

BLOCK COPOLYMERS DERIVED FROM THE ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION OF A MODIFIED VEGETABLE OIL

Timothy C. Mauldin, Ella F. Spiegel and Michael R. Kessler

Department of Materials Science and Engineering
Iowa State University
2220 Hoover Hall
Ames, IA 50011

Introduction

In recent years there has been a surge of interest in engineering block copolymers with custom material properties, achievable by varying block structure and chain length. Notably, block copolymers exhibiting microphase separation have found a commercial niche as a valuable class of materials known as thermoplastic elastomers, which merges the useful mechanical properties of two classes of polymers (thermoplastic and elastomeric) traditionally known as discrete material types. However, the growing industrial demand for these materials is beginning to conflict with the now ubiquitous goal to reduce our dependency on petroleum-based monomers (e.g. styrene, butadiene, isoprene, etc.) from which most thermoplastic elastomers are derived. Olefin metathesis polymerization^{1,2} of renewable chemicals—such as the unsaturated fatty acids of vegetable oils—are ideally suited to form biopolymers mimicking the elastomeric blocks of these copolymers since olefin metathesis retains double bonds to form unsaturated polymers (as in traditional elastomers polybutadiene and polyisoprene). Here, we synthesize copolymers containing a bio-derived elastomeric block made via Acyclic Diene Metathesis (ADMET)³⁻⁵ polymerization of a modified vegetable oil, grow triblock copolymers, and characterize the resulting copolymer properties.

Experimental

Materials. All reagents were purchased from Aldrich Chemical Co. Toluene and tetrahydrofuran (THF) were distilled over Na/benzophenone immediately prior to use, pyridine was purchased anhydrous and stored over molecular sieves (4Å), and all other chemicals were used without further purification.

Instrumentation. Molecular weight measurements were determined by size exclusion chromatography (SEC) with polystyrene standards in chloroform. Differential Scanning Calorimetry was performed with a Q2000 Model DSC (TA Instruments) under a flow of dry nitrogen gas (50 ml/min) at heating/cooling rates of 15 K/min. Thermogravimetry of polymers was done with a Q50 Model TGA (TA Instruments) under air (60 ml/min) at a rate of 20 K/min. ¹H-NMR spectra were recorded with a 300 MHz spectrometer using *d*-trichloromethane as solvent and residual chloroform as an internal standard.

Synthesis of ADMET monomer. Thionyl Chloride (50 ml, 0.42 mol) was added dropwise to a solution of toluene (50 ml) and 10-undecenoic acid (36.9 g, 0.20 mol) in an oven-dried flask under dry nitrogen gas. After stirring for 6 hours at room temperature, toluene and excess thionyl chloride were removed by vacuum distillation. To the resulting product, 25 ml of fresh toluene was twice added and removed under vacuum to eliminate residual thionyl chloride. Without further purification, 100 ml THF was added to the product, to which a solution of pyridine (17.7 ml, 0.22 mol) and ethylene glycol (12.4 g, 0.20 mol) in 25 ml of THF was added dropwise. After 14 hours stirring at room temperature, the reaction mixture was concentrated to ~75 ml, diluted with 200 ml diethyl ether, and washed with water (2 x 100 ml) and brine (1 x 100 ml). Volatiles were evaporated, and the crude product was purified by silica gel chromatography (hexane/ethyl acetate = 7/1 (v/v)) to reveal a clear liquid (83%). ¹H-NMR (300 MHz, CDCl₃) δ: 5.73-5.86 (m, 2H); 4.89-5.04 (m, 4H); 4.26 (s, 4H); 2.31 (t, 4H, J = 7.2 Hz); 1.99-2.06 (m, 4H); 1.55-1.67 (m, 4H); 1.15-1.43 (m, 20H) ppm.

Synthesis of ATRP initiator. ATRPi was synthesized as reported earlier⁶ without modification.

ADMET Polymerization. 1st generation Grubbs' catalyst (5 mg, 6.1 x 10⁻³ mmol) was recrystallized⁷ in a 10 ml, oven-dried flask to aid its dissolution in the ADMET monomer. ADMET monomer (0.5 g, 1.25 mmol) was added to the catalyst at 35 °C, which was stirred rapidly under mild vacuum. After ~30 minutes the viscosity of the reaction rapidly increased, at which point the heat was increased to 70 °C and the reaction flask opened to heavy vacuum. After 24 hours, vacuum was broken and the bulk solid was

dissolved in 10 ml THF, precipitated with 50 ml methanol, and vacuum filtered. The resulting polymer was dried under vacuum at 90 °C until a constant mass was attained to reveal a tan, opaque film (93%).

Synthesis of initiator end-capped polymer. The above procedure was repeated with 1 wt. % triblock initiator initially dissolved in the ADMET monomer.

Results and Discussion

Acyclic Diene Metathesis is a condensation polymerization of an α,ω-diene, which in this study was synthesized from a vinyl-terminated fatty acid, derived from castor oil, shown in **Figure 1**. ADMET is an especially well-suited polymerization technique for fatty acids, which typically contain a high degree of unsaturation, and other ADMET polymerizations of fatty acid derivatives have yielded a wide array of polymers with different properties.⁸⁻¹⁰

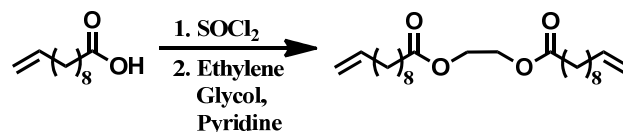


Figure 1. Synthesis of ADMET monomer.

The olefin metathesis catalyst Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride, (1st generation Grubbs' catalyst), which is known to produce high molecular weight and low polydispersity polymers [1], was used to perform ADMET. The polymerization was run at elevated temperatures and under vacuum in order to drive off the formation of ethylene gas, hence driving the reaction to form polymer **1** (**Figure 2**).

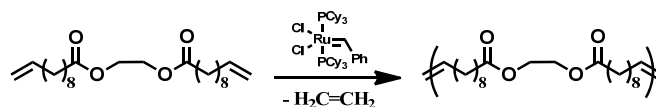


Figure 2. ADMET polymerization of an α,ω-diene using the 1st generation Grubbs' catalyst to form polymer **1**.

Yields for the ADMET polymerization were typically high (90-95%), and clean formation of polymer from monomer was observed via ¹H-NMR (**Figure 3**). Three proton peaks resulting from terminal olefins are observed in the ADMET monomer in the ranges of 5.73-5.86 (H_c of the monomer) and 4.89-5.04 ppm (H_a and H_b of the monomer). These peaks are absent in polymer **1** and are instead replaced with peaks representative of two internal vinylic protons (H_a and H_b of the polymer).

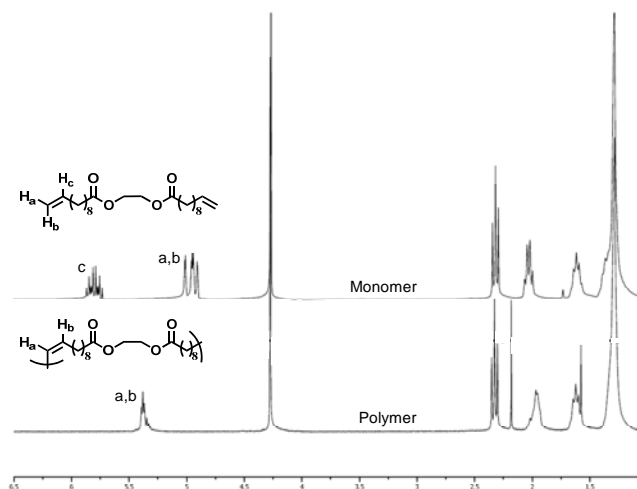


Figure 3. ¹H-NMR spectra (300 MHz, CDCl₃) of ADMET monomer (top spectra) and ADMET polymer (bottom spectra) with vinyl protons peaks assignments denoted as H_a, H_b, or H_c.

The ADMET polymer was characterized by GPC, DSC and TGA, the results of which are summarized in **Table 1**. Number-average molecular weight of polymer **1** was 33,700 g/mol with a polydispersity index of 1.81, the latter of which is common for ADMET with the 1st generation Grubbs' catalyst and surprisingly low for a step-growth polymerization. DSC revealed that polymer **1** is a semi-crystalline polymer, which undergoes both a glass transition (42 °C) and a melting transition (55 °C). Thermogravimetry revealed good thermal stability, as the polymer only lost 5% weight by 388 °C.

Table 1. Characterization for polymers 1 and 2.

Polymer	M _n (g/mol)	PDI	T _g (°C)	T _m (°C)	T _D ^a (°C)
1	33700	1.81	42	55	388
2	28500	1.93	41	56	374

In order to synthesize block copolymers, a telechelic polymer with endgroups capable of initiating polymerization mechanisms is needed. To achieve this, the ADMET polymerization was ran on the ADMET monomer in the presence of 1 wt. % of a terminal monoene (which can react via ADMET, end-capping the polymer) that also contains an initiator functional group (**Figure 4**). The monoene contained either an alcohol or a 2-bromo-2-methylpropionate group, capable of initiating either ring-opening or atom-transfer radical polymerizations, respectively. The resulting polymer (polymer **2**) had a slightly lower molecular weight and slightly higher PDI, which is expected for a polymerization containing an end-capping monomer. Thermal properties of polymer **2** were very similar to polymer **1**.

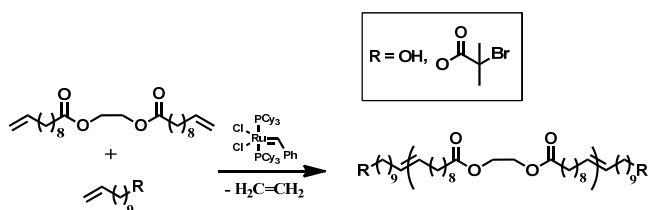


Figure 4. ADMET polymerization in the presence of an end-capping initiator to form a telechelic polymer.

From polymer **2**, triblock copolymers were formed under standard ring-opening polymerization (ROP) conditions of polylactic acid or standard atom-transfer radical polymerization (ATRP) conditions of polystyrene.

Conclusions

ADMET polymerization of an α,ω -diene derived from a renewable resource (castor oil) was used to synthesize the center block of a triblock copolymer. The center block copolymer was synthesized in good yield to form a semi-crystalline polymer with a molecular weight of 33,700 g/mol. At the expense of a minor loss in molecular weight, the ADMET polymer was made in the presence of an end-capping monoene, which was able to form a telechelic polymer with endgroups capable of initiating further polymerization. ROP- and ATRP-based end blocks were synthesized under standard polymerization conditions.

Acknowledgements. The authors kindly acknowledge Dr. Xia Sheng and Dr. Mahendra Thunga for their helpful discussions.

References

- (1) Baughman, T.W. and Wagener, K.B. *Adv. Polym. Sci.* **2005**, *176*, 1.
- (2) Bielawski, C.W. and Grubbs, R.H. *Prog. Polym. Sci.* **2007**, *32*, 1.
- (3) Wagener, K.B.; Boncella, J.M. and Nel, J.G. *Macromolecules* **1991**, *24*, 2649.
- (4) Wagener, K.B. and Smith, D.W. *Macromolecules* **1991**, *24*, 6073.
- (5) Schwendeman, J.E.; Church, A.C. and Wagener, K.B. *Adv. Synth. Catal.* **2002**, *344*, 597.
- (6) Matyjaszewski, K.; Miller, P.J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B.B.; Siclovan, T.M.; Kickelbick, G.; Vallant, T.; Hoffmann, H. and Pakula, T. *Macromolecules* **1999**, *32*, 8716.
- (7) Jones, A.S.; Rule, J.D.; Moore, J.S.; White, S.R. and Sottos, N.R. *Chem. Mater.* **2006**, *18*, 1312.

- (8) Rybak, A. and Meier, M.A.R. *ChemSusChem* **2008**, *1*, 542.
- (9) Fokou, P.A. and Meier, M.A.R. *Macromol. Rapid Commun.* **2008**, *29*, 1620.
- (10) Fokou, P.A. and Meier, M.A.R. *J. Am. Chem. Soc.* **2009**, *131*, 1664.