynamic mechanical analysis

Dynamic mechanical analysis was used to probe the morphology of the ordered structure as well as the ODT of the diblocks. The material and the methodology are described in the materials and methods section (1- Materials and methods). Prior to measurement, the samples were annealed for one hour in a vacuum oven at 130 °C. The samples were then loaded in the rheometer at a temperature between 110 °C and 130 °C (i.e., higher than the highest \( T_g \) in the samples).
do so, \( G'(\omega) \) and \( G''(\omega) \) were fitted with a power law function \((y=ax^b)\) using the Originlab® software.

The inset of Figure S11 represents these fittings for PLA-17.4-P(S-s-GMA)-11.1-X\(_{\text{GMA}}\)-29.2 at 130°C \((\varepsilon = 1\%)\). The values of the exponent \( b \) are reported in Table S4 for all the block polymers used in this study.

**Figure S11:** Temperature dependence of the storage modulus for PLA-17.4-P(S-s-GMA)-11.3-X\(_{\text{GMA}}\)-29.2 (heating rate 1 °C min\(^{-1}\), angular frequency \( \omega = 1 \) rad s\(^{-1}\) and shear strain \( \varepsilon = 1\%)\). Power law fittings on both side of the precipitous drop of \( G'(T) \) gives the tangents to the curve. The intersection of the tangents provides the onset of the drop identified as the ODT. The temperature corresponding to the onset is used as an estimation of \( T_{ODT} \). The error \((\Delta r)\) was estimated as the temperature increment over which the modulus drop occurred, i.e., the temperature increments between the onset point and the last points of contact between the \( G' \) plot and the tangents below and above the modulus drop. Inset: Frequency dependence of the storage and loss moduli at 130 °C. The fitting of \( G'(\omega) \) at low frequency \((0.1 \leq \omega \leq 1 \text{ rad s}^{-1})\) gives the exponent of the power law scaled by the storage modulus.

With the exception of a few samples, the storage and loss moduli obey the \( G' \sim G'' \sim \omega^{1/2} \) power law that is expected for a lamellar ordering.\(^{11}\) One sample scales as \( G' \sim G'' \sim \omega^{1/3} \), the exponent value that is expected for a cylindrical morphology\(^{12}\) (PLA-10.5-P(S-s-GMA)-13.8-X\(_{\text{GMA}}\)-14.1). A series of samples scaled as \( G' \sim G'' \sim \omega^{3/4} \). The exponent value \( 3/4 \) is not typical of any classical morphologies. For most of these samples, the structure was identified as lamellar by SAXS.
As explained in the materials and methods section, the T_{ODT}'s of the block polymers were determined from linear dynamic temperature sweeps acquired using a heating rate of 1 °C min^{-1} with an angular frequency ω = 1 rad s^{-1} and a shear strain ε = 1%. The precipitous drop in G' was used to determine the value of T_{ODT} as follow:^13,14 the linear regions (in log scale) on both sides of the precipitous drop were fitted with a power law function (y=\textit{ax}^b, use of Originlab®). The two fitted regions give the tangents to the plot on both side of the discontinuous drop of G' and their intersection provide the onset of the drop which is identified as the ODT. The T_{ODT} is then obtained by resolving the simple equation: \textit{aT}^b = \textit{a}'T'^b where (\textit{a},\textit{b}) and (\textit{a}',\textit{b}') are the parameters of the tangents below and above T_{ODT} respectively. Figure S11 represents the plot of G' as a function of T for PLA-17.4-P(S-s-GMA)-11.1-X_{GMA}-29.2. The tangents are plotted in red. The error (Er) was estimated as the temperature increment over which the modulus drop occurred, i.e., the temperature increments between the onset point and the last points of contact between the G' plot and the tangents below and above the modulus drop (see Figure 11). Typically, Er = ± 5 °C.
**Table S4:** Characterization of the morphology and the ODT of the PLA-\(\beta\)-P(S-s-GMA) block polymers by rheology and SAXS. The polymers are noted PLA-\(\alpha\)-P(S-s-GMA)-\(\beta\)-X_{GMA-\gamma} where \(\alpha\) is the molecular weight of the PLA block (in kg mol\(^{-1}\), determined from NMR), \(\beta\) is the molecular weight of the P(S-s-GMA) block (in kg mol\(^{-1}\), determined from NMR) and \(\gamma\) is the molar fraction of GMA in the P(S-s-GMA) block, \(X_{GMA}\).  
\(^a\)Volume fraction of the P(S-s-GMA) block.  
\(^b\)Molar percentage of GMA in the P(S-s-GMA) block.  
\(^c\)Exponent of the power law scaling for the low frequency viscoelastic response (\(G'\)) of the block polymer.  
\(^d\)Disordered block polymers that do not exhibit a ODT.  
\(^e\)Polymer that do not obey a power law typical of a classical morphology.  
\(^f\)Morphology of the block polymer as deduced from the value of the exponent of the power law scaled by the storage modulus.  
\(^g\)ODT of the block polymer estimated as the temperature corresponding to the onset of the discontinuous drop of the storage modulus.  
\(^h\)The scattering vector corresponding to the principal peak of the SAXS pattern. The numbers within the brackets correspond to the scattering vectors of the higher order peaks. Unless specifically noted, these values were measured at 25 °C.  
\(^i\)Morphology deduced from the position of higher order peaks.  
\(^j\)ODT's estimated by the broadening of the principal scattering peak.

|       | PLA-7.7          | PLA-8.5          | PLA-10.5         | PLA-13.2         | PLA-14.1         | PLA-17.4         | PLA-19.7         | PLA-27.6         | PLA-32.0         |
|-------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| \(f^a\) | 0.54             | 0.50             | 0.51             | 0.51             | 0.54             | 0.54             | 0.49             | 0.49             | 0.49             |
| \(X_{GMA}^b\) | 7.7              | 8.2              | 27.8             | 14.4             | 17.0             | 21.5             | 21.1             | 17.0             | 23.0             |
| Power law\(^c\) | NA              | 0.41             | 0.235[0.471, 0.708, 0.944] | 0.214[0.425, 0.638] | 0.204[0.407, 0.610] | 0.55[0.75, 0.708, 0.944] | 0.214[0.425, 0.638] | 0.55[0.75, 0.708, 0.944] | 0.44[0.407, 0.610] |
| Morphology\(^f\) | NA              | LAM             | LAM              | LAM              | LAM              | LAM              | LAM              | LAM              | LAM              |
| \(T_{ODT}^g\) | 120             | 166             | 204              | 132              | 168              | 192              | 233              | 234              | 253              |
| q (nm\(^{-1}\))\(^h\) | 0.399[0.794] | 0.338[0.677, 1.013] | 0.312[0.621, 0.935] | 0.325[0.650, 0.973] | 0.235[0.471, 0.708, 0.944] | 0.214[0.425, 0.638] | 0.242[0.485, 0.729] | 0.214[0.425, 0.638] | 0.204[0.407, 0.610] |
| Morphology\(^f\) | NA              | NA              | NA               | NA               | NA               | NA               | NA               | NA               | NA               |
| \(T_{ODT}^i\) | 130<T<140 | 181<T<183 | -                | -                | -                | -                | 190<T<200 | 180<T<185 | 173<T<175 |

Unless specifically noted, these values were measured at 25 °C.
b- SAXS

For some of the samples, the morphology and the $T_{ODT}$ of the block polymer were further evaluated by SAXS. As explained in the materials and methods section, the samples were hermetically loaded in a DSC pan. They were annealed 1 h at 120 °C or 130 °C prior to measurement. The structure was first analyzed by using the SAXS pattern acquired at 25 °C unless otherwise noted (for some of the samples the first SAXS pattern was acquired at higher temperature). The ODT was then identified by the broadening of the principal scattering peak. The $T_{ODT}$ is given by the temperature corresponding to the total disappearance of the sharp principal scattering peak. $T_{ODT}$ values obtained by SAXS were assigned an error corresponding to the temperature difference between the two consecutive acquisitions corresponding to the disappearance of the peak. The structure, the principal peak as well as the higher order peaks and the $T_{ODT}$ measured by SAXS are reported in Table S4 for all the samples that were analyzed using this method.

![Figure S12](image.png)

**Figure S12:** SAXS patterns obtained for PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2. Temperature was increased by 1 °C increments in order to precisely identify the disappearance of the sharp peaks (marked by inverse triangles and characteristic of residual order). The sample was annealed 2 min at each temperature. This way, the $T_{ODT}$ was 174±1 °C.
c- Control of $T_{\text{ODT}}$

The inclusion of GMA in the PS block of a PS-PLA copolymer increases the solubility parameter of the styrenic block making it more compatible with PLA. For this reason, the $T_{\text{ODT}}$ of PLA-$b$-P(S-s-GMA) is a decreasing function of the molar percentage of GMA, $X_{\text{GMA}}$, in the crosslinkable block (see Table S4). Figure S13 represents the evolution of $T_{\text{ODT}}$ as a function of $X_{\text{GMA}}$ for one representative series of diblocks where the molecular weight ($M_n$) and the volume fraction ($f$) of PLA were kept essentially constant. This method of control of $T_{\text{ODT}}$ offers flexibility and allows for easy tuning of the parameters of the system. For instance, the molar mass of the block polymer, which in turn controls the size of the nanodomains, can be widely varied while maintaining $T_{\text{ODT}}$ in an appropriate temperature window. In particular, $T_{\text{ODT}}$ must be lower than the degradation temperature, $T_d$, of the block polymer and in the temperature range of $T_{\text{curing}}$, the temperatures for which the curing reaction becomes kinetically viable. In practice, $T_{\text{curing}}$ values resulting in gel times, $t_{\text{gel}}$, longer than a day were ruled out. The temperature range corresponding to viable $T_{\text{curing}}$ is fixed by the crosslinking agent selected to react with the epoxide functions of GMA (See section 7-b- Study of the curing reaction by rheology, for more details and $t_{\text{gel}}$ measurements). Figure S14 further illustrates this idea with a 3D plot of the evolution of $T_{\text{ODT}}$ as a function of the size of the PLA block ($M_n(\text{PLA})$, x axis) and the molar percentage of GMA in the crosslinkable block ($X_{\text{GMA}}$, y axis). Clearly, the $T_{\text{ODT}}$ and the size of the block can be controlled by varying the GMA molar percentage.

Figure S13: Plot of the order-disorder transition temperature ($T_{\text{ODT}}$) as a function of the molar percentage of GMA in the crosslinkable block ($X_{\text{GMA}}$) for one representative series of PLA-$b$-P(S-s-GMA) obtained from PLA-13.2. The $T_{\text{ODT}}$ values were measured by dynamic mechanical analysis. The bottom dotted horizontal line indicates the position of the annealing temperature, $T_{\text{annealing}} = 110$ °C. The top dotted horizontal line indicates the position of the lowest degradation temperature observed for PLA-$b$-P(S-s-GMA), $T_d$ (mass loss > 5% measured by thermogravimetric analysis). $T_d \sim 250$ °C. The red area indicates the temperature window with viable gel times, $t_{\text{gel}}$: 1 day $\geq t_{\text{gel}} \geq 72$ s for $130 \, ^\circ\text{C} \leq T_{\text{curing}} \leq 210 \, ^\circ\text{C}$. 

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**Figure S14:** 3D-plot of the order-disorder transition temperature ($T_{ODT}$) (z axis) as a function of the size of the PLA block (x axis) and the molar percentage of GMA in the crosslinkable block ($X_{GMA}$, y axis). The data points are labelled with the size of the P(S-$s$-GMA) block. The $T_{ODT}$’s were estimated by dynamic mechanical analysis.

**5- Synthesis of the initiator of the crosslinking reaction, BTPH**

**a- Material**

All the starting materials used for the synthesis of the initiator (triphenyl phosphine, benzyl bromide, and potassium hexafluoroantimonate) were purchased from Sigma Aldrich and used as received.

**b- Synthesis**

The two steps of the synthesis are illustrated in Figure S15. The protocol is adapted from procedures reported in the literature.\textsuperscript{15-17}

**Step 1:** Benzyl bromide (17 g, 2 eq.) was added dropwise to a solution of triphenyl phosphine (13 g, 1 eq.) in acetonitrile (40 ml). The solution was stirred overnight at room temperature. A precipitate was formed and was filtered to give a white powder. It was washed with acetonitrile
and dried under vacuum overnight. The resulting product, benzyl triphenylphosphonium bromide (18.2 g, yield = 85 %), was characterized by $^1$H-NMR spectroscopy, Figure S16 (7.97-6.94 ppm, 20H, aromatic protons, 5.18 ppm, 2H, benzylic protons).

Step 2: A solution of benzyl triphenylphosphonium bromide (4 g, 9.2 mmol, 1 eq.) in MeOH (50 ml) was added dropwise to a solution of potassium hexafluoroantimonate (7.62 g, 3 eq., 27.7 mmol) in water/MeOH (50 ml, 1/1, v/v) at 60 °C. The solution was cooled down to room temperature and stirred overnight. A precipitate was formed and was filtered to give a white powder. It was purified twice by reprecipitation in a mixture of ethanol and acetonitrile (22/3 v/v). The resulting product was dried under vacuum overnight at 110 °C. Benzyl triphenylphosphonium hexafluoroantimonate (2.2 g, yield = 41 %) was characterized by $^1$H-NMR in DMSO-$d_6$, Figure S17 (7.97-6.94 ppm, 20H, aromatic protons, 6.18 ppm, 2H, benzylic protons).

Figure S15: The two steps for the synthesis of the initiator of the crosslinking reaction. Step 1: nucleophilic substitution. Step 2: anion metathesis.

Figure S16: $^1$H-NMR spectrum of benzyl triphenylphosphonium bromide (DMSO-$d_6$).
Figure S17: $^1$H-NMR spectrum of benzyl triphenylphosphonium hexafluoroantimonate (DMSO-$d_6$).

6- Preparation of the samples: PLA-$b$-P(S-s-GMA)+BTPH

a- General procedure

In a representative example, PLA-$b$-P(S-s-GMA) (3 g) was dissolved in a vial with THF (6 g). In a separate vial, BTPH (100 mg) is dissolved with THF (3 g). This solution was gently warmed with a heat gun to accelerate the process and then cooled down to room temperature. The solution of BTPH was then added to the solution of PLA-$b$-P(S-s-GMA) to give a clear and yellow
solution. The resulting mixture was quickly degassed under reduced pressure to remove bubbles and dissolved gas and then poured in a tared aluminum mold. THF is first evaporated overnight at room temperature and under atmospheric pressure. The film is then placed under dynamic flow of N₂ for one day in an oven set at 60 °C. The temperature was increased to 80 °C and the film was maintained under N₂ flow for 12 more hours. Gravimetric analysis shows that most of the solvent was removed after this stage. The film was then annealed at 110 °C for 1 h (still under N₂ circulation). A new mass measurement was consistent with the complete evaporation of THF. The film was then removed from the aluminum mold while it was still warm.

**b- Thermal latency**

A series of SEC and SAXS measurements demonstrate that the molecular characteristics, the morphology and the T_{ODT} of the PLA-b-P(S-s-GMA)+BTPH samples obtained after the procedure described in section 6-a, are essentially the same as the corresponding pristine polymer, PLA-b-P(S-s-GMA). This proves that the extent of the curing reaction is negligible after all the processing steps used for the preparation of the samples.

**SEC and SAXS after annealing**

After annealing at 110 °C, the film is fully soluble in THF (no gel fraction). It is possible to analyze the molecular characteristics of the polymer (Mₙ and dispersity) by SEC.

Figure S18 compares the SEC traces of the neat polymer PLA-17.4-P(S-s-GMA)-11.3-X_GMA-29.2 and the SEC of PLA-17.4-P(S-s-GMA)-11.3-X_GMA-29.2+BTPH0.3wt%, the sample obtained after the procedure described above (Section 6-a), including annealing at 110 °C for 1 h. The SEC traces are essentially the same and the molecular characteristics are unchanged.

Similarly, Figure S19 compares the SAXS patterns obtained at room temperature for the neat polymer PLA-17.4-P(S-s-GMA)-11.3-X_GMA-29.2 and the SAXS patterns obtained at room temperature for PLA-17.4-P(S-s-GMA)-11.3-X_GMA-29.2+BTPH0.3wt%, the sample prepared according to the procedure described above (Section 6-a, including annealing at 110 °C for 1 h). The patterns indicate that the morphology of the sample was the same in presence of the initiator. The scattering peaks and the d spacing were essentially unchanged.
Figure S18: SEC traces for the neat polymer PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2 (solid line, $M_n = 36.3$ kg mol$^{-1}$, $D=1.07$) and PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPh0.3 wt% after annealing (dotted line, $M_n = 38.1$ kg mol$^{-1}$, $D=1.07$)

Figure S19: SAXS patterns for the neat polymer PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2 (solid line, $q^* = 0.234$ nm$^{-1}$, $d_{\text{spacing}} = 26.8$ nm) and PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPh0.3 wt% after annealing (dotted lines, $q^* = 0.226$ nm$^{-1}$, $d_{\text{spacing}} = 27.8$ nm)

$T_{\text{ODT}}$ after annealing

The influence of the initiator on the $T_{\text{ODT}}$ of the polymer was estimated by SAXS measurements. For these experiments, the annealing time between two successive acquisitions (at different temperatures) is 1 min (as compared to 2 min for the neat samples). This is important for the
samples with high T_{ODT} values as we want to prevent the onset of curing prior to the observation of T_{ODT}. For the same reason, the use of a continuous (1 °C min\(^{-1}\)) temperature ramp in rheological measurements is not an appropriate method to measure the T_{ODT} of the samples containing the initiator as the curing reaction usually starts before the precipitous drop of the storage moduli characteristic of the ODT.

Figure S20 represents the SAXS patterns acquired at various temperature for PLA-17.4-P(S-s-GMA)-11.1-X_{GMA}-29.2 (neat) and PLA-17.4-P(S-s-GMA)-11.1-X_{GMA}-29.2+BTPH0.3wt%. The broadening of the principal scattering peak was observed within the same temperature window for the two samples, indicating that the presence of the initiator has no significant influence on the value of T_{ODT}. Similar observations were made for PLA-17.4-P(S-s-GMA)-11.3-X_{GMA}-29.2 (Figure S21).

Table S5 summarizes the molecular characteristics obtained by SEC and the morphology and ODT information obtained via SAXS measurements for three polymers before (i.e. neat) and after addition of the initiator of the curing reaction. In all cases, the results support the idea that the initiator has very little influence on the characteristics of the pristine polymer.

Figure S20: SAXS patterns acquired at various temperature for PLA-17.4-P(S-s-GMA)-11.1-X_{GMA}-29.2 (neat, a) and PLA-17.4-P(S-s-GMA)-11.1-X_{GMA}-29.2+BTPH0.3wt% (b).
Figure S21: SAXS patterns acquired at various temperature for PLA-17.4-P(S-\(s\)-GMA)-11.3-X\(_{\text{GMA}}\)-29.2 (neat, \(T_{\text{ODT}} = 174 \pm 1 \, ^\circ\text{C}\), a) and PLA-17.4-P(S-\(s\)-GMA)-11.3-X\(_{\text{GMA}}\)-29.2+BTPH0.3wt\% (\(T_{\text{ODT}} = 178 \pm 1 \, ^\circ\text{C}\), b).
Table S5: Molecular characteristics (from SEC), morphology and T<sub>ODT</sub> (from SAXS) for three polymers before (i.e. neat) and after addition of the initiator of the curing reaction, BTPH. The polymers are noted PLA-α-P(S-s-GMA)-β-X<sub>GMA</sub>γ where α is the molecular weight of the PLA block (in kg mol<sup>-1</sup>, determined from NMR), β is the molecular weight of the P(S-s-GMA) block (in kg mol<sup>-1</sup>, determined from NMR) and γ is the molar fraction of GMA in the P(S-s-GMA) block, X<sub>GMA</sub>. <sup>a</sup>Characteristics of the system diblock+initiator after annealing (1h, 110 °C). <sup>b</sup>Number-average molar mass of the diblock obtained from THF SEC. <sup>c</sup>Molar mass dispersity of the diblock determined using LS-SEC. <sup>d</sup>Scattering vector corresponding to the principal peak of the SAXS pattern. The numbers within the brackets correspond to the position of the scattering vector of the higher order peaks. <sup>e</sup>Morphology deduced from the higher order peaks. <sup>f</sup>T<sub>ODT</sub>’s estimated by the broadening of the principal scattering peak.

| Polymer | Neat | BTPH0.3wt%<sup>a</sup> | Neat | BTPH0.3wt%<sup>a</sup> | Neat | BTPH0.3wt%<sup>a</sup> |
|---------|------|------------------------|------|------------------------|------|------------------------|
| SEC | M<sub>n</sub> (kg mol<sup>-1</sup>)<sup>b</sup> | D<sup>c</sup> | q (nm<sup>-1</sup>)<sup>d</sup> | Morphology<sup>e</sup> | T<sub>ODT</sub> (°C)<sup>f</sup> |
| PLA-17.4-P(S-s-GMA)-11.1-X<sub>GMA</sub>29.2 | 35.0 | 1.08 | 0.226[0.452, 0.679] at 25 °C | LAM | 180 < T < 185 |
| | 37.2 | 1.11 | 0.223[0.444, 0.668] at 25 °C | LAM | 180 < T < 185 |
| PLA-17.4-P(S-s-GMA)-11.3-X<sub>GMA</sub>29.2 | 36.3 | 1.07 | 0.234[0.467, 0.699] at 25 °C | LAM | 173 < T < 175 |
| | 38.1 | 1.07 | 0.226[0.447, 0.671] at 25 °C | LAM | 177 < T < 179 |
| PLA-17.4-P(S-s-GMA)-10.3-X<sub>GMA</sub>38.4 | 32.7 | 1.08 | 0.244[0.488] at 110 °C | LAM | 120 < T < 124 |
| | 33.5 | 1.07 | 0.228[0.454, 0.678] at 50 °C | LAM | 110 < T < 120 |
7- Curing procedure for monolithic samples

a- Curing in the rheometer oven under N\textsubscript{2} atmosphere

Samples were cured by rapid exposure to the curing temperatures, T\textsubscript{curing}. The convection oven of an Ares rheometer was used as the heating source. Advantageously, the oven is small and is very rapidly equilibrated to the desired temperature. It is also easily placed under N\textsubscript{2} atmosphere.

In a representative example, 200 to 500 mg of PLA-\(\alpha\)-P(S-s-GMA)-\(\beta\)-X\textsubscript{GMA}-\(\gamma\)+BTPH0.3wt\% (where \(\alpha\) is the molecular weight of the PLA block (in kg mol\textsuperscript{-1}, determined from NMR), \(\beta\) is the molecular weight of the P(S-s-GMA) block (in kg mol\textsuperscript{-1}, determined from NMR) and \(\gamma\) is the molar fraction of GMA in the P(S-s-GMA) block, \(X\textsubscript{GMA}\)) were placed on a piece of Teflon and rapidly introduced in the oven previously set and equilibrated (5 min) at the desired temperature, T\textsubscript{curing}.

PLA-\(\alpha\)-P(S-s-GMA)-\(\beta\)-X\textsubscript{GMA}-\(\gamma\)+BTPH0.3wt\% is prepared according to the procedure described in Scheme S1. The curing times, t\textsubscript{curing}, are chosen such t\textsubscript{curing} > 3t\textsubscript{gel} (see Table S6).

b- Study of the curing kinetics by rheology

In order to efficiently cure the samples, we estimated the gel time (t\textsubscript{gel}, i.e. the curing time necessary to form a gel) of the curing reaction by rheological measurements at various temperatures. t\textsubscript{gel} were measured from isothermal time sweep experiments using T = T\textsubscript{curing}, an angular frequency \(\omega = 1\) rad s\textsuperscript{-1} and a shear strain \(\varepsilon = 1\%\) (see section 1- Materials and methods for more details). t\textsubscript{gel} was estimated as the point of crossover of the storage modulus G\textsuperscript{′} and the loss modulus G\textsuperscript{′′}.

PLA-17.4-P(S-s-GMA)-11.9-X\textsubscript{GMA}-32.1+BTPH0.3wt\% (prepared according to the procedure described in Scheme S1) was used in this study. 0.5 g of the sample was loaded in the rheometer (parallel plate geometry, 25mm) at 130 °C. The temperature was then rapidly increased to T\textsubscript{curing} (10 °C min\textsuperscript{-1}) and the time sweep was immediately started. Figure S22 illustrates the plots of the storage and loss moduli as a function of time for four curing temperatures.

The plot of ln(t\textsubscript{gel}) (t\textsubscript{gel} in seconds) as a function of 1000/T, where T is the temperature in Kelvin, gives a linear plot as is expected for an Arrhenius relationship (Figure S23). This is typically observed for the curing of epoxy resins. The slope and the interception gives an apparent activation energy, \(E_a\), and an apparent frequency factor, \(A\), respectively.\textsuperscript{19} They can be used to estimate t\textsubscript{gel} at any temperatures. Here, \(E_a =145\) kJ mol\textsuperscript{-1}. This value is consistent with values reported in the literature for the curing of epoxy resins initiated by thermolatent cationic initiators.\textsuperscript{20} It was also confirmed through the study of the kinetics of the reaction by dynamic scanning calorimetry, DSC (see appendix).

The gel time measured by rheology or calculated with the Arrhenius plot at various temperatures are reported in Table S6. Interestingly, the calculated gel time for T\textsubscript{curing} = 25 °C is 12000 years,
indicating that the curing of the system polymer+initiator is not kinetically viable at room temperature (Moreover, the calculated \( t_{gel} \) is probably underestimated as the curing kinetics were calculated for molten polymers while at room temperature the two blocks are glassy. It is even less likely to observe the initiation and the propagation of the curing reaction because of limited molecular motions in vitrified polymers).

Similarly, the gel time at 110 °C is 10 days. During the annealing step of the samples, the temperature is maintained at 110 °C for only 1 h (see section 6-a). Thus, the extent of the curing reaction after annealing is probably negligible and these results support well the other experimental observations (SEC, SAXS) indicating that the characteristics of the polymer are not affected by the initiator after all the processing steps used for the preparation of the samples (see section 6-a for the description of the entire procedure and section 6-b for the SEC and SAXS experiments).

**Figure S22:** Plots of the storage and loss moduli, \( G' \) (solid line) and \( G'' \) (dotted line), respectively, as a function of time for the curing of PLA-17.4-P(S-s-GMA)-11.9-X_{GMA}-32.1+BTPH0.3wt% at four different temperatures (\( \omega = 1 \text{ rad s}^{-1}, \varepsilon = 1\% \)). The vertical arrows indicate the point of crossover of \( G' \) and \( G'' \) used as an estimation of \( t_{gel} \).
**Figure S23**: Arrhenius plot of $\ln(t_{gel})$ (t$_{gel}$ in seconds) as a function of $1000/T$ (T in Kelvin) for the system PLA-17.4-P(S-s-GMA)-11.9-X$_{GMA}$-32.1+BTPH0.3wt%.

**Table S6**: Gel times, t$_{gel}$, for PLA-17.4-P(S-s-GMA)-11.9-X$_{GMA}$-32.1+BTPH0.3wt% at various curing temperatures. 

| Curing temperature (°C) | t$_{gel}$ determined by rheological measurements$^a$ | t$_{gel}$ extrapolated using Arrhenius parameters$^b$ | t$_{curing}$$^c$ |
|------------------------|-----------------------------------------------|-------------------------------------------------|-----------------|
| 25                     | -                                             | $12 \times 10^3$ y                               | -               |
| 110                    | -                                             | 10.3 d                                          | -               |
| 120                    | -                                             | 3.3 d                                           | -               |
| 130                    | -                                             | 1.1 d                                           | 3 d             |
| 140                    | -                                             | 9.2 h                                           | 35 h            |
| 150                    | -                                             | 3.4 h                                           | 10 h            |
| 160                    | 1.3 h                                         | -                                               | 4 h             |
| 170                    | 32 min                                        | -                                               | 3 h             |
| 180                    | 13 min                                        | -                                               | 2 h             |
| 190                    | 6 min                                         | -                                               | 1.5 h           |
| 200                    | -                                             | 2.6 min                                         | 1 h             |
| 210                    | -                                             | 1.2 min                                         | 30 min          |
| 220                    | -                                             | 34 s                                            | 30 min          |

$^a$Gel times that were experimentally measured by dynamic mechanical analysis. 

$^b$Gel times estimated by extrapolation from the Arrhenius plot obtained with the experimental gel times (Figure S23).

$^c$Curing time, t$_{curing}$, typically used to efficiently cure the samples ($t_{curing} \geq 3 \times t_{gel}$).
c- Stability of the system during curing experiments

In order to evaluate the influence of the curing reaction on the degradation of the polymer, we performed thermogravimetric analysis (TGA) of PLA-17.4-P(S-s-GMA)-11.3-X\textsubscript{GMA}-29.2+ BTPH0.3wt% at temperatures corresponding to the curing temperatures, T\textsubscript{curing} (heat and hold experiments).

5 to 10 mg of PLA-17.4-P(S-s-GMA)-11.3-X\textsubscript{GMA}-29.2+ BTPH0.3wt% are placed in an aluminum pan. Using a TA Q500 instrument, the samples are rapidly heated up (20 °C min\textsuperscript{-1}) to a temperature corresponding to T\textsubscript{curing}, under N\textsubscript{2} atmosphere (conditions similar to the curing procedure in the oven of the ARES rheometer). The temperature was held at T\textsubscript{curing} and the mass loss (%) was measured as a function of time.

Figure S24 represents the mass loss as a function of time for two curing temperatures: 180 °C and 220 °C. The vertical arrows indicate the typical curing time, t\textsubscript{curing}, corresponding to these curing temperatures. The mass loss after t\textsubscript{curing} was always less than 5%. A very small mass loss (~1.5%) is observed at the beginning of both experiments which is likely due to a small amount of residual solvent from the casting procedure.

![Figure S24: Thermogravimetric analysis during heat and hold experiments for PLA-17.4-P(S-s-GMA)-11.3-X\textsubscript{GMA}-29.2+ BTPH0.3wt% at two different temperatures: 180 °C and 220 °C. The vertical arrows indicate the typical curing time, t\textsubscript{curing}, corresponding to these curing temperatures.](image)

**d- Gel fraction after curing**

Once the sample were cured, the efficiency of the crosslinking reaction was estimated by measuring the gel fraction of the cured samples. To do so, a small amount (typically 40 to 50 mg)
of the cured sample was accurately weighed \((m_i)\) and then immersed in THF (a good solvent of \(\text{PLA-b-P(S-s-GMA)}\)) overnight. The insoluble fraction was then filtered and dried overnight under reduced pressure at room temperature. The dried gel fraction is weighed again \((m_g)\) and the gel fraction (%) is given by eq. (13):

\[
m_g/m_i \times 100 \quad \text{eq. (13)}
\]

The values measured for two different polymers are reported in Table S7.

| \(T_{\text{curing}}\) (°C) | \(t_{\text{curing}}\) (h) | Gel fraction (%) | \(t_{\text{curing}}\) (h) | Gel fraction (%) |
|--------------------------|--------------------------|------------------|--------------------------|------------------|
| 160                      | 5.5                      | 98               | 5                        | 96               |
| 170                      | 5.4                      | 100              | 3.5                      | 97               |
| 175                      | 2                        | 100              | -                        | -                |
| 180                      | 2                        | 100              | 2                        | 99               |
| 190                      | 2.5                      | 100              | 2.5                      | 100              |
| 200                      | -                        | -                | 1                        | 99               |
| 210                      | -                        | -                | 1.5                      | 100              |
| 220                      | -                        | -                | 1.5                      | 100              |

**Table S7**: Curing times \((t_{\text{curing}})\) and gel fractions for the crosslinking of \(\text{PLA-17.4-P(S-s-GMA)-11.1-X_{GMA}-29.2+BTPH0.3wt\%}\) and \(\text{PLA-17.4-P(S-s-GMA)-11.3-X_{GMA}-29.2+BTPH0.3wt\%}\) at different temperatures, \(T_{\text{curing}}\).
8- Stability of the crosslinked structures

**Figure S25:** Variable temperature SAXS patterns for a sample of PLA-17.4-P(S-s-GMA)-11.1-X_GMA-29.2+BTPH0.3wt% previously crosslinked at $T_{curing} = 160 \, ^\circ C$ (5 h), i.e. below $T_{ODT}$ ($T_{curing} - T_{ODT} = -18 \, ^\circ C$). (a) SAXS pattern acquired at $T = 25 \, ^\circ C$ ($T$ is the temperature used for the SAXS measurement), $T - T_{ODT} = -153 \, ^\circ C$, where $T_{ODT}$ is the $T_{ODT}$ of the pristine polymer (i.e., PLA-17.4-P(S-s-GMA)-11.1-X_GMA-29.2+BTPH0.3wt% prior to curing). (b) SAXS pattern acquired at $T = 230 \, ^\circ C$, $T - T_{ODT} = +52 \, ^\circ C$ (c) SAXS pattern acquired at $T = 250 \, ^\circ C$, $T - T_{ODT} = +72 \, ^\circ C$. For (b) and (c), SAXS pattern are acquired at temperatures that are well above the $T_{ODT}$ of the pristine polymer. They are still characteristic of a lamellar ordering indicating that the morphology has been efficiently locked in during the crosslinking step prior to the variable temperature SAXS measurements.

**Figure S26:** SAXS patterns acquired at room temperature for three samples of PLA-17.4-P(S-s-GMA)-11.1-X_GMA-29.2+BTPH0.3wt% cured at $T_{curing} = 190 \, ^\circ C$ for 2.5 h, i.e. for $T_{curing} - T_{ODT} = +12 \, ^\circ C$. (a) The crosslinked sample was annealed at 120 °C for 1 hour prior to the SAXS measurement, (b) The crosslinked sample was annealed at 120 °C for 15 hours prior to the SAXS measurement (c) The crosslinked sample was annealed at 160 °C for 1 hour prior to the SAXS measurement. In each case, the SAXS pattern is characteristic of a disordered structure indicating that even after annealing (for different period of time and at various temperature well above the $T_g$’s of the pristine polymer), the crosslinked sample cannot recover the lamellar morphology characteristic of the pristine polymer. This is indicative that the disordered structure has been efficiently locked in during the crosslinking step.
9- Detailed SAXS results for PLA-17.4-P(S-s-GMA)-11.3-X\textsubscript{GMA}-29.2+BTPH0.3wt%

a- SAXS patterns

Figure S27: SAXS pattern acquired at room temperature before (solid line) and after (dashed line) etching in a basic solution, for samples of PLA-17.4-P(S-s-GMA)-11.3-X\textsubscript{GMA}-29.2+BTPH0.3wt% cured at (a) 170 °C, (b) 180 °C, (c) 200 °C, (d) 210 °C, and (e) 220 °C.
Note: Figure S27b: $T_{\text{curing}} = 180 \, ^\circ\text{C}, \Delta T = +2 \, ^\circ\text{C}$

The SAXS pattern of the sample cured at nominally 180 °C (Figure S27b) exhibits a sharp principal peak even though this curing temperature is (slightly) higher than the $T_{\text{ODT}}$ of the system ($\Delta T = +2 \, ^\circ\text{C}$). Strong compositional fluctuations in the close proximity of $T_{\text{ODT}}$ may be responsible for this observation of apparent ordering. Indeed, with respect to the description of the fluctuation as a “pattern transition”, it is possible that the morphology of the dynamic system (i.e., uncrosslinked) appears as disordered on the time scale of the measurement but becomes ordered once it is kinetically trapped by the crosslinking reaction.

Interestingly, a broad reflection peak was observed after etching indicating that, despite the sharp scattering peak obtained for the system before etching, the crosslinked structure is probably not lamellar. Again, this observation suggests that, in the very close proximity of $T_{\text{ODT}}$, the structure is most likely a subtle intermediate between a morphology reminiscent of lamellae and a disordered network. It is also possible that the morphology is not fully uniform across the sample. Domains with different degree of ordering may coexist as it was observed in other block polymer systems. This hypothesis is further supported by results observed in SEM (see Figure S30b and S31c).

These phenomena that are apparent when curing close to the $T_{\text{ODT}}$ are still under investigation and not fully resolved.

### b- Variation of the domain spacing before and after curing

| T (°C) | Domain spacing, $d$ (nm) | $\Delta d/d$ (%) |
|--------|------------------------|------------------|
|        | PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2 Neat, SAXS acquired at T | PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2 Crosslinked at T, SAXS acquired at room temperature |
| 160    | 25.6                   | 27.8             | 8.4 |
| 170    | 25.6                   | 27.2             | 6.1 |
| 180    | 26.2                   | 26.5             | 1.3 |
| 190    | 26.5                   | 25.8             | -2.5 |
| 200    | 26.5                   | 25.8             | -2.5 |
| 210    | 26.2                   | 25.6             | -2.0 |
| 220    | 25.8                   | 25.3             | -2.0 |

**Table S8:** Domain spacing as measured by SAXS experiments for PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2 samples before and after curing. For the uncured samples (i.e. neat), the SAXS patterns were acquired at high temperatures, corresponding to the curing temperatures. For the cured samples the SAXS patterns were acquired at room temperature. *Temperatures corresponding either to the temperature used for heating the neat polymer during the SAXS experiments or the temperature used to crosslink the polymer ($T_{\text{curing}}$) during the curing experiments.
10- Etching of the cured monoliths

a- Procedure

The PLA domain of the cured samples is removed by chemical etching using a basic solution of sodium hydroxide (0.5 mol L\(^{-1}\)) in a mixture of water and methanol (H\(_2\)O/MeOH, 6/4, v/v).\(^{24}\) The typical procedure is: 200 to 500 mg of a cured monolith were accurately weighed (m\(_i\)), placed in a vial and immersed in the methanolic solution of sodium hydroxide (0.5 mol L\(^{-1}\)). The system is heated at 45 °C for 3 d.

The monolith was then thoroughly rinsed with deionized water and dried with a Kimwipe. It was cooled down to the temperature of liquid nitrogen and rapidly placed under vacuum at room temperature. After 12 h under vacuum, the monolith was weighed again (m\(_e\)).

b- Mass loss after etching

The removal of PLA was first confirmed by mass loss measurements using eq. (14):

\[
m_e/m_i \times 100 \quad \text{eq. (14)}
\]

The values calculated with eq. (14) must be in good agreement with the weight fraction of the P(S-s-GMA) block in the pristine PLA-b-P(S-s-GMA) block polymer used to obtain the cured monoliths. Mass loss measured for two polymers are reported in Table S9. The gravimetric measurements indicate that the removed mass is 3 to 7% lower than expected, based on the initial weight fraction of PLA in the block polymer. Small isolated inclusions of PLA that are trapped within the crosslinked P(S-s-GMA) matrix may account for the lower than expected mass loss. However, there is no other indication of these PLA inclusions when the etched samples are analyzed by IR spectroscopy and DSC (see below). Another possibility is that a small amount of PLA was degraded during the curing step, prior to etching. The heat and hold experiments presented in Figure S24 indicate that a mass loss of about 4% is usually observed after exposure of the samples to \(T_{\text{curing}}\), the curing temperature, for a period of time corresponding to \(t_{\text{curing}}\), the curing time. This value (4%) correlates well with the differences between the experimental and the theoretical mass losses, post-etching (3 to 7%, see Table S9).
Table S9: Mass loss after chemical etching of the PLA domain (NaOH 0.5 mol L^{-1}, H\textsubscript{2}O/MeOH, 6/4, v/v, 3 days, 45 °C) for PLA-17.4-P(S-s-GMA)-11.1-X\textsubscript{GMA}-29.2+BTPH0.3wt% and PLA-17.4-P(S-s-GMA)-11.3-X\textsubscript{GMA}-29.2+BTPH0.3wt% monoliths cured at different temperatures. \(^{a}\)The system was not cured at these curing temperatures.

| $T_{\text{curing}}$ (°C) | PLA-17.4-P(S-s-GMA)-11.1-X\textsubscript{GMA}-29.2 | PLA-17.4-P(S-s-GMA)-11.3-X\textsubscript{GMA}-29.2 |
|--------------------------|-------------------------------------------------|-------------------------------------------------|
|                          | Mass loss measured (%) | Mass loss expected (%) | Mass loss measured (%) | Mass loss expected (%) |
| 160                      | 57                 | 61                 | 54                 | 61                 |
| 170                      | 55                 | 61                 | 54                 | 61                 |
| 175                      | 57                 | 61                 | 56                 | 61                 |
| 180                      | 58                 | 61                 | 56                 | 61                 |
| 190                      | 55                 | 61                 | 56                 | 61                 |
| 200                      | \(^{a}\)             | 61                 | 57                 | 61                 |
| 210                      | \(^{a}\)             | 61                 | 58                 | 61                 |
| 220                      | \(^{a}\)             | 61                 | 57                 | 61                 |
**c- IR spectra before and after etching**

The removal of PLA was further confirmed by IR measurements. We used a Bruker Alpha Platinum spectrometer equipped with an ATR platform. The C=O vibration of PLA (1748 cm\(^{-1}\)) completely disappears after etching, proving that the PLA domain was removed. The C=O vibration of GMA (1727 cm\(^{-1}\)) is not affected by the etching process, proving that the procedure selectively removes PLA and does not significantly impact the P(S-s-GMA) domains. Figure S28 illustrates the IR spectra for a PLA-17.4-P(S-s-GMA)-11.3-X\(_{\text{GMA}}\)29.2+BTPH0.3wt% monolith cured at 190 °C, before and after etching.

**Figure S28**: IR spectra for a PLA-17.4-P(S-s-GMA)-11.3-X\(_{\text{GMA}}\)29.2+BTPH0.3wt% monolith cured at 190 °C, before and after etching.
d- DSC thermograms before and after etching

Another method to confirm the removal of PLA is DSC. The disappearance of the transition corresponding to the $T_g$ of PLA in the DSC thermogram of the etched material is an additional proof of efficient etching. Figure S29 illustrates the DSC thermograms for PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% monoliths cured at 160 °C, 180 °C, 190 °C and 220 °C before and after etching. They are compared to the thermogram of the corresponding neat polymer (PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2).

![DSC thermograms for PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% monoliths cured at 160 °C, 180 °C, 190 °C and 220 °C before and after etching.](image)

**Figure S29**: DSC thermograms for PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% monoliths cured at 160 °C, 180 °C, 190 °C and 220 °C. The regular solid line corresponds to the sample after curing and before etching. The bold solid line corresponds to the sample after curing and etching. The dashed line is the thermogram of the corresponding neat polymer (i.e. without initiator).
### Table S10: Domain spacing as measured by SAXS experiments for cured samples of PLA-17.4-P(S-s-GMA)-11.3-X\textsubscript{GMA}-29.2+BTPH0.3wt% before and after etching. aSamples crosslinked in the ordered state and for which the structure is collapsed after etching.
11- Scanning electron microscopy (SEM) results for PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTBH0.3wt%.

$T_{curing} = 170 \, ^\circ C$, $\Delta T = -8 \, ^\circ C$  

$T_{curing} = 180 \, ^\circ C$, $\Delta T = +2 \, ^\circ C$

$T_{curing} = 200 \, ^\circ C$, $\Delta T = +22 \, ^\circ C$

$T_{curing} = 210 \, ^\circ C$, $\Delta T = +32 \, ^\circ C$

$T_{curing} = 220 \, ^\circ C$, $\Delta T = +42 \, ^\circ C$

**Figure S30**: Representative SEM images of samples of PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTBH0.3wt% cured at (a) 170 °C, (b) 180 °C, (c) 200 °C, (d) 210 °C, and (e) 220 °C. Samples were etched in a basic solution, cryo-fractured and coated with Pt (∼2nm) prior to imaging.
**Figure S31:** Representative SEM images of samples of PLA-17.4-P(S-s-GMA)-11.3-X<sub>GMA</sub>-29.2+BTPH0.3wt% cured at (a) 160 °C, (b) 170 °C, (c) 180 °C, (d) 190 °C, (e) 200 °C, (f) 210 °C, and (g) 220 °C. Samples were etched in a basic solution, cryo-fractured and coated with Pt (∼2nm) prior to imaging. Images were captured at a lower magnification than Figure S30.
Note: Figure S30b and Figure S31c: $T_{\text{curing}} = 180 \, ^\circ\text{C}$, $\Delta T = +2 \, ^\circ\text{C}$

SEM confirms that $T_{\text{curing}}=180 \, ^\circ\text{C}$ is an intermediate case with the coexistence of dense domains, reminiscent of sheet-like structures, evenly distributed within a porous and disordered matrix. This correlates well with the results obtained in SAXS (Figure S27b).
12- Transmission Electron Microscopy (TEM) for PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% crosslinked at 190 °C and etched

a- Sample preparation

A monolith of PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% was crosslinked at 190 °C for 1h (crosslinking above T_{ODT}, ΔT = +12 °C). For this curing experiment, the sample was crosslinked in an autoclave under high pressure (500 Psi, Argon) in order to avoid the expansion of the air bubbles remaining trapped in the sample after the casting procedure (see section 6-1). Sorption measurement indicates no signifiative change of the surface area and pore volume of this sample compared to the sample crosslinked under atmospheric pressure. Prior to electron imaging, the sample was microsectioned at T = −120 °C using a LEICA UC6 microtome with a Diatome diamond knife. The sample was collected on carbon coated grids (200 mesh). The thickness of the section was roughly 150 nm. A drop of basic solution (0.5 M solution of NaOH in water/methanol 6/4(v/v)) was placed on the TEM grid for 1 h to remove PLA.

b- Regular TEM

The specimen was examined using a Tecnai TF30 300 kV FEG (FEI-Company, Hillsboro, OR, and Eindhoven, The Netherlands) at 78,000x (Figure S32 a) and 93,000x (Figure S32 b) nominal magnifications.

Figure S32: Transmission electron microscopy (TEM) images of PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% crosslinked at 190 °C and etched with a basic solution. The P(S-s-GMA) phase is dark, the porous phase is bright. Samples were cryo microtomed at −120 °C. The specimen was examined using a Tecnai TF30 300 kV FEG (FEI-Company, Hillsboro, OR, and Eindhoven, The Netherlands) at (a) 78,000x and (b) 93,000x nominal magnifications
c- TEM tomography

We collected a single-axis tilt series with a Tecnai TF30 300 kV FEG (FEI-Company, Hillsboro, OR, and Eindhoven, The Netherlands) transmission electron microscope using SerialEM from −60° to +60° with 1° increments at 78,000x nominal magnification and the resulting micrographs were aligned and reconstructed using the Etomo component of the IMOD software applying a simple back projection algorithm. The reconstructed image was then opened using the Slicer tool in 3DMOD. The image was rotated to align the top surface of the image with the viewing screen. Snapshots were taken for slices spanning the thickness of the sample. 12 representative snapshots are displayed in Figure S33.

Figure S33: Snapshots of slices of the reconstructed tomogram of PLA-17.4-P(S-γ-GMA)-11.3-XGMA-29.2+BTPH0.3wt% crosslinked at 190 °C and etched with a basic solution. The montage is comprised of every 5th slice from the 60 slice reconstruction. The images are numbered in order of appearance as we go through the thickness of the sample. Note: As the edges of the sample are approached in the 3D reconstruction, there is a noticeable decrease in the clarity of the images (in particular, images 9 to 12) likely as a result of inhomogeneities in the thickness of the sample microsection as well as missing information due to the "missing wedge" phenomenon.
The slices were compiled into a movie using ImageJ: Movie S1. The montage of Figure S33 as well as Movie S1 illustrate the interconnection of the pores (bright regions) through the thickness of the sample. These data support the idea of a bicontinuous network of pores.

Additionally, a volume rendering was performed in UCSF Chimera by applying a 3D Gaussian filter to the same tomogram with a threshold chosen to match the porosity of the rendered volume to the volume fraction of PLA in the P(S-s-GMA)-b-PLA diblock.27, 28 Pores are colored blue in the filtered image, while the cross-linked P(S-s-GMA) matrix is transparent (Figure S34a). To examine the connectivity of the pores, the “color blob tool” in UCSF Chimera was used. By selecting a feature in the filtered reconstruction, the tool colors a continuous channel that contains the selected feature red. Figure S34b highlights one such channel, displaying a highly connected pore network that spans the sample, consistent with a percolating morphology.

Isolated regions of pores are also observed within the cross-linked matrix. These regions may represent discontinuities within the porous network, a partial collapsing of the etched structure or may possibly be an artifact of TEMT related to the so-called “missing wedge”.25

**Figure S34**: Volume rendering performed in UCSF Chimera by applying a 3D Gaussian filter to the tomogram of PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% crosslinked at 190 °C and etched with a basic solution. (a) Pores are colored blue while the cross-linked P(S-s-GMA) matrix is transparent. In (b), we used the “color blob tool” to highlight a channel of pores. This channel spans the samples and is consistent with a percolating morphology.
a- Nitrogen sorption, Isotherms

**Figure S35:** Nitrogen sorption isotherm for samples of PLA-17.4-P(S-s-GMA)-11.3-X_{GMA}-29.2+BTPH0.3wt% cured at (a) 160 °C, (b) 170 °C, (c) 180 °C, (d) 190 °C, (e) 200 °C, (f) 210 °C, and (g) 220 °C. Samples were etched in a basic solution prior to measurement. Open circles (○) correspond to the adsorption branch, and filled circles (●) to the desorption branch.
**b- Nitrogen sorption, pore size distributions**

**Figure S36:** Mesopore size distributions based on QSDFT analysis of the adsorption branch for samples of PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% cured at (a) 160 °C, (b) 170 °C, (c) 180 °C, (d) 190 °C, (e) 200 °C, (f) 210 °C, and (g) 220 °C. Samples were etched in a basic solution prior to measurement.
Notes on the samples in Figure S35c and Figure S36c: $T_{curing} = 180 \degree C$, $\Delta T = +2 \degree C$

Figure S35c

The plateau of the isotherms is on average 100 cm$^3$.g$^{-1}$ lower than for the other porous samples (crosslinked at higher temperatures). As a result, the material cured at 180 °C exhibits the lowest pore volume, 0.22 cm$^3$.g$^{-1}$, and surface area, 90 m$^2$.g$^{-1}$. Again, this is attributed to the close proximity to the T$_{ODT}$.

Figure S36c

The pore size distributions, modeled using the adsorption branch of the isotherms and a quenched solid density functional theory kernel (QSDFT), exhibits a wide multimodal peak indicating a broad pore size distribution. This is most probably a consequence of the partial collapsing of the structure as illustrated by the presence of dense domains observed in SEM (Figure S30b and S31c).
14- SAXS results for PLA-10.5-P(S-s-GMA)-9.7-XGMA-14.4+BTPH0.3wt%

a- $T_{ODT}$ measurements

Figure S37: SAXS patterns obtained for PLA-10.5-P(S-s-GMA)-9.7-XGMA-14.4. The sample was annealed 2 min at each temperature. The $T_{ODT}$ was determined as 182±1 °C by the broadening of the principal scattering peak. For $T < T_{ODT}$, higher ordering peaks are marked by inverse triangles and are consistent with a lamellar morphology.

Note: It was not possible to directly measure the $T_{ODT}$ of PLA-10.5-P(S-s-GMA)-9.7-XGMA-14.4+BTPH0.3wt%. The sample reacts before disordering. However, a lamellar structure was confirmed with the same d spacing as for PLA-10.5-P(S-s-GMA)-9.7-XGMA-14.4 (the neat polymer).
b- SAXS patterns of cured samples before and after etching

**Figure S38:** SAXS pattern acquired at room temperature before (solid line) and after (dashed line) etching in a basic solution, for samples of PLA-10.5-P(S-s-GMA)-9.7-X\textsubscript{GMA}-14.4+BTPH0.3wt% cured at (a) 180 °C, (b) 190 °C, (c) 200 °C, and (d) 210 °C.
Note: Similar to the sample of PLA-17.4-P(S-s-GMA)-11.3-X_{GMA}-29.2+BTPH0.3wt% crosslinked at 180 °C, we note that the SAXS pattern of the sample of PLA-10.5- P(S-s-GMA)-9.7-X_{GMA}-14.4+BTPH0.3wt% crosslinked at 190 °C exhibits a sharp principle scattering peak despite a curing temperature above the T_{ODT} of the uncrosslinked system. Again, this unexpected behavior is attributed to the close proximity to the T_{ODT}. Here, for T_{curing} = 190 °C, ΔT = +8 °C. However, we consider the T_{ODT} of the neat polymer (without the initiator, see Figure S37 above). As demonstrated for PLA-17.4-P(S-s-GMA)-11.3-X_{GMA}-29.2+BTPH0.3wt%, the T_{ODT} is slightly increased upon addition of the initiator. Consequently, if PLA-10.5- P(S-s-GMA)-9.7-X_{GMA}-14.4+BTPH0.3wt% exhibits similar behavior, then T_{curing} would be closer to T_{ODT} than it would be for the neat polymer.

Moreover, the T_{ODT} of PLA-10.5- P(S-s-GMA)-9.7-X_{GMA}-14.4+BTPH0.3wt% is high, >180°C. At these temperatures, the kinetics of the curing reaction is really fast (see section 7-b). It is possible that, for T_{curing} = 190°C, the system forms a gel before it fully disorders. It is also possible that a rapid increase of the molar mass in the initial stages of the crosslinking reaction results in an increase of the apparent T_{ODT} of the system (T_{ODT})_{app}, so that (T_{ODT})_{app} > T_{curing} > (T_{ODT})_{init}, where (T_{ODT})_{init} is the T_{ODT} of PLA-10.5- P(S-s-GMA)-9.7-X_{GMA}-14.4+BTPH0.3wt% before exposure of the sample to the curing temperature, T_{curing}.

The observation made in SAXS is confirmed by SEM and nitrogen sorption results (See below Figure S39 to S42).
Detailed SEM results for PLA-10.5- P(S-s-GMA)-9.7-X\textsubscript{GMA}-14.4+BTPH0.3wt% 

$T_{\text{curing}} = 180 \, ^\circ \text{C}, \Delta T = -2 \, ^\circ \text{C}$

$T_{\text{curing}} = 190 \, ^\circ \text{C}, \Delta T = +8 \, ^\circ \text{C}$

$T_{\text{curing}} = 200 \, ^\circ \text{C}, \Delta T = +18 \, ^\circ \text{C}$

$T_{\text{curing}} = 210 \, ^\circ \text{C}, \Delta T = +28 \, ^\circ \text{C}$

**Figure S39:** Representative SEM images of samples of PLA-10.5- P(S-s-GMA)-9.7-X\textsubscript{GMA}-14.4+BTPH0.3wt% cured at (a) 180 °C, (b) 190 °C, (c) 200 °C, and (d) 210 °C. Samples were etched in a basic solution, cryo-fractured and coated with Pt (∼2nm) prior to imaging.
Figure S40: Representative SEM images of samples of PLA-10.5- P(S-s-GMA)-9.7-X_{GMA}-14.4+BTPH0.3wt% cured at (a) 180 °C, (b) 190 °C, (c) 200 °C, and (d) 210 °C. Samples were etched in a basic solution, cryo-fractured and coated with Pt (∼2nm) prior to imaging. Images were captured at a lower magnification than in Figure S39.
16- Detailed Nitrogen sorptions results for PLA-10.5- P(S-s-GMA)-9.7-XGMA-14.4+BTPH0.3wt%

\[ T_{\text{curing}} = 180 \, ^\circ\text{C}, \, \Delta T = -2 \, ^\circ\text{C} \]
\[ T_{\text{curing}} = 190 \, ^\circ\text{C}, \, \Delta T = +8 \, ^\circ\text{C} \]

Surface area \( \sim 0 \, \text{m}^2 \, \text{g}^{-1} \)
Pore volume \( \sim 0 \, \text{cm}^3 \, \text{g}^{-1} \)

\[ T_{\text{curing}} = 200 \, ^\circ\text{C}, \, \Delta T = +18 \, ^\circ\text{C} \]
\[ T_{\text{curing}} = 210 \, ^\circ\text{C}, \, \Delta T = +28 \, ^\circ\text{C} \]

Surface area = 89 m\(^2\) g\(^{-1}\)
Pore volume = 0.18 cm\(^3\) g\(^{-1}\)

Surface area = 107 m\(^2\) g\(^{-1}\)
Pore volume = 0.2 cm\(^3\) g\(^{-1}\)

**Figure S41:** Nitrogen sorption isotherm for samples of PLA-10.5- P(S-s-GMA)-9.7-XGMA-14.4+BTPH0.3wt% cured at (a) 180 °C, (b) 190 °C, (c) 200 °C, and (d) 210 °C. Samples were etched in a basic solution prior to measurement. Open circles (○) correspond to the adsorption branch, and filled circles (●) to the desorption branch.
Figure S42: Mesopore size distributions based on QSDFT analysis of the adsorption branch for samples of PLA-10.5- P(S-s-GMA)-9.7-X_{GMA}-14.4+BTPh0.3wt% cured at (a) 180 °C, (b) 190 °C, (c) 200 °C, and (d) 210 °C. Samples were etched in a basic solution prior to measurement.
17- Fabrication of composite membranes for ultrafiltration tests

a- Wire-wound rod membrane fabrication

A polyethersulfone (PES) support membrane (obtained from Sterlitech, 100 nm average pore diameter, 47 mm diameter disc) was immersed in water for 1 min to backfill the pores. The wetted membrane was then placed on top of a Teflon sheet. A PLA-b-P(S-s-GMA) selective layer (PLA-17.4-P(S-s-GMA)-11.3-X_{GMA}-29.2+BTPH0.3wt%) was then coated onto the top of the PES by depositing an 8 wt.% polymer solution in chlorobenzene in front of the PES support and drawing the solution across the surface using a wire-wound rod. The coated film was then allowed to dry for 1 min under ambient conditions before being placed in a preheated oven set to 60 °C for 30 minutes. The temperature was then reduced to 40 °C and the membrane was allowed to dry overnight. After the films were dried, they were annealed for 1 h at 100 °C (above \(T_g\)) and were then cured for 1 hour at 190 °C (above \(T_{ODT}\)) on top of the Teflon sheet, following the procedure used for monolithic samples. Once cooled, a 25 mm diameter disc was punched from the center of the larger membrane for ultrafiltration experiments.

The morphology of the etched samples (etching procedure described below) was examined using SEM. Cryo-fractured samples were coated with an ~3 nm thick Pt film to reduce charging and examined using an accelerating voltage of 3 kV and a 10 µA current using a Hitachi S-4700 cold FEG-SEM. Top-view specimens were examined to analyze the surface coverage and morphology of the selective layer and a cross-sectional view was used to determine the thickness of the selective layer, Figure S43. The film thickness was determined to be approximately 500 nm based on an average of 10 different measurements taken across the span of the membrane, using ImageJ.
Figure S43: Top (a) and cross-sectional (b) views of the PLA-17.4-P(S-s-GMA)-11.3-XGMA-
29.2+BTPH0.3wt% selective layer coated from an 8 wt.% solution in chlorobenzene using a wire-
wound rod. Top (c) and cross-sectional (d) images of a bare PES support subjected to the same
thermal processing parameters (1 h heating at 190 °C) are included for comparison.

b- Ultrafiltration Experiments

A 2.5 cm diameter disc of the UF membrane was placed in an Amicon 8010 stirred
ultrafiltration cell. To test the sample for the presence of holes or defects, a pressure difference of
0.5 bar was applied prior to etching the PLA. If no water permeation was observed after 1 h, the
membrane was determined to be defect/hole free with all of the pores of the PES covered by the
PLA-b-P(S-s-GMA) film. PLA was then selectively etched by filling the cell with a solution of
aqueous base (0.5 M NaOH in 40/60 w/w of MeOH/H2O) for 45 minutes. Following the etching
process, the membrane was first flushed with 10 mL of a 50/50 (v/v) methanol/water mixture
followed by flushing with 10 mL of DI water.

Water flux was measured in triplicate for three different pressure drops. Pure water permeability
was calculated as the slope of a linear fit of water flux to pressure difference. The bare PES support
displayed a permeability of 3700 L m⁻² h⁻¹ bar⁻¹ under the experimental set-up. After coating the
PES support with a P(S-s-GMA)-b-PLA selective layer, there was a notable decrease in the
permeability due to increased mass transport resistance, with a pure water flux of 7.4 Lm⁻² h⁻¹bar⁻¹
observed for the 500 nm thick film, Figure S44a.
Figure S44: Water flux for 500 nm P(S-s-GMA)-b-PLA selective layer on a PES was measured at three different pressure drops in triplicate before (a) and after (b) challenging with Dextran solutions. Pure water permeability was calculated via a linear fit of water flux vs. pressure difference. A significant reduction in permeability was observed after passing a Dextran solution through the membrane likely due to fouling. Additionally, the selective layer was shown to be mechanically stable at the highest pressure difference permitted by the UF cell, 3.4 bar. The specifications for the UF cell prevented the investigation of higher pressures.

Rejection experiments were performed using a 0.5 mg mL$^{-1}$ solution of TRITC-Dextran ($M_w = 155$ kg mol$^{-1}$, $R_h = 7$ nm) in DI water.$^{31}$ The Dextran solution was flushed through the membrane under a pressure drop of 0.5 bar and stirring speed of 600 rpm and the permeate was collected in a clean vial. The UV-Vis absorption of the permeate at $\lambda = 521$ nm, maximum absorption for TRITC, was then compared to the absorption of the feed at $\lambda = 521$ nm to determine rejection. Using this method, a rejection of 98% was observed for the 500 nm selective layer (Figure S45a).
Figure S45: Rejection of a 0.5 mg mL\(^{-1}\) TRITC-Dextran solution (M = 150 kg mol\(^{-1}\), \(R_h \sim 7\) nm) was calculated as 98% using UV-Vis (a). Rejection was calculated as the ratio of the absorbance of the feed solution (solid curve) to the absorption of the permeate (dashed curve) at 521 nm. Size-selectivity of the P(S-GMA)-b-PLA selective layer was demonstrated by passing a mixed feed of Dextran standards. Rejection was calculated from 100*(1-(permeate area)/(feed area)) from a mixed feed of Dextrans using SEC (solid curve in b). The size-selectivity experiment was repeated for a bare PES membrane as a comparison (dashed curve in b). Molecular weight was calculated from the elution time by constructing a calibration curve of Dextran standards and \(R_h\) was calculated from the molecular weight using a known relation from the literature. MWCO was calculated as approximately 50 kg mol\(^{-1}\), corresponding to a \(R_h\) of approximately 5 nm. Additionally, each Dextran standard was passed through the P(S-GMA)-b-PLA membrane separately and rejection was calculated as the ratio of the peak area for the permeate to the feed (blue circles in b).

To further examine the size-selectivity of the 500 nm film, a mixed feed of Dextran standards was passed through the membrane.\(^{32,33}\) The feed was prepared by dissolving 1 mg mL\(^{-1}\) each of 5 kg mol\(^{-1}\), 12 kg mol\(^{-1}\), 50 kg mol\(^{-1}\), 80 kg mol\(^{-1}\), 150 kg mol\(^{-1}\), and 410 kg mol\(^{-1}\) Dextran in the mobile phase of an aqueous SEC (0.1 M Na\(_2\)SO\(_4\)/1% acetic acid) and a 0.05 M KH\(_2\)PO\(_4\) buffer. The resulting solution was then passed through the membrane at a pressure difference of 0.5 bar with a stirring speed of 600 rpm and the permeate was collected in a clean glass vial. SEC was then performed on the feed and permeate solutions. Rejection was calculated as 100*(1-(permeate area)/(feed area)).\(^{30,31}\) Elution time was converted to molecular weight by constructing a calibration curve of Dextran standards. The overlaid elugrams of each of the standards used to construct this calibration curve are included in Figure S46. The calculated molecular weights were then used to determine the corresponding \(R_h\) using the relation for Dextran in water (eq. 14):\(^{31}\)

\[
\log(R_h) = 0.47 \times \log(M) - 1.513 \quad (eq. 14)
\]

A molecular weight cut off (MWCO) of approximately 50 kg mol\(^{-1}\) was observed (Figure S45b, solid curve), corresponding to a \(R_h\) of approximately 5 nm which is in reasonable agreement with
the 10 nm pore diameter calculated from N₂ sorption. An increase in rejection at low molar masses was observed, which was attributed to adsorption of these low molar mass chains into/onto the selective layer. For comparison, the rejection experiment for the mixed feed was performed on a bare PES support (dashed curve in Figure S45b). The bare PES support displayed negligible rejection for all molar masses examined in this experiment.

Additionally, each of the Dextran standards (5, 12, 50, 80, 150, 410 kg mol⁻¹) used in the mixed feed were passed through the membrane individually from 1 mg mL⁻¹ feed solutions. Rejection of each standard was calculated by taking the ratio of the integrated peak area for the feed divided by the area for the permeate from SEC. The rejection of each individual standard is marked by a blue dot in Figure S45b. A qualitatively similar trend to the mixed feed is observed with a MWCO of 100 kg mol⁻¹ and an increase in rejection at low molecular weights. It should be noted that the rejection values calculated for the individual standards does not quantitatively match the rejection for the corresponding molecular weight from the mixed feed experiment. This deviation is attributed to the molar mass dispersity of the Dextran standards, i.e. there is significant overlap across the elugrams (see Figure S46).

![Figure S46: Elugrams for the Dextran standards used in the rejection experiment. Each elugram was obtained for a single Dextran molecular weight and the resulting elugrams were then overlaid. A linear fit of the molecular weights vs. Elution volume was then performed to construct a calibration curve that was used to convert elution volume to molecular weight.](image)

**c- Mechanical Stability of the Membrane**

Following the series of rejection experiments, the membrane was rinsed overnight in DI water to clear some of the adsorbed Dextran. The mechanical stability of the membrane was then investigated by applying pressure differences in excess of 1 bar. Pressure differences of 1.4, 2.1, 2.8, and 3.4 bar were applied and the flux was recorded. Flux followed a generally linear increase with increasing pressure in accordance with the Hagen-Poiseuille equation, supporting that the membrane remained mechanically stable at these pressure differences. The filtration cell used in these experiments has a recommended maximum pressure of 3.9 bar, so higher pressures were not recorded. Pure water permeability was calculated as 0.53 Lm⁻²h⁻¹bar⁻¹ from a linear fit of water
flux vs. applied pressure difference, Figure S44b. This value for permeability is significantly lower than what was calculated for the pristine membrane, which was attributed to the occurrence of fouling following the numerous rejection experiments as evidenced by the persistence of the pink coloring from the TRITC-Dextran even after extensive rinsing.

**d- Spin Coated Membrane Fabrication**

A polyethersulfone (PES) support membrane (obtained from Sterlitech, 100 nm average pore size, 47 mm diameter) was immersed in water for 1 min to backfill the pores. The wetted membrane was then placed on a glass plate mounted onto the chuck of a spin coater. A 2 wt% PLA-17.4-P(S-s-GMA)-11.3-X<sub>GMA</sub>-29.2+BTPH0.3wt% solution in chlorobenzene was then deposited on the PES and a film was spin coated at 1500 rpm for 1 minute. The membrane was then allowed to dry under ambient conditions for 1 min before placing it onto a Teflon sheet. The coated film was then annealed for 1 h at 100 °C and cured for 1 h at 190 °C. After curing, the membrane was irradiated with UV for 30 minutes to improve adhesion of the selective layer to the PES. Identical spin coating parameters for the same polymer onto an HMDS-modified Si wafer resulted in an ~150 nm thick film, as measured by ellipsometry. The morphology for this film on an HMDS modified Si wafer was observed using AFM, Figure S47b.

Following the fabrication procedure, a disc was prepared for the UF experiments as described in section 17-b. The membrane displayed a pure water permeability of 195.8 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, Figure S48. Rejection of a TRITC-Dextran standard (M = 150 kg mol<sup>-1</sup>, R<sub>h</sub> ~ 7 nm) was 96% based on UV-Vis, Figure S49. Size-selectivity for a mixed feed of Dextrans was determined using an identical procedure as described in section 17-b. A sharp MWCO of of 100 kg mol<sup>-1</sup>, corresponding to an R<sub>h</sub> of ~ 6 nm, was observed, although the rejection was lower than for the rod coated membrane, Figure S49. This is likely a result of the presence of some defects and holes in this significantly thinner film, which can be observed in SEM, Figure S47. The higher MWCO than is observed for the rod coated membrane also is likely due to the presence of these imperfections, as they allow larger molecular weight Dextrans to permeate as compared to a pristine membrane.
Figure S47: SEM image of the top surface (a) for a PLA-17.4-P(S-ß-GMA)-11.3-XGMA-29.2+BTPH0.3wt% membrane spin coated at 1500 rpm from a 2 wt.% solution in chlorobenzene onto a PES support. An AFM phase image (b) for an analogous film spin coated onto an HMDS-modified Si wafer.

Figure S48: Pure water permeability for a PLA-17.4-P(S-ß-GMA)-11.3-XGMA-29.2+BTPH0.3wt% membrane spin coated at 1500 rpm from a 2 wt.% solution in chlorobenzene was calculated as 195.8 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ based on a linear fit of water flux vs. pressure difference.
Figure S49: Rejection experiments for a PLA-17.4-P(S-s-GMA)-11.3-XGMA-29.2+BTPH0.3wt% membrane spin coated at 1500 rpm from a 2 wt.% solution in chlorobenzene. Rejection of a TRITC-Dextran standard (M = 150 kg mol\(^{-1}\), \(R_h \approx 7\) nm) was calculated as 96% using UV-Vis (a). A rejection curve was constructed for a mixed feed of Dextrans (b). A MWCO of 100 kg mol\(^{-1}\) was observed, corresponding to a \(R_h\) of approximately 6 nm.

18- Appendix: enthalpies of the curing reaction as measured by DSC

The kinetics of the reaction was further investigated by dynamic scanning calorimetry (DSC). This is a classical approach used in thermoset technology\(^{34,35}\). Samples are submitted to a temperature ramp and the resulting thermogram represents the heat of the reaction. The exothermic ring opening of epoxies makes this technique amenable for kinetics studies of the curing reactions of epoxy resins.

Several methods permit the extraction of the kinetics information embedded in the peak. First, a qualitative consideration of the temperature corresponding to the exothermic peak, \(T_{\text{max}}\), provides relevant information regarding the activity of the initiator. Intuitively, the higher \(T_{\text{max}}\), the “more latent” is the initiator. For the quantitative analysis of the thermograms, the simplest and most accurate approach is based on the analysis of the variation of \(T_{\text{max}}\) as a function of the heating rate, \(q\). For a given system, the reaction is conducted at various heating rates. By assuming that the extent of the reaction at the exothermic peak is constant, the variation of \(\ln(q)\) as a function of \(\ln(T_{\text{max}})\) provides an Arrhenius-plot whose slope and y-intercept provide the activation energy, \(E_a\), and the frequency factor, \(A\), of the reaction respectively.

Samples of 5 to 10 mg of PLA-17.4-P(S-s-GMA)-11.1-XGMA-29.2+BTPH0.3wt% were scanned at 3 different heating rates in 40 \(\mu\)L aluminum pans under nitrogen atmosphere. Samples were rapidly stabilized at 25 °C (2min) and then heated to 260 °C while monitoring the heat flow.

Figure S50 illustrates the thermograms for the three heating rates. \(T_{\text{max}}\) is an increasing function of the heating rate. \(T_{\text{max}}\) values are reported in Table S11. These values are high and consistent with
the temperature range observed for the curing of commercial epoxy resins initiated by the same initiator, BTPH.\textsuperscript{15} They confirm that, in this system, the initiator is thermolatent, i.e. the curing reaction is initiated at high temperatures. The inset of Figure S50 represents the Arrhenius plot obtained by using the values of $T_{\text{max}}$ for the three different heating rates, $q$. This plot gives $E_a = 140$ kJ mol$^{-1}$. The value is in near perfect agreement with the apparent activation energy estimated using rheological measurements (see section 7-b, $E_a = 145$ kJ mol$^{-1}$).

![Figure S50](image)

**Figure S50:** Heat flow for the curing of PLA-17.4-P(S-s-GMA)-11.1-X$_{\text{GMA}}$-29.2+BTPH0.3wt% at various heating rates. The inset represent the Arrhenius plot obtained by plotting $\ln(q)$ as a function of $\ln(T_{\text{max}})$ where $T_{\text{max}}$ (in K) is the temperature corresponding to the peak exotherm for the thermogram obtained with the heating rate $q$ (in °C min$^{-1}$).

The integration of the exothermic peak provides the enthalpy of the reactions. The values, in joules per gram of sample (J g$^{-1}$), are reported in Table S11 for the three different heating rates. By using the number of moles of epoxy per gram of polymer for PLA-17.4-P(S-s-GMA)-11.1-X$_{\text{GMA}}$-29.2 (0.99 mole of epoxy/g of polymer) we can calculate the enthalpy of the reactions in kJ mol$^{-1}$ of epoxy. These values are also reported in Table S11. They are consistent with typical values reported in the literature for commercial epoxy resins ($\Delta H \sim 75$-105 kJ mol$^{-1}$ of epoxy)\textsuperscript{34}.
| Heating rate (°C min⁻¹) | $T_{\text{max}}$ (°C)$^a$ | Enthalpy of reaction (J g⁻¹)$^b$ | Enthalpy of reaction (kJ mol⁻¹ of epoxy)$^c$ |
|-------------------------|--------------------------|-------------------------------|-----------------------------------|
| 2                       | 202                      | 102                           | 103                               |
| 5                       | 215                      | 111                           | 112                               |
| 8                       | 220                      | 102                           | 103                               |

Table S11: Kinetics information for the dynamic curing of PLA-17.4-P(S-ς-GMA)-11.1-XGMA-29.2+BTPH0.3wt% at three different heating rates in DSC. $^aT_{\text{max}}$ is the temperature corresponding to the exothermic peak of the thermograms. $^b$Enthalpy of the reaction in joule per gram of polymer, obtained by integration of the exothermic peaks. $^c$Enthalpy of reaction in joule per mol of epoxy, obtained by considering the number of moles of epoxy function contained in PLA-17.4-P(S-ς-GMA)-11.1-XGMA-29.2.
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