Application of Time Resolved MALDI-TOF Mass Spectral Analysis to Elucidate Chain Transfer Mechanism during Polymerization of Oxazoline Monomers Containing Thioethers

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Supporting Information

Scheme S1: Synthesis of the functionalized 2-isopropenyl-2-oxazoline monomers.¹

Experimental Procedure

Materials:

Acetonitrile (reagent grade, Fisher Scientific) was purified by distillation at 75 °C and placed over molecular sieves until used. Methyl tosylate (98%) was purified by distillation at 140 °C and placed over molecular sieves until used. 2-isopropenyl-2-oxazoline ($\geq 99\%$), thiophenol (97%), methyl thioglycolate (95%), and sodium trifluoroacetate (98%) were purchased from

Aldrich and used without further purification. 1,8,9-anthracenetriol (puriss. for MALDI-MS) was purchased from Fluka and used without further purification. All other solvents were reagent grade, purchased from Fisher Scientific, and used without further distillation or purification.

Instrumentation:

Mass spectral data was acquired using a Bruker Autoflex III (Billerica, MA) Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometer (MALDI) with delayed extraction using the reflector and positive ion mode. Mass spectral data was also obtained with a Bruker MicrOTOF ElectroSpray Ionization (ESI) Mass Spectrometry with an Agilent 1200 series binary pump (Santa Clara, CA).

For polymer products of monomer **1**, solutions of 1,8,9-anthracenetriol matrix (20 mg mL⁻¹) in chloroform, NaTFA (2 mg mL⁻¹) as the counter ion in THF, and 2 mg mL⁻¹ of sample in THF were used. MALDI samples were then prepared by using a matrix solution/counter ion solution/sample solution ratio of 1:1:1. The pulsed ion extraction delay was set to 0 ns, with ion source 1 voltage of 19.00 kV, and ion source 2 voltage of 16.47 kV, a lens voltage of 8.30 kV, a low mass gate at 800 amu, and a laser power set to 55 %. For polymer products of monomer **S1**, solutions of 1,8,9-anthracenetriol matrix (20 mg mL⁻¹) in chloroform, NaTFA (2 mg mL⁻¹) as the counter ion in THF, and 2 mg mL⁻¹ of sample in THF were used. MALDI samples were then prepared by using a matrix solution/counter ion solution/ sample solution with a ratio of 1:2:1. The pulsed ion extraction delay was set to 50 ns, with ion source 1 voltage of 19.00 kV, and ion source 2 voltage of 16.70 kV, a lens voltage of 6.40 kV, a low mass gate at 600 amu, and a laser power set to 31 %. Number average molecular weight (M_n) and polydispersity (PDI) were calculated using PolyTools software.

Gel Permeation Chromatography (GPC) was carried out on a Waters model 1515 series pump (Milford, MA) with three-column series from Polymer Laboratories, Inc. consisting of PLgel 5 μ m Mixed D (300mm x 7.5 mm, molecular weight range 200-400,000), PLgel 5 μ m 500 Å (300 mm x 7.5 mm, molecular weight range 500-30,000), and PLgel 5 μ m 50 Å (300mm x 7.5 mm, molecular weight range up to 2000) columns. The system was fitted with a Model 2487 differential refractometer detector and anhydrous tetrahydrofuran was used as the mobile phase (1 mL min⁻¹ flow rate) at 25°C. The resulting molecular weight was based on calibration using linear polystyrene standards.

Proton (and Carbon) Nuclear Magnetic Resonance (NMR) spectra were obtained from a 400 MHz (100 MHz) Varian Mercury spectrometer (Palo Alto, CA), using TMS = 0.00 ppm calibration and a 500 MHz (125 MHz) Bruker spectrometer (Billerica, MA), using TMS=0.00 ppm calibration with deuterated solvents at room temperature.

Infrared (IR) Spectroscopy was implemented using a NEXUS 670 FT-IR E.S.P. (Madison, WI). Samples were made using approximately 4 mg of polymer and 5 mg of KBr which was ground into a fine powder by mortar and pestle and compacted into a pellet.

The monomers were prepared according to the previously reported procedure.¹

General Procedure for the Polymerization of Functionalized 2-isopropenyl-2-oxazoline.

The desired 2-isopropenyl-2-oxazoline functionalized monomer¹ was dried under vacuum overnight to remove any water. All glassware was flame-dried. Distilled Acetonitrile (4-6 mL) was added to the reaction flask under N₂ gas with a syringe. Initiator to monomer ratio of 1:130 was used. Distilled methyl tosylate (0.0129g, 0.0696 mmol) was added to the reaction via syringe. Functionalized 2-isopropenyl-2-oxazoline monomer (eg. Monomer **1**, 2g, 9.0462 mmol) was added via syringe. The reaction was heated to 65°C. Aliquots (0.25 ml) of the bulk reaction

were removed at various times utilizing a clean disposable syringe. Immediately after removal from the reaction, the samples were cooled in an ice bath and 0.1ml of H₂O were added to the samples to quench any reactive chains. The sample was then concentrated to remove acetonitrile with a rotary evaporator. MALDI-TOF MS was then taken of the samples with no further purification. GPC was also taken of the polymer after reacting for 24 hours (Overall conversion after 24 hours: 19%).

Characterization of polymer products from monomer 1. MALDI-TOF MS was taken at a matrix/counter ion/ sample ratio of 1:1:1, with 1,8,9-anthracenetriol matrix (20 mg/mL), NaTFA (2mg/mL) as the counter ion, and 2 mg/mL of sample. Representative characterization data follow. ¹H NMR (CDCl₃, δ, ppm): 1.0-1.4 (br (-CH₃)), 2.6-2.8 (br (-CHCH₂S-)), 2.8-3.1 (br (-CCHCH₃CH₂-)), 3.1-3.8 (br (-NCH₂CH₂-)), 6.9-7.4 (br (CH from (Ph))). ¹³C NMR (CDCl₃, δ, ppm): 19 (-CH₃), 37 (-CCHCH₃CH₂-), 38 (-CHCH₂S-), 48 (-NCH₂CH₂-), 126 (Ar(C)), 137 (Ar(C)), 139 (Ar(C)), 146 (Ar(C)), 186 (-NCOCH-). IR: 1600 (Ar(C=C)), 1640 (tertiary amide(C-N)), 3050 (Ar(C-H)), 3080 (Ar(C-H)), 3300 (O-H), 3500 (O-H).

Characterization of polymer products of monomer S1. MALDI-TOF MS was taken at a matrix/counter ion/ sample ratio of 1:2:1, with 1,8,9-anthracenetriol matrix (20 mg/mL), NaTFA (2 mg/mL) as the counter ion, and 2 mg/mL of sample. Representative characterization data follow. ¹H NMR (CDCl₃, δ, ppm): 1.10-1.30 (br (-CH₃)), 2.55-2.70 (br (-CHCH₂S-)), 2.85-3.10 (br (-CCHCH₃CH₂-)), 3.10-3.30 (br (-SCH₂C-)), 3.40-3.60 (br (-NCH₂CH₂-)) 3.60-3.75 (br (-COOCH₃)). ¹³C NMR (CDCl₃, δ, ppm): 19 (-CH₃), 34 (-CCHCH₃CH₂-), 36 (-CCH₂S-), 37 (-SCH₂COOCH₃), 46 (-NCH₂CH₂-), 52 (-COOCH₃), 172 (-CH₂COOCH₃), 176 (-NCOC-). IR: 1640 (tertiary amide (C-N)), 1735 (ester (C=O)), 3500 (O-H), 3200 (O-H).

Figure S1: Results for MALDI-TOF MS end group analysis using linear regression protocol previously reported² for the four products of the polymerization of monomer **1** present after 5 hours. (Intercept- Na^+ = End Group Mass)

Figure S2. MALDI-TOF MS spectrum of products from monomer **S1** after 3 hours.

(monoisotopic exact mass used in calculations and for observation mass for all distributions)

Note: A new distribution was observed during the polymerization of methyl thioglycolate functionalized monomer (**S1**) corresponding to a methyl initiated and OCH_3 terminated polymer (**S7**).

Figure S3: MALDI-TOF MS of formation of chain transfer products at various time intervals for products of monomer **S1**. (signal counts normalized relative to compound **S2** at each time point)

Figure S4: Results for MALDI-TOF MS end group analysis using linear regression protocol previously reported² for the four products of the polymerization of monomer **S1** present after 5 hours.

1. Cortez, M. C.; Grayson, S. M. *Macromolecules* **2010**, *43*, 4081-4090.
2. Li, Y.; Hoskins, J. N.; Sreerama, S. G.; Grayson, M. A.; Grayson, S. M. *J. Mass Spectrom.* **2010**, *45*, 587-611.