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Renewable, Degradable, and Chemically Recyclable Cross-Linked Elastomers

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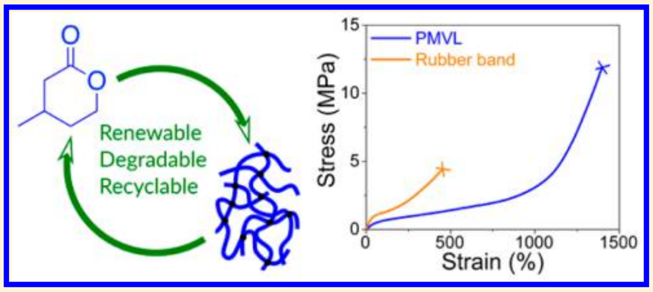
Ⓢ *Supporting Information*

ABSTRACT: Most commercial elastomers, typified by vulcanized natural rubber, are cross-linked polymers and as such cannot easily be reprocessed or recycled. While some are derived from renewable resources, the majority are produced from petroleum feedstocks and do not easily degrade. In this study, renewable elastomers based on β-methyl-δ-valerolactone were produced using two different methodologies: (1) tandem copolymerization/cross-linking with a bis(six-membered cyclic carbonate); (2) cross-linking of a linear poly(β-methyl-δ-valerolactone) homopolymer with a free-radical generator. The mechanical properties of these materials were investigated; tensile strengths of up to 12 MPa and elongations of up to 2000% were observed. Inclusion of a filler (fumed silica) was used to enhance the performance of the elastomers without significant loss of elasticity, with some composites exhibiting tensile strengths nearly double that of the neat elastomer. Aqueous degradation studies indicated that the materials were capable of degradation in acidic and basic conditions at 60 °C. Moreover, these cross-linked elastomers can also be chemically recycled, yielding monomer in high purity and yield (>91% and 93%, respectively).



■ INTRODUCTION

Cross-linked polymers (CPs) encompass almost a third of the synthetic polymer industry and are vital in a wide variety of products including tires, contact lenses, elastomers, adhesives, and foams.[1] While cross-linking confers a number of advantages, including high thermal stability and solvent resistance, this structure also prevents these materials from being reprocessed. Postconsumer CPs are consequentially disposed of in landfills or by incineration, leading to significant loss of value.[1] Additionally, the vast majority of synthetic polymers—including CPs—are petroleum-derived and nondegradable. Their production and disposal is therefore unsustainable in the long term. In recent years, considerable effort has been devoted to the development of CPs that are recyclable, some of which are also renewable.[2−8]

Among the palate of renewable polymers, aliphatic polyesters are particularly attractive because they are easily synthesized and, in many cases, are also biodegradable and biocompatible.[9−11] In numerous previous examples, aliphatic polyesters have been used to prepare thermoplastic elastomers (TPEs) that mimic styrenic block polymers in both design and performance.[12−22] Conveniently, the thermal and mechanical properties of these TPEs can be easily tuned by altering the size and composition of the discrete polymer blocks. Unfortunately, TPEs typically have poor solvent resistance and low thermal stability and often exhibit significant stress softening (known as the Mullins effect).[23] Finally, polyester TPEs often require rigorous reaction conditions to ensure proper morphology; variations in the dispersity and presence of adventitious initiators can result in a dramatic reduction of toughness.

These issues are often resolved by the use of CPs because they exhibit both high thermal stability and solvent resistance. A number of methods have been developed for cross-linking polyesters to improve their thermal, physical, and mechanical properties. These methodologies frequently employ hydroxy-multifunctional polyesters, or polyesterols, such as poly(lactide) (PLA) and poly(ε-caprolactone) (PCL). Polyesterols can be cross-linked using condensation reactions or further functionalized and subsequently cross-linked.[6,24−30] Because the polyesterols are synthesized by either step-growth condensation or ring-opening transesterification polymerization (ROTEP), their reactive groups are generally terminal. In theory, the coupling efficiency should not be influenced by the molar mass; in practice, low molar mass ($M_n \leq 5$ kg mol^{-1} to the reactive end group) is often necessary to precisely target a balanced stoichiometry for the cross-linking reaction such that it reaches high conversion. As a result, the range of accessible molar masses between cross-links (M_x) is rather constrained. Improvements in the mechanical properties of CPs have been attributed to large M_x values. Most notably, ultimate elongation increases with M_x. Furthermore, higher M_x values allow entanglements to form, which behave as transient physical

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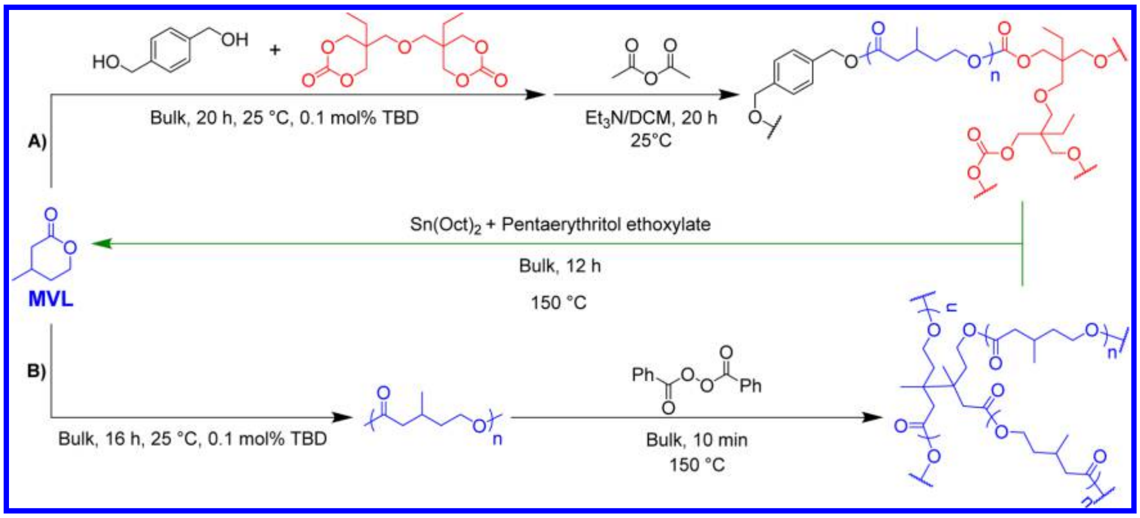
Scheme 1. Synthesis of Cross-Linked PMVLs



cross-links; a lower molar mass between entanglements (M_e) in the constituent polymer will increase the number of physical cross-links, also improving the mechanical properties.[31]

Other strategies have been developed for polyesters to overcome these deficiencies. One method, tandem copolymerization/cross-linking, allows for the direct conversion of monomers to CPs. Although this approach eliminates processing steps, it comes with its own challenges. For example, because of problems with solubility, high concentrations of bis(ε-caprolactone) cross-linkers (8−28 mol %) are often required, rendering it difficult to tune the mechanical properties of the CPs in a controlled manner.[32,33] Bis(six-membered cyclic carbonates) have been utilized at much lower loadings (1 mol %) when copolymerized directly with ε-caprolactone (CL), but this system likely suffered from reactivity differences as well.[34,35] The inclusion of trimethylene carbonate (50 mol %) allowed for lower concentrations of cross-linker (0.05 mol %) and resulted in an amorphous material; however, the mechanical properties of the resulting material were poor.

A second method that has been used to access tunable polyester elastomers is ROTEP of alkene-functionalized lactone comonomers with saturated aliphatic lactones (e.g., CL) to produce statistical copolymers.[36−38] These copolymers can be cross-linked in subsequent steps using free-radical or thiol−ene click reactions. While the properties of these CPs can be easily tuned, the alkene comonomers are often prohibitively expensive and/or challenging to synthesize on a large scale.[37] Alkene-functionalized macrolactones are more economical; however, their polymerization may also require the use of enzymatic polymerization catalysts, which can be limiting.[38] Interestingly, free-radical generators are capable of cross-linking fully saturated polyesters.[34,39−42] Typically, this involves the thermal cross-linking of the polyester with an organic peroxide. Although this allows for facile tuning of the mechanical properties, these studies have been confined to high glass transition temperature (T_g) and/or semicrystalline materials, which are not ideal for elastomers. In fact, there is a dearth of literature on tough, cross-linked amorphous, low-T_g polyesters; the preceding examples have indicated poor tensile properties due to limits on M_x dictated by the methodologies used.[26,27,43,44] Those with competitive properties generally have a T_g value that is above −40 °C, limiting the scope of their potential applications.[27,33,35]

We have demonstrated that β-methyl-δ-valerolactone (MVL) can be produced renewably on a large scale and can be polymerized in bulk to afford poly(β-methyl-δ-valerolactone) (PMVL).[17] The properties of amorphous PMVL ($T_g = -52$ °C and $M_e = 4.3$ kg mol^{-1}) make it an attractive polymer for use in a wide range of applications. For example, we have explored the use of PMVL in tough plastics, TPEs, soft polyurethane foams, and thermoplastic polyurethanes.[17,20,45] Furthermore, PMVL has been shown to depolymerize in the presence of a catalyst, allowing for controlled recovery of a pure monomer.[45]

Herein, we report the production of cross-linked elastomers prepared from PMVL. We use two different synthetic strategies: a tandem copolymerization/cross-linking reaction of MVL with a bis(six-membered cyclic carbonate) and cross-linking of linear PMVL with a free-radical generator (Scheme 1). We investigate the impact of synthetic conditions and fumed-silica (FS) incorporation on the mechanical properties of PMVL elastomers. Furthermore, we study the degradation of these materials in aqueous media. Finally, we show that these materials can be recycled to recover MVL in high purity and yield.

■ EXPERIMENTAL SECTION

Materials. All reagents were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received unless otherwise stated. 1,5,7-Triazabicyclodec-5-ene (TBD) was purified by vacuum sublimation (70 °C, 30 mTorr). Dichloromethane (DCM), tetrahydrofuran (THF), and methanol were purchased from Fisher Scientific (Hampton, NH); DCM and THF were purified via a GC-SPS-4-CM glass contour 800-L solvent purification system obtained from Pure Process Technologies (Nashua, NH). 3-Methyl-1,5-pentanediol was obtained from TCI (Portland, OR) and used without further purification. β-Methyl-δ-valerolactone (MVL) was produced by one of two methods as described in previous studies and purified by fractional distillation (3×) over calcium hydride (72 °C, 1 Torr).[45,46] 5,5′-[Oxybis(methylene)]bis(5-ethyl-1,3-dioxan-2-one) (B6CC), a bis(six-membered cyclic carbonate), was also produced as described in a previous study and recrystallized from THF (3×).[7] Aerosil R 812 was kindly provided by Evonik Industries (Parsippany, NJ). Rubber bands were purchased from the University of Minnesota chemistry stockroom; they were manufactured in Thailand for Universal (Deerfield, IL). All glassware was heated to 105 °C overnight prior to use.

Modified Synthesis of MVL from 3-Methyl-1,5-pentanediol.[46] 3-Methyl-1,5-pentanediol (1 L, 974 g, 8.24 mol) and copper chromite (50 g, 0.16 mol, 2 mol %) were charged in a 2-L three-neck round-bottomed flask fitted with a Dean−Stark apparatus, a thermometer, and a glass stopper. The apparatus was then attached to a bubbler filled with silicon oil. A heating mantle was used to heat the round-bottomed flask to 240 °C under vigorous stirring. The temperature of the reaction rapidly rose to 170 °C, followed by the collection of water (ca. 5 mL) and an unknown organic liquid (ca. 5 mL). Following the removal of these impurities, the reaction temperature rose rapidly to ca. 210−220 °C, followed by the evolution of H_2 gas. The reaction was allowed to continue for 20 h and then cooled. At this time, the ^{1}H NMR spectrum of the solution indicated ca. 95% conversion of the diol. The crude product, a mixture of MVL monomer and PMVL polymer, was then purified by fractional distillation under reduced pressure.

First, a forerun was removed (1 Torr, 55−72 °C, 50 g), followed by a second fraction (1 Torr, 72−75 °C, 850 g). The higher boiling fraction was a clear, colorless liquid containing a minor amount of 4-methyl-3,4,5,6-tetrahydro-2*H*-pyran-2-ol. The concentration of this impurity in MVL was estimated to be ∼0.2 mol % using the ^{1}H NMR signal corresponding to the methine proton at 5.3 ppm. To remove lactol, the crude MVL was stirred with phosphorus pentoxide (5 g) at 120 °C for 12 h; this resulted in dehydration of the lactol impurity and polymerization of MVL (∼60% conversion of MVL was observed) presumably with water or lactol as the initiating species. The solution of polymer in monomer was then distilled under the conditions previously described until ca. 10% of the liquid remained in the pot. Analysis of the resulting MVL via ^{1}H NMR spectroscopy indicated that it no longer contained any lactol impurity, within the detection limit of the instrument used. To obtain high-purity monomer, MVL was then distilled two more times under reduced pressure from calcium hydride, each time discarding the first 5% of the distillation liquid, to yield a clear colorless liquid (65−75% yield).

To evaluate the monomer purity, test polymerizations were conducted in bulk at room temperature using 0.1 mol % TBD as the catalyst in the absence of exogenous initiator. The molar mass of the resultant polymer is expected to depend on the concentration of adventitious initiators, which can be roughly estimated via size-exclusion chromatography. For this work, we classified MVL as low purity if polymerization results in PMVL with $M_n < 100$ kg mol^{-1}, moderate purity if $M_n > 100$ kg mol^{-1}, and high purity if $M_n > 200$ kg mol^{-1}. The copper chromite residue after the first distillation has been used in up to four successive reactions without a noticeable decrease in activity. ^{1}H NMR (500 MHz, $CDCl_3$; 25 °C): δ 4.40 [m, $-OCH_2CH_2-$, 1H], 4.25 [m, $-OCH_2CH_2-$, 1H], 2.66 [m, $-COCH_2CH(CH_3)-$, 1H], 2.20 [m, $-COCH_2CH(CH_3)-$, 1H], 2.03−2.13 [m, $COCH_2CH(CH_3)CH_2-$ and $-COCH_2CH(CH_3)-$, 2H], 1.9 [m, $-CH(CH_3)CH_2CH_2O$, 1H], 1.55 [m, $-CH(CH_3)CH_2CH_2-$, 1H], 1.05 [d, $-CH_2CH(CH_3)CH_2-$, 3H].

Synthesis of a Cyclic Carbonate Cross-Linked PMVL (CC). Under a nitrogen atmosphere, MVL (7.00 g, 61.4 mmol, high purity) was charged in a 20 mL scintillation vial along with varying amounts of B6CC (46−371 mg, 0.15−1.23 mmol, 0.25−2 mol % to MVL) and 1,4-benzenedimethanol (BDM; 0−19 mg, 0−0.14 mmol). The mixture was stirred until completely homogeneous, and then a solution of TBD in DCM (100 mg/mL, 85 μL solution, TBD = 0.1 mol % relative to MVL) was injected using a gastight syringe. The polymerization solution was allowed to stir for ca. 10 s and then poured into a Pyrex Petri dish (inner diameter = 90 mm). The contents of the Petri dish were allowed to cure overnight at room temperature under nitrogen (ca. 20 h) to ensure maximum conversion. The resulting elastomer was then removed from the dish, and a 1 M solution of acetic anhydride and triethylamine in DCM (0.35−1.40 mL, ca. 5 equiv relative to hydroxyl moieties or TBD if no BDM was used) was dripped over the top of the film via a syringe. The elastomer was allowed to sit in air for another 20 h and then placed in an oven under reduced pressure at 80−90 °C for 48 h to remove DCM, acetic anhydride, triethylamine, and residual MVL monomer. This process afforded a clear, colorless, and odorless cross-linked PMVL film (88−91% mass yield). Samples prepared using this method are named CC-*X*-*Y*, where *X* and *Y* represent mol % B6CC and theoretical molar mass (kg mol^{-1}) if no cross-linking were to occur, respectively. For example, a sample with 1.00 mol % B6CC and a theoretical molar mass of 100 kg mol^{-1} based on the amount of BDM added (assuming 100% monomer conversion and no cross-linker added) would be denoted CC-1.00-100.

Synthesis of a MVL Homopolymer. Under a nitrogen atmosphere, MVL (100.00 g, 875 mmol, moderate purity) was charged in a 1-L round-bottomed flask with a Teflon-coated magnetic stir bar. A solution of TBD in DCM (1.22 mL, 100 mg of TBD/mL of DCM, 0.1 mol % TBD to MVL) was added to the monomer; then the flask was sealed with a rubber septum, and the mixture was stirred for 16 h. Following this, a 1 M benzoic acid solution in DCM was added (9 mL, 10 equiv of benzoic acid to TBD), and the polymer solution was diluted with additional DCM to ca. 500 mL. Once the polymer was fully dissolved, the solution was precipitated into methanol (5 L) and then dried over a stream of nitrogen for 2 days, dried under vacuum at room temperature for 3 days, and finally dried in an oven under reduced pressure at 60−70 °C for 2 days. The resulting PMVL was highly viscous, clear, and colorless (85−88% yield). ^{1}H NMR (500 MHz, $CDCl_3$; 25 °C): δ 4.13 [m, $-OCH_2CH_2-$, 2H], 2.34 [m, $-COCH_2CH(CH_3)-$, 1H], 2.20 [m, $-COCH_2CH(CH_3)-$, 1H], 2.10 [m, $-CH_2CH(CH_3)$-CH_2-, 1H] 1.72 [m, $-CH(CH_3)CH_2CH_2-$, 1H], 1.55 [m, $-CH(CH_3)CH_2CH_2-$, 1H], 1.00 [d, $-CH_2CH(CH_3)CH_2-$, 3H]. RI-SEC ($CHCl_3$): M_n = 162 kg mol^{-1}, $Đ$ = 1.29. DSC: T_g = −52 °C. TGA: T_d (5% mass loss, air) = 240 °C.

Production of Peroxide Cross-Linked PMVL (PC) and PC−FS Composities. PMVL homopolymer (2.00 g) and benzoyl peroxide (BPO; 20−100 mg, 1−5 wt %) were loaded into a twin-screw extruder (DSM Xplore 5 mL micro compounder; Geleen, The Netherlands) at 70 °C (10 h half-life for BPO) and allowed to mix for 10 min before a grayish-yellow material (ca. 80% recovery) was extruded. Composites were also prepared with 10, 20, or 30 wt % FS fed into the extruder (2 wt % BPO relative to PMVL was used for all composites), yielding a colorless and translucent material. The homogeneous polymer mixture was placed in a 5 cm (W) × 5 cm (L) × 0.05 cm (T) aluminum mold that was placed between two 12 cm × 12 cm aluminum plates with a thin Teflon sheet (0.05 mm thick) over each plate. This was then placed in a press mold (Wabash MPI, Wabash, IN) at 150 °C and 3 tons of pressure for 10 min and rapidly cooled to room temperature over 5 min, affording a translucent, grayish-yellow elastomer. In the presence of FS, the materials appeared colorless and translucent. Samples are named PC-Z-FSQ, where Z represents the wt % BPO relative to PMVL and Q represents the wt % FS fed into the extruder. For instance, a sample with 1 wt % BPO and 0 wt % FS would be denoted as PC-1.0-FS0.

Depolymerization of CC-0.50-100 or PC-2.0-FS0. CC-0.50-100 or PC-2.0-FS0 (ca. 1.00 g cut into small pieces), stannous octoate (1 drop, ca. 20 mg), and pentaerythritol ethoxylate (1 drop, ca. 20 mg, M_n = 797 g mol^{-1}) were placed in a 10 mL round-bottomed flask equipped with a simple vacuum distillation apparatus. The mixture was heated to 150 °C overnight at 1 Torr, yielding a clear and colorless liquid (91% recovery for CC-0.50-100 and 93% for PC-2.0-FS0 after mass correction for the cross-linker was performed). The ^{1}H NMR spectrum of the distillate was identical with that of pure MVL (Figure S13).

Characterization Methods.[6] ^{1}H NMR spectroscopy was performed on a 500 MHz Bruker Avance III HD with SampleXpress spectrometer (Billerica, MA). Solutions were prepared in 99.8% $CDCl_3$ (Cambridge Isotope Laboratories). All spectra were acquired at 20 °C with 64 scans and a 2 s delay. Chemical shifts are reported in ppm with respect to $CHCl_3$ (7.26 ppm).

Uniaxial tensile testing and hysteresis measurements were conducted using dogbone-shaped tensile bars [ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 14 mm for PC samples or 0.5 mm (T) × 5 mm × 38 mm (L) and a gauge length of 22 mm for CC samples]. The samples were aged for 48 h at 25 °C in a desiccator prior to testing. Tensile measurements were performed on a Shimadzu Autograph AGS-X series tensile tester (Columbia, MD) at 25 °C with a uniaxial extension rate of 50 mm min^{-1}. Young's modulus (E) values were calculated using the *Trapezium* software by taking the slope of the stress−strain curve from 0 to 10% strain. Reported values are the average and standard deviations of five replicates from the same sample. A total of 20 cycles were performed during hysteresis measurements to 67% strain at 50 mm min^{-1}, and the energy loss was calculated by subtracting the area under the curve of the contraction from the area under the curve of the extension in each cycle. The residual strain was taken as the point at which the return cycle reached its minimum stress. All graphical representations of hysteresis data were smoothed using a 100-point adjacent-averaging smoothing function in *Origin* data analysis software in order to remove noise.

Dynamic mechanical thermal analysis (DMTA) was performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) using dogbone-shaped films [ca. 0.5 mm (T) × 3 mm (W) × 25 mm (L) and a gauge length of 14 mm]. DMTA experiments were conducted in tension film mode, where the axial force was first adjusted to 0.2 N of tension (sensitivity of 0.01 N) to ensure no buckling of the sample. The proportional force mode was set to force tracking to ensure that the axial force was at least 100% greater than the dynamic oscillatory force. The strain adjust was then set to 30% with a minimum strain of 0.05%, a maximum strain of 5%, and a maximum force of 0.2 N in order to prevent the sample from going out of the specified strain range. A temperature ramp was then performed from −70 to +200 °C at a rate of 5 °C min^{-1}, with an oscillating strain of 0.05% and an angular frequency of 6.28 rad s^{-1}. T_g was calculated from the maximum value of the loss modulus. The effective molar mass between cross-links ($M_{x,eff}$), which consists of contributions from cross-links and entanglements, was calculated using the storage modulus (E') at 25 °C and eq 1

$$E'(T) = 3G'(T) = 3RT\nu_e = \frac{3\rho RT}{M_{x,eff}} \quad (1)$$

where E' and G' are the storage and shear moduli, respectively, R is the universal gas constant, T refers to the absolute temperature in the rubbery region (ca. 298 K), ν_e is the cross-link density, and ρ is the density of PMVL[17] (ca. 1.1 g cm^{-3}).

Differential scanning calorimetry (DSC) was conducted on a TA Instruments Discovery differential scanning calorimeter (New Castle, DE). The instrument was calibrated using an indium standard. All samples were prepared using T-Zero hermetic pans (ca. 5 mg) under a N_2 purge of 50 mL min^{-1}. The samples were initially cooled to −80 °C and then heated to 100 °C at 10 °C min^{-1}. The samples were then cooled back to −80 °C at 10 °C min^{-1} and heated again to 100 °C at the same rate. Values for T_g were acquired at the midpoint of each transition in the second heating curve using the *Trios* software. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 analyzer (New Castle, DE) under air at a heating rate of 10 °C min^{-1} to 550 °C. A typical sample size was between 8 and 15 mg.

Solvent-extraction experiments were performed by placing a small amount of sample (ca. 20−100 mg) into a 20-mL vial filled with DCM. The vial was then closed and stirred for 48 h before removal of the solvent by gravity filtration. The recovered sample was dried under reduced pressure for 48 h at 20 mTorr, after which the sample was weighed and the gel percent was determined.

Hydrolytic degradation of the elastomers was investigated in accelerated conditions using 1 M aqueous solutions of NaOH or HCl at 60 °C as well as in biologically relevant conditions using an aqueous phosphate-buffered saline (PBS; pH = 7.4) solution at 37 °C. Nine replicates of each CP sample were prepared (50 mg each). The replicates were immersed in triplicate in the aforementioned aqueous solutions in separate 20 mL scintillation vials and heated to their respective temperatures. The insoluble mass was recorded after removal of each sample from the solution and patting it dry with a Kimwipe, after which the sample was reimmersed in the same solution. Solutions were checked weekly with litmus paper to ensure that their pH remained stable; none of the solutions showed pH variance by this method. The data presented in the plots of insoluble mass % (percentage of original mass) over time include the averages and standard deviations of the triplicate samples in their respective media.

Refractive index size-exclusion chromatography (RI-SEC) was performed on an HP/Agilent 1100 series size-exclusion chromatograph at 35 °C using three successive PLgel Mixed C columns and a PLgel 5 μm guard column with an HP 1047A RI detector (Santa Clara, CA). $CHCl_3$ was used as the mobile phase with an elution rate of 1 mL min^{-1}. M_n and $Đ$ were determined based on a 10-point calibration curve using EasiCal polystyrene standards purchased from Agilent.

■ RESULTS AND DISCUSSION

We first investigated PMVL elastomers synthesized using a tandem methodology (Scheme 1A). A bis(six-membered cyclic carbonate) was chosen as a cross-linker because of its high solubility in neat MVL and also because it was anticipated that MVL and B6CC would have similar reactivity. The equilibrium monomer concentration of MVL is 90% at room temperature; thus, we removed the residual monomer postpolymerization and prior to testing the material properties.[17]

Table 1. Tandem Cross-Linking of PMVL with B6CC

CC-*X*-*Y*[a]	mass recovery (%)[b]	gel %[c]	E' at 25 °C (MPa)[c]	$M_{x,\text{eff}}$ (kg mol^{-1})[c,d]	$M_{x,\text{theo}}$ (kg mol^{-1})[c,e]	$T_{g,\text{DMTA}}$ (°C)[c,f]	$T_{g,\text{DSC}}$ (°C)[c,h]	T_d (°C)[c,i]
CC-0.25-100	88	89	1.2	6.8	40	−49	−48	274
CC-0.50-100	91	95	1.8	4.5	21	−48	−48	262
CC-0.75-100	89	98	1.9	4.3	13	−48	−47	266
CC-1.0-100	89	99	2.1	3.9	10	−48	−48	269
CC-2.0-100	89	100	2.7	3.0	5.1	−47	−46	269
CC-1.0-NI[g]	76	98	2.8	2.9	10	−47	−47	268
CC-1.0-50	88	97	1.8	4.5	10	−48	−47	262
CC-1.0-75	89	96	1.6	5.1	10	−48	−47	263
CC-1.0-150	89	99	2.2	3.7	10	−48	−47	266
CC-1.0-200	89	100	1.7	4.8	10	−48	−47	262

[a] X = mol % B6CC to MVL and Y = theoretical M_n (kg mol^{-1}) assuming no cross-linker was added and 100% monomer conversion. [b] Recovery of mass after heating in a vacuum oven for 48 h at 80 °C. [c] Determined after removal of residual monomer. [d] Determined using E' from DMTA in eq 1. [e] Calculated by dividing the mass of the polymer recovered by the moles of B6CC and assuming no contribution from entanglements. [f] Calculated from the maximum of the loss modulus. [g] NI stands for no initiator; M_n in the presence of no B6CC with high-purity monomer is >200 kg mol^{-1} relative to polystyrene standards in RI-SEC with $CHCl_3$ as the mobile phase. [h] Taken on the second heating ramp at a rate of 10 °C min^{-1}. [i] Taken under air, defined as the temperature at which 5% mass loss is observed.

Because PMVL is able to depolymerize in the presence of a catalyst, we scanned a variety of methodologies to deactivate TBD so that any residual monomer could be removed under reduced pressure and the material could operate at elevated temperatures without uncontrollable depolymerization. Guanidine-based organocatalysts are most commonly deactivated using a large excess of benzoic acid, yet we observed that excess benzoic acid sublimed under vacuum and that the films depolymerized in these conditions. We posit that there remained an acid adduct of TBD that was capable of depolymerizing PMVL because similar acid adducts of organocatalysts are capable of transesterification.[47] Additionally, deactivation of TBD through exposure to air generally took up to 2 weeks at ambient conditions, suggesting that diffusion of oxygen and carbon dioxide into the polymer is slow.

Therefore, we developed a method to convert the hydroxyl end groups of PMVL to acetate groups; we suspected that acetylation chemistries would also deactivate the residual TBD. To accomplish this, we applied a solution of acetic anhydride and triethylamine in DCM (5 equiv with respect to hydroxyl moieties or TBD if no added initiator was added) to the surface of the film. After the solution was allowed to diffuse through the film for 20 h, we subjected the material to reduced pressure to remove residual monomer. We found that this could be accomplished with mild heating (80−90 °C) without significant depolymerization. We observed that this end-capping strategy also increased the decomposition temperature (T_d) of the polymers by 10−15 °C compared with that of CC samples, in which we deactivated TBD with 2 weeks of air exposure. The significant increase in the T_d can be attributed to the lack of hydroxyl groups, which are required for depolymerization of PMVL to occur via an "unzipping" mechanism. The amount of cross-linker did not appear to affect the mass recovery after excess monomer removal, nor was there a significant difference in their T_ds. On the other hand, the yield of an elastomer produced with no initiator was significantly lower (76%), likely because of a slower polymerization rate; if polymerization had been allowed to proceed, higher conversion would be likely. This indicates that some initiator is necessary to attain high monomer conversion in a reasonable period of time.

Once the monomer removal protocol was established, two sets of CC samples were investigated. At a fixed ratio of MVL to added BDM initiator (specifically, 876:1), we first varied the concentration of B6CC from 0.25 to 2.0 mol % relative to MVL. All of the materials with B6CC concentrations greater than or equal to 0.25 mol % gelled within 10 min. To ensure that conversion of MVL monomer reached equilibrium, the films were allowed to cure overnight (ca. 20 h). After monomer removal, extraction experiments revealed high gel percentages that increased slightly with the cross-linker content (Table 1). Next, we fixed the ratio of MVL to B6CC (specifically at 100:1) and varied the amount of added initiator. No clear trend in the gel percentage was observed when the concentration of the initiator was varied. Furthermore, the T_g of all of the materials was between −47 and −49 °C compared to −52 °C for PMVL homopolymer; this observation suggests that the molecular structure and amount of cross-linker did not significantly contribute to the thermal properties of the material. These results are summarized in Table 1.

With the materials in hand, we sought to determine their tensile properties and compare them to those of a conventional elastomer, specifically vulcanized natural rubber (generic rubber band, Universal, Deerfield, IL). Remarkably, both CC-0.25-100 and CC-0.50-100 exhibited significantly higher tensile strength and elongation than rubber bands as well as a substantial strain hardening effect (Figure 1A). Interestingly, both CC-0.75-100 and CC-1.00-100 showed uniaxial extension properties very similar to those of a rubber band, although their tensile strength drops significantly compared to the samples with lower cross-linker content. A second batch of analogous materials exhibited nearly identical properties, indicating that this behavior is reproducible. As expected, increasing the amount of cross-linker resulted in a reduction of the strain at break while slightly increasing Young's modulus. However, there was no clear correlation between the cross-linker content and ultimate tensile strength. Cross-linked rubbers often show a maximum in the tensile strengths at intermediate cross-link densities, which would initially explain this trend.[48] However, the increase in the tensile strength for CC-2.0-100 does not correlate, suggesting that other undeterminable factors may be involved. Data summarizing the mechanical characteristics as a function of the cross-linker content are available in the Supporting Information (Figure S5).

Hysteresis experiments revealed that the energy loss and residual strain per cycle decreased monotonically with the B6CC content, with the sample containing 2.0 mol % B6CC

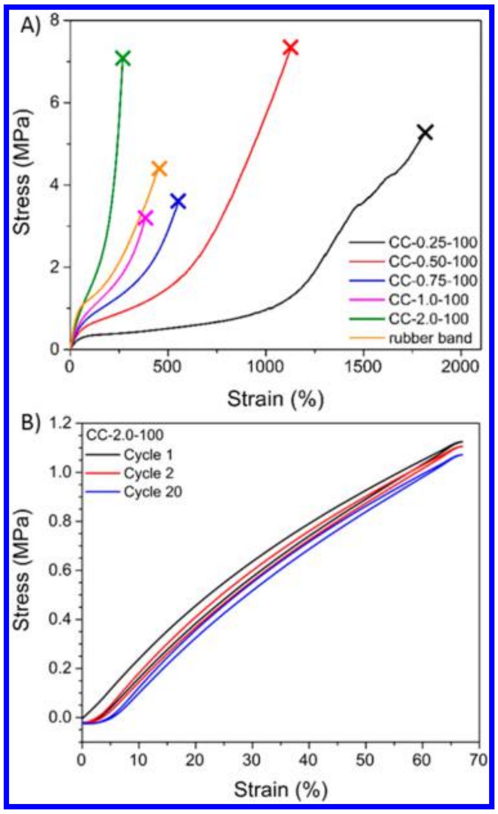


Figure 1. (A) Representative tensile data for CC elastomers cross-linked with varying amounts of B6CC and keeping BDM constant. (B) Representative hysteresis data for a cross-linked elastomer (CC-1.0-100). See Table S1 and Figure S5 for more information.

exhibiting the least amount of hysteresis loss over 20 cycles (Figures 1B and S9 and Table S3). The results obtained via DMTA indicated a similar trend in the stiffness of the elastomers; samples with more cross-linker exhibited a higher plateau modulus (Figure S1A). Samples with the least amount of cross-linker displayed a slightly negative sloping plateau modulus at temperatures above the T_g. This effect is likely due to dangling chain ends because this phenomenon has been seen previously in materials with high levels of this network defect.[49] The effective molar mass between cross-links ($M_{x,eff}$) of the materials was much lower than expected (Table 1); because M_e of linear PMVL is 4.3 kg mol^{-1}, this result is likely due to inherent entanglements contributing to $M_{x,eff}$.[50] Therefore, it is also possible that relaxation of the transient entanglements within the network is also contributing to the negatively sloping modulus exhibited by samples with low cross-linker content.

We next tested the set of materials prepared at fixed B6CC content with varying amounts of initiator (indicated in the bottom half of Table 1). Uniaxial extension tests revealed that increasing the amount of initiator caused the material to lose significant toughness (Figures 2 and S6), although no significant change in the hysteresis loss was observed (Figure S10). We hypothesize that the loss of toughness is due to an increase in the network defects from a higher amount of active initiation sites; network defects can cause a significant reduction in the mechanical properties because the applied stress will be localized rather than equally divided among the strands in the network.[30] Furthermore, the absence of an initiator did not produce a more desirable material; thus, the addition of some initiator is preferred to obtain higher mass recovery after monomer removal and high conversion of monomer.

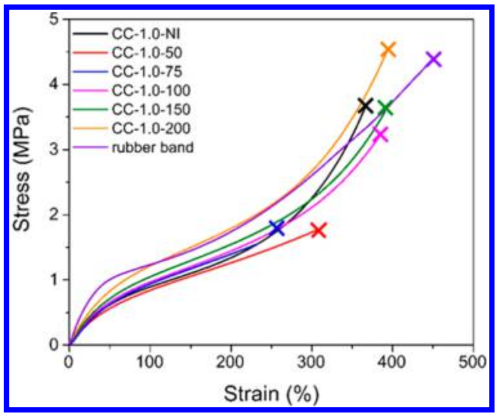


Figure 2. Representative tensile data showing the influence of varying amounts of BDM, while B6CC is kept constant, on the tensile properties. See Table S1 and Figure S6 for more information.

When the impact of reactivity ratio differences is neglected, if the ratio of MVL to BDM is fixed, M_x should increase with a decreasing amount of B6CC in the initial feed because less tetrafunctional junctions will be formed. On the other hand, M_x should not vary significantly if the ratio of MVL to BDM is varied because BDM is difunctional and will not introduce cross-link junctions. Indeed, the plateau modulus and $M_{x,eff}$ increase as the amount of B6CC is decreased, whereas no clear trend is seen when the amount of BDM is varied (Figures S1A and S2B and Table 1).

In addition to the tandem copolymerization/cross-linking strategy, we also explored a sequential approach where linear PMVL homopolymer was synthesized and cross-linked using a free-radical generator (Scheme 1B). This was accomplished by melt-blending linear PMVL with BPO in a twin-screw extruder at 70 °C and curing in a press mold at 150 °C. We fixed the initial molar mass of the PMVL prepolymer (M_n = 162 kg mol^{-1}) and varied the mass percent of BPO in the blend. In some cases, a hydrophobic FS filler, Aerosil R 812, was also added. The characteristics of these samples and blends are summarized in Table 2.

To our knowledge, the exact mechanism by which saturated polyesters cross-link in the presence of radicals has not been studied. Hermans and Eyk suggest that the reaction of cyclohexane with BPO produces carbon radicals capable of a variety of reactions, most commonly resulting in dimers and other oligomers.[51] The tertiary carbon atom within the backbone of PMVL is the most stable position for carbon radicals, and thus we assume that the longer-lived radicals at the tertiary carbon atoms allow for a more efficient reaction than those at the methylene units along the backbone. Indeed, the PC elastomers exhibited higher gel fractions compared to PCL cross-linked with BPO, which contains no tertiary carbon atoms.[41]

The reaction of PMVL with BPO did not afford a high degree of cross-linking at 0.1 and 0.5 wt % BPO. PC elastomers prepared with 2 and 3 wt % BPO exhibited very desirable tensile properties (Figures 2 and S7 and Table 2) and outperformed all CC samples. At BPO loadings of 4 and 5 wt %, the materials began to drastically lose toughness, exhibiting significant decreases in the tensile strength and elongation; furthermore, these samples no longer exhibited significant strain hardening. Indeed, this phenomenon has

Table 2. Postpolymerization/Cross-Linking of PMVL with BPO

PC-Z-FSQ[a]	gel %	FS (%)	E' at 25 °C (MPa)	$M_{x,eff}$ (kg mol^{-1})[b]	$T_{g,DMTA}$ (°C)[c]	$T_{g,DSC}$ (°C)[d]	T_d (°C)[e]
PC-1.0-FS0	76	0	1.4	5.8	−50	−50	264
PC-2.0-FS0	93	0	1.7	4.8	−49	−50	244
PC-3.0-FS0	95	0	1.8	4.5	−50	−49	246
PC-4.0-FS0	96	0	2.1	3.9	−50	−49	242
PC-5.0-FS0	97	0	2.1	3.9	−49	−48	241
PC-2.0-FS10	96	9	2.4	3.4	−49	−50	256
PC-2.0-FS20	95	16	2.9	2.8	−50	−51	259
PC-2.0-FS30	95	25	5.0	1.6	−48	−51	256

[a] Z = wt % BPO with respect to PMVL, and FSQ = wt % FS with respect to PMVL; all samples produced with 162 kg mol^{-1} PMVL relative to polystyrene standards in RI-SEC with $CHCl_3$ as the mobile phase. [b] Calculated using E' from DMTA in eq 1. [c] Determined from the maximum of the loss modulus from DMTA. [d] Taken on the second heating ramp at a rate of 10 °C min^{-1}. [e] Taken under air, defined as the temperature at which 5% mass loss is observed.

previously been observed with vulcanized rubber and has been attributed to variations in the viscoelastic properties of the material rather than a reduction in its inherent strength.[48] However, Smith and Chu posit that no simple correlation can be attributed to this occurrence because the tensile failure depends on a variety of factors.[52] All of the PC samples exhibited a grayish-yellow discoloration. We surmise that the yellow discoloration in the absence of FS is due to a slight oxidative degradation, while the gray discoloration is due to impurities present in the extruder. Indeed, samples prepared by solvent casting in DCM also had a yellow discoloration; however, no gray discoloration was observed. No significant differences in the mechanical or thermal properties were observed between samples prepared by solvent casting and extrusion.

Similar to the CC elastomers, the radically cross-linked materials exhibited higher plateau moduli and better hysteresis recovery when the loading of BPO was increased (Figures S3 and S11). At low BPO loading, we also observe a negatively sloping plateau modulus, similar to that of CC samples with low B6CC loading, which we attributed to dangling chain ends[49] and relaxation of the transient entanglements within the network. The large increase in the tensile strength from CC to PC was not entirely expected. We hypothesize that the difference in the reactivity ratios between MVL and B6CC may have resulted in more network defects and a less uniform distribution of cross-links than that in the PC elastomers. The radicals formed in the production of PC samples should theoretically have an equal probability of reacting with each repeat unit, which would result in a more uniform distribution of cross-links. As previously discussed, an applied force is more evenly dispersed in materials with evenly distributed cross-links than in those with more network defects; as a result, the more uniform materials should be significantly stronger.[30]

In an attempt to further improve the properties of the PMVL elastomers and to reduce the total cost of the elastomer, we prepared composites containing the FS Aerosil R 812.[53] We recently demonstrated that this FS could be homogeneously dispersed in cross-linked hydrogenated polyolefins and also impart dramatic improvements in the mechanical properties.[54] Although we also attempted to produce filler-reinforced materials using the tandem cross-linking strategy, we observed that the TBD catalyst used for the copolymerization reaction was intolerant of the FS. However, we found that FS-reinforced elastomers could easily be prepared using a sequential radical melt-blending route. For all samples, the BPO loading was fixed at 2 wt % with respect to PMVL, and blends containing 10−30 wt % FS were prepared. The TGA data indicated that in all cases the incorporation of FS into the polymer matrix during twin-screw extrusion was slightly lower than the feed amount (Table 2). Because TGA of Aerosil R 812 exhibited no mass loss up to 550 °C, we believe that this minor discrepancy is due to inefficient extrusion rather than FS degradation, loss of water, or volatile small molecules adsorbed to the surface of the filler.

As expected, the mechanical properties of the PC elastomers improved dramatically when blended with FS (Figures 3B and S8 and Table S2). The tensile strengths of the composites were improved by 50−83% relative to the neat elastomer, and the elongation at break remained nearly constant at all filler loadings. Furthermore, Young's modulus increased from 1.4 to 2.2 MPa when 25 wt % FS was incorporated. This significant stiffening effect from the FS was also observed by DMTA; the plateau modulus rose from 1.7 to 5.0 MPa when 25 wt % FS

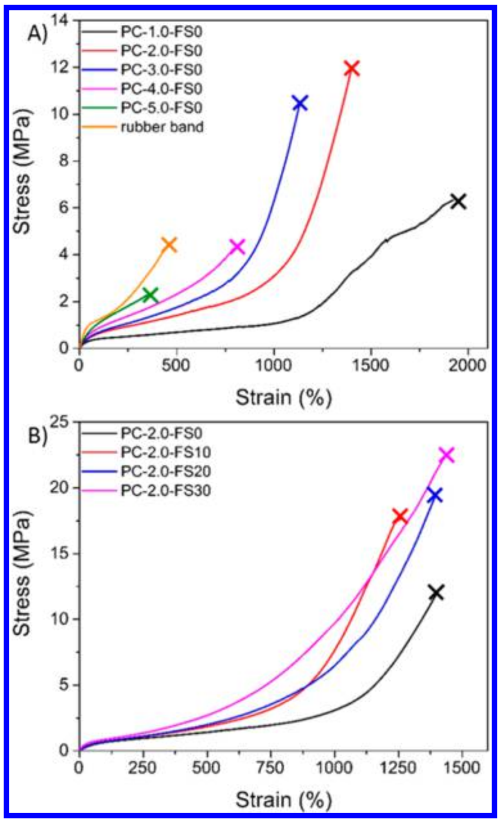


Figure 3. (A) Representative tensile data for PC elastomers and a commercially available generic rubber band. The 1 wt % BPO sample (black line) begins to tear near the grip above 1500% strain, making the observable tensile strength at break lower than its actual value. (B) Tensile data for PC−FS composites prepared with 2 wt % BPO relative to the mass of PMVL. See Table S2 for more information.

was incorporated (Figure S4 and Table S2). As we anticipated, increasing the amount of FS filler also increased the extent of the Mullins effect observed during hysteresis (Figure S12 and Table S3). Even at 9 wt % incorporation of FS, the appearance of the resulting elastomer was colorless and translucent in contrast to the samples in the absence of FS, which were a grayish-yellow color. It is likely that the FS behaves as a white dye in the materials.

To demonstrate the recyclability of the PMVL elastomers, we determined the percentage of monomer that was recoverable via chemical depolymerization of CC-0.50-100 and PC-2.0-FS0. While CC should be easily depolymerizable, the backbones of the PC materials are chemically altered by the radical cross-linking reaction. We were therefore unsure as to whether the covalent linkages formed during the radical reactions would inhibit depolymerization. To facilitate MVL recovery via depolymerization, we added stannous octoate and pentaerythritol ethoxylate (a high-boiling tetraol) to the elastomers and heated them to 150 °C overnight under vacuum. Both CC and PC elastomers were capable of depolymerization. We were able to recover 91% of pure MVL from CC-0.50-100 and 93% from PC-2.0-FS0 (Figure S13).

Finally, we investigated hydrolytic degradation of the elastomers in aqueous media. Samples were placed in PBS (pH = 7.4), 1 M hydrochloric acid, and 1 M sodium hydroxide (Figure 4). The elastomers proved to be resilient to degradation in PBS solutions at physiological conditions (37 °C) and in acidic solutions at room temperature, although PC-2.0-FS0 exhibited slight degradation in the basic solutions at room temperature (Figure 4A). The poor hydrolytic degradability is likely due to the hydrophobic nature of the materials. Increasing the temperature to 60 °C dramatically improved the degradation of the samples in both acid and base (Figure 4B). Because hydrochloric acid can behave as a polymerization catalyst for MVL, it is also capable of depolymerizing PMVL at elevated temperature and, therefore, capable of degrading the samples. We hypothesize that the increased temperature improved penetration of the polar moieties into the network, allowing accelerated basic degradation of PC-2.0-FS0. Interestingly, CC-0.50-100 appeared to be highly resistant to the basic solution, even at 60 °C; this is somewhat counterintuitive given that esters are easily cleaved in the presence of hydroxide ions. The Young's modulus, plateau modulus, and gel content of PC-2.0-FS0 and CCP-0.50-100 are almost identical, suggesting either that the carbonate moieties lend chemical resistance or that peroxide cross-linking may alter the chemical structure of PMVL in a way that leaves it more susceptible to degradation in basic conditions.

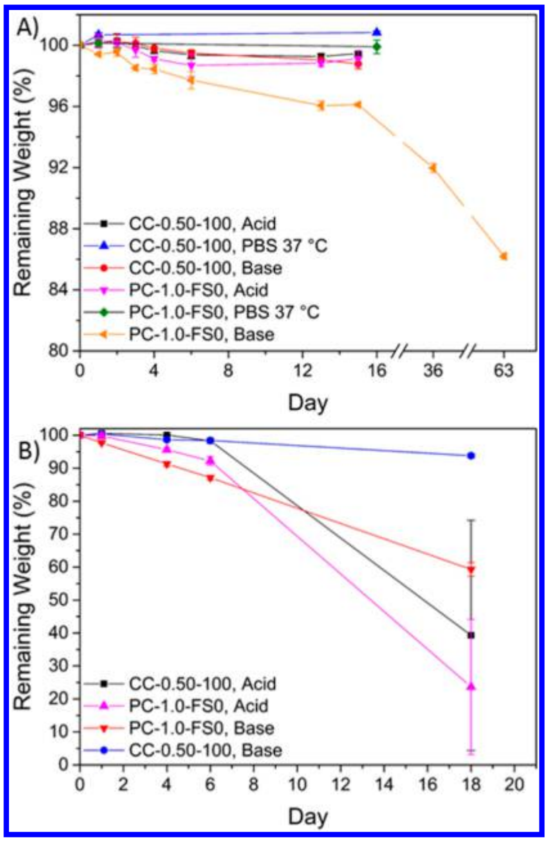


Figure 4. Degradation studies of CC-0.50-100 and PC-2.0-FS0 in aqueous PBS (37 °C), 1 M hydrochloric acid (aqueous), and 1 M sodium hydroxide (aqueous). Samples were studied at (A) room temperature (excluding PBS buffer) and (B) 60 °C. Degradation was not performed in a PBS buffer at 60 °C because we sought to mimic physiological conditions.

■ CONCLUSIONS

We have demonstrated that elastomers with a wide range of mechanical properties can be produced from PMVL. Both tandem and radical cross-linking methodologies can be successfully implemented depending on the desired processing conditions and physical/mechanical properties of the material. The mechanical properties of the reported materials were far superior to similar low-T_g, amorphous polyester elastomers reported in the literature, and the toughness could be improved further by incorporating FS. The Young's modulus and tensile strength were improved by 57% and 83%, respectively, without sacrificing the elongation at break by incorporating up to 25 wt % FS in PC. Furthermore, PC—FS materials were produced with tensile strengths and elongations at break similar to those of synthetically challenging TPEs based on MVL and lactide.[17] The ability to produce tough composite elastomers facilely with PC will greatly improve its viability as a commodity rubber. Moreover, the recyclability of CC and PC was successfully demonstrated because they were both able to depolymerize in the presence of catalyst to provide up to 93% recovery of MVL. Finally, both polymers showed the ability to degrade under acidic conditions at 60 °C, while only PC was capable of degradation in basic conditions; this apparent degradation is promising toward the sustainability of these materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b02931.

DMTA, TGA, DSC, and hysteresis data (PDF)

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Notes

The authors declare the following competing financial interest(s): Marc A. Hillmyer has equity and royalty interests in, and serves as secretary and on the Board of Directors of Valerian materials, a company involved in the commercialization of MVL. The University of Minnesota also has equity and royalty interests in Valerian Materials. These interests have been reviewed and managed by the University of Minnesota in accordance with its Conflict of Interest policies. The other authors declare no competing financial interest.

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■ ABBREVIATIONS

B6CC = oxybis(methylene)bis(5-ethyl-1,3-dioxan-2-one)
BDM = benzenedimethanol
BPO = benzoyl peroxide
CC = cyclic carbonate cross-linked poly(β-methyl-δ-valerolactone)
CL = ε-caprolactone
CPs = cross-linked polymers
DMTA = dynamic mechanical thermal analysis
DSC = differential scanning calorimetry
E = Young’s modulus
E' = storage modulus
FS = fumed silica
G' = shear modulus
M_e = molar mass between entanglements
M_n = number-average molar mass
MVL = β-methyl-δ-valerolactone
M_x = molar mass between cross-links
$M_{x,eff}$ = effective molar mass between cross-links
$M_{x,theo}$ = theoretical molar mass between cross-links
PC = peroxide cross-linked poly(β-methyl-δ-valerolactone)
PC–FS = peroxide cross-linked poly(β-methyl-δ-valerolactone) fumed-silica composites
PCL = poly(ε-caprolactone)
PLA = poly(lactide)
PMVL = poly(β-methyl-δ-valerolactone)
Q = wt % fumed silica relative to polymer
RI-SEC = refractive index size-exclusion chromatography
ROTEP = ring-opening transesterification polymerization
TBD = 1,5,7-triazabicyclodec-5-ene
T_d = 5% decomposition temperature
T_g = glass transition temperature
TGA = thermogravimetric analysis
TPEs = thermoplastic elastomers
X = mol % oxybis(methylene)bis(5-ethyl-1,3-dioxan-2-one)
Y = theoretical molar mass of polymer based on the initiator added and no cross-linker added
Z = wt % benzoyl peroxide relative to polymer
ν_e = cross-link density

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