

Triptycene-Containing Polyetherolefins Via Acyclic Diene Metathesis Polymerization

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ABSTRACT: Several new triptycene-containing polyetherolefins were synthesized via acyclic diene metathesis (ADMET) polymerization. The well-established mechanism, high selectivity and specificity, mild reaction conditions, and well-defined end-groups make the ADMET polymerization a good choice for studying systematic variations in polymer structure. Two types of triptycene-based monomer with varying connectivities were used in the synthesis of homopolymers, block copolymers, and random copolymers. In this way, the influence of the triptycene architecture and concentration in the polymer backbone on the thermal behavior of the polymers was studied. Inclusion of

increasing amounts of triptycene were found to increase the glass transition temperature, from $-44\text{ }^{\circ}\text{C}$ in polyoctenamer to $59\text{ }^{\circ}\text{C}$ in one of the hydrogenated triptycene homopolymers (**H-PT2**). Varying the amounts and orientations of triptycene was found to increase the stiffness (**H-PT1**), toughness (**PT1₁-b-PO₁**) and ductility (**PT1₁-ran-PO₃**) of the polymer at room temperature. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 1695–1706

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INTRODUCTION Olefin metathesis is a powerful and popular method of carbon–carbon bond formation. Initially observed as a scrambling of double bonds in the presence of transition metal catalysts,¹ the potential for application in polymer synthesis was almost immediately recognized. Early investigations were carried out in the 1960s at Philips Petroleum,² and at DuPont, where the reaction was used to synthesize polynorborene.³ However, it was not until the mechanism was proposed by Hérisson Chauvin⁴ in 1971 that the potential of olefin metathesis polymerization was suggested. The first polymerizations via olefin metathesis utilized cyclic monomers, which drives the polymerization with the release of ring strain.^{1,2} Ring-opening metathesis polymerization (ROMP) remains an important field of research today; however the development of selective and highly active catalysts^{5,6} has increased the specificity of the reaction to allow for acyclic monomers.

Acyclic diene metathesis polymerization (ADMET) was first applied to synthesize polymers of high molecular weight in 1991, using a non-Lewis acidic highly active tungsten catalyst.⁷ The success of ADMET polymerization relies on the elimination of competing side reactions that can be substan-

tial with Lewis acidic catalysts and on the facile removal of the olefin byproduct (usually ethylene), which drives the reaction equilibrium towards the polymer product. Because the polymerization goes by a step-growth mechanism, a selective, high-yielding process is crucial to produce high molecular weight polymers. ADMET polymerization has been used to synthesize a variety of polymers including purely linear polyethylene,⁸ well-ordered copolymers,⁹ chiral polymers,¹⁰ silicon-containing polymers,¹¹ and conducting polymers.¹² Among other polymers, ADMET polymerization quickly demonstrated its utility as a method for unsaturated polyether synthesis.¹³ At high molecular weight, unsaturated polyethers comprise a useful class of thermoplastic elastomers in which the carbon-oxygen bond introduces a greater degree of flexibility in the polymer backbone and a low T_g .¹⁴

Triptycene is a paddle-wheel shaped molecule that is well-known to impart interesting properties when incorporated into the backbone of a polymer.¹⁵ The rigid three-dimensional structure of triptycene interrupts the close packing of polymer chains and the associated interchain interactions when imparted into a polymer matrix.^{16–18} For this reason, triptycene often imparts solubility and processability to

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polymers, and in the instance of thermoplastic elastomers also prevents crystallization. Enhanced thermal stability is often also observed with triptycene incorporation, along with improvements in polymer mechanical properties including increased stiffness, toughness, ductility, and ultimate tensile strength.^{19–21}

In this study, we have systematically introduced triptycene into the backbone of ADMET-synthesized polyethers to investigate the thermal and mechanical effects of triptycene incorporation. Two different triptycene olefin monomers were synthesized to study the effect of incorporation into the polymer backbone in different geometries (Fig. 1). **T1** allows a 1,4 connection through the phenyl ring in the polymer backbone and **T2**, allows a bridgehead connection through the polymer backbone.

Three types of triptycene-containing polymers were prepared. First, homopolymers of the α - ω diene triptycenes with differing connectivities were synthesized in good yield and high molecular weight (\sim 40 kDa) containing 44.7 weight % triptycene. Second, block copolymers of **T1** and cyclooctene (CO) were synthesized with monomer ratios of 1:1 and 1:3 and varying molecular weights. Finally, random copolymers of **T1** and 1,9-decadiene were synthesized with monomer ratios of 1:1 and 1:3. Polyoctenamer (PO), synthesized by the ADMET polymerization of 1,9-decadiene, was chosen as the control polymer for the three types of triptycene polymer. The thermal properties were investigated with thermogravimetric analysis (TGA) and dynamic scanning calorimetry (DSC). To understand the viscoelastic behavior of the polymers, dynamic mechanical analysis (DMA) was performed and tensile tests were executed at room temperature to determine variations in ambient properties. From these studies, we show that triptycene inclusion systematically increases the glass transition temperatures and improves the strength, toughness, and ductility of a polymer with different incorporation methods.

EXPERIMENTAL

Materials and Instrumentation

Anhydrous tetrahydrofuran (THF) was obtained using a solvent purification system (Innovative Technologies). 1,2-dichlorobenzene was distilled, passed through an activated alumina column, and degassed by bubbling Argon through before use. Grubbs' first generation and Grubbs-Hoveyda cat-

alysts were provided by Materia. Wilkinson's hydrogenation catalyst was obtained from Catalyst Technologies and used as received. All other chemicals were of reagent grade and used as received from Sigma Aldrich. All reactions were performed under Argon using standard Schlenk techniques unless otherwise noted.

¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a Mercury 300 spectrometer, and the ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were obtained on a Varian Associates Innova 500 spectrometer. Reaction conversions and relative purity of crude products were monitored by thin layer chromatography performed on EMD silica gel coated (250- μ m thickness) glass plates and ¹H and ¹³C NMR. Gel permeation chromatography (GPC) was performed at 40 °C using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns (10 microns PD, 7.8 mm ID, 300-mm length) in HPLC grade THF (0.05–0.07%, w/v sample concentration). Retention times were calibrated against narrow molecular weight polystyrene standards (Polymer Laboratories; Amherst, MA) to produce number average molecular weight (M_n) and weight average molecular weight (M_w) values.

TGA was performed using a TA Instruments Q4000 Series instrument under nitrogen at a scan rate of 20 °C/min from 50 to 600 °C. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q1000 series equipped with a controlled cooling accessory (LNCS) at a heating rate of 10 °C/min. Transition temperatures were referenced to indium and freshly distilled *n*-octane and transition enthalpies were referenced to indium. DMA and tensile testing were performed on a TA Instruments Q800 Dynamic Mechanical Analyzer. Samples were prepared for the test by casting a film from a filtered 20 mg/mL solution of the polymer in chloroform in a Teflon dish. Test strips were cut to be 28 \times 6.2 \times 0.05 mm³ with a razor blade. DMA tests were conducted starting at -80 or -140 °C (starting temperature determined by T_g via DSC) and terminating when mechanical integrity was lost ($T = 0$ – 100 °C). 0.1% strain was applied at 1 Hz while the temperature was ramped at 10 °C/min. Tensile tests were run at 23 °C with a strain-controlled ramp of 3 N/min. Both the DMA and tensile tests were conducted on a minimum of three samples for each polymer type.

Synthesis

Synthesis of Triptycene-1,4-diol

Synthesis was accomplished via literature procedure.²²

Synthesis of Triptycene-9,10-diol

Synthesis was accomplished via literature procedure.^{23–25} 9,10-diethynyl-9,10-dihydroanthracene-9,10-diol (5 g, 19.2 mmol), and [Rh(cod)Cl]₂ (237 mg, 0.48 mmol) were suspended in 150 mL dry toluene under argon. Norbornadiene (8.8 g, 96 mmol) was added and the flask was sealed and heated at 105 °C for 20 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (4:1, Hexanes:EtOAc) to give 8.52 g Triptycene-9,10-diol.

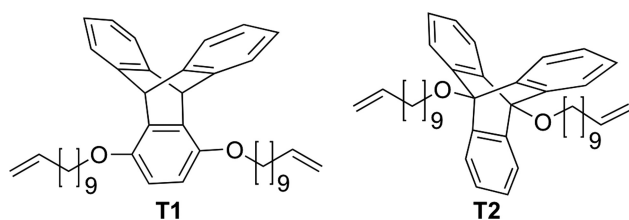


FIGURE 1 Chemical structures of **T1** (1,4-bis(undec-10-en-1-yloxy)-triptycene), a triptycene monomer with a 1,4 connection and **T2** (9,10-bis(undec-10-en-1-yloxy)-triptycene), a triptycene monomer with a bridgehead connection.

Yield: 75%. ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.56$ (dd, $J = 5.6, 3.2, 6\text{H}$), 7.12 (dd, $J = 5.6, 3.2, 6\text{H}$), 3.4 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): $\delta = 144.7, 125.7, 118.8, 79.6$. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{14}\text{O}_2$ [M+H] 287.1072, found 287.1080.

Synthesis of T1 (1,4-Benzene Substituted Monomer)

Triptycene-1,4-diol (7 g, 24.5 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (4.26 g, 24.5 mmol), Bu_4NBr (2.37 g, 7.3 mmol), NaOH (12.7 g, 318 mmol), 11-bromo-1-undecene (21 mL, 98 mmol), were dissolved in 100 mL $\text{THF}:\text{H}_2\text{O}$ (1:1) and refluxed 8 h. The reaction was cooled to room temperature and partitioned between water and diethyl ether. The aqueous phase was extracted with diethyl ether once more, and the combined organic fractions were washed with 3 M NaOH three times, dried over Mg_2SO_4 and evaporated *in vacuo*. The residue was dissolved in a minimum amount of dichloromethane and precipitated from EtOH at 0°C twice to give 13.5 g **T1**.

Yield: 94%. m.p. $94\text{--}95^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.41$ (dd, $J = 5.2, 3.2, 4\text{H}$), 6.99 (dd, $J = 5.2, 3.2, 4\text{H}$), 6.50 (s, 2H), $5.90\text{--}5.79$ (m, 2H), 5.89 (s, 2H), $5.06\text{--}5.01$ (m, 2H), $4.98\text{--}4.95$ (m, 2H), 3.94 (t, $J = 6.4, 4\text{H}$), 2.09 (m, 4H), 1.84 (m, 4H), 1.55 (m, 4H), $1.50\text{--}1.33$ (m, 20H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): $\delta = 148.7, 146.0, 139.4, 135.9, 125.1, 123.9, 114.4, 110.9, 69.9, 47.7, 34.1, 29.9, 29.7, 29.6, 29.4, 29.2, \text{ and } 26.4$. HRMS (ESI) calcd. for $\text{C}_{42}\text{H}_{54}\text{O}_2$ [M+Na] 613.4016, found 613.4016. Elemental analysis: calc. C 85.37%, H 9.21%, found C 85.41%, H 9.26%.

Synthesis of T2 (Bridgehead Substituted Monomer)

Triptycene-9,10-diol (4 g, 14 mmol), 11-bromo-1-undecene (25 mL, 107 mmol), and NaH (5 g, 130 mmol) were dissolved in 100 mL of DMF and heated at 70°C for 15 h. The reaction was cooled to room temperature and partitioned between water and diethyl ether. The aqueous phase was extracted with diethyl ether twice more, and the combined organic fractions were washed with water, brine, dried over Mg_2SO_4 and evaporated *in vacuo*. The residue was recrystallized from EtOH twice to give 3.3 g **T2**.

Yield: 40%. m.p. $133\text{--}134^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.56$ (dd, $J = 5.2, 3.2, 6\text{H}$), 7.05 (dd, $J = 5.2, 3.2, 6\text{H}$), $5.90\text{--}5.79$ (m, 2H), $5.05\text{--}4.99$ (m, 2H), $4.97\text{--}4.94$ (m, 2H), 4.57 (t, $J = 7, 4\text{H}$), $2.18\text{--}2.05$ (m, 8H), 1.67 (m, 4H), $1.52\text{--}1.35$ (m, 20H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): $\delta = 145.0, 139.5, 125.1, 121.2, 114.4, 85.2, 67.5, 34.1, 32.0, 29.9, 29.7, 29.4, 29.2, \text{ and } 26.5$. HRMS (ESI) calcd. for $\text{C}_{42}\text{H}_{54}\text{O}_2$ [M+H] 591.4197, found 591.4179. Elemental analysis: calc. C 85.37%, H 9.21%, found C 84.43%, H 9.10%.

Synthesis of PT1 (1,4-Substituted Homopolymer)

In an Schlenk flask, a saturated solution of **T1** (591 mg) in 1,2-dichlorobenzene (1.2 mL, 50 wt %) was degassed by bubbling argon through the solution for 3 h. Under strong argon flow, 1 mol % (8.23 mg) of Grubbs' first generation catalyst was added. The system was then placed under dynamic vacuum at 70 Torr absolute pressure via an aspirator attached to one arm. The reactor was heated to 45°C and left to stir for 72 h. Then, ADMET was terminated by

dissolving polymer in a degassed solution of 20 mL chloroform and 2 mL ethyl vinyl ether. The solution was allowed to stir for 3 h. After that time, polymers were precipitated from cold methanol, to yield 500 mg of **PT1**.

Yield: 86%. ^1H NMR (500 MHz, CDCl_3 , ppm): $\delta = 7.40$ (dd, $J = 3.2, 2.0, 4\text{H}$), 6.98 (dd, $J = 3.3, 1.8, 4\text{H}$), 6.49 (s, 2H), 5.89 (s, 2H), $5.50\text{--}5.36$ (m, 2H), 3.93 (t, $J = 3.9, 4\text{H}$), $2.10\text{--}1.95$ (m, 4H), 1.84 (m, 4H), 1.55 (m, 4H), $1.50\text{--}1.30$ (m, 20H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): $\delta = 148.7, 146.1, 135.9, (130.7, 130.2, 125.1, 124.0, 110.9, 69.9, 47.7, 32.9, 30.0, 29.9, 29.8, 29.7, 29.5, 27.5, 26.5$. GPC: M_n : 44,000 Da, M_w : 83,000 Da, polydispersity indice (PDI): 1.9. TGA: 150°C (5% weight loss). DSC: T_g : 22°C .

Synthesis of PT2 (Bridgehead Homopolymer)

The same polymerization method described for **PT1** was used, starting with 589 mg **T2**. 500 mg of polymer **PT2** was obtained.

Yield: 87%. ^1H NMR (500MHz, CDCl_3 , ppm): $\delta = 7.58$ (dd, $J = 5.3, 3.2, 6\text{H}$), 7.03 (dd, $J = 5.3, 3.0, 6\text{H}$), $5.52\text{--}5.33$ (m, 2H), 4.55 (t, $J = 7.0, 4\text{H}$), $2.25\text{--}1.92$ (m, 8H), 1.65 (m, 4H), $1.57\text{--}1.21$ (m, 20H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): $\delta = 145.0, 130.6, 130.1, 125.1, 121.2, 85.2, 67.5, 32.9, 29.9, 29.8, 29.5, \text{ and } 26.5$. GPC: M_n : 49,000 Da, M_w : 91,000 Da, PDI: 1.8. TGA: 420°C (5% weight loss). DSC: T_g : 37°C .

Synthesis of H-PT1

In a 125 mL Parr bomb glass sleeve, **PT1** (400 mg) was dissolved in 40 mL degassed toluene. A few milligrams of Wilkinson's hydrogenation catalyst were added, and the bomb was charged with 400 psi of hydrogen. The reaction was allowed to proceed for 3 days at 70°C . The polymer solution was concentrated and precipitated in cold methanol to yield 350 mg of **H-PT1**.

Yield: 90% ^1H NMR (500 MHz, CDCl_3) $\delta = 7.42$ (s, 4H), 7.00 (s, 4H), 6.51 (s, 2H), 5.90 (s, 2H), 3.95 (s, 4H), 1.85 (s, 2H), 1.56 (s, 2H), 1.33 (m, 14H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): $\delta = 151.2, 148.5, 138.5, 138.4, 127.6, 126.4, 113.4, 72.4, 50.2, 32.5, 32.4, 32.2, \text{ and } 29.0$. GPC: M_n : 46,000 Da, M_w : 86,000 Da, PDI: 1.9. TGA: 390°C (5% weight loss). DSC: T_g : 43°C .

Synthesis of H-PT2

The same method as described above for **H-PT1** was used, starting with 500 mg of **PT2**, to give 432 mg of **H-PT2**.

Yield: 89%. ^1H NMR (500 MHz, CDCl_3 , ppm): $\delta = 7.59$ (dd, $J = 5.3, 3.2, 6\text{H}$), 7.04 (dd, $J = 5.3, 3.2, 6\text{H}$), 4.57 (t, $J = 6.8, 4\text{H}$), $2.23\text{--}2.04$ (m, 4H), 1.65 (m, 4H), $1.58\text{--}1.18$ (m, 22H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): $\delta = 145.0, 125.0, 121.2, 85.2, 67.5, 32.0, 30.0, 29.9, \text{ and } 26.5$. GPC: M_n : 42,000 Da, M_w : 99,000 Da, PDI: 2.1. TGA: 450°C (5% weight loss). DSC: T_g : 50°C , T_m : 122°C (ΔH : 14.7 J/g), T_c : 117°C (ΔH : 9.4 J/g).

Synthesis of PT1₁-b-PO₃low (Block Copolymer in 1:3 Ratio)

The same ADMET polymerization method described for **PT1** was used, starting with 300 mg **T1**. Instead of quenching the

polymerization with ethyl vinyl ether, a degassed solution containing 350 mg CO in 1,2-dichlorobenzene as added, followed by the addition of Grubbs' first generation catalyst. The solution was sealed under argon atmosphere for about 48 h. After this period of time, polymerization was terminated by the addition of degassed ethyl vinyl ether (2 mL), and the solution was allowed to stir for 3 h. Polymer was then precipitated from cold methanol to yield 483 mg of **PT1₁-b-PO₃low**.

Yield: 82%. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.40 (dd, *J* = 3.30, 1.90 Hz, 4 H), 6.98 (dd, *J* = 3.57, 2.06 Hz, 4H), 6.49 (s, 2H), 5.88 (s, 2H), 5.33–5.49 (m, 7H), 3.93 (t, *J* = 6.18 Hz, 4H), 1.93–2.13 (m, 14H), 1.79–1.88 (m, 4H), 1.50–1.59 (m, 5H), 1.25–1.47 (m, 41H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ = 148.6, 146.0, 135.8, 130.7, 130.6, 130.6, 130.5, 130.1, 127.9, 125.1, 123.9, 110.8, 69.9, 47.7, 32.9, 32.8, 30.1, 30.0, 30.0, 29.9, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 27.5, 27.4, and 26.5. GPC: *M*_n(prepolymer): 13,100 Da, *M*_w(prepolymer): 34,500 Da, PDI_(prepolymer): 2.6. *M*_n(PT11-b-PO3low): 28,800 Da, *M*_w(PT11-b-PO3low): 52,200 Da, PDI_(PT11-b-PO3low): 1.8. DSC: *T*_g: -15 °C

Synthesis of PT1₁-b-PO₃med

The same method as described above for the block copolymer **PT1₁-b-PO₃low** was used, starting with 400 mg **T1** and 115 mg CO (1:1 **T1**: CO monomer molar ratio), which gave 289 mg **PT1₁-b-PO₃med**.

Yield: 63 %. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.40 (dd, *J* = 3.29, 2.05 Hz, 4H), 6.94–7.02 (m, 4H), 6.49 (s, 2H), 5.88 (s, 2H), 5.33–5.48 (m, 9H), 3.93 (t, *J* = 6.10 Hz, 4H), 1.92–2.12 (m, 18H), 1.78–1.89 (m, 4H), 1.49–1.59 (m, 5H), 1.23–1.47 (m, 49H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ = 148.7, 146.05, 135.9, 130.6, 130.1–29.3, 27.5, 26.5, and 1.28. *M*_n(prepolymer): 28,100 Da, *M*_w(prepolymer): 53,600 Da, PDI_(prepolymer): 1.9. *M*_n(PT11-b-PO3med): 40,800 Da, *M*_w(PT11-b-PO3med): 73,400 Da, PDI_(PT11-b-PO3med): 1.8. TGA: 420 °C (5% weight loss). DSC: *T*_g: -24 °C, *C*_p = 3.7 J/g °C.

Synthesis of PT1₁-b-PO₃high

The same method as described above for the block copolymer **PT1₁-b-PO₃low** was used starting with 380 mg **T1** and 120 mg CO (1:1 **T1**: CO monomer molar ratio) to give 385 mg **PT1₁-b-PO₃high**.

Yield: 64%. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.42 (br. s., 4H), 7.00 (br. s., 4H), 6.51 (br. s., 2H), 5.90 (br. s., 2H), 5.34–5.53 (m, 7H), 3.95 (br. s., 4H), 2.03 (d, *J* = 11.67 Hz, 15H), 1.85 (br. s., 4H), 1.57 (d, *J* = 7.14 Hz, 6H), 1.38 (br. s., 43H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ = 148.7, 146.1, 135.9, 130.6, 130.1, 127.9, 125.1, 123.9, 110.9, 69.9, 47.7, 32.9, 30.0–29.3, 27.5, and 26.5. *M*_n(prepolymer): 47.300 Da, *M*_w(prepolymer): 89,800 Da, PDI_(prepolymer): 1.9. *M*_n(PT11-b-PO3high): 69,600 Da, *M*_w(PT11-b-PO3high): 111,200 Da, PDI_(PT11-b-PO3high): 1.6. TGA: 421 °C (5% weight loss). DSC: *T*_g: -16 °C, *C*_p = 2.8 J/g °C.

Synthesis of PT1₁-b-PO₁ (Block Copolymer in 1:1 Ratio)

The same method as described above for the block copolymer, **PT1₁-b-PO₃low**, was used, starting with (1:1 **T1** to CO monomer molar ratio) to give.

Yield: 74%. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.36 (dd, *J* = 3.16, 2.06 Hz, 4H), 6.95 (dd, *J* = 3.16, 2.20 Hz, 4H), 6.45 (s, 2H), 5.85 (s, 2H), 5.32–5.46 (m, 2H), 3.89 (t, *J* = 6.45 Hz, 4H), 1.92–2.09 (m, 4H), 1.76–1.85 (m, 4H), 1.46–1.56 (m, 4H), 1.23–1.44 (m, 22H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ = 148.6, 145.9, 135.8, 130.5, 130.1, 125.0, 123.8, 110.8, 69.8, 47.6, 32.8, 30.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 27.4, and 26.4. GPC: *M*_n(prepolymer): 11,700 Da, *M*_w(prepolymer): 24,100 Da, PDI_(prepolymer): 2.1. *M*_n(PT11-b-PO1): 13,400 Da, *M*_w(PT11-b-PO1): 24,400 Da, PDI_(PT11-b-PO1): 1.8. TGA: 420 °C (5% weight loss). DSC: *T*_g: 25 °C, *C*_p = 2.8 J/g °C.

Synthesis of PT1₁-ran-PO₃ (Random Copolymers in a 1:3 Ratio)

The same method as described above for ADMET homopolymerization was used, with a degassed solution of 621 mg 1,9-decadiene and 858 mg **T1** (1:3 **T1**: 1,9-decadiene monomer ratio) in 1,2-dichlorobenzene (3 mL, 50 wt %) with 1 mol % Grubbs' first generation catalyst (49 mg). After 3 days of reaction, polymerization was terminated by the addition of degassed ethyl vinyl ether (2 mL), and the solution was allowed to stir for 3 h. Polymer was then precipitated from cold methanol to yield 1.06 g of polymer, **PT1₁-ran-PO₃**.

Yield: 73%. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.41 (dd, *J* = 3.30, 1.90 Hz, 4H), 6.99 (dd, *J* = 3.30, 1.80 Hz, 4H), 6.50 (s, 2H), 5.89 (s, 2H), 5.35–5.50 (m, 7H), 3.94 (t, *J* = 6.31 Hz, 4H), 1.94–2.12 (m, 16H), 1.85 (m, 4H), 1.51–1.60 (m, 6H), 1.26–1.48 (m, 42H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ = 148.6, 145.9, 135.8, 130.5, 130.5, 130.0, 125.0, 123.9, 110.8, 69.8, 47.6, 32.8, 32.8, 30.0, 29.9, 29.9, 29.8, 29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.2, 27.4, and 26.4. GPC: *M*_n: 33,500 Da, *M*_w: 59,800 Da, PDI: 1.8. TGA: 409 °C (5% weight loss). DSC: *T*_g: -17 °C, *C*_p = 3.2 J/g °C.

Synthesis of PT1₁-ran-PO₁ (Random Copolymers in a 1:1 Ratio)

The same method as described above for ADMET random copolymerization of **PT1₁-ran-PO₁** was used, starting with 856 mg **T1** and 207 mg 1,9-decadiene to give 760 mg of **PT1₁-ran-PO₁**.

Yield: 81%. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.42 (dd, *J* = 3.30, 1.80 Hz, 4H), 7.00 (dd, *J* = 3.20, 1.80 Hz, 4H), 6.50 (s, 2H), 5.90 (s, 2H), 5.34–5.52 (m, 4H), 3.94 (t, *J* = 6.25 Hz, 4H), 1.95–2.13 (m, 8H), 1.79–1.91 (m, 4H), 1.51–1.62 (m, 6H), 1.23–1.49 (m, 28H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ = 148.7, 146.1, 135.9, 130.8, 130.7, 130.6, 130.2, 130.1, 128.0, 125.1, 124.0, 110.9, 69.9, 47.5, 32.9, 32.9, 30.1, 30.0, 30.0, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.3, and 26.5. GPC: *M*_n: 44,400 Da, *M*_w: 77,700 Da, PDI: 1.8. TGA: 403 °C (5% weight loss). DSC: *T*_g: 12 °C, *C*_p = 3.2 J/g °C.

RESULTS AND DISCUSSION

Synthesis of the Homopolymers

The two triptycene diols were synthesized via literature procedures^{22,23} and alkylated with standard Williamson ether synthesis conditions, using sodium hydride as the base, to yield the monomers **T1** and **T2**.^{24,25} 11-bromo-1-undecene

was chosen as the alkyl spacer and the relatively long chain insured that the steric bulk of the triptycene did not interfere at the catalyst reaction site. ADMET polymerizations of **T1** and **T2** were carried out under standard conditions for a solid monomer, which involved dynamic vacuum using high boiling solvent (1,2-dichlorobenzene) at 40 °C.^{26,27} Grubbs' first generation catalyst (**G1**) was selected because it is known to prevent terminal olefin isomerization,²⁸ and thereby assures a completely linear polymer with perfectly spaced triptycene units. Successful polymerization of these monomers to polymers **PT1** and **PT2** was confirmed via NMR (*vide infra*) and GPC, which showed polymer number average molecular weights (M_n) of 44 and 49 kDa respectively (Scheme 1).

To be assured of clean reaction, the polymerization was monitored via ¹H NMR. Monomer **T1** is characterized by three distinct aromatic protons at 6.47, 6.96, and 7.38 ppm and the bridgehead proton at 5.90 ppm. The aliphatic protons appear between 1.24 and 3.91 ppm. The two terminal olefin protons appear at 4.9 and 5.0 ppm and the internal olefin appears at 5.8 ppm. Clean polymerization of **PT1** is characterized by the complete disappearance of the terminal olefin protons at 4.9 and 5.0 ppm and emergence of a new internal olefin peak at 5.4 ppm (Supporting Information Fig. S1). Similarly, monomer **T2** shows aromatic peaks of the triptycene, however the two equivalent aromatic peaks at 7.05 and 7.56 ppm suggest the bridgehead substitution. This substitution is further characterized by the lack of the bridgehead proton. Here the protons of the aliphatic linkage appear from 1.35 to 4.57 ppm, with the internal olefin peak appearing at 5.9 ppm and the two terminal olefins appearing at 5.0 and 5.1 ppm. Polymerization is observed via the loss of the monomer olefin peaks and the appearance of one new internal olefin peak at 5.4 ppm (Fig. 2).

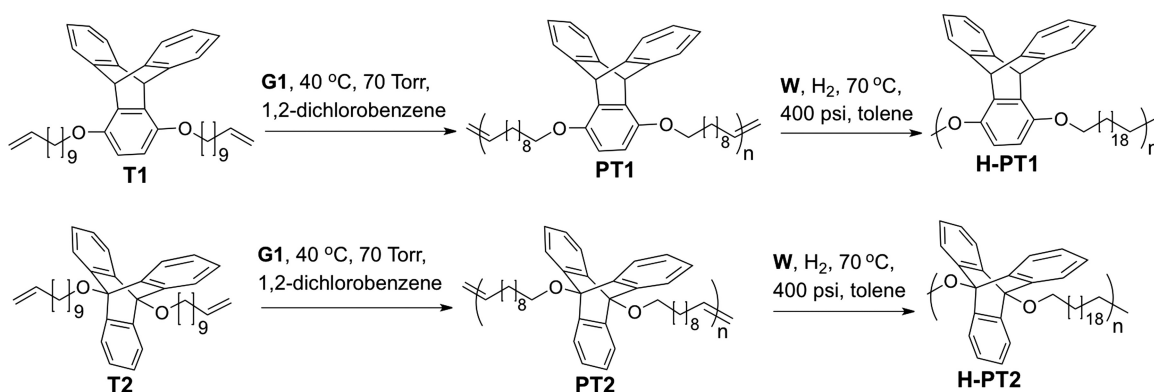
Further confirmation can be ascertained from the ¹³C-NMR. **T1** exhibited characteristic aromatic carbon signals at 148.7, 146.0, 135.9, 125.1, 123.9, and 110.9 ppm, with the bridgehead carbon appearing at 47.7 ppm. Aliphatic carbons were characterized by peaks 26.4–34.1 ppm. The complete conversion of **T1** to **PT1** was verified by the disappearance of the

terminal olefin carbons at 139.5 and 114.4 ppm and the appearance of new internal olefins at 130.7 and 130.2 ppm (Fig. 3). From the ratio of these carbons, the isomerization of the double bond can be characterized as 76% *trans* and 24% *cis* olefin, which is in similar to the preference for *trans* olefin formation observed in other ADMET polymers.²⁹

Similarly, the ¹³C-NMR shifts of **T2** were studied. Three aromatic carbons are observed at 145.0, 125.1, and 121.2 ppm and the bridgehead carbon appears at 85.2 ppm, downfield from where it appears in **T1**, due to the direct attachment of the electronegative oxygen. The aliphatic carbons appear between 26.5 and 67.5 ppm and the terminal olefin is characterized by two carbons at 139.5 and 114.4 ppm. After polymerization to **PT2**, two new internal olefins are observed at 130.6 and 129.9 ppm, corresponding to approximately 79% *trans* and 21% *cis* isomers (Supporting Information Fig. S2).

Comparatively few studies have been performed using the more active Hoveyda–Grubbs first generation (**HG1**) catalyst as an alternative to **G1** in ADMET polymerization.²⁸ To test the efficacy of the **HG1** catalyst, ADMET polymerization of **T2** was attempted under the same conditions. Polymer **PT2_{HG1}** was obtained in good yield with an M_n of 44 kDa, roughly the same as the molecular weight obtained with **G1**. Furthermore, the product showed no shift in the internal olefin signal at 5.4 ppm in the ¹H and at 130.6 ppm (*trans*) and 129.9 ppm (*cis*) in the ¹³C-NMR. Although it is not conclusive, this data suggests that no isomerization has taken place, and it is proposed that **HG1** can be used as an alternative to **G1** in the synthesis of precisely functionalized polymers. This result is in contrast to previously reported investigations.³⁰

Metathesis polymerization products (**PT1** and **PT2**) were subsequently hydrogenated with Wilkinson's catalyst (**W**) under 400 psi of hydrogen gas in a Parr Bomb to give hydrogenated polymers **H-PT1** and **H-PT2** (Scheme 1). This methodology was chosen because it is highly efficient and can be performed without the danger of elevated temperatures.³¹ The molecular weight of the polymers were preserved (Table 1) and spectroscopic characterization via ¹H and ¹³C-NMR revealed complete saturation. Specifically, in **H-PT1** the



SCHEME 1 ADMET polymerization of monomers **T1** (1,4 benzene substituted) and **T2** (bridgehead substituted) to give polymers **PT1** and **PT2**. Subsequent hydrogenation to give polymers **H-PT1** and **H-PT2** is also shown.

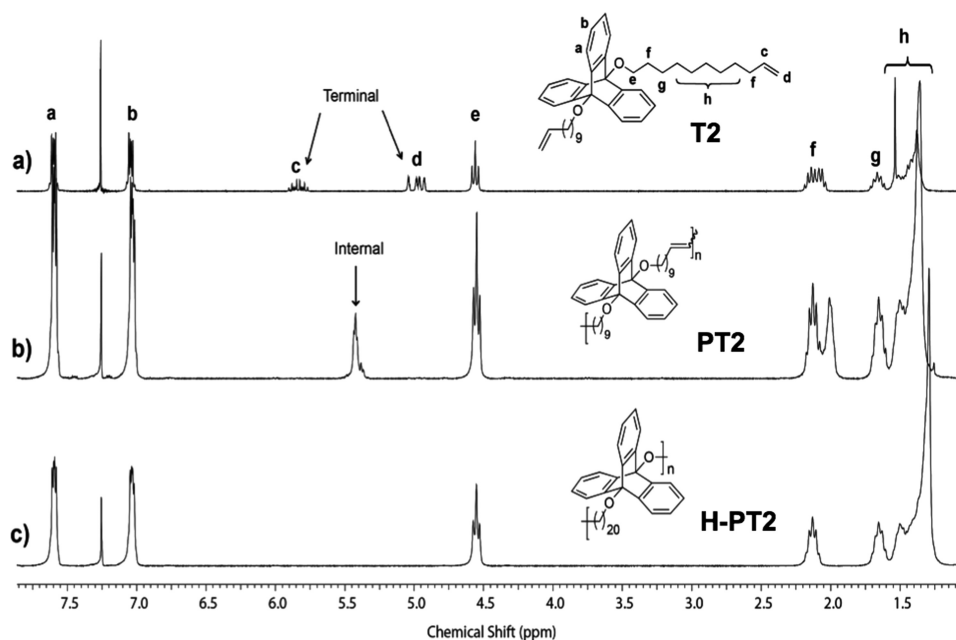


FIGURE 2 ¹H NMR of bridgehead triptycene derivatives. (a) Triptycene monomer, T₂, (b) Triptycene polyolefin, PT₂, and (c) Hydrogenated triptycene polyolefin, H-PT₂.

proton signals at 5.4 ppm, corresponding to the internal olefin, and the carbon signals at 130.7 and 130.2 ppm, corresponding to the carbons of the *trans* and *cis* double bond isomers, disappeared and were replaced with additional signals in the aliphatic regions. Similarly, in H-PT₂, the internal olefin proton signals at 5.4 ppm the *trans* and *cis* olefin carbon signals at 130.6 and 129.9 ppm disappear, suggesting complete hydrogenation (Supporting Information Fig. S2).

Synthesis of the Block Copolymers

Block copolymerization was the first strategy used to investigate the effect of lower triptycene content in the unsaturated polyethylene polymer backbone. In contrast to random and alternating copolymers, block copolymers often phase separate, which can lead to different and interesting properties. Here, the two phases of the block copolymer were chosen to be the ADMET polymer synthesized from the 1,4 benzene

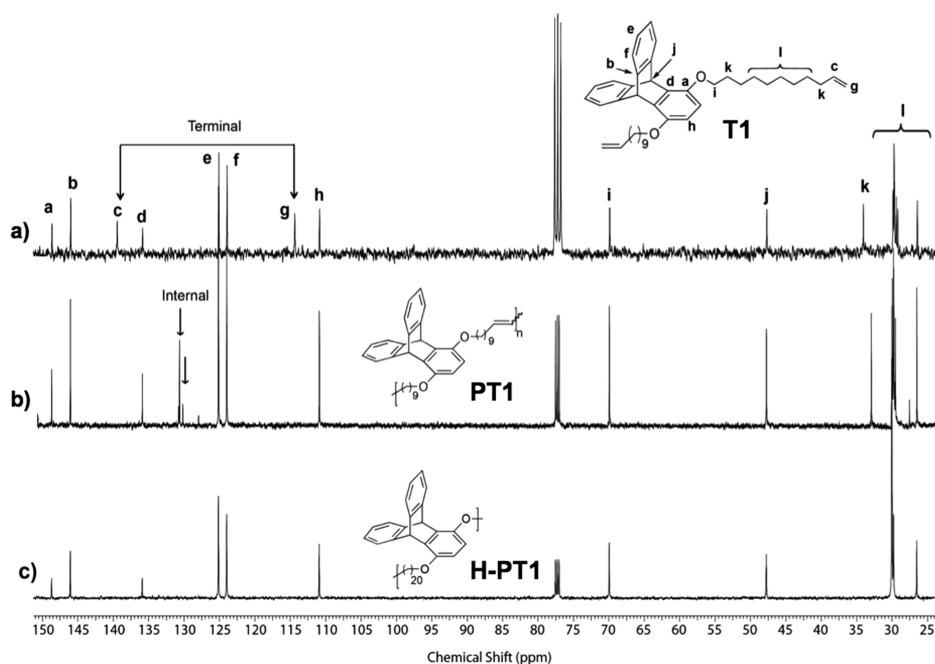


FIGURE 3 ¹³C NMR of bridgehead triptycene derivatives. (a) Triptycene monomer, T₁, (b) Triptycene polyolefin, PT₁, and (c) hydrogenated triptycene polyolefin, H-PT₁.

TABLE 1 Summary of Polymer Molecular Weights and Thermal Properties

Polymer	PO Amount ^a	M_n^b (kDa)	PDI	T_d^c (°C)	Char Weight (%)	T_g DSC (°C)	T_g DMA (°C)	Mole % T1/T2 (%)	Weight % Triptycene (%)
Polyoctenamer	1	–	–	345	0	–40 ^d	–44	0	0
PT1	0	44	1.8	420	2	22	–	100	45
H-PT1	0	46	2.1	450	12	43	45	100	45
PT2	0	49	1.8	230	2	37	–	100	45
H-PT2	0	42	2.1	390	77	50	59	100	45
PT1_{1-b-PO₃low}	2.4	28	1.8	295	0	–15	–23	29	30
PT1_{1-b-PO₃med}	2.3	41	1.8	420	1	–24	–24	30	31
PT1_{1-b-PO₃high}	2.4	70	1.6	421	1	–16	–24	29	31
PT1_{1-b-PO₁}	0.08	13	1.8	390	0	25	27	93	44
PT1_{1-ran-PO₃}	2.6	34	1.8	350	2	–17	–23	28	30
PT1_{1-ran-PO₁}	0.81	44	1.8	380	2	12	0	55	39

^a Molar ratio of PO in the polymer with reference to 1 mole **T1**/ **T2**.

^b Polymers **PT1_{1-b-PO₃low}**, **PT1_{1-b-PO₃med}**, **PT1_{1-b-PO₃high}**, and **PT1_{1-b-PO₃high}** have PT blocks of $M_n = 13, 28, 47,$ and 12 kDa, respectively. This is detailed in Supporting Information Table S1.

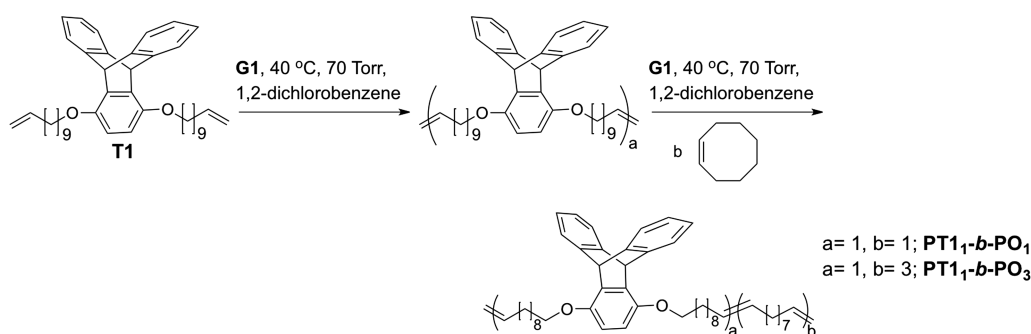
^c Given as the 95% weight loss temperature.

^d Literature value.³¹

substituted monomer, **T1**, and the ROMP product of *cis*-CO. ROMP was chosen for the addition of the second block because of the high reactivity of CO and the high molecular weight of the resulting polymers.³² Block copolymers were synthesized in the ratio of 1:1 and 1:3 parts **T1** to **CO**. The molecular weight was also systematically varied for the 1:3 copolymer to observe the effect of M_n on thermal and mechanical properties. Although mostly blocky in nature, these polymers may be scrambled due to secondary methathesis reactions within the first ADMET blocks. It is assumed that ROMP is preferred because it is faster, however, cross-methathesis between the ADMET block and CO block is possible. This side reaction does not change the composition of the copolymer, but would make the copolymer somewhat less defined.

To synthesize the 1:3 block copolymer, **T1** was subjected to the ADMET polymerization conditions used to synthesize **PT1**. After 72 h, a portion of the reaction was quenched and the ADMET polymerization was verified to be successful with the observation of molecular weights (M_n) from 12 to 47 kDa and PDIs of 1.9–2.6 via GPC (Supporting Information

Table S1). As illustrated in Scheme 2, subsequent addition of CO and additional G1 to the system initiated ROMP and after 6 h, the reaction was terminated. In this manner, the block copolymers containing one part **T1** to three parts CO (poly-triptycene 1-*block*-polyoctenamer₃, **PT1_{1-b-PO₃}**) were synthesized with molecular weights of 29 kDa (**PT1_{1-b-PO₃low}**), 41 kDa (**PT1_{1-b-PO₃med}**), and 70 kDa (**PT1_{1-b-PO₃high}**). The PDIs also drop to 1.6–1.8, which is expected for the ROMP polymerization, which usually gives PDIs of 1.2 for the homopolymer.³³ The ratio **T1** to CO was verified via ¹H-NMR (Supporting Information Fig. S3). To calculate the monomer ratios, the integration of the methylene group at 3.9 ppm, adjacent to the **T1** ether, is compared with the integration of the olefin protons at 5.4 ppm. In **PT1**, this ratio is 4:2, and in **PT1_{1-b-PO₃low}**, the ratio is 4:6.4, which corresponds to an experimental ratio of one **T1** to 2.4 CO monomers. Similarly, the ratios of **PT1_{1-b-PO₃med}** and **PT1_{1-b-PO₃high}** are calculated to be 2.3 and 2.4 CO to 1 **T1**, respectively. Controlling the monomer ratios to give a block copolymer with one part **T1** to one part CO proved to be difficult due to the rapid polymerization of the CO via


SCHEME 2 Block copolymerization of **PT1_{1-b-PO₁}** and **PT1_{1-b-PO₃}**. Three molecular weights of **PT1_{1-b-PO₃}** were synthesized.

ROMP. The block copolymer synthesized using 1:1 monomer ratios, **PT1₁-b-PO₁**, resulted in a polymer with only 0.08 parts CO to 1 part **T1**, as determined by the ratio of the protons at 3.9 and 5.4 ppm. The molecular weight of 13.4 kDa, is still well above the entanglement molecular weight,³⁴ so accurate comparisons can be made. In the case of all the block copolymers, successful attachment of the CO block was confirmed by the monomodal growth of the molecular weight in the GPC curve (Supporting Information Fig. S4).

Synthesis of the Random Copolymers

Random copolymerization was considered as a second strategy to decrease the overall triptycene content in the olefin backbone. Previous work demonstrated that the ADMET random copolymerization of 1,9-decadiene with branched alkenes, such as 1-propene, decreased the concentration of branched alkyl units in the polymer backbone.³⁵ As the dodecyl chain connecting the triptycene to the reactive olefin is relatively long, it is expected that the reactivity ratios of **T1** and 1,9-decadiene will be similar, giving a thorough distribution of triptycene chains along the alkyl backbone. The triptycene monomer, **T1**, was subjected to random copolymerization with 1,9-decadiene in monomer ratios of 1:1 and 1:3 using standard ADMET conditions, as described above.

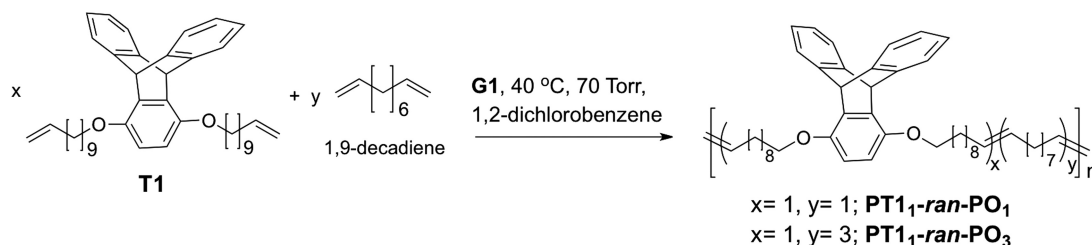
Two random copolymers were synthesized. **PT1₁-ran-PO₁**, was synthesized using a one to one monomer feed ratio of **T1** and 1,9-decadiene and **PT1₁-ran-PO₃**, was synthesized using a one to three monomer feed ratio of **T1** and 1,9-decadiene (Scheme 3). These polymers were characterized by GPC to reveal high molecular weights of 45 and 34 kDa, respectively. Further characterization via ¹H-NMR suggests the purity and the establishment of the desired connections with minimal structural isomerization, through the visibility of all of the peaks found in **PT1** (Supporting Information Fig. S3). The ratio of the 1,9-decadiene to **T1** incorporated into the polymer backbone was calculated in the same manner as for the block copolymers, comparing the ratio of the proton peaks at 3.9 and 5.4 ppm. **PT1₁-ran-PO₁** was found to contain 1 part **T1** to 0.8 parts 1,9-decadiene and **PT1₁-ran-PO₃** was found to contain 1 part **T1** to 2.6 parts 1,9-decadiene. The monomer feed ratios are close to the final composition in the polymer and therefore it can be ascertained that the reactivity of the two monomers is similar. Furthermore, random copolymerization can be established as a reliable method to control polymer composition in this system.

Thermal Properties

Thermal properties of the polymers were investigated by TGA and DSC. Polymer decomposition temperatures (T_d), reported as the 5% weight loss temperature under nitrogen, varied from 230 °C in **PT2** to 450 °C in **H-PT2**. It is possible that despite the vacuum drying, a small amount of solvent remains trapped within **PT2**, which would account for the lower temperature weight loss around the boiling point of 1,2-dichlorobenzene. The other polymers displayed intermediate values. The lower stability of the bridgehead polymer can be understood as the stability of the decomposition products. Char weights are negligible for PO, the copolymers, and **PT1** and **PT2**. This could possibly be explained by the release of ethene in the decomposition process. Char weights were 12 and 77 wt % for **H-PT1** and **H-PT2**, respectively. Considering the high aromatic content of the triptycene moieties in these polymers, graphitization likely takes place at high temperatures, which is suggested by the high char weights (Fig. 4).

Among the copolymers, the block copolymers exhibited higher thermal stability on average than the random copolymers. The decomposition temperatures of the random copolymers, **PT1₁-ran-PO₁** and **PT1₁-ran-PO₃**, were 380 and 350 °C, respectively. This is in accordance with previous research, which has found that triptycene can increase the thermal stability of polymers.^{18–20} Interestingly, the block copolymers do not show increasing thermal stability with higher triptycene content. Presumably, this is because the molecular weight of **PT1₁-b-PO₁** is lower than the weights of the **PT1₁-b-PO₃** copolymers. Overall, the T_d did not dramatically increase with the incorporation of triptycene, which is different than what has been found previously.

DSC revealed glass transitions temperatures (T_g s) from –40 °C for the PO homopolymer to 50 °C for the hydrogenated polytritycene (**H-PT2**). Polymers **PT1** and **PT2** show the highest T_g s of the polyolefins at 22 and 37 °C, respectively. The higher T_g exhibited by **PT2** suggests that the bridgehead connection to the polymer backbone blocks interchain mobility more efficiently than the incorporation with triptycene introduced via the 1,4-benzene connection. Hydrogenation brings the T_g s up to 43 °C for **H-PT1** and 50 °C **H-PT2**. Additionally, a melting transition (T_m) can be observed for **H-PT2** at 122 °C. However, no melting transition is observed in **H-PT1**. It can be ascertained that the three benzene moieties surrounding the bridgehead connection are not as effective as the 1,4 connection at blocking crystallization of



SCHEME 3 Synthesis of the random copolymers, **PT1₁-ran-PO₁** and **PT1₁-ran-PO₃**.

the polyethylene chains. This difference may be related to the more efficient threading of the chains in the 1,4 system which is driven by the desire to minimize the intermolecular free volume (IMFV) around the triptycene.¹⁵

The random copolymers exhibit T_g s between the two homopolymers, which is expected. **PT1₁-ran-PO₁** with the greater amount of **T1**, exhibits a T_g of 12 °C and **PT1₁-ran-PO₃** exhibits a T_g of -17 °C, closer to the T_g of the pure PO (Fig. 5). Interestingly, the block copolymers also exhibit T_g s at intermediate values between the PO and **PT1**. This is interesting because block copolymers typically display two distinct T_g s when phase separated, one arising from each block, with the T_g s equivalent to the two homopolymer T_g s.³⁶ From this data, we can ascertain that the blocks of the polymer are not phase separated, as in traditional block copolymers. **PT1₁-b-PO₁**, which is in actuality comprised of only 7 mol % PO, exhibits a drop in T_g to 25 °C. It is not surprising that two phases are not observed in these polymers; with the small percentage of CO incorporated, the polymer is more accurately described as end-capped by the short PO segments. This large change in T_g despite the small change in polymer structure is a result of the disproportionate influence of polymer chain ends on the mobility of the polymer.

For the three different molecular weights of **PT1₁-b-PO₃**, the influence on T_g is even greater. By DSC, the T_g drops to -15 °C for **PT1₁-b-PO₃low**, -24 °C for **PT1₁-b-PO₃med**, and -16 °C for **PT1₁-b-PO₃high**. Even for **PT1₁-b-PO₃high**, with both polymer blocks individually well above their entanglement molecular weight, no second transition temperature can be observed. This is understood to arise from the spacing of the triptycenes by alkyl chains on the monomer **T1** far enough apart such that they do not overlap or aggregate to form a hard block. Instead, the alkyl chains of other polymers fill space around the triptycene to minimize the IMFV and provide an interlocking material that is homogeneous. The non-systematic variations in the T_g exhibited by the 1:3 block copolymers were further investigated using DMA.

DMA

DMA was used to further probe the thermal properties and to study the effect of triptycene incorporation on the mechanical properties of the polymers. For this test, the temperature was varied from -80 °C or appropriately lower for the lower T_g polymers, to the temperature at which the polymer starts to flow and mechanical integrity is lost. With T_g s above room temperature, the homopolymers were the first to be tested, and the results show good agreement with the transitions observed in the DSC traces. PO shows a peak in the loss modulus (G'') at -44 °C, indicating the glass transition temperature. After this transition, the storage and loss modulus fall off slowly, leading PO to exhibit some elastic properties at room temperature. In contrast, **H-PT1** shows a glass transition temperature above room temperature. The peak in G'' occurring at 45 °C is sharp and elastic properties are lost immediately after the transition. Below the T_g , a distinct storage modulus (G') plateau at 950 MPa is observed. Polymer **H-PT2** is characterized by the highest T_g of the

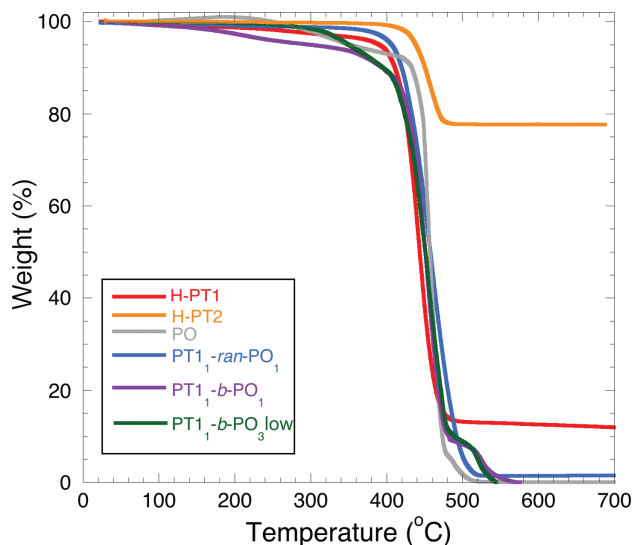


FIGURE 4 Thermogravimetric traces of the unsaturated homopolymers and representative copolymers. The remainder of the polymers' TGA traces can be found in Supporting Information Figure S5.

studied polymers, which appears as a peak in G'' at 59 °C. Like PO, the peaks trails off slowly, and some elastic behavior is observed even at 100 °C. Presumably, the properties will fall off sharply at the T_m of 122 °C, observed in the DSC traces (Fig. 6).

Interestingly, the two types of block copolymer show different behaviors. **PT1₁-b-PO₁** shows a sharp peak in G'' at 27 °C, suggesting a T_g that is in accordance with that found by DSC (25 °C). G' exhibits a plateau at around 1300 MPa and G'' peaks sharply and falls off rapidly at the T_g , which is very similar to the behavior observed for **H-PT1**. This is not surprising, as **PT1₁-b-PO₁** contains a very low weight % of PO. Interestingly though, a small peak in the loss modulus

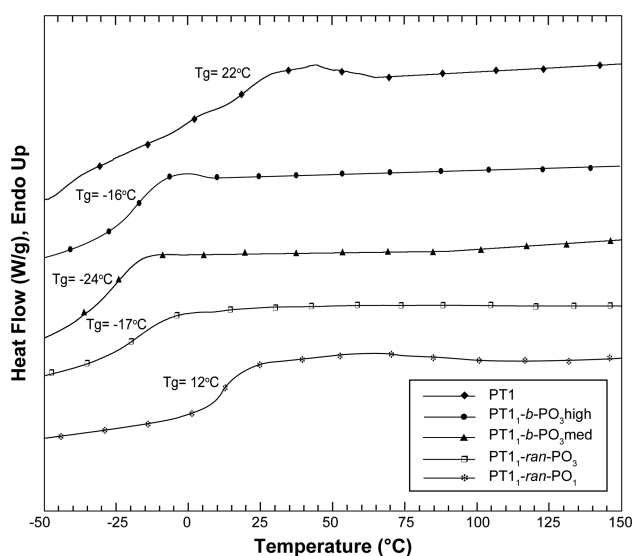


FIGURE 5 DSC results for representative polymers **PT1**, **PT1₁-b-PO₃high**, **PT1₁-b-PO₃med**, **PT1₁-ran-PO₃**, and **PT1₁-ran-PO₁**.

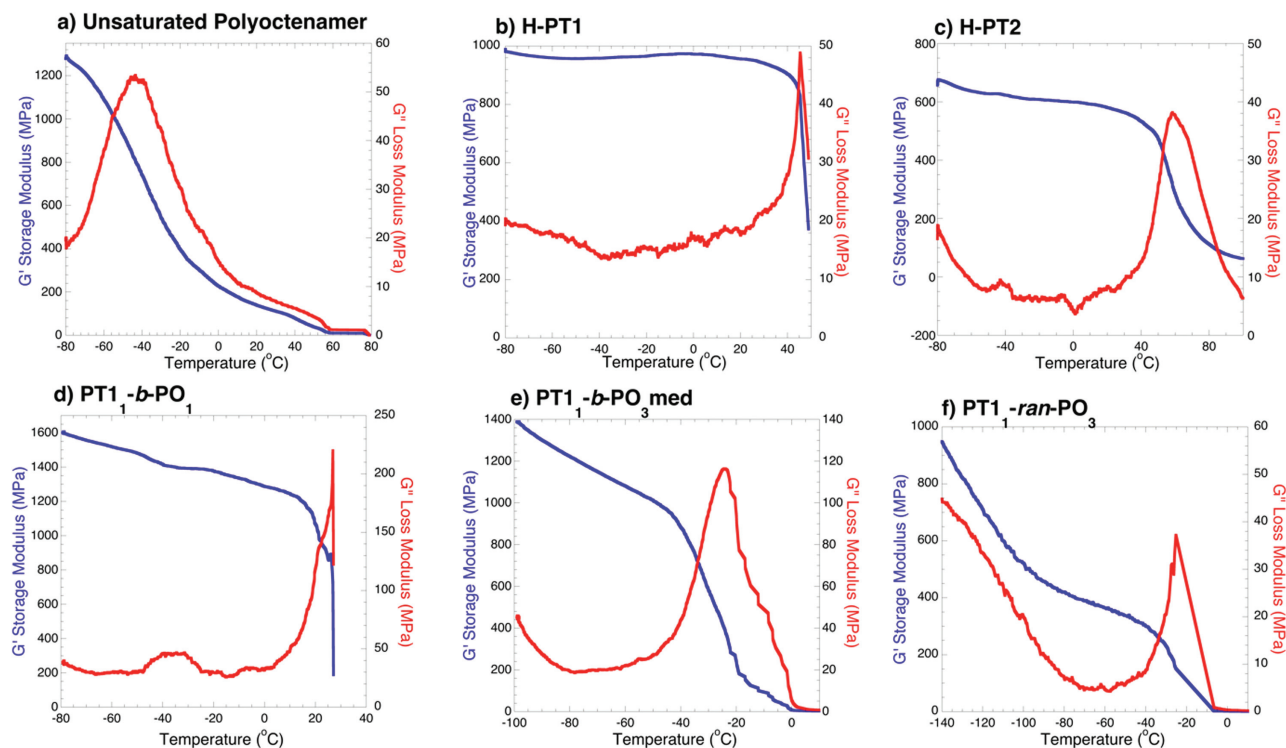


FIGURE 6 DMA curves for (a) unsaturated PO, (b) H-PT1, (c) H-PT2, (d) PT1₁-b-PO₁, (e) PT1₁-b-PO₃med, and (f) PT1₁-ran-PO₃. DMA curves for PT1₁-b-PO₃low, PT1₁-b-PO₃high, and PT1₁-ran-PO₁ can be found in Supporting Information Figure S6. Scans were taken over a temperature range between -140 and 90 °C, as appropriate for the thermal properties of the polymer.

appears at -40 °C, which could be attributed to a small degree of phase separation by the PO chain ends. The variability in the DSC T_g observed in the 1:3 block copolymers is not observed in the DMA results. The three molecular weights of PT1₁-b-PO₃ show a peak in G'' at -23 °C for PT1₁-b-PO₃low and -24 °C for both PT1₁-b-PO₃med and PT1₁-b-PO₃high. The lack of variability in T_g strongly suggests that even at 29 kDa, the polymer is well above its entanglement molecular weight. In these copolymers, the storage modulus plateau increases with increasing molecular weight, which is expected. No peak in G'' is observed around -40 °C, offering further evidence that these block copolymers do not phase separate.

The random copolymers exhibit a different type of temperature-dependent mechanical behavior. The magnitude of the loss modulus is high at low temperatures, which suggests a good degree of mobility in the polymer chains. A shorter plateau region is also observed in the storage modulus. For PT1₁-ran-PO₁, the plateau modulus appears over the temperature range of -100 to -20 °C at a magnitude of only 450 MPa. The T_g is observed at 0 °C, which is slightly lower than what is observed in the DSC experiments (12 °C). PT1₁-ran-PO₃ exhibits almost no plateau modulus in G' and a peak in G'' at -23 °C. Interestingly, this is the same temperature T_g that is observed for the 1:3 block copolymers, further confirming the lack of phase separation in the block copolymers.

Room Temperature Tensile Properties

To compare the most tangible viscoelastic properties of the polymers, the room temperature tensile properties were studied. Samples were prepared in the same manner as for the

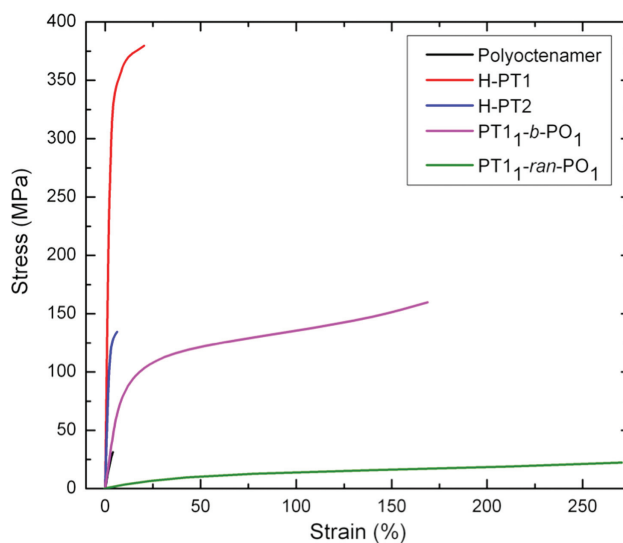


FIGURE 7 Room temperature (23 °C) stress/strain curves for the homopolymers and 1:1 copolymers. Given their low glass transition temperatures, PT1₁-ran-PO₃ and each of the molecular weights of the PT1₁-b-PO₃ showed minimal mechanical integrity at room temperature.

DMA tests and loaded into the DMA for a constant strain test to failure at 23 °C. PO, which is above its T_g at room temperature, displays an ultimate tensile stress (UTS) of 31 MPa at an elongation of 4%. Homopolymers **H-PT1** and **H-PT2** were the stiffest of the polymers tested, with the most remarkable properties being displayed by **H-PT1**. This polymer showed increased strength, with a UTS of 380 MPa at a deformation of 20% strain. Among the block copolymers, **PT1₁-b-PO₁** showed the greatest mechanical integrity, which is expected, given its glass transition around room temperature. The addition of the short PO segments significantly toughens the material in comparison to the **H-PT1** homopolymer. The UTS is reduced to 160 MPa from that found in **H-PT1**, however, the strain at failure is now 170% (Fig. 7). The three molecular weights of **PT1₁-b-PO₃** show minimal mechanical integrity at room temperature, due to their low T_g s. Of the random copolymers, **PT1₁-ran-PO₁** is quite ductile, with the strain at failure being 270%. The significantly lower UTS of 22 MPa is likely due to increased PO content in comparison to the block copolymer, **PT1₁-b-PO₁**. Like the 1:3 block copolymers, **PT1₁-ran-PO₃** displays minimal mechanical integrity at room temperature.

CONCLUSIONS

Three different types of triptycene containing polymers were synthesized using ADMET polymerization to yield polymers of high molecular weight (13–70 kDa). Two homopolymers were synthesized with differing connectivities of the triptycene to the backbone. **PT1** was synthesized from 1,4-bis(undec-10-en-1-yloxy)-triptycene, which is connected to the polymer backbone through the 1,4-positions on a phenyl group. **PT2** was synthesized from 9,10-bis(undec-10-en-1-yloxy)-triptycene, which was connected to the polymer backbone through the triptycene bridgehead positions. Both of these polymers were efficiently hydrogenated to give polymers **H-PT1** and **H-PT2**. The 1,4-benzene connected triptycene monomer, **T1**, was used to make both block and random copolymers. Block copolymers were synthesized with a triptycene block by ADMET and the second block of *cis*-CO was added using ROMP conditions. The 1:1 block copolymer, **PT1₁-b-PO₁**, only contained 7 mol % PO and three molecular weights (28, 41, and 70 kDa) of the 1:3 block copolymer, **PT1₁-b-PO₃**, were synthesized. Random copolymers were synthesized from **T1** and 1,9-decadiene in monomer ratios of 1:1 for **PT1₁-ran-PO₁** and 1:3 for **PT1₁-ran-PO₃**. The thermal and mechanical properties of these polymers were compared and it was found that the incorporation of triptycene increases the glass transition temperature and thermal stability of the polymers. Tensile tests let us conclude that controlling triptycene content in the polymer backbone improves the strength, toughness, and ductility of polymers.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

- 1 A. W. Anderson, N. G. Merklings, (DuPont Co.) U.S. Patent, 2,721,189, October 18, 1955.
- 2 R. L. Banks, G. C. Bailey, *Ind. Eng. Chem. Prod. Res. Dev.* **1964**, *3*, 170–173.
- 3 W. L. Truett, D. R. Johnson, I. M. Robinson, B. A. Montague, *J. Am. Chem. Soc.* **1960**, *82*, 2337–2340.
- 4 J.-L. Hérisson, Y. Chauvin, *Makromol. Chem.* **1971**, *141*, 161–176.
- 5 R. R. Schrock, A. H. Hoveyda, *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 4592–4633.
- 6 S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975.
- 7 K. B. Wagener, J. M. Boncella, J. G. Nel, *Macromolecules* **1991**, *24*, 2649–2657.
- 8 J. E. O'Gara, K. B. Wagener, S. F. Hahn, *Makromol. Chem. Rapid Commun.* **1993**, *14*, 657–662.
- 9 (a) K. R. Brzezinska, T. J. Deming, *Macromolecules* **2001**, *34*, 4348–4354; (b) T. W. Baughman, K. B. Wagener, *Adv. Poly. Sci.* **2005**, *176*, 1–42; (c) M. M. Abdellatif, K. Nomura, *ACS Macro. Lett.* **2012**, *1*, 423–427.
- 10 (a) T. E. Hopkins, J. H. Pawlow, D. L. Koren, R. H. Deters, S. M. Solivan, J. A. Davis, F. J. Gomez, K. B. Wagener, *Macromolecules* **2001**, *34*, 7920–7922; (b) V. P. Bui, T. Hudlicky, *Tetrahedron* **2004**, *60*, 641–646.
- 11 (a) A. C. Church, J. H. Parlow, K. B. Wagener, *Macromolecules* **2002**, *35*, 5746–5751; (b) B. Marciniak, M. Majchrzak, *J. Organomet. Chem.* **2003**, *686*, 228–234.
- 12 (a) M. A. Hillmyer, Y. Qin, *Macromolecules* **2009**, *42*, 6429–6432; (b) P. A. Delgado, D. Y. Liu, Z. Kean, K. B. Wagener, *Macromolecules* **2011**, *44*, 9529–9532.
- 13 K. Brzezinska, K. B. Wagener, *Macromolecules* **1991**, *24*, 5273–5277.
- 14 G. L. Backer, Y. Chen, J. Qiao, *Chem. Mater.* **1999**, *11*, 2542–2547.
- 15 T. M. Swager, *Acc. Chem. Res.* **2008**, *41*, 1181–1189.
- 16 V. E. Williams, T. M. Swager, *Macromolecules* **2000**, *33*, 4069–4073.
- 17 J. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873.
- 18 T. M. Long, T. M. Swager, *J. Am. Chem. Soc.* **2003**, *125*, 14113–14119.
- 19 N. T. Tsui, A. J. Paraskos, L. Torun, T. M. Swager, E. L. Thomas, *Macromolecules* **2006**, *39*, 3350–3358.
- 20 N. T. Tsui, Y. Yang, A. D. Mulliken, L. Torun, M. C. Boyce, T. M. Swager, E. L. Thomas, *Polymer* **2008**, *21*, 4703–4712.
- 21 Y. Liu, S. R. Turner, G. Wilkes, *Macromolecules* **2011**, *44*, 4049–4056.
- 22 P. D. Bartlett, M. J. Ryan, S. G. Cohen, *J. Am. Chem. Soc.* **1942**, *64*, 2649–2653.
- 23 M. S. Taylor, T. M. Swager, *Org. Lett.* **2007**, *9*, 3695–3697.
- 24 B. VanVeller, D. Robinson, T. M. Swager, *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 1182–1186.
- 25 B. VanVeller, D. J. Schipper, T. M. Swager, *J. Am. Chem. Soc.* **2012**, *134*, 7282–7285.
- 26 T. Vorfalt, K. J. Wannowius, H. Plenio, *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 5533–5536.
- 27 J. Mei, B. S. Aitken, K. R. Graham, K. B. Wagener, J. R. Reynolds, *Macromolecules* **2010**, *43*, 5909–5913.

- 28** S. E. Lehman, J. E. Schwendeman, P. M. O'Donnell, K. B. Wagener, *Inorg. Chim. Act.* **2003**, *345*, 190–198.
- 29** K. L. Opper, K. B. Wagener, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 821–831.
- 30** H. Mutlu, L. Montero, O. Turunc, M. A. R. Meier, *Beilstein J. Org. Chem.* **2010**, *6*, 1149–1158.
- 31** J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* **1966**, *12*, 1711–1732.
- 32** F. Jing, M. Hillmyer, *J. Am. Chem. Soc.* **2008**, *130*, 13826–13827.
- 33** C. W. Bielawski, R. H. Gubbs, *Prog. Polym. Sci.* **2007**, *32*, 1–29.
- 34** 1 kDa for polyethylene. P. M. Wood-Adams, J. M. Dealy, A. W. deGroot, O. D. Redwine, *Macromolecules* **2000**, *33*, 7489–7499.
- 35** G. Rojas, E. B. Berda, K. B. Wagener, *Polymer*, **2008**, *49*, 2985–2995.
- 36** R. M. Ikeda, M. L. Wallach, R. J. Angelo, In *Block Copolymers*; S. L. Aggarwall, Ed.; Plenum Press: New York, N. Y., **1970**.