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Synthesis and Tunable Properties of Chemically Recyclable Multiblock Copolymers via Tandem Olefin Metathesis Polymerizations

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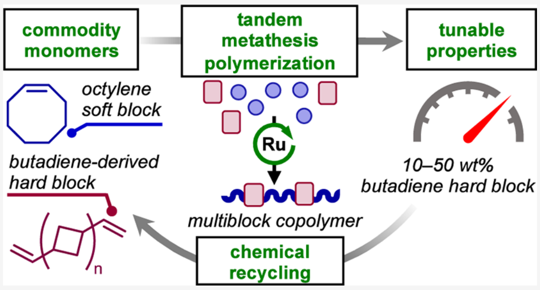
ABSTRACT: Chemical recycling, in which materials are depolymerized to monomer, enables access to repeated, closed-loop recycling. However, current routes to chemically recyclable polymers typically rely on synthesizing monomers with cleavable heteroatomic linkages or tailored ring strains. In this work, we report the synthesis of all-hydrocarbon chemically recyclable multiblock copolymers containing (1,n'-divinyl)-oligocyclobutane (DVOCB-(n)). DVOCB(n) is synthesized from the Fe-catalyzed reversible [2+2]-cycloaddition of butadiene, a commodity monomer, and is semicrystalline. Using commercially available all-hydrocarbon monomers, we developed a tandem ring-opening metathesis polymerization-acyclic diene metathesis approach which enabled the synthesis of materials with octylene soft segments and systematic variations in DVOCB(n) hard-segment length and content (10−50 wt % DVOCB(n)). We characterized the thermo-mechanical properties of the resulting multiblock copolymers using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and wide-angle X-ray scattering. By tuning the DVOCB segment length and content, DSC and DMA analysis revealed a broad spectrum of tunable melting temperatures (45−120 °C) and rubbery plateau moduli. Finally, ethenolysis of these copolymers was demonstrated and pristine DVOCB(n) recovered, thus offering potential end-of-life circularity for these materials.



■ INTRODUCTION

Commodity polymers (e.g., polyethylene, polypropylene, and poly(ethylene terephthalate)) are ubiquitous today.[1,2] Owing to their outstanding durability, processability, and low cost, these materials have found widespread utility in applications ranging from medical devices to food packaging. However, the recycling of commodity polymers remains a challenge. For mechanical recycling, waste streams must be physically sorted because the mixing of incompatible polymers results in phase separation, and a reduction in material properties.[3−5] Furthermore, mechanical recycling processes often cause chain scission that further reduces the material's strength, particularly after multiple rounds of mechanical recycling. Thus, there is a critical need to develop sustainable, end-of-life alternatives for plastics.[6,7]

Chemical recycling is an attractive supplement to mechanical recycling, in which polymers are depolymerized to their constituent monomers, enabling access to repeatedly recyclable materials.[8−11] Currently, most chemically recyclable polymers are based on materials that contain cleavable heteroatomic linkages,[12−16] or are comprised of monomers with tailored ring strains that enable depolymerization.[17−20] However, using specialized monomers is not cost- and scale-competitive with current feedstocks used to produce commodity polymers. Recent advances toward this challenge have demonstrated the catalytic dehydrogenation of postconsumer polyethylene (followed by ethenolysis),[21] and deconstruction of polyolefins to various small molecules.[22−27] However, true chemical recycling of all-hydrocarbon polymers back to pristine monomer remains a substantial challenge.[28]

Previously, Chirik and co-workers reported the iron-catalyzed [2+2] cycloaddition−oligomerization of 1,3-butadiene—a commodity monomer—to yield (1,n'-divinyl)-oligocyclobutane (DVOCB(n)), where n corresponds to the average number of cyclobutyl rings in the oligomer (Figure 1A). As an oligomer, DVOCB is semicrystalline as measured by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS).[29] Furthermore, the melting temperature (T_m) of the oligomer is directly controlled by the oligomer length, which enables access to materials with a wide

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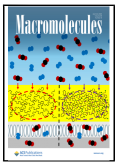

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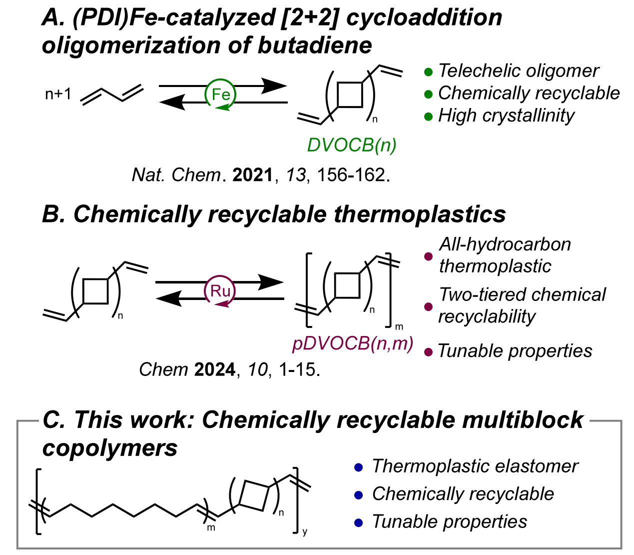

Figure 1. Previous and current work in chemically recyclable butadiene-derived materials.

range of tunable thermal properties. Specifically, the T_m of DVOCB increases from 60 to 150 °C as n increases from 4 to 10. Notably, in the presence of iron or nickel catalysts, DVOCB undergoes retro-[2+2] cycloaddition to regenerate butadiene[29,30] or vinylcyclohexene,[31] respectively, offering a rare example of chemical recycling for an all-hydrocarbon material.

Recent work has reported the chain extension of DVOCB-(n) via acyclic diene metathesis (ADMET) polymerization to yield poly(DVOCB(n)), pDVOCB.[30] A thermoplastic, pDVOCB possesses high thermal stability ($T_{d5\%}$ = 365 °C for 5% weight loss), and a high melting temperature (T_m > 240 °C) (Figure 1B).[30] Furthermore, the thermal properties of pDVOCB are influenced by the length of the constituent DVOCB oligomer, allowing for tunable material properties without increasing synthetic complexity. pDVOCB exhibits two tiers of chemical recycling: (1) reverse ADMET (ethenolysis) of pDVOCB to DVOCB oligomer, and (2) retro-[2+2] cycloaddition of DVOCB to butadiene. Importantly, the thermal properties of the pDVOCB are retained through rounds of depolymerization−repolymerization.

$(A-B)_m$ multiblock copolymers in which the A component is a semicrystalline hard segment (which enables physical cross-linking), and the B segment forms a soft, rubbery domain, are versatile materials that can be tuned to combine elastomeric mechanical properties with melt processability.[32,33] Multiblock copolymers can behave as thermoplastic elastomers (TPEs), finding applications in automotive parts,[34] footwear,[35] and electrical insulators.[32] Building on previous studies with pDVOCB, we envisioned chemically recyclable copolymers containing hard (DVOCB) and soft (polyalkenamer) segments (Figure 1C). Here we describe the synthesis of multiblock copolymers with systematic variations in DVOCB segment length and composition which enabled access to materials with a broadly tunable range of properties.

■ EXPERIMENTAL SECTION

Materials. All reagents and solvents were obtained from commercial vendors and used as received unless otherwise noted. Grubbs second generation catalyst (G2, M204), *cis*-cyclooctene (95%), ethyl vinyl ether (99%), and mesitylene (98%) were purchased from Sigma-Aldrich. Cyclooctene was purified by distillation prior to use. Benzoquinone was purchased from Oakwood Chemical. The high-temperature cyclic alkylaminocarbene ruthenium metathesis catalyst (M1002) ($RuCl_2(CAAC)(=CHAr)$; CAAC = (2,6-$^iPr_2$-C_6H_3)-3,5,5-Me_3-3-Ph-pyrrolidin-2-ylidene, Ar = C_6H_4-2-O^iPr) was provided by Umicore AG & Co. KG. Chloroform-*d* (99.8%) was purchased from Cambridge Isotope Laboratories. DVOCB(n) was synthesized according to the previous literature procedure, with a typical chain-length dispersity ($Đ$) ≤ 1.05.[30]

Multiblock Copolymer Synthesis. All manipulations were carried out using standard vacuum line and Schlenk techniques, and all glassware was oven-dried prior to use. To an oven-dried Schlenk flask equipped with a magnetic stir bar were added DVOCB(n), cyclooctene, and benzoquinone (5 mol % relative to total monomers). Mesitylene was added to a final monomer concentration of 5 M. The mixture was degassed by freeze−pump−thaw (3 cycles), warmed to rt, and backfilled with N_2. The flask was placed in an oil bath at 80 °C, whereupon the DVOCB dissolved. M1002 was added in one portion. To prevent loss of volatile COE monomer, the reaction was initially stirred at 80 °C for 2 h, then the temperature was increased to 135 °C. The polymerization continued to stir for 48−72 h. To terminate the polymerization, the reaction was cooled to rt, quenched with ethyl vinyl ether (500 μL), and diluted with toluene. The polymer was precipitated into cold methanol thrice to provide an off-white solid.

ADMET Depolymerization. ADMET depolymerization of the multiblock copolymer containing 40 wt % DVOCB(5) was conducted according to the previously published procedure.[30] To an oven-dried 35 mL Schlenk flask equipped with a magnetic stir bar were added 50 mg polymer, benzoquinone (5 mol % relative to total monomers), and 5 mL of toluene. The mixture was deoxygenated by bubbling with argon for 20 min. In a nitrogen-filled glovebox, M1002 (1.0 mol % relative to total monomers) was dissolved in minimum dry toluene, removed from the glovebox in a syringe, and added to the reaction flask under a constant argon flow. The flask was sealed and the mixture was frozen with liquid nitrogen. The headspace was evacuated and ethylene (20 equiv relative to total monomers) was added to the reaction using a calibrated gas bulb. The flask was sealed and warmed to room temperature, then stirred at 120 °C for 2 h. The temperature was then lowered to 50 °C and the mixture stirred for 16 h to improve ethylene solubility while maintaining polymer solubility at partial depolymerization. After cooling to room temperature, the flask was opened under air to release excess ethylene, and the reaction was quenched with 1 mL ethylvinylether. The reaction solution was concentrated by reduced pressure and the resulting residue was purified by redissolving in boiling hexanes and filtering through a pad of silica. The volatiles were removed by reduced pressure to yield recovered DVOCB(5) as a white semisolid.

Characterization. ^1H NMR data were collected at 25 °C using a Bruker AVANCE 400 MHz NMR instrument (32 scans, 2 s relaxation delay). All ^1H chemical shifts are reported in ppm relative to $SiMe_4$ using the ^1H (chloroform-*d*: 7.26 ppm) chemical shift of the solvent as a standard.

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and dispersity ($Đ$) were characterized by size exclusion chromatography (SEC) using two 30 cm Agilent PLgel 5 μm Mixed-C columns operating at 35 °C, a Wyatt Optilab T-rEX differential refractive index (DRI) detector (25 °C, 658 nm wavelength), and a miniDAWN TREOS three-angle light scattering instrument (rt, 658 nm). Tetrahydrofuran (inhibitor-free HPLC, Sigma-Aldrich) was used as the mobile phase. Absolute M_w was measured using multiangle light scattering, using dn/dc (mL g^{-1}) = 0.1114 + 0.020 × (wt fraction$_{DVOCB(n)}$) (Figure S6). The DRI elution time was calibrated with narrow-distribution polystyrene standards, and $Đ$ was determined from that calibration curve. Finally, M_n was calculated as $M_n = M_w/Đ$.

Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q500 Thermogravimetric Analyzer, with 3−10 mg of polymer in platinum sample pans. Under air or nitrogen gas at a constant flow rate of 60 mL min^{-1}, the samples were heated from ambient and held isothermally at 110 °C for a minimum of 15 min to

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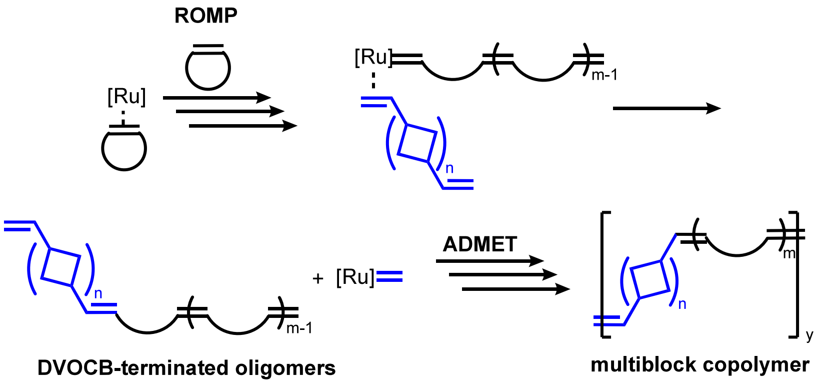


Figure 2. DVOCB(n) chain transfer in tandem ROMP-ADMET. Chain-transfer with DVOCB(n) results in DVOCB(n)-terminated and vinyl-terminated oligomers early in the polymerization. After COE is consumed, ADMET (and the release of ethylene) results in the formation of multiblock copolymers.

remove residual water or solvent, then heated to 500 °C at 10 °C min^{-1}. Degradation temperatures ($T_{d5\%}$) are reported at 5% mass loss relative to the mass after the 110 °C isothermal hold.

Peak melting temperatures (T_m) and enthalpies (ΔH_m) were examined using differential scanning calorimetry with a PerkinElmer DSC 7, with sample masses ranging from 3−7 mg. Samples were first heated from room temperature to 175 °C at 10 °C min^{-1}, then cooled to −45 °C at 10 °C min^{-1}, followed by a second heat to 175 °C at 10 °C min^{-1}. All data reported herein are from the second heat.

Storage and loss moduli from −120 to 155 °C were measured using dynamic mechanical analysis (DMA) with a PerkinElmer DMA-8000, in tension mode at 1 Hz and a heating rate of 5 °C min^{-1}. The glass transition temperature in these materials could not be clearly resolved using DSC, so the T_g is reported as the peak in the loss modulus (E'') curve.

Uniaxial tensile tests were performed at room temperature on the copolymer films using an Instron 5865. Samples for the Instron test were cut to ca. 3.0 mm wide × 10.0 mm gauge length × 0.3 mm thick. The ends of the polymer film were glued into two plastic holders (Figure S13) and mounted into the Instron grips. Tensile tests were conducted at a constant crosshead speed of 3% engineering strain per minute and proceeded until sample break. Cyclic strain tests were used to measure elastic recovery. The percent elastic recovery, R, was calculated for each cycle i using $R_i = \left(\frac{\varepsilon_a - (\varepsilon_s - \varepsilon_r)}{\varepsilon_a}\right) \times 100\%$, where ε_a is the prescribed strain from the initial length (10%), ε_r corresponds to the strain at which the stress crosses zero while increasing strain during cycle i, and ε_s is the strain at which the stress crosses zero while increasing strain during cycle $i + 1$.

Wide-angle X-ray scattering (WAXS) measurements were performed in transmission on a Xenocs Xeuss 3.0 using a Cu K$_\alpha$ source. In situ heating measurements utilized a Linkam stage, heating at 5 °C min^{-1} with an in-house temperature calibration curve.[36] Polymer samples for scattering measurements were prepared by melt pressing polymer powder into a disk (ca. 0.5 mm thick and 5.0 mm diameter), which was then loaded into a Linkam heating cell, ensuring good thermal contact. To match the DSC thermal history, samples were then heated above their final melting temperature and cooled to 10 °C at 10 °C min^{-1}, prior to WAXS data collection on heating. The isotropic two-dimensional scattering patterns were azimuthally integrated and are presented against the magnitude of the momentum transfer vector $q = (4\pi/\lambda)\sin\theta$, where θ is half the scattering angle and λ is the wavelength of the Cu K$_\alpha$ radiation (1.5418 Å). The precise sample-to-detector distance was determined for each specimen by matching the position of the most intense WAXS peak to that measured on a Bruker Discover D8 diffractometer, both at room temperature.

■ RESULTS AND DISCUSSION

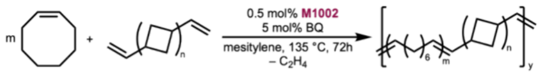
Acyclic diene metathesis (ADMET) polymerization is a versatile technique used to synthesize precision polyolefins,[37,38] hyperbranched polymers,[39] and segmented copolymers.[40] In ADMET, α,ω-diene monomers are condensed, with the release and constant removal of ethylene, in a stepwise fashion to grow high molecular weight polymers.[41] Historically, ADMET polymerizations are conducted neat using commercially available Grubbs (Ru) or Schrock-type (Mo or W) catalysts under high vacuum (<100 mTorr) to facilitate the removal of ethylene.[42] However, several literature reports detail ADMET polymerization in solution, typically with a high-boiling solvent, and either a steady flow of N_2 or a light vacuum to remove ethylene from the headspace of the reaction vessel to drive the reaction to high conversion.[43−45]

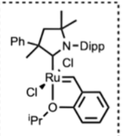
Typical soft segments in multiblock copolymers include polyethers,[46] ethylene−octene copolymers,[47] or ethylene-propylene-diene terpolymers.[48] For the soft segment of DVOCB(n) multiblock copolymers, polyoctylene was selected, which can be synthesized via either: (1) ring-opening metathesis polymerization (ROMP) of cyclooctene (COE),[49−51] or (2) ADMET polymerization of 1,9-decadiene (DDE).[52,53] *trans*-Polyoctylene rubber (commercialized by Evonik as VESTENAMER) is semicrystalline (T_m = 55 °C), but possesses a low crystallinity, and a glass transition temperature much lower than room temperature (T_g = −67 °C).[54,55] Thus, we reasoned that polyoctylene could serve well as the soft segment for our DVOCB multiblock copolymers.

DVOCB(n), where n corresponds to the average number of cyclobutyl groups in the oligomer, was synthesized by the iron-catalyzed [2+2] oligomerization of butadiene as previously reported.[30] To synthesize DVOCB(n) multiblock copolymers, we initially conducted bulk ADMET copolymerizations of 1,9-decadiene (DDE) and DVOCB(5) using Grubbs first-generation catalyst (G1) in which high vacuum was used to promote removal of ethylene throughout the polymerization. However, the growth of polymer molecular weight was slow as determined by size exclusion chromatography (SEC) with multiangle light scattering (MALS) detection ($M_n^{(SEC)}$ < 5 kDa in 48 h), and DVOCB(5) was not fully incorporated into the final polymer structure. While a slow growth of molecular weight is expected for ADMET polymerizations,[42] these low molecular weights were insufficient for studying the thermomechanical properties of the resulting copolymers.

However, because ROMP is a chain-growth polymerization, the growth of molecular weight is faster than in acyclic metathesis. Thus, we hypothesized that a tandem ROMP-ADMET approach could be used to further increase the molecular weight of the DVOCB(*n*) copolymers. We conducted a simultaneous cometathesis polymerization of cyclooctene (COE) with telechelic DVOCB(*n*) (Figure 2). In our system, the formation of multiblock copolymers occurs in three overlapping stages. First, ROMP of COE rapidly builds molecular weight, while concurrent chain-transfer with the vinyl-terminated DVOCB generates a "dead" chain and rapidly initiates propagation of a new chain, resulting in COE-DVOCB diblock oligomers (Figure 2).[56,57] ^{1}H NMR spectra of crude reaction aliquots indicated that the COE monomer was essentially all consumed (>90% conversion) in the first 5 min after catalyst addition (Figure S1), and SEC measurements of these same aliquots revealed M_n values less than 2.0 kg mol^{-1} at this time (Figure S2), corresponding to the diblock oligomer. Once the COE monomer is consumed, the removal of ethylene drives the formation of high molecular weight polymers, as is typical for ADMET polymerizations.[42,58] Finally, metathesis exchange reactions between polymer chains scramble the COE segments resulting in random multiblock copolymers.

Due to the relatively high melting points of DVOCB(*n*) and the resulting copolymers, tandem ROMP-ADMET copolymerizations were conducted at elevated temperature using a commercially available cyclic alkylaminocarbene catalyst (M1002), as this catalyst is stable and effective for ADMET polymerization at elevated temperatures (>100 °C).[59] Using this approach, we synthesized a series of COE copolymers with systematic variations in DVOCB(5) content (Figure 3, entries 2−6). ^{1}H NMR spectroscopy confirmed the successful incorporation of DVOCB(5) into each copolymer, as the DVOCB content in the product closely matched that calculated from the DVOCB:COE feed ratio (typically within 1 wt %, see Table S2). While benzoquinone (BQ) is added to the reaction mixture to suppress olefin isomerization, previous work has demonstrated that isomerization still occurs even in the presence of BQ at these elevated temperatures.[60,61] NMR end-group analysis (by integrating the proton resonance signals corresponding to the terminal vinyl group, isomerized (ethylidene) DVOCB(*n*) end group, and the olefin backbone, Figures S3 and S4) of these materials indicated M_n values of 11.5−28.6 kg mol^{-1}, in reasonable agreement with the values of $M_n^{(SEC)}$. Furthermore, the dispersity ($Đ$) for each polymer determined by SEC was ≅2, as expected for a polycondensation. For comparison, a polyCOE homopolymer synthesized via ROMP using Grubbs second generation catalyst is included (Figure 3, entry 1 and Table S1). Notably, because COE is commercially synthesized via the partial hydrogenation of cyclooctadiene—prepared from the [4+4] cycloaddition of butadiene—these materials are effectively "all-butadiene" copolymers.[62]





M1002

Entry	n	DVOCB(*n*)^a (wt%)	$M_n^{(NMR)a}$ (kg mol^{-1})	$M_n^{(SEC)b}$ (kg mol^{-1})	$Đ^c$
1	–	0^d	19.3	19.7	2.26
2	5	10	28.6	28.4	3.32
3	5	20	18.1	13.4	2.91
4	5	30	15.9	14.0	3.34
5	5	40	11.5	21.3	3.37
6	5	50	13.1	17.2	3.31
7	6	10	23.5	11.0	2.04
8	6	20	21.1	9.3	1.85
9	6	30	17.4	17.3	2.47
10	6	40	12.4	16.6	2.57
11	6	50	20.3	15.7	2.38

Figure 3. Tandem ROMP-ADMET copolymerization of COE and DVOCB(*n*) to yield poly(octenamer-*co*-DVOCB(*n*)). (a) Determined from ^{1}H NMR spectroscopy. (b) Determined by M_n = $M_w^{(SEC-MALS)}/Đ$ in THF. (c) M_w/M_n from differential refractive index (DRI) elution time trace. (d) Synthesized via ROMP of COE using Grubbs 2nd generation catalyst at rt.

Thermogravimetric analysis (TGA) in nitrogen of selected copolymers indicated $T_{d5\%}$ around 420 °C, comparable to other hydrocarbon polymers such as polyethylene and polypropylene ($T_{d5\%}$ > 400 °C).[63,64] However, when performed in air, we observed a slight mass increase around 300 °C prior to mass loss (Figure S10), which we attribute to oxidation of the unsaturated units upon heating.[65]

Differential scanning calorimetry (DSC) was conducted to further investigate the effect of copolymer composition on the thermal properties. Copolymers containing low amounts of DVOCB(5) exhibited melting transitions at low temperatures (∼40−50 °C), characteristic of pCOE crystallinity (Figure 4A). However, these melting transitions become broader, weaker, and shift to lower temperatures as DVOCB(5) content is increased. At 30 wt % DVOCB(5), melting of DVOCB(5) crystallites becomes evident (>80 °C). Copolymers containing higher contents of DVOCB(5) (>30 wt %) exhibited T_ms that are competitive with commercial all-hydrocarbon TPEs. An example is DOW's INFUSE olefin block copolymers (OBCs), which contain polyethylene hard segments alternating with ethylene/octene soft segments; depending on the copolymer composition, INFUSE OBCs exhibit tunable T_ms between 90−110 °C.[66] The thermal properties of all the copolymers are summarized in Table S4.

Dynamic mechanical analysis (DMA) was used to determine the viscoelastic response of each material as a function of temperature (Figure 4B). The T_g was estimated from the temperature corresponding to the peak in the loss modulus (E'', dashed line), and ranged from−60 to −45 °C, depending on the DVOCB(5) content (Table S4). Polymers containing higher weight fractions of DVOCB(5) exhibited a higher modulus above 50 °C, and higher temperatures for the onset of rubbery flow, consistent with the increased crystallinity above 60 °C observed by DSC.

Previous work demonstrated that the melting point of DVOCB(*n*) is directly linked to the oligomer length, where increasing *n* from 4 to 10 systematically increases T_m from 60 to 150 °C.[30] Thus, to further demonstrate the tunability of our multiblock copolymers, additional copolymerizations were conducted with the longer, higher-melting DVOCB(6) oligomer, under identical reaction conditions (Figure 3, entries 7−11). As observed with the DVOCB(5) copolymers, at low (≤20 wt %) contents of DVOCB(6), crystallinity is dominated by the octylene units, which exhibit T_ms between 25 and 45 °C. DVOCB(6) crystallinity contributes substantially when the DVOCB(6) content is 30 wt % or above, resulting in higher T_ms relative to the DVOCB(5) copolymers at the same hard segment content (Figure 5A). Similar to the DVOCB(5) copolymers, DMA analysis indicated T_gs ranging from −60 to

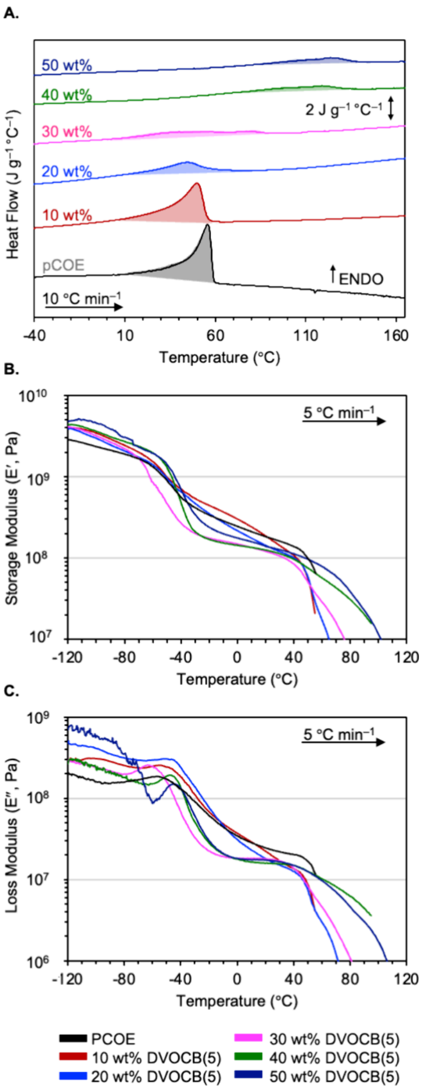


Figure 4. Thermal properties of the poly(COE-*co*-DVOCB(5)) series. (A) DSC thermograms (2nd heat) at a constant heating rate of 10 °C min^{-1}. (B) DMA storage and (C) loss moduli measured at 5 °C min^{-1} and 1 Hz.

−45 °C. As expected, increasing the DVOCB(6) content increased the rubbery plateau width, indicative of the contribution from DVOCB(6) crystallinity (Figure 5B). At 25 and 50 °C, the storage modulus for both copolymer series initially decreases as the DVOCB(n) content increases, consistent with a reduction in octylene crystallinity as also observed by DSC (Figures S11A,B). Subsequently, as the DVOCB(n) hard segment crystallinity begins to contribute, the modulus increases. Taken together, DSC and DMA show that a broad spectrum of thermal properties is accessible by simply altering the copolymer composition.

Previous DSC analysis of DVOCB(n) indicated the presence of multiple endothermic transitions before melting.[29] Variable temperature wide-angle X-ray scattering (VT-WAXS) of the DVOCB(n) oligomers revealed that the lower-temperature endothermic events could be attributed to a crystal-to-rotator phase transition before reaching the melting temperature.[36] Similarly, rotator phases have been observed for the chain-extended polymers of DVOCB(n), pDVOCB.[30] To further investigate the morphological origin of the endotherms observed with our copolymers, we performed VT-WAXS to probe for the presence of DVOCB crystallinity in the DVOCB(6) copolymers (Figure 6). For comparison, VT-WAXS profiles of pCOE homopolymer, and the remaining DVOCB(6) copolymers, are included in the SI.

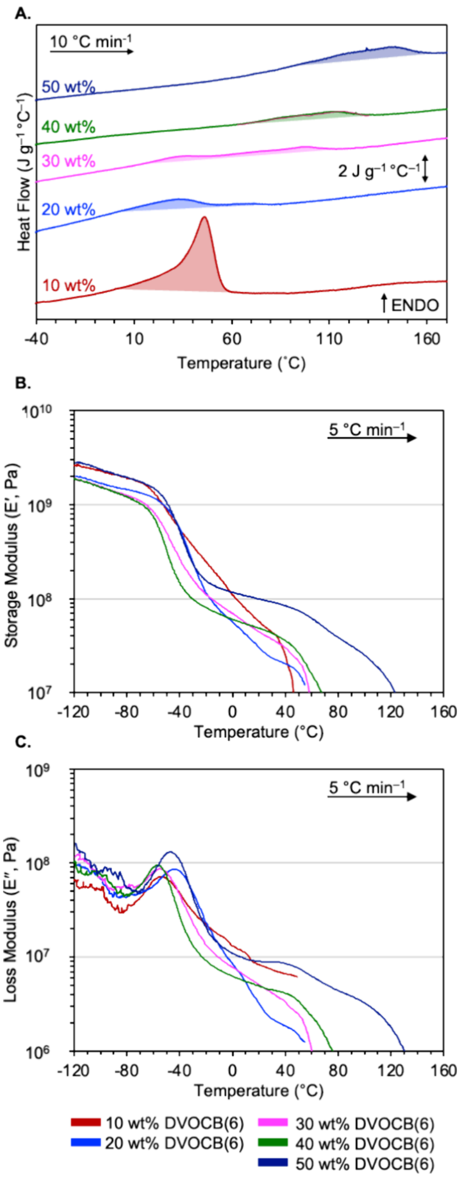


Figure 5. Thermal properties of the poly(COE-*co*-DVOCB(6)) series. (A) DSC thermograms (2nd heat) at a constant heating rate of 10 °C min^{-1}. (B) DMA storage and (C) loss moduli measured at 5 °C min^{-1} and 1 Hz.

In the 10 wt % DVOCB(6) copolymer, two distinct peaks in the WAXS profile were observed (Figures 6A and S12A,B), which indicate octylene crystallinity, similar to reported WAXS patterns for the triclinic phase of pCOE homopolymers.[67,68] Upon heating, both peaks exhibit a parallel decrease in intensity, suggesting the melting of a single phase, as corroborated by DSC analysis. Conversely, the 20 wt % DVOCB(6) copolymer shows a single peak at room temperature that is shifted to a slightly higher q compared to the primary peak in pCOE homopolymer (Figure S12C). This single peak may correspond to a rotationally disordered pCOE crystal, akin to those reported in previous studies of *trans*-

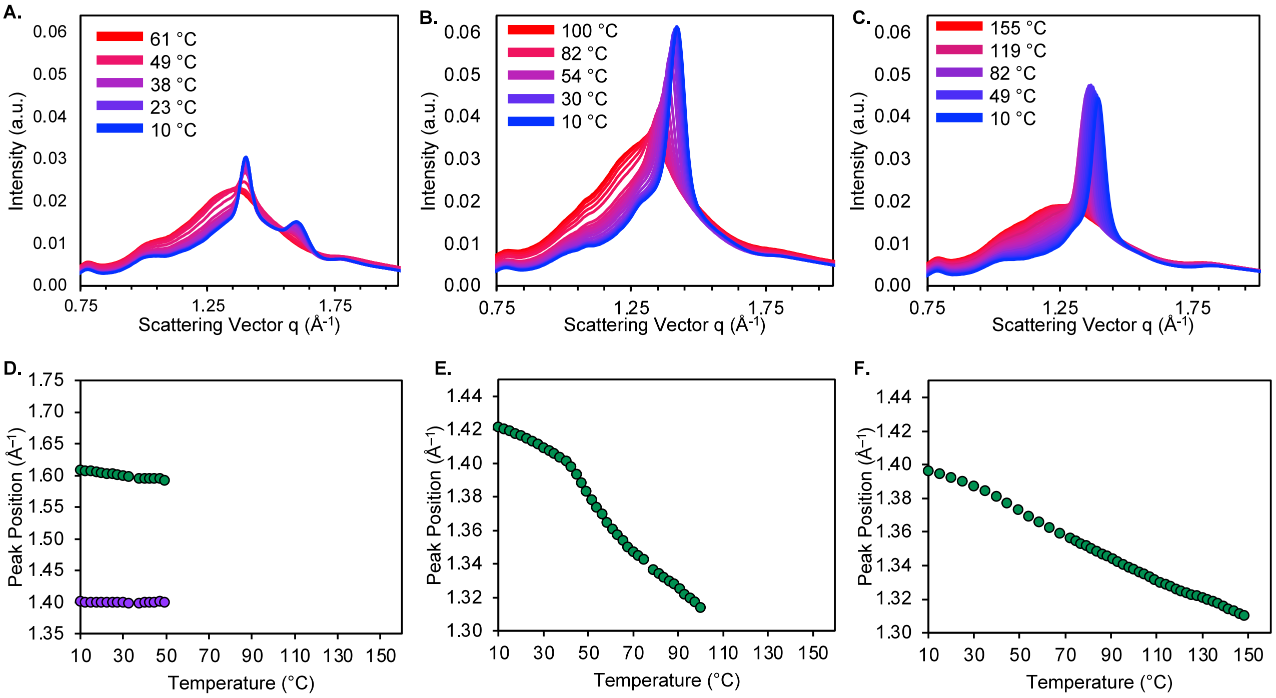


Figure 6. Variable-temperature WAXS of melt-pressed samples of (A) 10 wt %, (B) 30 wt %, and (C) 50 wt % DVOCB(6) copolymers. Plots of peak position versus temperature for (D) 10 wt %, (E) 30 wt %, and (F) 50 wt % DVOCB(6) copolymers. Only selected temperatures are labeled for clarity in plots A–C.

polybutadiene.[69,70] The 30 and 40 wt % DVOCB(6) copolymers (Figures 6B and S12D,E) also display a single narrow peak which not only decreases in intensity upon heating, but also shifts to lower *q*; plots of peak position versus temperature revealed three distinct regimes of *q* versus *T* (Figures 6E and S12D,E). We hypothesize that at room temperature, the WAXS pattern reflects a superposition of scattering from distinct octylene and DVOCB(6) rotator phases. Heating (to ≅50 °C) melts the octylene rotator phase, leaving the DVOCB(6) rotator phase, which subsequently melts at higher temperature (≅100 °C for 30 wt % DVOCB(6), Figure 6E). At 50 wt % DVOCB(6), the crystallinity of DVOCB(6) becomes predominant (Figures 6C,F and S12F), resulting in a WAXS pattern closely resembling that for pDVOCB homopolymers.[30] We estimated the percent of the DVOCB(*n*) which has crystallized in each copolymer containing ≥30 wt % DVOCB(*n*) by comparing the $\Delta H_m^{(\mathrm{DVOCB}(n))}$ (Table S3) to $\Delta H_m^{(\mathrm{copolymer})}$ (Table S4) according to eq S1. As expected, the percent DVOCB(*n*) crystallinity increases with increasing DVOCB(*n*) content; however, it remains modest (<30%) for both DVOCB(*n*) (n = 5, 6) copolymer series (Tables S3 and S4).

The tensile properties of a subset of the DVOCB(*n*) copolymers were measured through uniaxial stress–strain tests. Copolymers with higher DVOCB(*n*) content (≥30 wt % DVOCB(*n*)) displayed a distinct yield point occurring at less than 20% strain (Figures 7 and S14–S17). These copolymers continued to deform beyond the yield point, ultimately reaching a breaking strain as high as 100%. This represents a substantial increase in the breaking strain compared with previously synthesized pDVOCB homopolymers (10–80%).[30] Additionally, a 30 wt % DVOCB(6) copolymer was also subjected to a cyclic strain test, in which the sample was repeatedly strained and released below its yield point. While the elastic recovery from the first cycle was only R_1 = 89%, the material exhibited progressively less hysteresis in subsequent cycles, with the elastic recovery improving to R_2 = 98% on the second cycle and reaching R_5 = 99% on the fifth cycle (Figure 7).

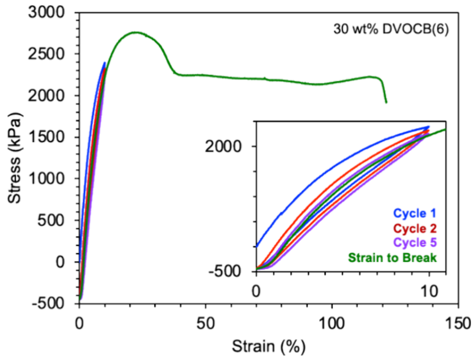


Figure 7. Coupled hysteresis experiment of selected cycles (at a strain of 10%) finished with a strain-to-failure (green line) for a 30 wt % DVOCB(6) copolymer. The inset shows an expanded view at low strain demonstrating the strain recovery of the copolymer. Only cycles 1, 2, and 5 are shown for clarity.

Finally, the chemical recyclability of these materials was examined. To date, several examples of metathesis depolymerization reactions have been reported in which an unsaturated polymer undergoes acyclic metathesis with either ethylene (ethenolysis),[21,30] or another small molecule olefin[71,72] to deconstruct a polymer. We performed ethenolysis using a 40 wt % DVOCB(5) sample in which the copolymer was subjected to ethylene in the presence of a new charge of the same Ru catalyst (M1002) used for polymerization.[30] Ethenolysis provided nearly complete deconstruction of the polymer to the original DVOCB(5) oligomer. ^{1}H NMR spectroscopy indicated that the DVOCB(5) oligomer is essentially unchanged after depolymerization when compared to virgin DVOCB(5), as evidenced by comparing the relative peak integrations in the ^{1}H NMR spectrum (Figures 8 and S18). However, a small amount (4%) of the olefinic proton area in the ethenolysis product appears near a chemical shift of 5.4 ppm, matching the appearance of the internal olefins in the copolymers and in pCOE homopolymer. We attribute this to a small fraction of pCOE oligomers not completely cleaved to 1,9-decadiene (DDE) under the time and temperature protocol used for ethenolysis. The DDE produced in the ethenolysis reaction was not recovered during the reaction workup here due to its volatility, but it could in principle be isolated from the other volatiles by distillation. DDE is readily converted to COE by ring-closing metathesis,[73] allowing its reuse in the synthesis of new multiblock copolymers of COE and DVOCB.

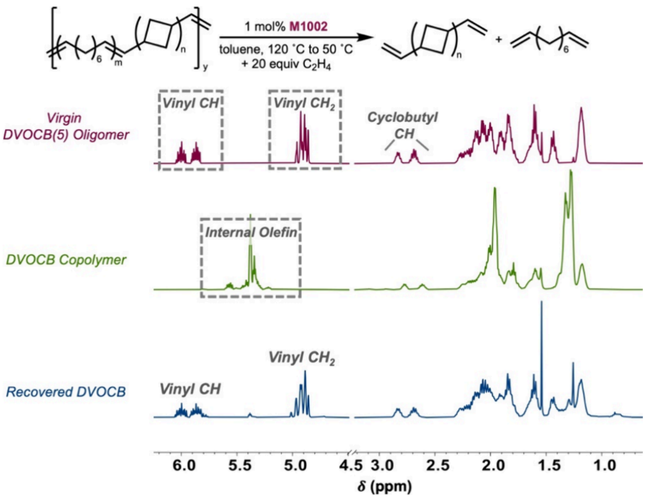


Figure 8. Recovery of DVOCB(5) from 40 wt % multiblock copolymer via ethenolysis.

■ CONCLUSIONS

In summary, we synthesized a series of copolymers with systematic variations in the content of DVOCB, a semicrystalline chemically recyclable oligomer derived from butadiene. Tandem ROMP-ADMET copolymerization of DVOCB(n) with COE produced multiblock copolymers containing hard (DVOCB(n)) and soft (COE) segments. We observed a direct correlation between DVOCB(n) content in the copolymer and both T_m and the width of the rubbery plateau. Overall, this work sheds light on the synthesis, properties, and potential end-of-life circularity for these novel chemically recyclable multiblock copolymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c00292.

> Representative NMR characterization, SEC traces, summary of thermal and mechanical data for DVOCB(n) copolymers, and variable temperature WAXS of the remaining DVOCB(6) copolymers (PDF)

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Notes

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