One-Pot Synthesis of Depolymerizable δ-Lactone Based Vitrimers

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A depolymerizable vitrimer that allows both reprocessability and monomer recovery by a simple and scalable one-pot two-step synthesis of vitrimers from cyclic lactones is reported. Biobased δ-valerolactone with alkyl substituents (δ-lactone) has low ceiling temperature; thus, their ring-opening-polymerized aliphatic polyesters are capable of depolymerizing back to monomers. In this work, the amorphous poly(δ-lactone) is solidified into an elastomer (i.e., δ-lactone vitrimer) by a vinyl ether cross-linker with dynamic acetal linkages, giving the merits of reprocessing and healing. Thermolysis of the bulk δ-lactone vitrimer at 200 °C can recover 85–90 wt% of the material, allowing reuse without losing value and achieving a successful closed-loop life cycle. It further demonstrates that the new vitrimer has excellent properties, with the potential to serve as a biobased and sustainable replacement of conventional soft elastomers for various applications such as lenses, mold materials, soft robots, and microfluidic devices.

1. Introduction

Petroleum-derived synthetic polymers are one of the most important technological advancements in recent human history and have become increasingly dominant in modern industry, bringing enormous benefits to our life quality. However, the excessive use of these plastics also leads to increasing concerns about our environment and sustainability.[1–3] Massive non-degradable and non-recyclable plastic waste now creates severe pollution both on land and in the oceans, and extensive efforts have been made to mitigate the environmental impact.[1,4] New innovations in polymer science are urgently needed to create renewable, degradable alternatives with the competing performance of existing non-recyclable polymers.[5,6]

Covalent adaptable network polymers, or vitrimers, have recently emerged as potential sustainable replacements for conventional thermosets.[7,8] Vitrimers have cross-linked networks with dynamic covalent linkages that enable thermal malleability and reprocessability while maintaining the integrity of the cross-linked network.[9–20] However, just like thermoplastic reprocessing, performance deterioration is unavoidable after multiple cycles of reprocessing due to chain scission, degradation, and oxidation.[21–24] Depolymerizing the vitrimer back to the original feedstocks could be an attractive strategy to enable the "monomer–polymer–monomer" closed-loop cycle, but it is challenging to achieve. In some instances, vitrimers have been shown to degrade into oligomers and small molecules. Still, these examples often involve harsh conditions, poor monomer recovery selectivity, and tedious separation processing before reusing, which could diminish the value of end-of-life vitrimers.[25–31] For these reasons, exploiting vitrimers that can directly depolymerize to reusable constituent monomers under mild conditions is appealing.

One pathway to achieve efficient depolymerization is to use monomers with low to moderate ceiling temperatures. Ceiling temperature (T_c) is a thermodynamic concept and is defined as the temperature where the rates of polymerization and depolymerization are equal. Above T_c, the polymer displays a tendency to depolymerize.[32–34] Many aliphatic polyesters from ring-opening transesterification polymerization (ROTP) of cyclic lactones have been reported to possess low ceiling

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temperatures.[35,36] Bulk ROTP of lactone monomers is a well-studied reaction to synthesize aliphatic polyesters. It is atom economical and solvent-free, and can be performed at room temperature or below, thereby reducing energy consumption compared with most other petroleum-based polymer feedstocks. It also has very well-controlled polymerization in which the molecular architecture and molecular weight can be easily adjusted by altering the initiator type and its ratio to the monomers.

Cyclic lactones widely exist in nature, and many have five (γ)- or six-membered (δ) rings. These bio-derived lactones are often used in the food and fragrance industry as additives due to their pleasant aroma. Additionally, these ring sizes generate polymers that are capable of depolymerizing to pristine monomers under mild conditions. Several alkyl substituted δ-valerolactone (δ-lactones) monomers have been reported as ROTP monomers, presenting ceiling temperature between 100 and 200 °C, a preferable depolymerization temperature range that satisfies the application at ambient conditions while enabling depolymerizing in a relatively low temperature.[35] However, unlike semicrystalline polycaprolactone, racemic poly(δ-lactone)s are amorphous viscous liquids with high flexibility due to the substituted alkyl side chain.[37,38] Therefore, they can only be used as soft polyester segment precursors to prepare block polymers or polyurethanes.[39–42] With different non-depolymerizable compositions added, those reported soft elastomers have limited depolymerizability.

To leverage the advantages of the reprocessability of vitrimers and depolymerizability of poly(δ-lactone), we anticipated that a depolymerizable vitrimer could be achieved if a dynamic linkage can be used to cross-link the otherwise viscous liquid-like poly(δ-lactone). Depolymerization of low-ceiling-temperature poly(δ-lactone) relies on the backbite of hydroxyl groups. Linkages or cross-linking at the hydroxyl site significantly inhibit such depolymerization reactions and increase stability. Here, we present the use of degradable acetal linkages to cross-link poly(δ-lactone). The acetal group is a pH-responsive group that is highly stable under neutral and basic conditions at room temperature, but rapidly hydrolyzes into aldehyde and alcohol under mild acidic conditions or elevated temperatures. The recovered hydroxyl groups then facilitate the depolymerization to monomer of the poly(δ-lactone). Through the proposed strategy, we have developed acetal cross-linked δ-lactone vitrimers in this work, which possess the dynamic properties of vitrimers while also being able to be depolymerized under mild conditions with a high recycling to monomer ratio. These vitrimers have excellent mechanical and optical properties and can be reprocessed, recycled, and depolymerized to recover virgin-quality monomers for reuse, achieving closed-loop life cycles. In addition to their sustainability benefits, the δ-lactone vitrimers have the potential to serve as a sustainable replacement for silicones or polydimethylsiloxane (PDMS), which are widely used in lenses, soft mold materials, soft robotics, and microfluidic devices but are not recyclable.

The inherent degradability of aliphatic polyesters from alkyl-substituted δ-lactone was utilized to cross-link with divinyl ether via a "click" reaction between hydroxyl and vinyl in a one-pot synthesis (as shown in **Figure 1**). Dynamic metathesis of acetals[43,44] is a thermally responsive exchange reaction but is not commonly used in vitrimer design due to hydrolytic degradation. To overcome this limitation, we exploited an organobase as a stabilizer to suppress hydrolysis, which significantly increases the stability of acetal linkages under ambient conditions while still permitting cleavage at elevated temperatures to recover the hydroxyl groups. Ultimately, 85–90 wt% of the δ-lactone vitrimers can be depolymerized into high-purity monomers for reuse. The proposed polymer design thus opens a new route to develop sustainable alternatives for a wide range of soft material applications.

2. Results and Discussion

2.1. Synthetic Chemistries for Degradable Pδ Vitrimers

In this work, the degradable poly(δ-lactone) (Pδ) vitrimer was synthesized in a simple one-pot, two-step procedure as illustrated in Figure 1a. First, glycerol was employed as an initiator to produce the 3-arm Pδ triol, resulting in a viscous polymer liquid. Second, a divinyl ether (1,4-Cyclohexanedimethanol divinyl ether) was added directly to cross-link the Pδ triol. The properties of the Pδ triols are summarized in Table S1 (Supporting Information). All feedstocks were completely utilized in the reaction without any byproduct. The final resultant thermoset Pδ vitrimer enabled thermal depolymerization under mild condition ($\approx$200 °C).

The organocatalyst diphenyl phosphate (DPP) is an efficient acid catalyst for controlled ROTP of δ-lactone, and we found it can also effectively catalyze the click reaction between vinyl ethers and alcohols, as demonstrated with the model reactions (details in, Reaction 1–2, Figures S1–S3, Supporting Information). Thus, the ROTP synthesized Pδ can be used directly for cross-linking without any post-treatment. The divinyl ether cross-linker was then added into Pδ in a certain molar ratio respective to the hydroxyl groups. The reaction was confirmed by FTIR spectra (Figure S4, Supporting Information). The characteristic peak intensity of O–H stretch at $\approx$3400 cm^{-1} gradually decreased with increasing cross-linker quantity, along with the characteristic C=C stretch at $\approx$1608 cm^{-1}, indicating the successful reaction between the Pδ and the divinyl ether. With excess cross-linker, the extra vinyl ether tended to homopolymerize,[45] which turned the sample from colorless to light yellow, as shown in Figure 1a. To avoid this side reaction, a slight stoichiometric excess of alcohol ($r = 0.9$ vinyl group: hydroxyl group in molar ratio) was employed, and the obtained sample was colorless and highly transparent. Moreover, the remaining unreacted hydroxyl moieties can facilitate the depolymerizability of Pδ. The gel fraction after the swelling test with acetone (detail in Supporting Information) is directly indicative of the cross-linked network. All tested samples with the above stoichiometric ratio possessed high gel content ranging from 92% to 95%.

Figure 1b illustrates the overall synthetic route for Pδ vitrimers. Three different δ-lactone monomers with alkyl substituent lengths 1 (δ1), 4(δ4), and 7(δ7) were compared. The Pδ vitrimer network was formed through the aforementioned one-pot, two-step reaction sequence, and the curing was efficient under a nitrogen atmosphere. The synthesized Pδ vitrimers were labeled as v-δ1, v-δ4, and v-δ7 according to their respective lactone monomers. It is noted that the dynamic metathesis of acetals[43,44] is a thermally responsive exchange reaction. Although several acetal-based vitrimer polymers were recently reported,[46,47] they are still not commonly used due to the instability of hydrolytic degradation of acetal linkages under ambient conditions.[48] As
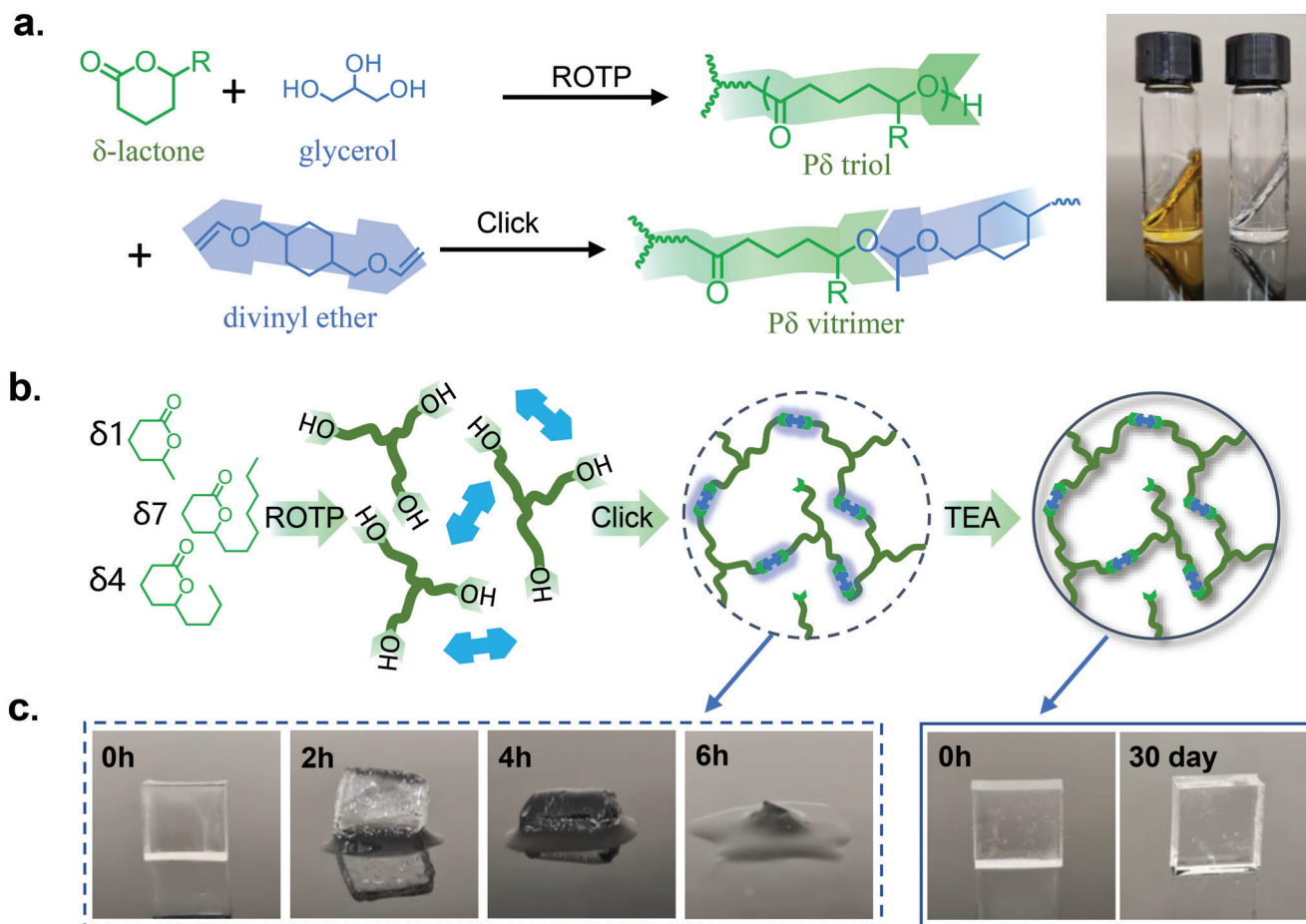
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Figure 1. Schematic illustration of Pδ vitrimer synthesis. a) The chemistry for Pδ and Pδ vitrimer synthesis, and the cured v-δ1 with excessed vinyl ether (light yellow) or hydroxyl (transparent). b) Schematic illustration of Pδ vitrimer from monomers to cross-linked network. c) Hydrolytic degradation of v-δ1 without and with post-treatment; the post-treated sample was stable after 30 days in the air.

shown in Figure 1c, the cured Pδ vitrimer degraded back to Pδ within 6 h. FTIR results confirmed the —OH peak was recovered after the hydrolysis of acetal linkage (Figure S5, Supporting Information). To address this issue, a soaking procedure was developed in the presence of triethylamine (TEA) to suppress hydrolysis. The organic weak base can neutralize the acid catalyst DPP to form a stable triethylamine salt (Figure S6, Supporting Information). Simply soaking the cured Pδ vitrimers in 1 wt% TEA in isopropyl alcohol (IPA) solution effectively preserved them from hydrolysis of acetal groups. The treated Pδ vitrimers were stable for more than one month without degradation in an open air condition with a humility of ≈14–16%.

2.2. Thermal and Mechanical Properties of Pδ Vitrimers

PDMS is one of the most used soft elastomers but is non-recyclable. Here, we evaluated the properties of synthesized Pδ vitrimers to validate the potential to be used as a sustainable substitute of PDMS. Since the alkyl substituent length could affect the thermomechanical and depolymerization behaviors of the Pδ vitrimers, the influence of their side chain lengths on

these properties was investigated. Dynamic mechanical analysis (DMA) results of the Pδ vitrimers displayed typical thermoset behaviors with a plateau of storage modulus above the glass transition temperature (T_g), as shown in **Figure 2**a. Increasing the side chain length resulted in lower T_g and lower storage modulus. The cross-linking densities were also quantitatively confirmed from the storage modulus at the rubbery plateau region, indicating that longer side chains impart lower cross-link density. The rigidity of their chain segment generally determined T_g of cross-linked polymers. Owing to the amorphous and flexible Pδ, the Pδ vitrimers possessed T_g below 0 °C as shown by the tan δ peaks in Figure 2a. Longer side chains decreased the T_g of cross-linked Pδ vitrimers, consistent with the T_g of linear Pδ counterparts (as shown in Figures S7-S9, Supporting Information). The T_g measured from differential scanning calorimetry (DSC) presented the same trend as shown in Figure 2b, with −30.8°C, −36.4 °C, and −50.8 °C for v-δ1, v-δ4, and v-δ7 respectively. All detailed data was presented in Table S2 (Supporting Information).

The Pδ vitrimers exhibited typical elastomeric stress–strain behaviors with Young's moduli from 0.27 to 1.24 MPa (Figure 2c). Increasing side chain length resulted in a softer elastomer with higher stretchability: v-δ1 can be stretched more than 80% before
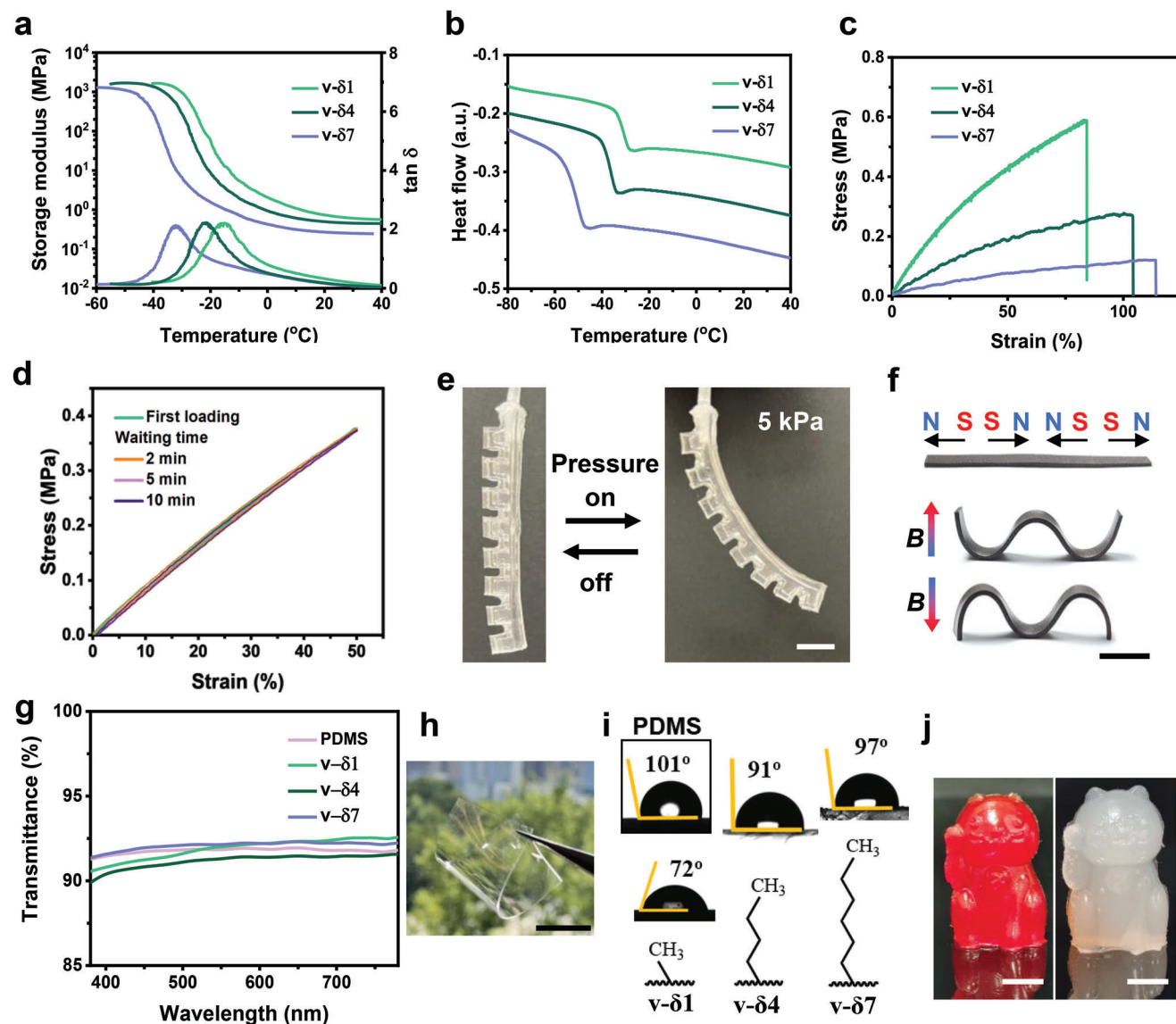
Figure 2. a–d) Properties and potential applications of Pδ vitrimers: Thermomechanical properties measured from DMA (a), DSC (b), uniaxial tensile tests (c), and cyclic tensile tests (d) of v-δ1 with a strain of 50%. e,f) Using Pδ vitrimers as actuators: e) A mold-cured pneumatic actuator and f) a magnetic actuator fabricated with v-δ1; the magnetic actuator has four segments with different magnetic poles (N–S), and B is the applied magnetic field. g,h) Optical properties: g) UV–vis transmittance and h) a photograph of v-δ. i,j) Potential use as molding materials: i) Water contact angle of Pδ vitrimers comparing with PDMS (inserted) and j) gelatin jelly and silicone rubber cured lucky cats with a v-δ7 fabricated mold. All scale bars: 1 cm.

failure, while v-δ7 can be stretched more than 110%. The properties can be modulated with different δ-lactone monomers or molecular weight to adapt to different applications (Figure S10, Supporting Information). In addition, as shown in Figure 2d, the loading and unloading curves of v-δ1 are superimposable with negligible hysteresis. It is worth noting that high stretchability and low hysteresis are desirable properties for sensor and actuator applications as they allow faster deformation and recovery. To date, soft materials, such as PDMS, are widely used in soft actuators, which have the advantage of interacting with fragile objects or living organisms; but PDMS is not recyclable due to the chemically cross-linked network.[49] The excellent mechanical properties of our δ-lactone vitrimers can provide an alterna-

tive sustainable replacement of these materials. Figure 2e shows a pneumatic actuator by using mold-cured v-δ1. The soft actuator by v-δ1 was able to bend by 70° when a very low pressure of 5 KPa was applied.

Another example, as shown in Figure 2f, is a magnetic soft material fabricated by v-δ1 embedded with 50 wt% magnetic particles of neodymium magnet (NdFeB). Magnetically responsive actuator enables programmable deformation, controlled by the magnetic field direction and magnitude.[50–54] Since magnetic fields can penetrate most materials, this type of soft actuator is ideal for enclosed area applications such as targeted drug delivery or minimally invasive surgery.[55–57] Most of the previous works used silicone or PDMS as the matrix material. Here, the rather

soft Pδ vitrimers are very sensitive to the applied stimulus (Video S1, Supporting Information). In Figure 2f, the magnetic soft material was magnetized first (top photo; N and S are directions of magnetic poles). When an upward magnetic field B = 50 mT was applied, the strip bent into a W-shape; when the magnetic field was switched, it bent into an M-shape. In addition, the Pδ vitrimers had a modulus from 0.27 to 1.24 MPa, covering the range of human skin (0.42–0.75 MPa),[58] which can be potentially further tuned by changing the molecular weight of Pδ or copolymerized with different Pδs for skin like actuator or sensor applications.

The amorphous Pδ vitrimers bring not only resiliency but also transparency. All Pδ vitrimers displayed similarly high transparency as commercial PDMS with a transmittance over 90% at the visible wavelength range as shown in Figure 2g. Figure 2h shows the as-prepared v-δ1 film, which exhibit high transparency.

We further compared the effect of alky side chain length on the surface property. As the linear alky chains were hydrophobic, the long chain v-δ5 and v-δ7 displayed higher hydrophobicity than v-δ1, as indicated by the increasing contact angle from v-δ1 to v-δ7. In addition, v-δ7 possessed similar contact angle as PDMS as shown in Figure 2i. The softness and hydrophobicity can be used to fabricate v-δ7 based depolymerizable and recyclable molds as replacements to PDMS molds. Figure 2j shows two lucky cats made of gelatin jelly and silicone rubber that were cured using the same v-δ7 mold. These examples confirmed that Pδ vitrimers possess physical properties similar to PDMS that are flexible and elastic, transparent and hydrophobic, demonstrating the ability as a sustainable substitute of PDMS.

2.3. Reprocessing, Reshaping, and Healing Enabled by Exchange Reactions in Pδ Vitrimers

Vitrimers exhibit unique features that allow the network topology rearrangement while maintaining their cross-linking. These features allow them to be welded, remolded, and reprocessed at elevated temperatures. In our Pδ vitrimers, these features were enabled by the acetal metathesis exchange reaction, which is shown schematically in **Figure 3**a and further validated with small molecule model reactions (detail in Figure S1–S3, Supporting Information). The dynamic properties of the Pδ vitrimers were evaluated by stress-relaxation tests. All Pδ vitrimers reached complete stress relaxation within a relatively short time under a mild temperature between 100 to 130 °C (as shown in Figure 3b for v-δ1), which validated the exchangeable acetal linkages of the vinyl ether cured Pδ vitrimers. As shown in Figure 3b, the relaxation modulus decreased exponentially over time and exhibited typical Arrhenius temperature-dependent behavior (351 s of 130 °C, 681 s of 120 °C, 1920 s of 110 °C, and 4371 s of 100 °C). The exchange kinetic analysis of the acetal linkage with the Arrhenius equation revealed relatively low activation energy (E_a). V-δ1 has the fastest reaction rate and lowest E_a of 108.3 KJ mol^{-1}, compared with 114.8 and 122.8 KJ mol^{-1} for v-δ4 and v-δ7 as shown in Figure 3c. Higher cross-linking density and reduced steric hindrance were favorable for the exchange reaction,[59] which was consistent with the experimental observation.

The reprocessability of Pδ vitrimer was validated with a conventional hot-press reprocessing with the broken tensile test samples. The mechanical properties of the reprocessed samples (v-δ1) were compared in Figure 3d. Slightly decrease in modulus on the second time reprocessed sample was observed, possibly due to the slight hydrolytic degradation during the hot pressing in the air. Further reprocessing significantly decreased the properties due to the low thermal stability of the degradable vitrimers (Figure S11, Supporting Information). The dynamic exchange of the acetal linkages allowed the rearrangement of network topology, making the cross-linked Pδ vitrimer malleable. The high transparency of Pδ vitrimer can be potentially utilized as materials for recyclable lenses. In a proof-of-concept demonstration, as shown in Figure 3e, a 2D flat v-δ1 film (Figure 3e-i) was reshaped using a hemispherical mold at 130 °C for 30 min (Figure 3e-ii) into a 3D hemisphere shape convex lens (Figure 3e-iii,iv). It offered more flexibility in shape adaptation than regular soft elastomers like PDMS, silicone rubber, or hydrogel. Figure 3f demonstrated another possible application as a remoldable microfluidic chip. The flat v-δ1 sample (Figure 3f–i) was hot-stamp imprinted (Figure 3f-ii, 130 °C for 30 min) with the predesigned microchannel pattern into a microfluidic chip (Figure 3f-iii). It could be rewritten into a different pattern by remolding (Figure 3f-iv, 130 °C for 30 min) for a new chip (Figure 3f-v).

Another important feature of vitrimers was the exchangeable reaction endowed healability and reprocessability. Soft actuators and sensors are often required in dynamic and complex stress/strain environments. Particularly for soft pneumatic actuators, any puncture damage would cause the loss of their function. Herein, the mold fabricated v-δ1 pneumatic actuator in Figure 2e was cut by a blade with complete separated damage (as shown in Figure 3g-i), and it could no longer be actuated because of the major leakage. The damaged actuator was then healed in a customized epoxy mold at 130 °C for 30 min. The separated part was welded airtightly together through surface exchange reactions. The bending deformation was recovered, as demonstrated in Figure 3g-ii. Figure 3h displayed the reprocessed v-δ1 sample after remolding from the cut small pieces. From these examples, it can be seen that besides having the properties that could be used to serve as a sustainable replacement of PDMS, our Pδ vitrimers also possessed the advantages such as reforming, healing, and reprocessing, which are unavailable in PDMS.

2.4. Depolymerization of Pδ Vitrimers

The Pδ vitrimers were able to depolymerize to the original δ-lactone monomers when they were at the end of their service lifetime, such as repeated reprocessing. The depolymerization route of Pδ vitrimer is illustrated in **Figure 4**a. The initial degradation temperature $T_{d5\%}$ (the temperature for 5% weight loss) was 196, 181, and 176 °C for v-δ1, vδ-4, and vδ-7, respectively, when the sample was heated at 10 °C min^{-1}. Upon heating to 200 °C, the acetal cross-linkages started to decompose to 1,4-cyclohexanedimethanol and acetaldehyde and evaporated, resulting in the hydroxyl capped Pδ aliphatic polyester, which can be simultaneously depolymerized and the monomer recovered through the backbiting reactions.[60] Although the degraded cross-linker constitutes only a small proportion of the vitrimers, it can still be recycled and used to synthesize new cross-linker for reuse. The thermal stability of Pδ vitrimers was examined by TGA
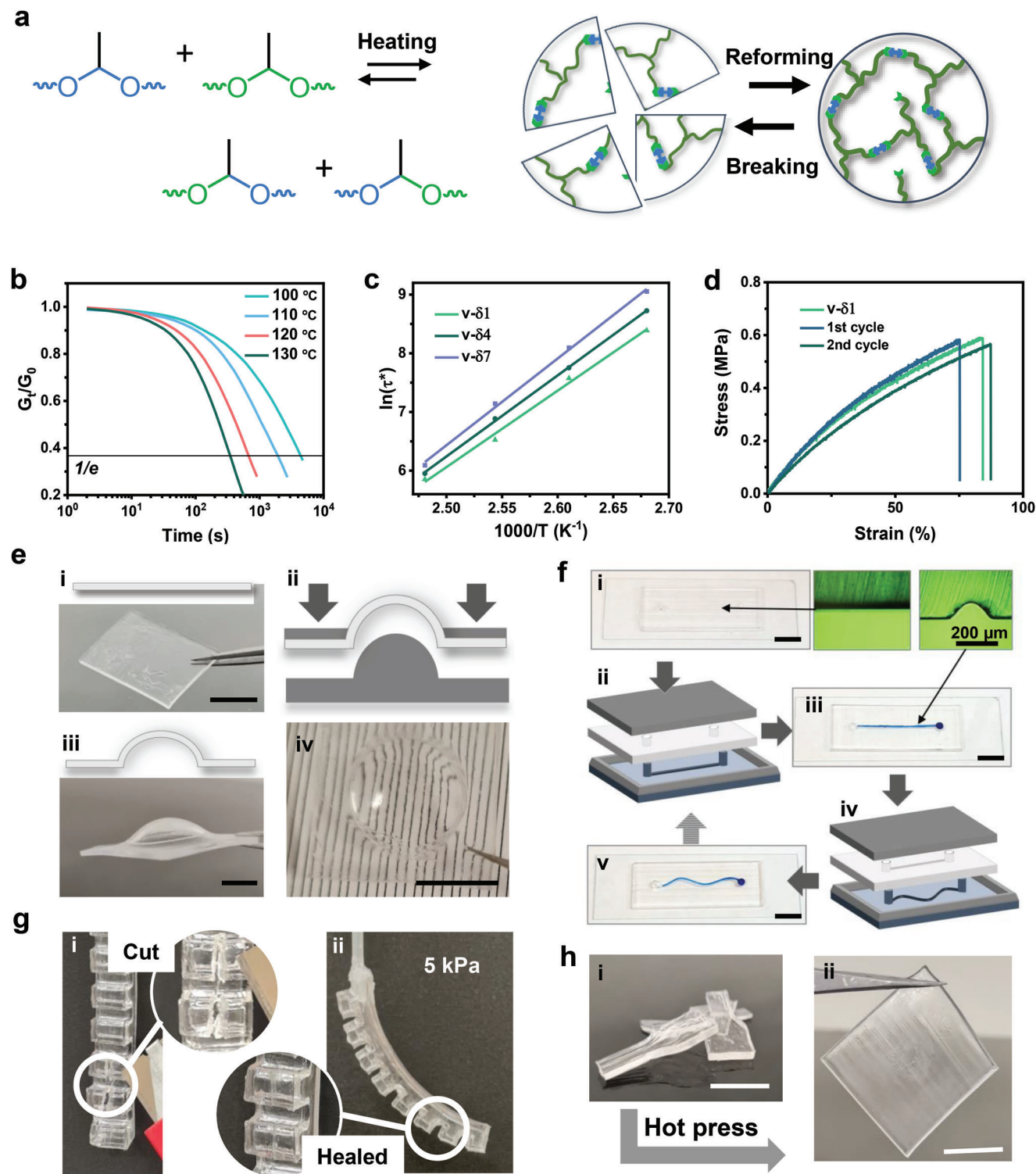
Figure 3. Dynamic network performance of Pδ vitrimers. a) Schematic of the chemistry of acetal metathesis exchange reaction and acetal vitrimer network breaking and reforming. b) Stress relaxation of v-δ1 at different temperature. c) Arrhenius plot of the characteristic relaxation time τ^* versus inverse temperature for Pδ vitrimers. d) Tensile comparison of reprocessed v-δ1. e) Reshape of v-δ1 film into a convex lens. f) Hot-stamping imprint of microchannel on v-δ1. g) Self-healing of v-δ1 actuator. h) Reprocessing of v-δ1 by hot-press molding. All scale bars: 1 cm.

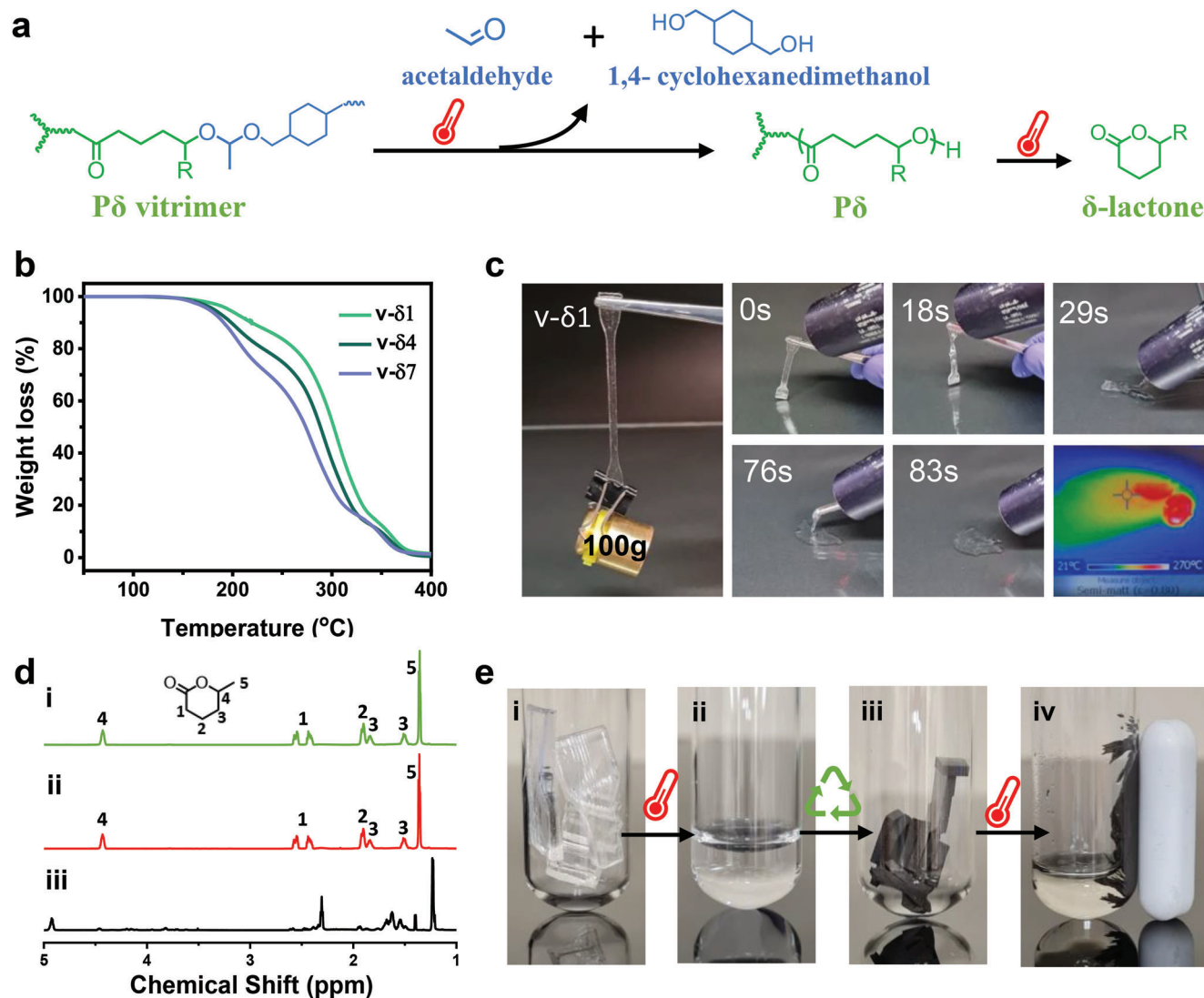**Figure 4.** Degradation and upcycling of Pδ vitrimer. a) Schematic of Pδ vitrimer depolymerization. b) TGA curves of Pδ vitrimers. c) Photo of v-δ1 degraded from solid to liquid oligomer with a thermal gun. d) Overlay of ^{1}H NMR spectra of: i) pristine δ-1 monomer, ii) recycled δ-1 monomer, and iii) undepolymerized oligomers from (c). e) Depolymerization of v-δ1 (i) into δ-1 (ii) and re-synthesis into v-δ1 magnetic composite (iii) and depolymerization again and separation the magnetic particles (iv).

as shown in Figure 4b. Moreover, all samples reached ≈100% weight loss at a temperature below 380 °C, due to the evaporation of the resulting small molecules. According to the previous report by Hillmyer et al., the ceiling temperatures for polymers made from δ1, δ4, and δ7 were ≈170, 140, and 130 °C, respectively.[35] Therefore, the vitrimers with longer alkyl groups were likely to depolymerize at a lower temperature, and the degradation behavior of the cross-linked Pδ vitrimers followed this trend. The acetal linkages started to degrade first and release more free hydroxyl groups on the chain ends of Pδ segments, and then the depolymerization of poly(δ-lactone) occurred. Figure 4c showed the v-δ1 sample degraded from cross-linked solid elastomer to viscous liquid polymer (Figure 4d) at a temperature ≈200–250 °C with a heat gun, which was due to degradation of the acetal linkage. Video S2 (Supporting Information) showed the rapid degradation of the v-δ1 sample turning into liquid within 2 min by a hot air gun. It's worth noting that as long as the polymer is stable under the application conditions, a lower degradation temperature is favorable for recycling. However, the thermal stability can be increased by tuning the stoichiometric ratio of the cross-linker (Figure S12, Supporting Information).[61]

The bulk thermolysis of Pδ vitrimer was also attempted, and all samples can be completely depolymerized at 200 °C in less than one hour. In many previous works using Pδ in copolymer design, the degraded mixture contained a large portion of undepolymerized oligomers.[41,42] In our approach, the depolymerization of Pδ vitrimers yielded entirely small molecules. Moreover, 85–90 wt% of the Pδ vitrimers were successfully recycled back to cyclic δ-lactone monomers, and the ratio can be increased further by increasing the poly(δ-lactone) molecular weight. δ-lactone monomers can be easily recollected with high purity (nearly 100% yield) by distillation under reduced pressure, as confirmed

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in Figure 4d. In situ TGA-IR of v-δ1 also directly confirmed the evaporated product was δ1 monomer (Figure S13, Supporting Information).

The recovery of the virgin-quality pure δ-lactone monomers enabled reuse for synthesizing new Pδ polymers with the same or different molecule architecture and molecular weight (Figures S14 and S15, Supporting Information). Figure 4e-i-iii demonstrated that the v-δ1 tensile samples were depolymerized into monomers, which were then used for the v-δ1 magnetic composite. Since the matrix can completely depolymerize into liquid monomers, the solid additives or fillers can be easily separated. The magnetic composite was depolymerized again at the end of use and the magnetic particles can be reused (Figure 4e-iv). Thus, the inherent value of the Pδ vitrimer waste could be maximized with the successful demonstration of a "polymer–monomer–polymer" closed-loop life cycle.

3. Conclusion

Deterioration of thermal and mechanical properties after cycles of reprocessing is generally a major bottleneck for reprocessing and recycling of polymers. To address this end-of-use issue, depolymerizing to recover the original reusable feedstock with a closed-loop life cycle is a promising strategy to maximize the value of vitrimer polymers. We have presented this concept with vitrimers synthesized with naturally derived δ-lactone monomers and acetal dynamic bonds. The Pδ vitrimers, prepared in a facile and scalable approach, can not only undergo reprocessing and recycling but also enable recovery of 85 to 90 wt% of the vitrimers back to the original monomers. We also demonstrated promising potential for a range of applications of the Pδ vitrimers that could be used as a sustainable replacement for PDMS. The Pδ vitrimers also have the desirable merits of reprocessing and healing that do not exist in PDMS. Overall, this work may lead to an appealing direction in designing new sustainable elastomers for soft material applications.

4. Experimental Section

Materials: δ-Hexalactone (δ-1), δ-nonalactone (δ-4), δ-dodecalactone (δ-7), glycerol, diphenyl phosphate(DPP), triethylamine(TEA) and 1,4-cyclohexanedimethanol divinyl ether and anhydrous isopropyl alcohol(IPA) were all purchased from Sigma–Aldrich (St. Louis, MO, USA). Monomers and glycerol were dried with a molecular sieve and kept in a nitrogen atmosphere.

Synthesis of Poly(δ-lactone) Triol (Pδ): The bulk ring-opening polymerizations were performed on a scale of 10 g monomer. The monomer (10 g), the initiator (glycerol), and the catalyst DPP were added into a 20 mL glass vial with a constant molar ratio [monomer]:[initiator]:[DPP] of 12:1:0.12. The reaction was conducted for 48 h at room temperature with stirring under a nitrogen atmosphere in a glove box.

Synthesis of Pδ Vitrimers: Cross-linked Pδ vitrimers were synthesized by curing the prepared triol with divinyl ether cross-linker (1,4-Cyclohexanedimethanol divinyl ether) in a molar ratio of [vinyl]:[hydroxyl] = 0.9. Under the nitrogen atmosphere glove box, divinyl ether was dropped into synthesized Pδ to mix well with the vortex mixer and then cast in a silicone mold. The mold was then transferred into a nitrogen-purged oven and cured for 1 h at 80 °C. The cured sample was soaked in dry IPA with 1 wt% TEA for 6 h and then dried at room temperature.

Network Reshaping and Reprocessing: Reshaping and reprocessing of Pδ vitrimers were conducted at 130 °C with a pressed mold for 30 min (convex lens, imprinting of microchannels, self-healing of actuator). Reprocessing recycles of Pδ vitrimers were hot pressed at 150 °C under the pressure of 5 MPa.

Depolymerization of Pδ Vitrimers: Pδ vitrimers were sealed with nitrogen in a glass pressure vessel equipped with a magnetic stir bar and depolymerized at 200 °C for at least 1 h. Monomers were then separated with a fractional vacuum distillation at 80 °C.

Detailed characterization and analysis are presented in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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