

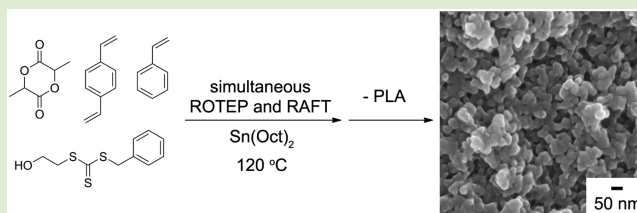
One-Step Synthesis of Cross-Linked Block Polymer Precursor to a Nanoporous Thermoset

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Supporting Information

ABSTRACT: Using a simultaneous block polymerization/in situ cross-linking from a heterofunctional initiator approach, we produced a nanostructured and cross-linked block polymer in a single step from a ternary mixture of monomers and used it as a precursor for a cross-linked nanoporous material. Using 2-(benzylsulfanylthiocarbonylsulfanyl)ethanol as a heterofunctional initiator, simultaneous ring-opening transesterification polymerization of D,L-lactide in the presence of tin 2-ethylhexanoate as a catalyst and reversible addition–fragmentation chain transfer polymerization of styrene at 120 °C produced a polylactide-*b*-polystyrene (PLA-*b*-PS) block polymer. Incorporation of divinylbenzene in the polymerization mixture allowed in situ cross-linking during the simultaneous block polymerization to result in the cross-linked block polymer precursor in one step. This material was converted into cross-linked nanoporous polymer by etching PLA in a basic solution.



Block polymers composed of chemically dissimilar blocks are interesting nanostructured materials with various applications^{1,2} that have been prepared by chain coupling, sequential addition of monomers, or mechanism-transformation approaches.³ The latter method combines different types of polymerization mechanisms by chain end transformation or use of heterofunctional initiators, allowing (sequential or simultaneous) incorporation of distinct monomers.³ For example, polylactide-*b*-polystyrene, a versatile precursor for block polymer based nanoporous materials,⁴ can be synthesized by a combination of either ring-opening transesterification polymerization (ROTEP) of lactide and anionic polymerization of styrene⁵ or ROTEP of lactide and controlled radical polymerization (CRP) of styrene^{6,7} (e.g., reversible addition–fragmentation chain transfer (RAFT) polymerization).^{8–10}

While the chain end transformation approach is useful for syntheses of block polymers,^{5,8a–e,9} the use of heterofunctional initiators potentially allows one-pot sequential block polymerization.^{6,7,8f} Furthermore, if there is no interference between two polymerization mechanisms, simultaneous polymerization of two monomers from a heterofunctional initiator can efficiently produce the desired block polymer in a single step.¹¹ Examples of simultaneous block polymerizations combining ROTEP of cyclic esters and CRP have been recently reported.^{7b,8f,12–16} In particular, an attempt to simultaneously polymerize styrene and D,L-lactide using ROTEP and atom transfer radical polymerization produced a block polymer with a somewhat large molar mass dispersity (\bar{D}) of 1.5, presumably due to interference between two polymerization mechanisms.^{7b} Very recently, simultaneous polymerization of L-lactide by ROTEP and styrene by RAFT polymerization was reported to produce PLLA-*b*-PS of 6 kg mol⁻¹ with a low dispersity ($\bar{D} = 1.14$).^{8f}

We reported synthesis of cross-linked nanoporous polymers derived from polylactide-*b*-poly(styrene-*co*-divinylbenzene) (PLA-*b*-P(S-*co*-DVB)) synthesized by RAFT copolymerization of styrene and divinylbenzene (DVB) as a cross-linker in the presence of a PLA macrochain transfer agent (PLA-CTA).¹⁷ Chain end transformation of hydroxyl-terminated PLA into PLA-CTA^{8a–e} allowed controlled growth of P(S-*co*-DVB) from the PLA chain end. The in situ block polymer formation induced microphase separation into a nanoscopic bicontinuous morphology that was arrested through cross-linking of the incorporated DVB. In contrast to macroporous polymers produced by polymerization-induced phase separation,¹⁸ the covalent connection between PLA and P(S-*co*-DVB) ensured structure formation with a small length dictated by microphase separation, and a reticulated nanoporous polymer with excellent thermal stability and good mechanical properties was produced after PLA etching.

To greatly simplify our approach to such nanostructured materials, we explored a one-step synthesis of nanostructured and cross-linked block polymer precursor from an admixture of commercially available monomers and a readily accessed chain transfer agent by a simultaneous block polymerization/in situ cross-linking method. We first investigated simultaneous block polymerization of styrene and D,L-lactide for the synthesis of PLA-*b*-PS using a heterofunctional initiator and then used this process for the simultaneous polymerization of styrene, DVB, and D,L-lactide to cross-link the PS and form the nanostructured material all in one simple thermally induced step. Cross-linked

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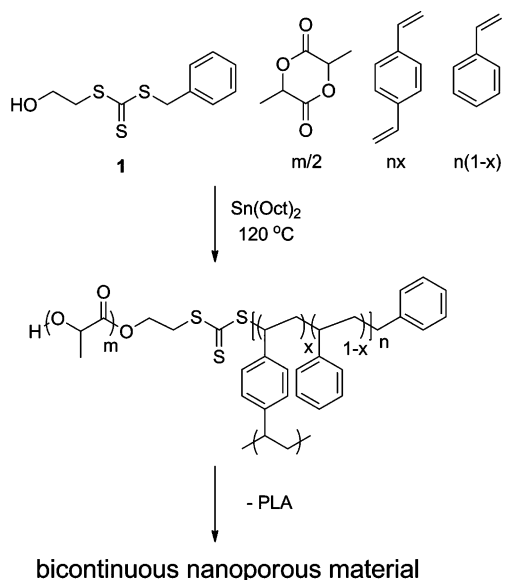
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nanoporous polymers were readily obtained by selective etching of PLA.

The route for the synthesis of PLA-*b*-PS and PLA-*b*-P(*S-co-DVB*) via simultaneous block polymerization is presented in Scheme 1. A hydroxyl-containing CTA, 2-(benzylsulfanyl-

Scheme 1. Simultaneous Block Polymerization/in Situ Cross-Linking of Styrene, DVB, and D,L-Lactide in the Presence of 1 to Generate a Precursor to a Cross-Linked Nanoporous Material



thiocarbonylsulfanyl)ethanol (**1**), was selected for the polymerization based on its established use for both ROTEP and RAFT polymerization.^{16,19–23} A particularly relevant study reported the synthesis of poly(ϵ -caprolactone)-*b*-polystyrene by simultaneous polymerization using **1** as an initiator and chain transfer agent for the enzymatic ROTEP of ϵ -caprolactone and RAFT polymerization of styrene, respectively.¹⁶ We chose tin 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) as a catalyst for ROTEP of D,L-lactide and 120 °C as the polymerization temperature because the bulk polymerization of styrene is thermally initiated (autoinitiation) at this temperature.²⁴

Compound **1** was synthesized according to a literature procedure,²⁵ and successful control over homopolymerization of styrene and D,L-lactide at 120 °C in the presence of **1** was confirmed (see Figures S1–S3 in the Supporting Information). Furthermore, both the sequential polymerization of styrene in the presence of CTA-containing PLA prepared using **1** and the sequential polymerization of D,L-lactide in the presence of hydroxyl-containing PS prepared using **1** at 120 °C produced the desired block polymer PLA-*b*-PS. These results indicate that both the trithiocarbonate and hydroxyl functionality remain intact during ROTEP and RAFT polymerizations, respectively (Figures S4 and S5, Supporting Information).

Simultaneous block polymerizations were conducted using mixtures of styrene, D,L-lactide, **1**, and $\text{Sn}(\text{Oct})_2$ at 120 °C. In a typical experiment, a mixture with molar ratio of [styrene]:[D,L-lactide]:[**1**]:[$\text{Sn}(\text{Oct})_2$] of 600:200:1:0.01 was prepared in a pressure vessel that was then heated to 120 °C. Simultaneous consumption of both D,L-lactide and styrene over time was apparent (Figure 1a). The level of $\text{Sn}(\text{Oct})_2$ controlled the lactide polymerization rate but did not impact the styrene polymerization rate (Figure S6, Supporting Information). The ¹H NMR spectrum of the resulting block polymer also supported formation of PLA-*b*-PS initiated by **1** (Figure S7, Supporting Information). Size exclusion chromatography (SEC) traces of the block polymers prepared by this method were unimodal and narrow ($\mathcal{D} = 1.2$ – 1.3) throughout polymerization indicating a well-controlled polymerization process (Figure 1b and c).

The PLA-*b*-PS obtained after a simultaneous polymerization (PS of 20 kg mol⁻¹ and PLA of 13 kg mol⁻¹, $f_{\text{PLA}} = 0.55$) showed two distinct glass transition temperatures by differential scanning calorimetry (DSC) and a small-angle X-ray scattering (SAXS) pattern corresponding to a lamellar morphology with the domain spacing of 28 nm (Figures S8 and S9, Supporting Information), confirming microphase separation of this diblock polymer.

A one-step synthesis of cross-linked block polymer precursor was achieved by conducting simultaneous polymerizations of the D,L-lactide, styrene, and DVB in the presence of **1** and $\text{Sn}(\text{Oct})_2$.²⁶ Simply heating a mixture of [styrene]:[DVB]:[D,L-lactide]:[**1**]:[$\text{Sn}(\text{Oct})_2$] = 480:120:190:1:0.13 to 120 °C for 20 h produced a translucent homogeneous monolith with 88% yield (after evaporation of unreacted styrene and DVB). SAXS

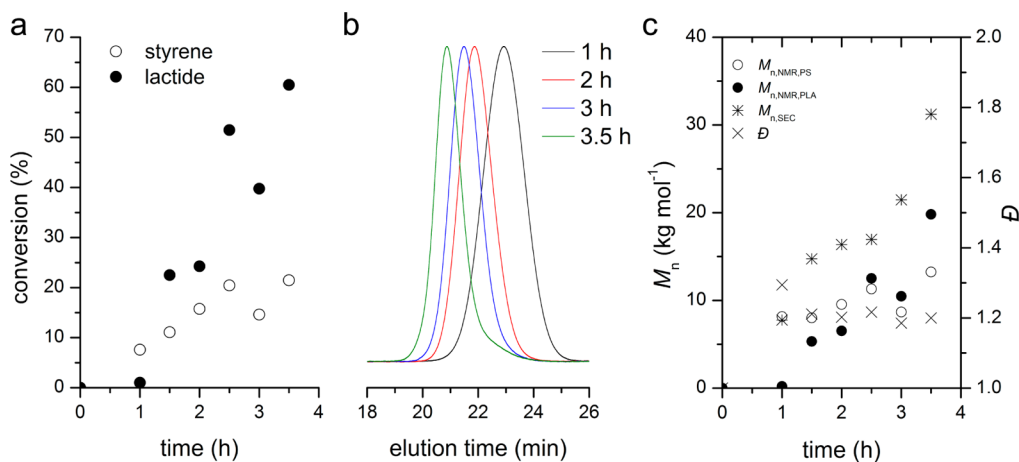


Figure 1. Simultaneous block polymerization kinetics of styrene and D,L-lactide in the presence of **1** and $\text{Sn}(\text{Oct})_2$ (0.01 equiv to **1**) at 120 °C. (a) Time vs conversion. (b) SEC traces over time. (c) Conversion vs M_n and \mathcal{D} based on polystyrene standards.

of the monolith did not reveal a clear principal scattering peak in contrast to the previous result (Figure S10, Supporting Information).¹⁷ This suggests a less well-defined structure that may be due to limited control over RAFT copolymerization of styrene and DVB (i.e., more intramolecular cross-linking of DVB²⁷ and generation of homoPS by chain coupling^{19a,28} as shown in Scheme S1, Supporting Information) (Figure S11, Supporting Information).

Treatment of the cross-linked monolith obtained from simultaneous polymerization with dilute aqueous base led to a 26% weight loss that was consistent with the weight fraction of D,L-lactide in the initial polymerization mixture (29%). The shape of the scattering curve was retained after PLA etching, but the scattering intensity significantly increased because of the high electron density contrast between PS and the pores, supporting successful formation of the porous structure (Figure S10, Supporting Information). Scanning electron microscopy (SEM) revealed that the nanoporous polymer possessed a percolating nanoporous network with pore diameter of 16 ± 4 nm after accounting for a 1 nm Pt coating (Figure 2). By

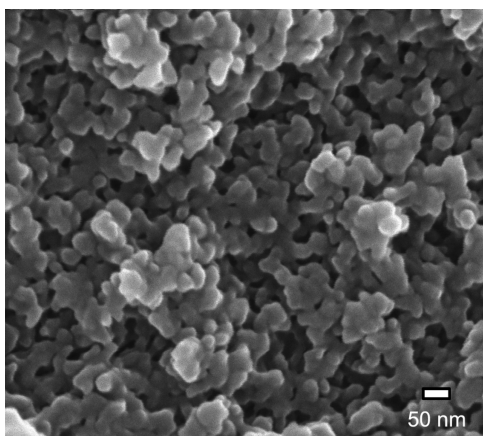


Figure 2. Scanning electron micrograph of the cross-linked nanoporous polymer derived from a polymerization mixture of [styrene]:[DVB]:[D,L-lactide]:[1]:[Sn(Oct)₂] = 480:120:190:1:0.13 that was heated to 120 °C for 20 h and etched in a basic solution. The sample was coated with Pt (1 nm thick) before imaging.

nitrogen adsorption at 77 K, the pore volume of the nanoporous polymer was estimated to be 0.37 mL g^{-1} , a value very close to the expected volume fraction of PLA in the precursor (0.39 mL g^{-1}) (Figure 3).²⁹ An “open” isotherm at the low relative pressure regime was consistent with the previous result¹⁷ and is tentatively attributed to dissolution of nitrogen within the cross-linked PS matrix.³⁰ Pore size distribution based on Barrett–Joyner–Halenda (BJH) analysis³¹ of the desorption branch gave a mean pore diameter of 13 nm (Figure 3, inset), and a specific surface area of $110 \text{ m}^2 \text{ g}^{-1}$ was obtained by the multipoint Brunauer–Emmett–Teller (BET) method (see Figure S12, Supporting Information, for comparison).³² As we previously demonstrated,^{5b,8b,c,17} the highly cross-linked PS matrix formed by RAFT copolymerization of DVB with styrene provided excellent thermal stability to the nanoporous polymer as evidenced by no obvious pore collapse signatures up to 150 °C in a DSC experiment (Figure S13, Supporting Information).

In summary, the simultaneous ROTEP and RAFT terpolymerization from the heterofunctional initiator **1** allowed formation of nanostructured and cross-linked PS-*b*-PLA

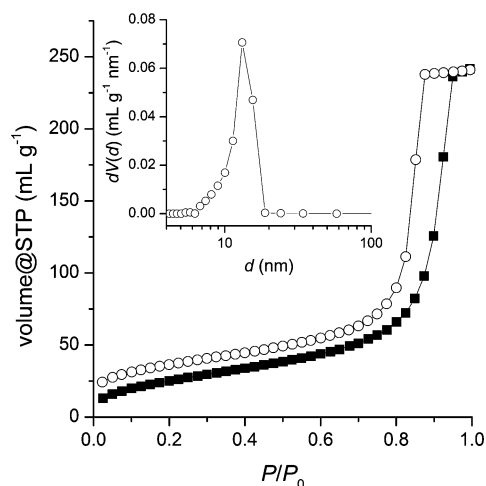


Figure 3. Nitrogen adsorption isotherm of the cross-linked nanoporous polymer at 77 K. The sample was derived from a polymerization mixture of [styrene]:[DVB]:[D,L-lactide]:[1]:[Sn(Oct)₂] = 480:120:190:1:0.13 that was heated to 120 °C for 20 h and etched in a basic solution. Filled squares: adsorption branch; empty circles: desorption branch. Inset: pore size distribution as a function of pore diameter (d) based on BJH analysis of the desorption branch.

precursor from a mixture of D,L-lactide, styrene and DVB in one step, and the resulting precursor was successfully transformed into a nanoporous and cross-linked PS by PLA etching. The simplicity of this strategy for the synthesis of cross-linked nanoporous polymers will be quite valuable for practical applications of these new materials.

■ ASSOCIATED CONTENT

Supporting Information

Materials and Methods, Figures S1–S13, and Scheme S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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