

Facile Preparation of Block Polymer films by RAFT Photopolymerization

(KAIST) ○Jaehoon Oh, Myungeun Seo

Abstract

We present a route to fabrication of nanoporous polymer films derived from crosslinked block polymer precursors via photoinitiated reversible addition-fragmentation chain transfer (RAFT) process. Photoinitiated copolymerization of a monomer and a crosslinker in the presence of a macro-chain transfer agent and a photoradical initiator rapidly produced a crosslinked block polymer precursor film which could be converted into a nanoporous polymer.

Introduction

Selectively removing a sacrificial block from a block polymer precursor can produce a nanoporous polymer with robust control over pore structure and size, making this class of materials attractive for applications such as filtration [1-2]. We recently reported a route to the synthesis of crosslinked block polymer precursors containing a disordered bicontinuous morphology by copolymerization of styrene and divinylbenzene in the presence of polylactide macro-chain transfer agent (PLA-CTA) [3]. Robust nanoporous polymers with three-dimensionally continuous pore structure were derived by PLA etching. However, application of the thermally-initiated reversible addition-fragmentation chain transfer (RAFT) process to nanoporous film fabrication has been challenging due to high reaction temperature.

Here we report that a photoinitiated RAFT polymerization can be an attractive alternative to the thermal polymerization as the photoinitiated polymerization proceeds much more rapidly even at room temperature. Using *S*-1-Dodecyl-*S'*-(*R,R'*-dimethyl-*R''*-acetic acid) trithiocarbonate, isobornyl acrylate (IBA), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a RAFT CTA, a monomer, and a photoradical initiator, we demonstrate successful control over polymerization of IBA via the RAFT process. Combining PLA-CTA and ethylene glycol diacrylate (EGDA) with IBA, we further show facile formation of a block polymer precursor film by photoinitiated RAFT that can be converted into nanoporous film.

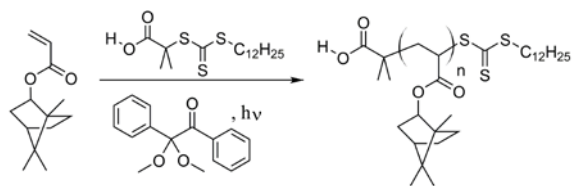
Experimental

IBA (Co)Polymerization. A polymerization mixture with a molar ratio of [N,N-dimethylformamide (DMF)]:[IBA]:[DMPA]:[CTA] = 300:150:0.1:1 was prepared and degassed. Polymerization was initiated by photoirradiation. The polymerization mixture was precipitated in methanol and the polymer was recovered by filtration. Replacing DMF and CTA with PLA-CTA and 1,4-dioxane, PLA-b-PIBA was synthesized following the identical protocol.

Fabrication of Nanoporous Polymer. A polymerization mixture containing [1,4-dioxane]:[IBA]:[DMPA]:[PLA-CTA] = 660:292:1.5:1 was prepared and degassed. Sandwiching the solution between glass slides and irradiating with light produced a transparent polymer film. Treating the film with 0.05 M NaOH (H₂O/methanol = 6/4) removed PLA to yield a nanoporous polymer film.

Result and Discussion

Photoinitiated RAFT polymerization of IBA is schematically depicted in Figure 1. While polymerization of IBA can be controlled by the thermally initiated RAFT process [4], the photoinitiated process was drastically more rapid producing high molecular weight PIBA with narrow dispersity ($D \sim 1.1$) was readily formed after only several minutes of long UV



[Scheme 1. Photoinitiated RAFT of IBA]

exposure [5] at room temperature. Size exclusion chromatography (SEC) traces of PIBA over polymerization time are shown in Figure 1a. We also verified that the polymerization follows a first-order kinetics and the molecular weight increases proportional to the conversion supporting successful control over the polymerization via RAFT mechanism (Figure 1b and c).

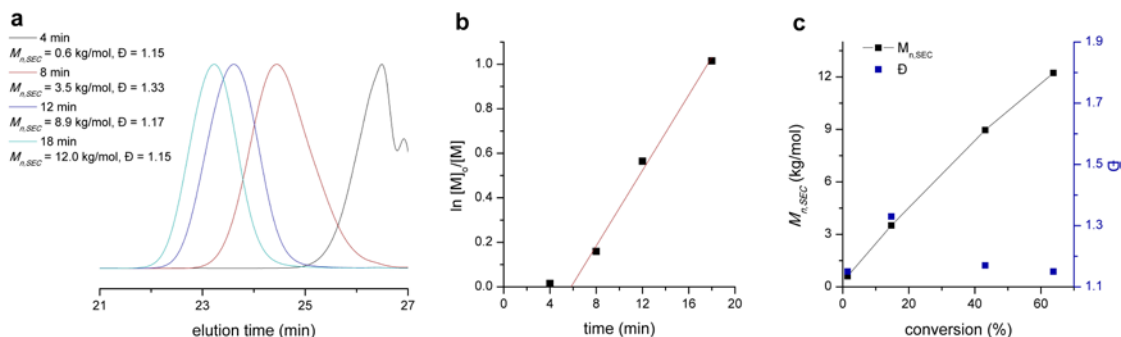


Figure 1. Photoinitiated RAFT polymerization of IBA. (a) SEC traces over time. (b) Kinetic plot. (c) Conversion vs. M_n and D plot

Following the same protocol, PLA-b-PIBA block polymers were also readily prepared from PLA-CTA as evinced by the SEC traces shown in Figure 2. Inspired by the result, a crosslinked block polymer film was fabricated by photoinitiated copolymerization of IBA with EGDA in the presence of PLA-CTA. After PLA etching, the target nanoporous film was readily obtained. The nanopore structure was evident in the scanning electron micrograph shown in Figure 3.

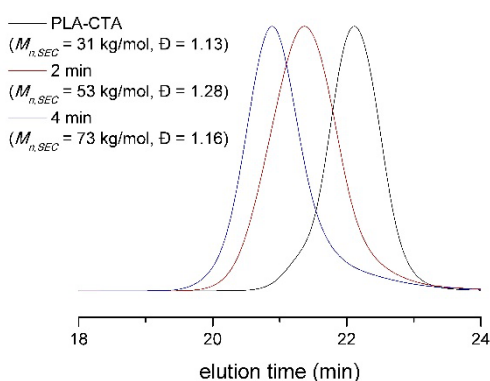


Figure 2. SEC traces of PLA-CTA and PLA-b-PIBAs formed over time.

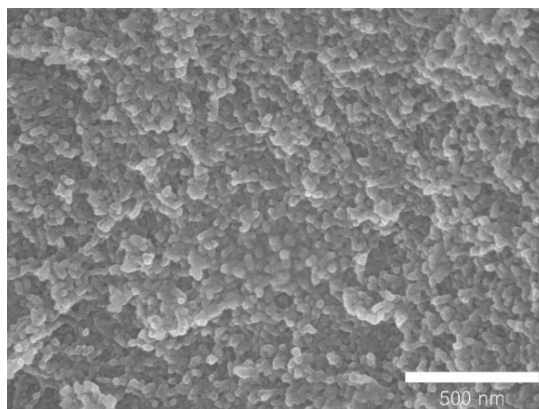


Figure 3. SEM image of the nanoporous film after Os coating.

Conclusion

A block polymer precursor film was obtained by photoinitiated RAFT copolymerization in one step and successfully converted into the nanoporous film by PLA etching. The nanoporous polymer film is expected to be useful as advanced membranes.

Reference

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