

## Cross Metathesis Functionalization of Polyolefins

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### SUPPORTING INFORMATION

#### Characterization

All air and moisture sensitive chemistry was carried out in a Braun Labmaster drybox or using standard Schlenk line techniques.  $^1\text{H}$  NMR spectra of polymers were recorded on a Varian Inova 500 MHz spectrometer and referenced to non-deuterated solvent shifts. Polymers that were insoluble at room temperature were recorded on a Varian Inova 500 MHz spectrometer at 130° C in 1,1,2,2-tetrachloroethane- $d_2$ . The molecular weights ( $M_n$  and  $M_w$ ) and polydispersity indexes ( $M_w/M_n$ ) were measured by a Waters Alliance GPCV 2000 size exclusion chromatograph (SEC). The SEC columns set (4 Waters HT 6E and 1 Waters HT 2) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt % di-*tert*-butylhydroxytoluene (BHT) at 1.0 mL/min at 140° C. The molecular weights and polydispersity indexes were measured relative to a polystyrene calibration curve. DSC analyses were performed on a TA Instruments Q1000 instrument equipped with a liquid nitrogen cooling source and an automated sampler. Typical DSC experiments were made in crimped aluminum pans under nitrogen with a heating rate of 10° C/min from -50 to +200° C. The reported DSC data from the second heating run was processed with the TA Q Series software.

#### Materials

The solvents were dried on solvent columns containing molecular sieves, alumina and activated copper. Propylene (Matheson, Polymer Grade) was purified by a column of molecular sieves and alumina. Methylaluminoxane (PMAO-IP, 12.9 wt. % Al in toluene, Akzo Nobel) was dried under vacuum at 60° C for 24 h. 1,5-Hexadiene (Aldrich) was stirred over  $\text{CaH}_2$  for 2 days, degassed with periodic freeze-pump-thaw cycles and distilled onto molecular sieves. Polymers were made as reported in Hustad, P. D.; Coates, G. W., *J. Am. Chem. Soc.*, **2002**, *124*, 11578. Monomers for cross metathesis reactions were commercially available and were used as received.

### **Cross metathesis of poly(ethylene-*co*-propylene)-*block*-poly(MCP-*co*-VTM) with 2,2,3,3,4,4,4-heptafluorobutyl acrylate**

The polymer (50 mg, 0.12 mmol VTM) was dissolved in chlorobenzene (2 mL), 1,1,2-trichloro-1,2,2-trifluoroethane (5 mL) and 2,2,3,3,4,4,4-heptafluorobutyl acrylate (10 equiv, 1.2 mmol, 0.22 mL) in a 50 mL round bottom flask equipped with a Straus adapter and a condenser. The solution was degassed with several freeze-pump-thaw cycles and put in a sand bath at 55°C. The catalyst solution (0.0024 mmol, 2.0 mg of **2** in 0.5 mL chlorobenzene) was added by syringe. A slight dynamic vacuum was applied. After 4 hours, the flask was allowed to cool to room temperature and the polymer was precipitated into methanol. The polymer was filtered, washed with excess methanol and dried under vacuum.

### **Cross metathesis of poly(*syndio*-propylene)-*block*-poly(propylene-*co*-MCP-*co*-VTM) with 4-pentene-1-ol**

The polymer (100 mg, 0.02 mmol VTM) was dissolved with 2 mL chlorobenzene, 2 mL of methylene chloride and 5-hydroxy-1-pentene (10 equivalents, 0.2 mmol, 0.024 mL) in a 50 mL round bottom flask equipped with a Straus adapter and a condenser. The solution was degassed with several freeze-pump-thaw cycles and put in a sand bath at 55°C. The catalyst was added by syringe (0.02 equivalents, 0.0004 mmol, 0.34 mg of **2** in 1 mL of chlorobenzene). The reaction was stirred under a slight dynamic vacuum. After 1 hour, the polymer was precipitated into methanol, filtered and dried under vacuum.

### **Cross metathesis of poly(MCP-*co*-VTM) with ethyl acrylate**

The polymer (50 mg, 0.2 mmol VTM) was dissolved with 2 mL chlorobenzene and 5 mL of methylene chloride in a 50 mL round bottom flask with a Straus adapter. Ethyl acrylate (10 equivalents, 2.0 mmol, 0.22 mL) and a solution of **2** (0.02 equivalents, 0.004 mmol, 3.4 mg in 0.5 mL of chlorobenzene) were added. The reaction was stirred for 7 hours at 55°C under a slight dynamic vacuum. The flask was cooled to room temperature and the polymer was precipitated into methanol. The polymer was filtered, washed with excess methanol and dried under vacuum.