*eXPRESS Polymer Letters Vol.10, No.8 (2016) 693–700*
*Available online at www.expresspolymlett.com*
*DOI: 10.3144/expresspolymlett.2016.62*

# Synthesis of polyisobutylene-polycaprolactone block copolymers using enzyme catalysis

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*Received 21 December 2015; accepted in revised form 12 March 2016*

**Abstract.** The synthesis of poly(isobutylene-*b*-ε-caprolactone) diblock and poly(ε-caprolactone-*b*-isobutylene-*b*-ε-caprolactone) triblock copolymers was accomplished using a combination of living carbocationic polymerization of isobutylene (IB) with the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). OH-PIB-allyl was prepared by living carbocationic polymerization of IB initiated with 1,2-propylene oxide/$TiCl_4$ followed by termination with allyltrimethylsilane. Hydroxyl telechelic HO-PIB-OH was obtained by living IB polymerization initiated by 2,4,4,6-tetramethyl-heptane-2,6-diol/$TiCl_4$, termination with allyltrimethylsilane and subsequent thiol-ene click reaction with mercaptoethanol. The structure of the hydroxyl PIBs was confirmed by $^1$H NMR (proton Nuclear Magnetic Resonance spectroscopy). OH-PIB-allyl and HO-PIB-OH were then successfully used as macroinitiators for the polymerization of ε-CL catalyzed by *Candida antarctica Lipase B* (CALB), yielding poly(ε-caprolactone-*b*-isobutylene) diblock and poly(ε-caprolactone-*b*-isobutylene-*b*-ε-caprolactone) triblock copolymers, respectively. Differential Scanning Calorimetry (DSC), Transition Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) demonstrated that the amorphous PIB and the semicrystalline PCL block segments phase separated, creating nanostructured phase morphology.

***Keywords:*** *polymer synthesis, enzyme catalysis, block copolymers, polyisobutylene, polycaprolactone*

## 1. Introduction

The design of novel macromolecular architectures is a continuous focus in polymer science. Many of these architectures, such as block copolymers, possess unique properties, which make them interesting candidates for special applications in nanotechnology and biomedical materials. Controlled ring-opening polymerization (ROP) of cyclic esters, such as lactide, glycolide, cyclic carbonate, and/or ε-caprolactone (ε-CL), have received significant attention due to the good mechanical properties, degradation behavior and biocompatibility of the resulting polymers [1–3]. Polyisobutylene (PIB) has been combined with materials widely used for biomedical applications (polyacrylates and -methacrylates, polysiloxanes, polylactones, polyurethanes, poly(ethylene oxide), and poly (vinyl alcohol)), and some devices that use PIB-based materials are approved by the Food and Drug Administration (FDA) [4–6]. One of the most relevant combinations is poly(styrene-*b*-isobutylene-*b*-styrene) (SIBS). SIBS is a very soft, transparent material resembling silicone rubber, with superior mechanical properties. It is used as a drug-eluting coating of coronary stents [6–8]. PIB is not degradable under biological conditions, however, its copolymers can be. Block copolymers of PIB with L-lactide [9] and pivalolactone [10] have been synthesized from primary hydroxyl functionalized PIBs and metal-containing activators. It was found that the blocks had phase-separated morphologies, and the crystallization behavior of the polylactide and polypivalolactone was influenced by the presence of the PIB blocks. However,

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we found only two papers discussing the synthesis of PIB-PCL block copolymers [11, 12]. Both papers used telechelic HO-PIB-OH macroinitiators obtained by multistep processes, and triethyl aluminum or $HCl \cdot Et_2O$ catalyst. The first paper concentrated on structural analysis without investigating the phase morphology of the products [11]. The second paper reported microphase-separation based on Differential Scanning Calorimetry (DSC) that found two transitions: $T_g = -60\,°C$ for the PIB segment and $T_m = 60\,°C$ for the PCL block [12].

This paper reports the facile synthesis of a poly(isobutylene-*b*-ε-caprolactone) diblock and poly(ε-caprolactone-*b*-isobutylene-*b*-ε-caprolactone) triblock copolymers using PIB-OH and HO-PIB-OH macroinitiators [13–15], and ROP of ε-CL catalyzed by *Candida antarctica lipase B* (CALB). Enzyme-catalyzed ROP [16–21] is one of the most promising tools and avoids the use of organo-metallic catalysts (Zn, Al, Sn or Ge), which are known to be cytotoxic to cellular systems and are often difficult to remove from polymeric products [2]. Gross and Hillmyer used anionically synthesized monohydroxyl-functional polybutadiene of various molecular mass ($M_n \sim$ 2600–19 000 g/mol) to initiate the ROP of ε-CL and pentadecalactone catalyzed by CALB to make diblock copolymers. However, the products contained 10–30 wt% homoPCL after methanol precipitation, so they developed a fractionation method to purify the diblocks [19]. Tang and coworkers [20, 21] used hydroxyl- and ester-functionalized polyoctadiene to initiate ROP of ε-CL and ω-pentadecalactone using CALB, but did not investigate the phase morphology of the resulting block copolymers. PIB-containing block copolymers have never been synthesized using CALB-catalyzed ROP of lactones. We report conditions leading to pure di- and triblock copolymers.

## 2. Experimental section

### 2.1. Materials

HO-PIB-allyl ($M_n = 4300$ g/mol, $Đ_M = 1.21$) [18] and HO-PIB-OH ($M_n = 4100$ g/mol, $Đ_M = 1.2$) [14, 15] macroinitiators were synthesized by recently reported facile new methodologies. ε-caprolactone (ε-CL, Sigma Aldrich, 97%), methylene chloride ($CH_2Cl_2$, ≥99.8%, EMD Chemicals) and toluene (Sigma Aldrich, 99%) were dried over $CaH_2$ (95%, Aldrich)) and distilled under vacuum. Methanol (MeOH, 99.8%, Fisher Scientific) was used as received. Lipase B from *Candida antarctica* immobilized on microporous acrylic resin (20 wt% CALB, Novozyme 435, Sigma Aldrich), deuterated chloroform ($CDCl_3$, 99.8%, Chemical Isotope Laboratories) were used as received.

### 2.2. Procedures

#### 2.2.1. Synthesis of poly(isobutylene-*b*-ε-caprolactone)

A solution of HO-PIB-allyl (0.18 g, $8.05 \cdot 10^{-3}$ mol/L) and dry toluene (5.0 mL) were transferred via syringe under dry $N_2$ atmosphere into a flask containing immobilized CALB (75 mg, 20% CALB, $4.33 \cdot 10^{-4}$ mol/L). The suspension, as well as a separate flask containing ε-CL, was equilibrated for 15 min at the reaction temperature (70 °C). Thereafter, ε-CL (0.2 g, 0.35 mol/L) was transferred to the reaction flask via syringe under dry $N_2$ atmosphere to start the polymerization. After 24 h reaction time the reaction mixture was cooled to room temperature and CALB was removed by filtration. The polymer was precipitated in methanol and dried under vacuum for 24 h at room temperature (yield 0.235 g, ε-CL conversion 28%).

#### 2.2.2. Synthesis of poly(ε-caprolactone-*b*-isobutylene-*b*-ε-caprolactone)

A solution of HO-PIB-OH (0.090 g, $8.13 \cdot 10^{-3}$ mol/L) and dry toluene (2.5 mL) were transferred via syringe under dry $N_2$ atmosphere into a flask containing immobilized CALB – (40 mg, 20% CALB, $4.45 \cdot 10^{-4}$ mol/L). The suspension, as well as a separate flask containing ε-CL, was equilibrated for 15 min at the reaction temperature (70 °C). Thereafter, ε-CL (0.2 mL, 0.67 mol/L) was transferred to the reaction flask via syringe under dry $N_2$ atmosphere to start the polymerization. After 24 h reaction time the reaction mixture was cooled to room temperature and CALB was removed by filtration. The polymer was precipitated in methanol and dried under vacuum for 24 h at room temperature (yield 0.14 g, ε-CL conversion 25%).

### 2.3. Characterization

#### 2.3.1. Size exclusion chromatography (SEC)

The molecular mass and molecular mass distribution ($Đ_M$) of the polymers were determined by SEC con-

sisting of a Waters 515 HPLC Pump, a Waters 2487 Dual Absorbance UV Detector (UV), a Wyatt OPTI-LAB DSP Interferometric Refractometer (RI), a Wyatt DAWN EOS multi-angle light scattering detector (LS), a Wyatt ViscoStar viscometer (VIS), a Wyatt QELS quasi-elastic light scattering instrument (QELS), a Waters 717 plus autosampler and 6 Styragel® columns (HR6, HR5, HR4, HR3, HR1 and H0.5). The columns were thermostated at 35 °C and THF, continuously distilled from $CaH_2$, was used as the mobile phase at a flow rate of 1 mL/min. The results were analyzed by using the ASTRA software (Wyatt Technology). Block copolymer dn/dc was calculated based on the weight fraction and dn/dc of the individual components; PCL = 0.053 [22] and PIB = 0.108 [23]. The results agreed with data obtained assuming 100% mass recovery.

#### 2.3.2. Nuclear Magnetic Resonance (NMR) spectroscopy

$^1$H NMR spectra were recorded on a Varian Mercury-500 NMR spectrometer in $CDCl_3$. The resonance at δ = 7. 27 ppm ($^1$H NMR) was used as internal reference. Spectra were acquired with 128 transients and a relaxation time of 5 sec.

#### 2.3.3. Differential scanning calorimetry (DSC)

DSC was carried out on a TA Q2000 instrument. 5 mg of the sample was subjected to heating/cooling cycles at 10 °C/min in the temperature range of –100 to 150 °C. Nitrogen atmosphere was used to minimize thermal degradation of the polymers. $T_g$ and $T_m$ were calculated as the mean value between the onset and end point temperatures of the second cycle.

#### 2.3.4. Optical microscopy

Optical images were collected with an Olympus BX51 optical microscope using reflected light.

#### 2.3.5. Transmission electron microscopy (TEM)

TEM was carried out on a Philips Tecnai 12 instrument at an accelerating voltage of 120 kV. Thin films were prepared on a carbon coated glass surface by spin coating one drop of a 1% polymer solution in THF. The carbon coated glass surface with the spin coated copolymer was immersed into a distilled water bath. The polymeric film along with the carbon layer floated onto the water surface, and then was picked up by clean TEM copper grids (400 mesh, SPI). Before TEM observation, the samples on the grids were annealed for 5 min at 70 °C and then 15 h at 40 °C. The samples were stained with 1% $OsO_4$.

#### 2.3.6. Atomic Force Microscopy (AFM)

AFM images were taken using a Veeco Instruments Multimode AFM with a Nanoscope IV controller, operated in the tapping-mode with height and phase images collected simultaneously. Silicon cantilevers with a nominal resonance frequency of 170 kHz (Aspire CT170R) were used, with typical medium-light tapping forces as characterized by a 2.0 V free amplitude and a 1.6 V set point amplitude.

## 3. Results and discussion

### 3.1. Synthesis of poly(isobutylene-*b*-ε-caprolactone) diblock

The enzyme-catalyzed ROP of ε-CL was initiated using the HO-PIB-allyl macroinitiator ($M_n$ = 4300 g/mol with $Đ_M$ = 1.21) as shown in Figure 1. In this case [monomer]/[OH] ~40 was used based on Storey's previous report [11]. Higher ratios were tried but did not yield clean diblocks.

Figure 2 shows the $^1$H NMR spectrum of PIB-*b*-PCL. The resonances at δ = 5.04 ppm (f) and δ = 5.77 ppm (e) belong to the allylic protons of the HO-PIB-allyl macroinitiator. Signals for structural analysis included those at 3.68 and 4.33 (h, J 6.5 Hz, $–CH_2–OH$), due to the methylene protons of PCL chain-end units and resonances at 4.11 ppm (g) and 2.32 ppm (m), due to the methylene protons in the PCL repeat unit. The $M_n$ of the poly(ε-caprolactone) block was calculated from the ratio of the integral of the methylene protons of the repeat unit of PCL (g) at δ = 4.23 ppm and the methylene proton of the allyl end group of

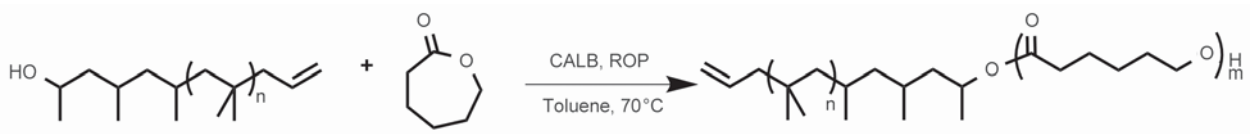


**Figure 1.** CALB catalyzed ROP of ε-CL using allyl-PIB-OH as macroinitiator. [HO-PIB-allyl] = $8.05 \cdot 10^{-3}$ mol/L, [ε-CL] = 0.35 mol/L; [CALB] = $4.33 \cdot 10^{-4}$ mol/L.

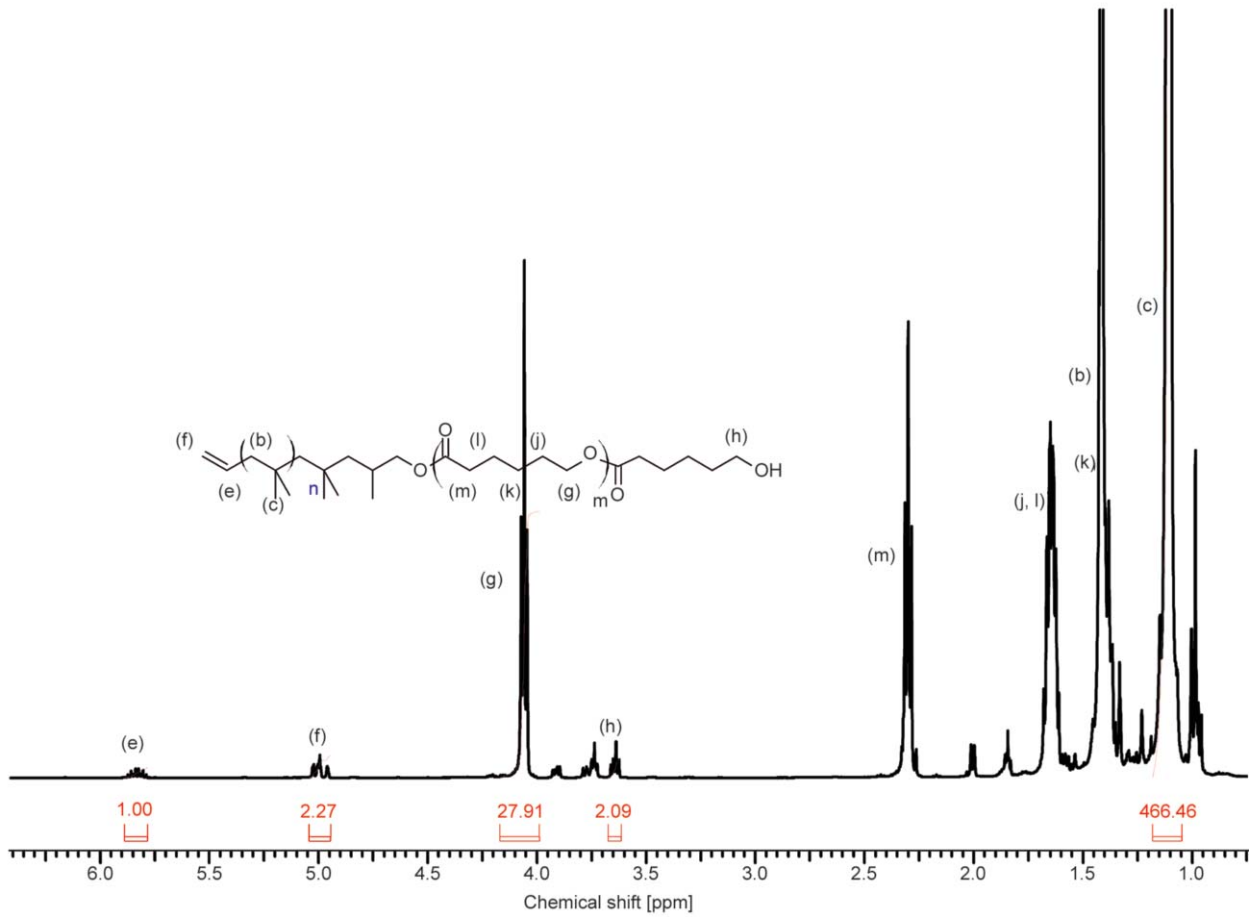


**Figure 2.** $^1$H NMR spectrum of PIB-*b*-PCL

HO-PIB-allyl (e) at δ = 5.77 ppm as $M_n$ = 1590 g/mol. Thus the total diblock molecular weight is $M_n$ = 5890 g/mol, corresponding to 26.8 wt% PCL. Figure 3 shows the SEC traces of the macroinitiator and the diblock copolymer (PIB-*b*-PCL).

Relative to the starting HO-PIB-allyl ($M_n$ = 4300 g/mol), the SEC RI traces of PIB-*b*-PCL diblock copolymer shifted to higher molecular mass and the molecular mass distribution remained narrow. The $M_n$ = 6100 g/mol and $Đ_M$ = 1.26 were determined by SEC using d*n*/d*c* = 0.093. This corresponds to a $PIB_{4300}$-*b*-$PCL_{1800}$ structure (29.5 wt% PCL), which is in good agreement with the NMR data.

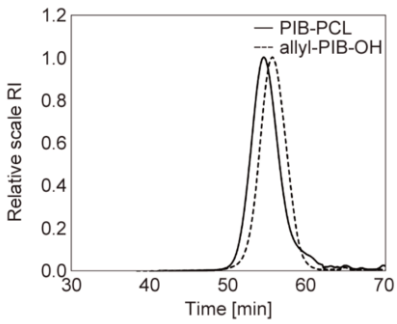


**Figure 3.** SEC traces of HO-PIB-allyl and PIB-*b*-PCL

### 3.2. Synthesis of poly(ε-caprolactone-*b*-isobutylene-*b*-ε-caprolactone) triblock

Figure 4 shows the triblock synthesis. HO-PIB-OH ($M_n$ = 4100 g/mol, $Đ_M$ =1.2) was used as a macroinitiator.

Figure 5 shows the $^1$H NMR spectrum of PCL-PIB-PCL. The signal of the methylene protons of the HO-PIB-OH macroinitiator (h) at 3.77 ppm disappeared. Signals for structural analysis included those at 3.68 and 4.33 (h, J 6.5 Hz, –$CH_2$–OH), due to the meth-

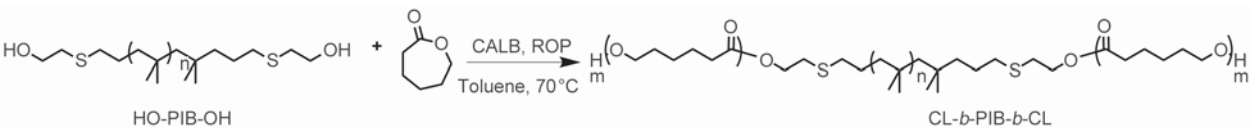


**Figure 4.** Synthesis of PCL-PIB-PCL. [HO-PIB-OH] = 8.13·10$^{-3}$ mol/L, [ε-CL] = 0.67 mol/L; [CALB] = 4.45·10$^{-4}$ mol/L.

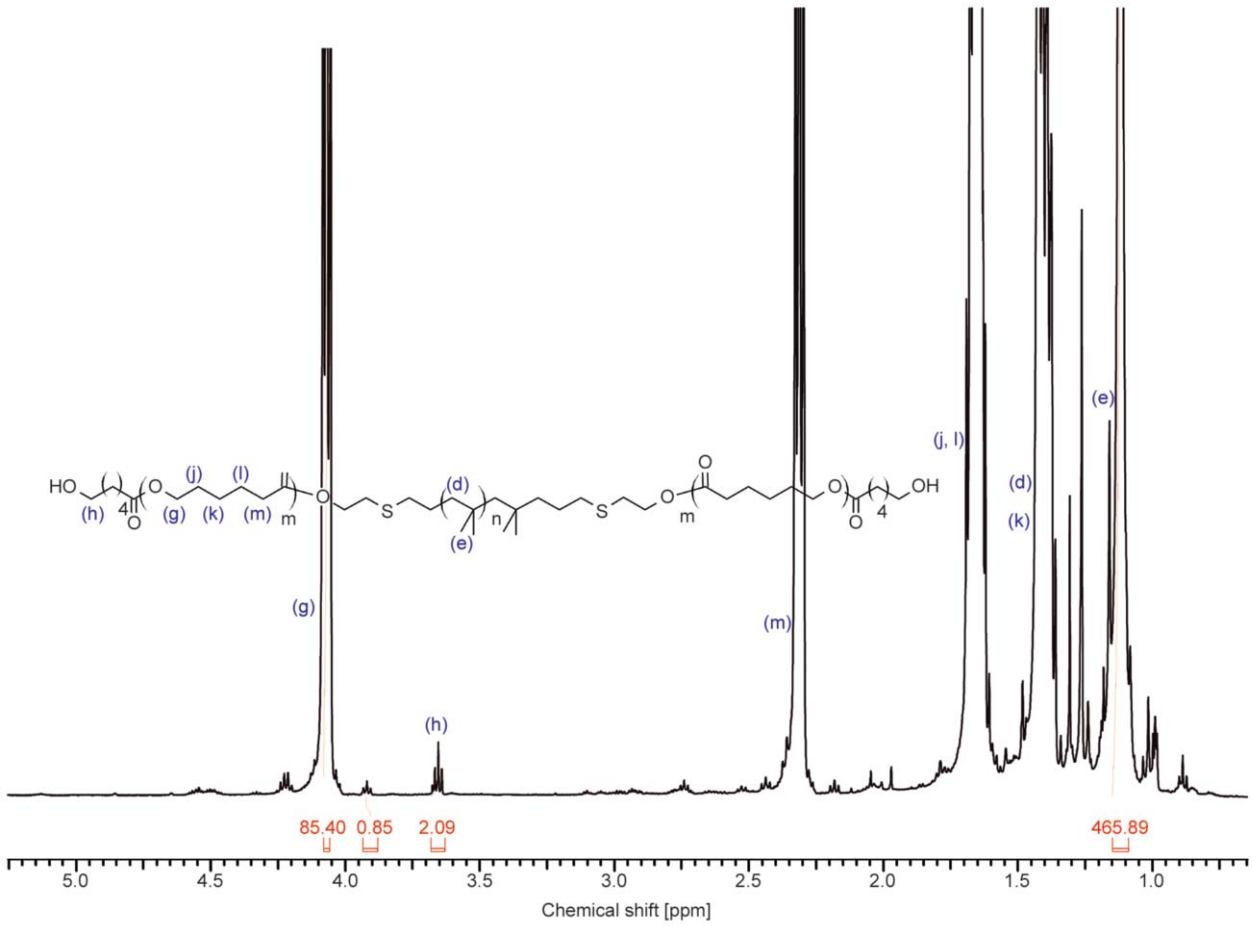


**Figure 5.** $^1$H NMR spectrum PCL-PIB-PCL

ylene protons of PCL chain-end units and resonances at 4.11 ppm (g) and 2.32 ppm (m), due to the methylene protons in the PCL repeat unit. The proton resonances at δ = 1.13 ppm (e) and δ = 1.45 ppm (d) correspond to the methyl and methylene protons, respectively, of the repeat unit of PIB.

$M_n$ = 2200 g/mol was calculated for the PCL blocks from the ratio of the integral of the methylene protons of the repeat unit of PCL (h) at δ = 3.99–4.11 ppm and the methyl protons of the repeat unit of PIB (e), and using $M_n$ = 4090 g/mol for the starting HO-PIB-OH. Thus the PIB center block is flanked on either side by PCL outer blocks, giving a structure of $PCL_{2200}$-*b*-$PIB_{4090}$-*b*-$PCL_{2200}$ and 52.8 wt% PCL content. The SEC traces are shown in Figure 6. SEC analysis yielded $M_n$ = 8400 g/mol ($Đ_M$ = 1.48), in good agreement with the NMR data.

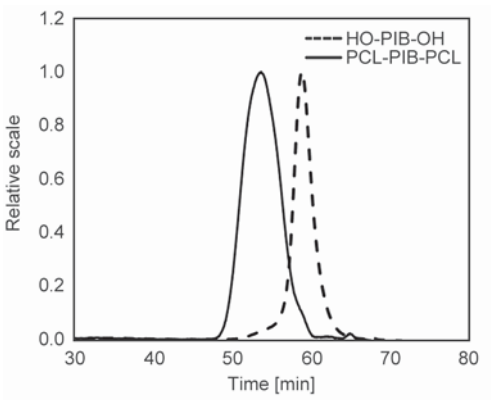


**Figure 6.** SEC traces of HO-PIB-OH and PCL-*b*-PIB-*b*-PCL

### 3.3. Phase morphology

DSC thermograms are presented in Figure 7.

The diblock copolymer exhibited the $T_g$ of the amorphous rubbery PIB segment at $T_g$ = –70.1 °C and another transition at 45.9 °C. The DSC of the triblock showed the PIB $T_g$ at –67.2 °C and a very sharp transition at 51.3 °C with a shoulder at 55.1 °C. $T_g$ = –60 °C and $T_m$ ranging between 59–64 °C were reported in the literature for PCL [24]. In our case, the $T_g$ transition for the PCL blocks was barely detectable at –60.2 °C These observations clearly indicate microphase-separation in the block copolymers between

the soft PIB phase and the PCL hard phases. The sharp and prominent high temperature transition in the DSC indicates that the PCL blocks in the triblock have very high crystalline fractions. This may be due to confinement by the PIB phases. We will investigate this phenomenon in more detail.

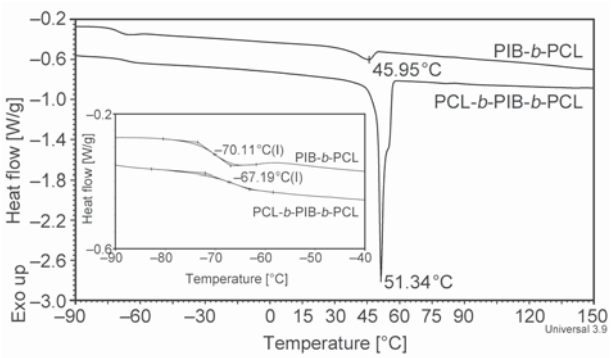


**Figure 7.** DSC thermograms of PIB-*b*-PCL and PCL-*b*-PIB-*b*-PCL

Figures 8a and b shows the optical images of the diblock and triblock copolymers. We have no explanation for these strange patterns: crystalline PCL normally displays the well-known 'Maltese cross' pattern [25].

The AFM images (Figures 9) are also unusual and need further investigation.

The TEM of the diblock in Figure 10a did not show clear features. The TEM of the triblock copolymer in Figure 10b indicates a lamellar structure, but the lamella thickness appears to be too large. This will require more detailed investigations. However, all images show phase-separation.

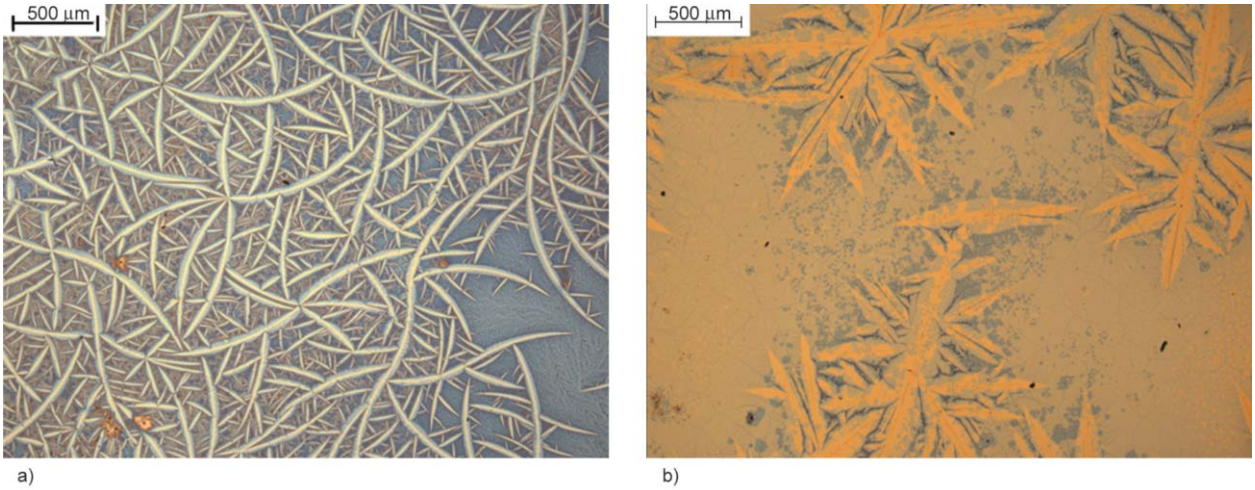


**Figure 8.** Optical images of (a) PIB-*b*-PCL and (b) PCL-*b*-PIB-*b*-PCL

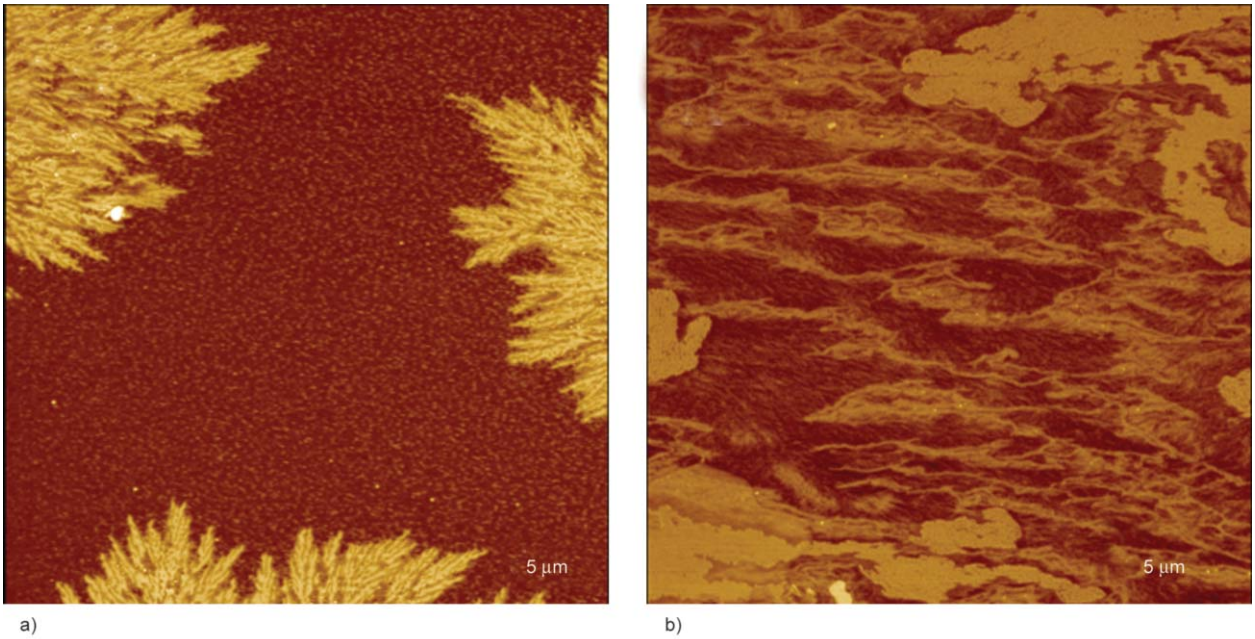


**Figure 9.** AFM images of (a) PIB-*b*-PCL and (b) PCL-*b*-PIB-*b*-PCL

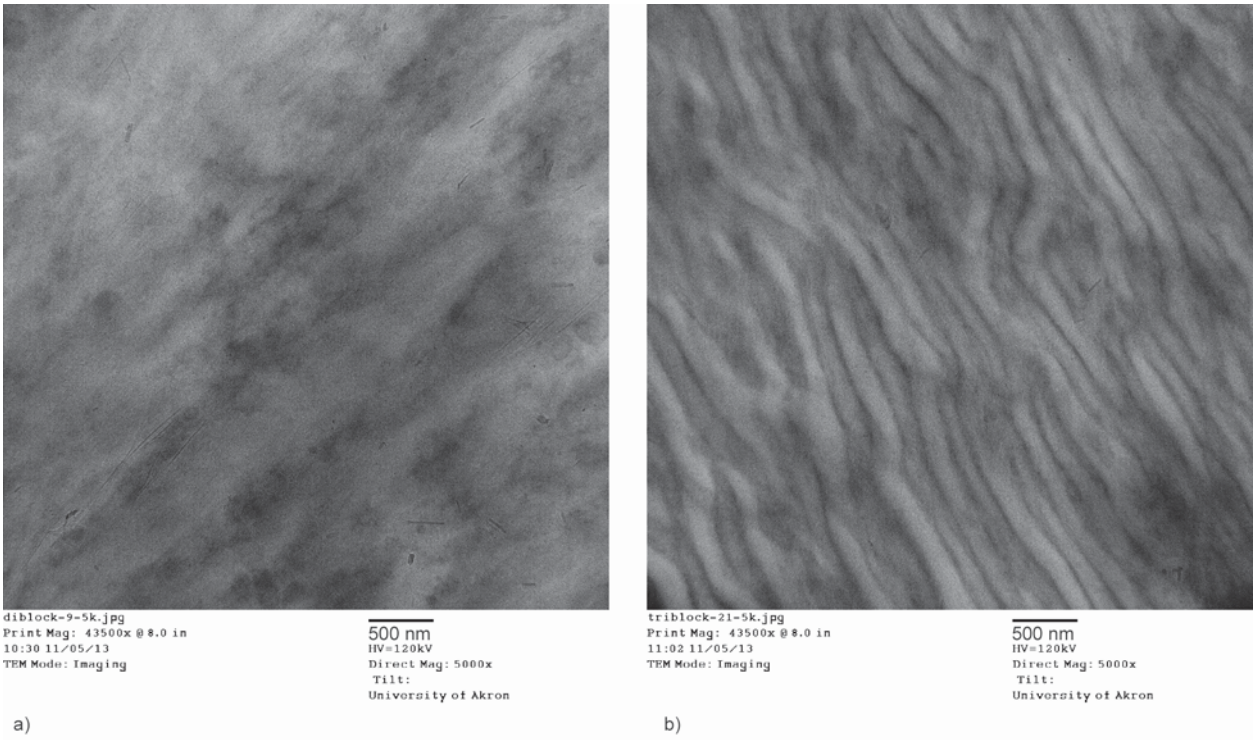


**Figure 10.** TEM images of (a) PIB-*b*-PCL and (b) PCL-*b*-PIB-*b*-PCL

## 4. Conclusions

The combination of carbocationic and enzymatic polymerization yielded PIB-*b*-PCL and PCL-*b*-PIB-*b*-PCL. The use of enzyme catalysis resulted in the metal-free synthesis of poly(caprolactone) blocks, which normally requires the use of tin or other transition metals, which are difficult to remove. This methodology can be expanded to the synthesis of other cyclic monomers to yield functional biomaterials containing degradable polyester blocks. The phase morphology of the blocks requires further investigation.

## Acknowledgements

This material is based upon work supported by the National Science Foundation under DMR-0804878 and the Ohio Board of Regents. We wish to thank The Ohio Board of Regents and The National Science Foundation for funds used to purchase the NMR (CHE-0341701 and DMR-0414599) and MS (CHE-1012636 and DMR-0821313) instruments used in this work.

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