

Supporting Information

Lipase-catalyzed ring-opening copolymerization of ω -pentadecalactone and δ -valerolactone by reactive extrusion

Changcun Li,^{a,b,c} Shuaijun Pan,^a Weijian Xu,^a Yanbing Lu,^{*a}

Peipei Wang,^b Fuming Zhang^b and Richard Alan Gross^{*b}

- a.* College of Chemistry and Chemical Engineering, Institute of Polymer Science and Engineering, Hunan University, Changsha 410082, China
- b.* Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York 12180, United States
- c.* Baling Petrochemical Company, SINOPEC Asset Management Corporation, Yueyang 414014, China.

Contents:

1) Experimental Section

1.1 Materials

1.2 Analytical Methods

- 1.2.1 Nuclear Magnetic Resonance (NMR) spectroscopy.
- 1.2.2 Gel Permeation Chromatography (GPC)
- 1.2.3 Differential Scanning Calorimetry (DSC)
- 1.2.4 Thermal Gravimetric Analysis (TGA)

1.3 Synthetic Protocols

- 1.3.1 Copolymerization of ω -pentadecalactone (PDL) and δ -valerolactone(VL) by Reactive Extrusion catalyzed by N435.
- 1.3.2 N435 catalyzed solution copolymerization of PDL and VL.
- 1.3.3 N435 catalyzed bulk copolymerization of PDL and VL.
- 1.3.4 N435 bulk copolymerization of PDL and VL to determine the reactivity ratios

2) Figures

Fig. 1 Photographs of Xplore® MC 15 micro twin-screw extruder and screws

Fig. 2 ¹H NMR spectra of P(PDL-co-VL) copolymers prepared by REX with N435 catalysis at predetermined reaction times.

Fig. 3 ¹³C NMR spectra of P(PDL-co-VL) copolymers prepared by REX with N435 catalysis at predetermined reaction times.

Fig. 4 ^{13}C NMR spectra of P(PDL-co-VL) copolymers prepared by N435-catalyzed solution copolymerization at predetermined reaction times.

Fig. 5 ^{13}C NMR spectra of P(PDL-co-VL) copolymers prepared by N435-catalyzed bulk copolymerization at predetermined reaction times.

Fig. 6 Reactivity ratios determination based on the Kelen-Tudos method.

1 Experimental Section

1.1 Materials

ω -Pentadecalactone (PDL, with a purity of 98%) and δ -valerolactone (VL) were purchased from Sigma-Aldrich. VL was dried by calcium hydride and distilled. Novozyme-435 lipase was a gift from Novozymes. It was dried in a vacuum desiccator (0.1 mmHg, 25 °C) for 1 day. Chloroform-d was purchased from Sigma-Aldrich and was dried by activated 4Å molecular sieves.

1.2 Analytical Methods

Prior to product characterizations, chloroform or tetrahydrofuran solutions of the copolymers were filtered to remove N435 beads and solvent was stripped by rotary evaporation.

1.2.1 Nuclear Magnetic Resonance (NMR) spectroscopy: Proton (^1H) and carbon (^{13}C) NMR spectra were determined at 25 °C using Bruker 600 and 800 MHz spectrometers. Samples were dissolved in $\text{CHCl}_3\text{-d}$ at 20 mg/mL. Data were analyzed using Bruker TopSpin 3.2 software. ^1H NMR spectra were also recorded to determine monomers conversion from the relative peak areas of signals corresponding to the ester methylene ($-\text{CH}_2\text{-O-C=O}$) of copolymer repeat units (4.07ppm), the ester methylene ($-\text{CH}_2\text{-O-C=O}$) of VL (4.35ppm) and the ester methylene ($-\text{CH}_2\text{-O-C=O}$) of PDL (4.13ppm). ^{13}C NMR spectra were recorded to determine the relative fractions of diad repeat unit sequences.

1.2.2 Gel Permeation Chromatography (GPC): Molecular weights were determined by gel permeation chromatography (GPC) using a Waters HPLC system. GPC software Breeze version 2 was used for data processing. Tetrahydrofuran (THF, HPLC grade) was used as the eluent at a flow rate of 1.0 mL/min at room temperature. Samples were dissolved in THF (0.2% wt/vol) and relative molecular weights were determined using a polystyrene standard curve.

1.2.3 Differential Scanning Calorimetry (DSC): Melting and crystallization temperatures were measured by TA Instruments DSC (Model Q2000) using premium pan/hermetic lid (low mass aluminum sample pans/lids) and a sample weight of 2-3 milligrams. Polymer samples were heated at 20 °C /min and cooled at 10°C/min. Melting temperatures were determined using the second heating scan. Data analysis of the DSC scans was performed using TA Universal Analysis 2000 software.

1.2.4 Thermal Gravimetric Analysis (TGA): Weight loss as a function of temperature was measured using a TA Instrument TGA (Model Q50). Ceramic pans were placed on a microbalance hook inside of the furnace chamber. Samples (~5-10 mg) were heated at a rate of 10°C/min. TA Universal Analysis 2000 software was used to analyze TGA data.

1.3 Synthetic Protocols

1.3.1 Copolymerization of ω -pentadecalactone (PDL) and δ -valerolactone(VL) by Reactive Extrusion (REX) catalyzed by N435: The molar ratio of the comonomers VL and PDL was 1:1. After distillation from CaH₂, VL (4.435g) was pipetted into a dry glass vial. PDL (10.644g) and N435 (1.5g) were weighed in aluminum pans. To get a uniformed mixture of N435 and PDL, PDL was melted by heating to 38°C and N435 was transferred to the PDL melt. The mixture of PDL and N435 beads was agitated to mix and then cooled to room temperature. The extrusion compartment of the Xplore® MC 15 micro twin-screw extruder was heated to 150°C with nitrogen purge for 30 min to remove water and thereafter cooled under ambient conditions to 30°C. VL was transferred into the extruder chamber using a glass pipette and the stirring rate was set at 60 rpm. Then powdered PDL and N435 were transferred into the extruder chamber using a solid particle feeding propeller device. The extruder temperature was set at 90°C and maintained at that temperature throughout the reaction. Furthermore, the reaction chamber was continuously purged with nitrogen gas and samples were removed from the reactor through the outlet valve at predetermined reaction times.

The force produced by screw rotation is a function of REX temperature, N435 loading and reaction time. The extruder force at any given time is determined by the reaction viscosity. In other words, more viscous products require more energy to maintain a constant mixing speed.

1.3.2 N435-catalyzed solution copolymerization of PDL and VL: The molar ratio PDL to VL was 1:1 and the ratio of N435 to monomers was 10 wt %. PDL (10.647g), VL (4.494g) and N435 (1.52g) dried as described above were transferred into a 100mL three-necked flask. Dry toluene was added to the reaction mixture such that the ratio of solvent to monomers was 2:1 v/w. The copolymerization was maintained at 90°C, with magnetic stirring (60 rpm) and a nitrogen purge.

1.3.3 N435 catalyzed bulk copolymerization of PDL and VL: The reaction was performed as described in 1.3.2 except without solvent.

1.3.4 N435 bulk copolymerization of PDL and VL to determine the reactivity ratios: The procedure followed is exactly as describe in 1.3.3 except the reaction

was maintained at 45°C to decrease the reaction rate.

2.0 Figures



Fig. 1 Photographs of Xplore® MC 15 micro twin-screw extruder (A) and screws (B).

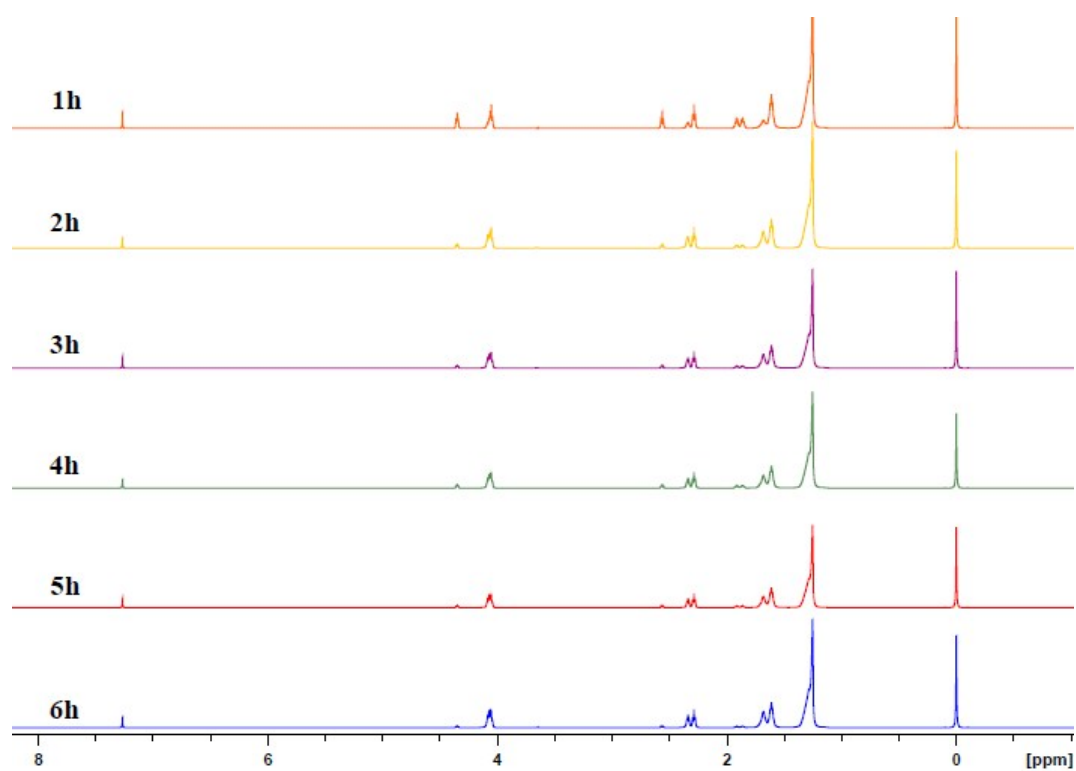


Fig. 2 ¹H NMR spectra of P(PDL-co-VL) copolymers prepared by REX with N435 catalysis at predetermined reaction times.

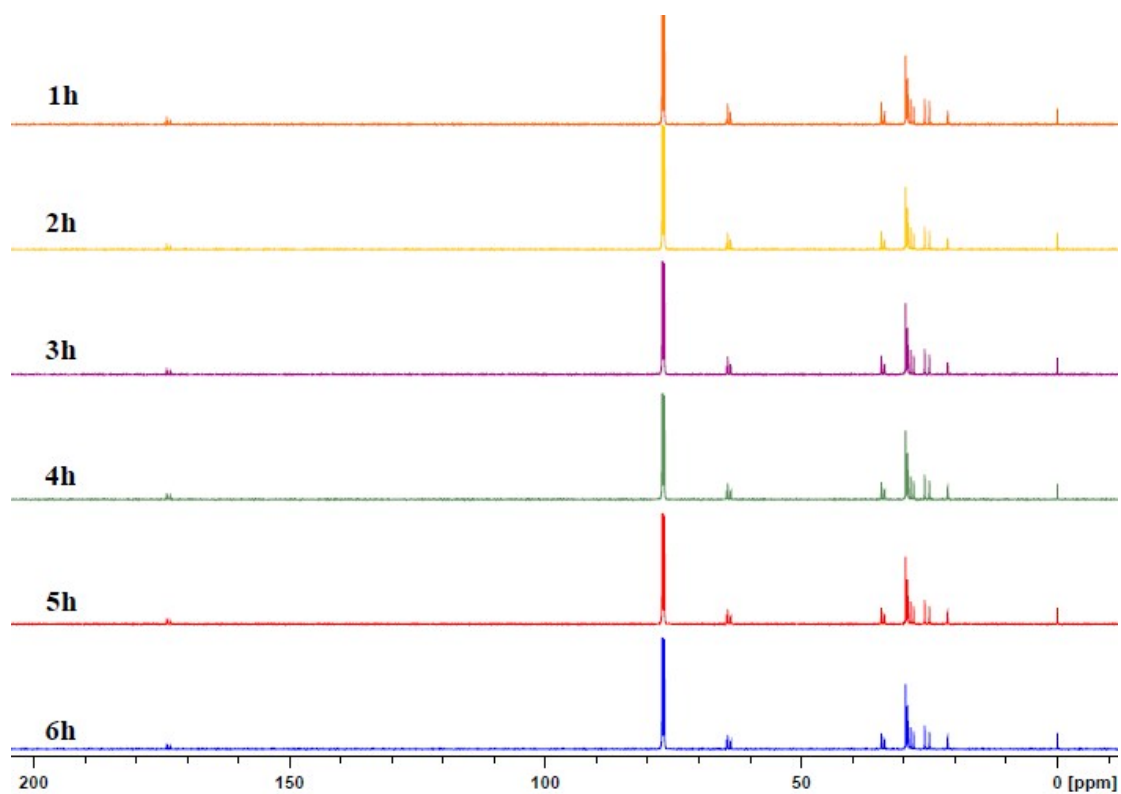


Fig. 3 ^{13}C NMR spectra of P(PDL-co-VL) copolymers prepared by REX with N435 catalysis at predetermined reaction times.

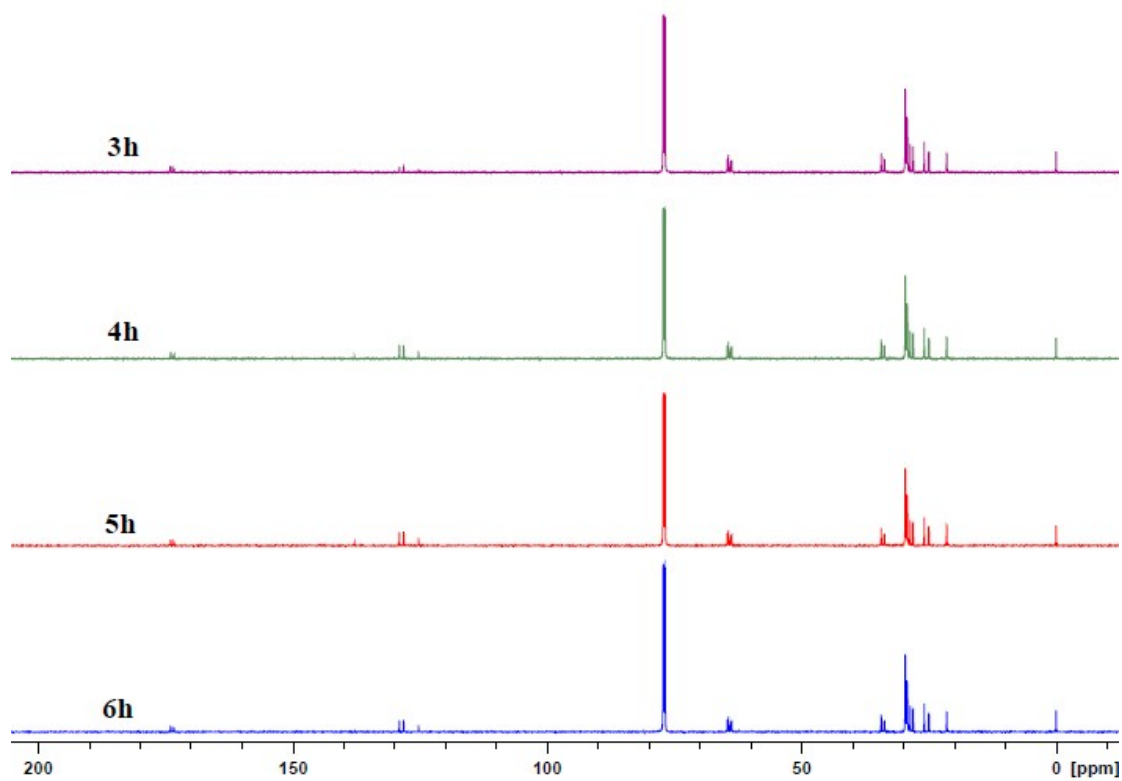


Fig. 4 ^{13}C NMR spectra of P(PDL-co-VL) copolymers prepared by N435-catalyzed solution copolymerization at predetermined reaction times

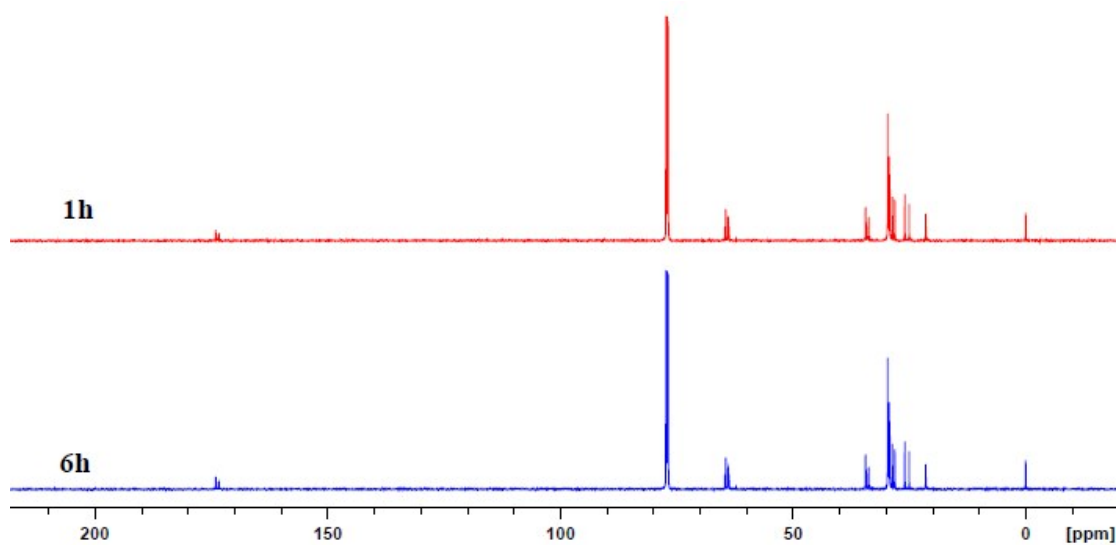


Fig. 5 ^{13}C NMR spectra of P(PDL-co-VL) copolymers prepared by N435-catalyzed bulk copolymerization at predetermined reaction times.

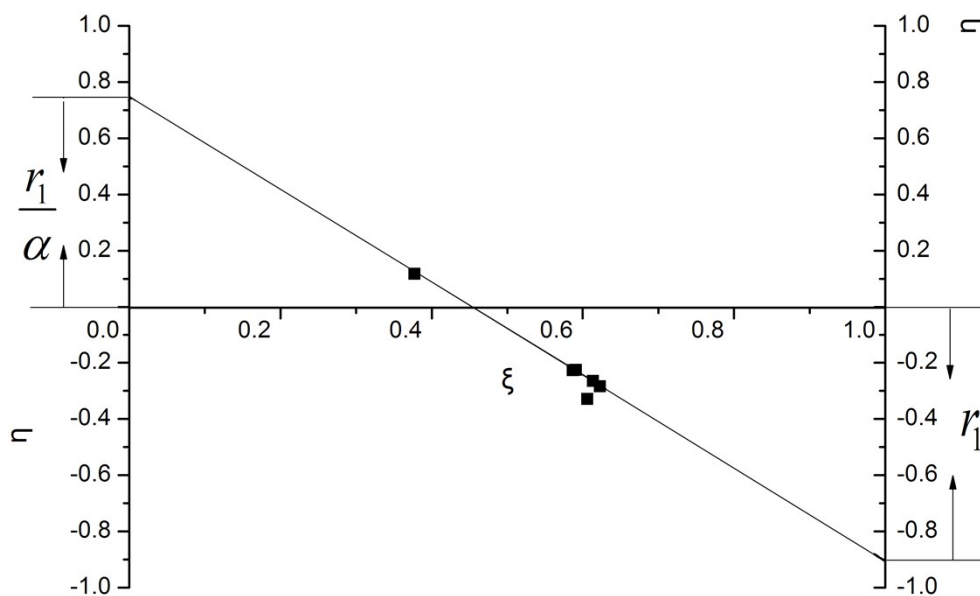


Fig. 6 Reactivity ratios determination based on the Kelen-Tudos method.