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Poly(4-ketovalerolactone) from Levulinic Acid: Synthesis and Hydrolytic Degradation

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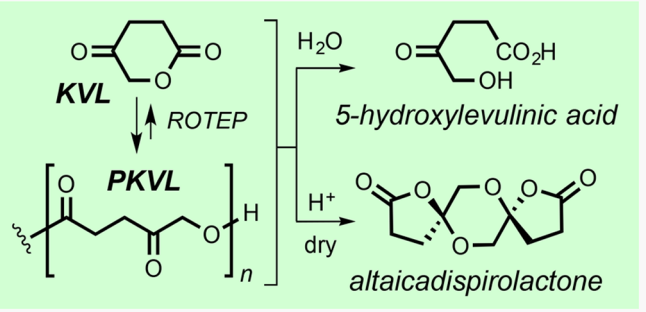
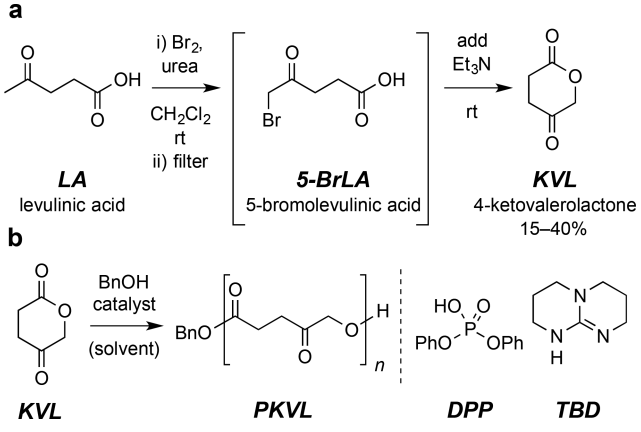
ABSTRACT: We report here the synthesis of poly(4-ketovalerolactone) (PKVL) via ring-opening transesterification polymerization (ROTEP) of the monomer 4-ketovalerolactone (KVL, two steps from levulinic acid). The polymerization of KVL proceeds to high equilibrium monomer conversion (up to 96% in the melt) to give the semicrystalline polyketoester PKVL. PKVL displays glass transition temperatures of 7 °C and two melting temperatures at 132 and 148 °C. This polyester can be chemically recycled through hydrolytic degradation. Under aqueous neutral or acidic conditions, the dominating pathway for polyester hydrolysis is through backbiting from the chain end. Under basic conditions, midchain cleavage, accelerated by the ketone carbonyl group in the backbone, promotes the hydrolysis of nearby backbone ester bonds. The final hydrolysis product is 5-hydroxylevulinic acid, the ring-opened hydrolysis product of KVL. PKVL was also observed to degrade under the action of a Brønsted acid to a bis-spirocyclic dilactone natural product altaicadispirolactone, which is a dimer of KVL. This constitutes a rare example of a one-step synthesis of a secondary metabolite of nontrivial structure in which a polymer was the starting material and the sole source of matter. Analogous ROTEP of the isomeric four-membered lactone 4-acetyl-β-propiolactone (APL) was also explored, although this chemistry was not as well-behaved as the KVL to PKVL polymerization.



INTRODUCTION

Here we report the synthesis of 4-ketovalerolactone (KVL) from levulinic acid (LA) (Scheme 1) and its ring-opening transesterification polymerization (ROTEP) to produce the polyester poly(4-ketovalerolactone) (PKVL). This study was motivated by (i) the ready availability of levulinic acid[1] from biomass, (ii) the well-established utility of many cyclic esters (lactones) to function as monomer precursors to polyesters,[2−5] and (iii) the possibility of generating a new class of bioderived polymeric material of utility. The structural similarity between PKVL and polyglycolide (PGA) is shown in Figure 1.

Scheme 1. (a) Two-Step Synthesis of KVL from Levulinic Acid; (b) ROTEP of KVL to Produce PKVL



Levulinic acid can be produced cost effectively and in high yield through acid-catalyzed hydrolysis of lignocellulosic biomass.[6−12] LA was identified as one of the 12 most promising platform chemicals from biomass by the National Renewable Energy Laboratory of the U.S. Department of Energy in 2004.[1] It has been used to produce a number of bioderived chemicals and materials including succinic acid, food flavoring and fragrance compounds, solvents, plasticizers, antifreeze agents, biofuels and fuel additives, resins, polymers, and other building blocks useful in fine chemical synthesis.[7−9]

Plant biomass (from CO_2 and H_2O via photosynthesis) can provide abundant and renewable precursors that can be converted into reactive monomers for polymerization reactions. This has the potential providing materials by routes with

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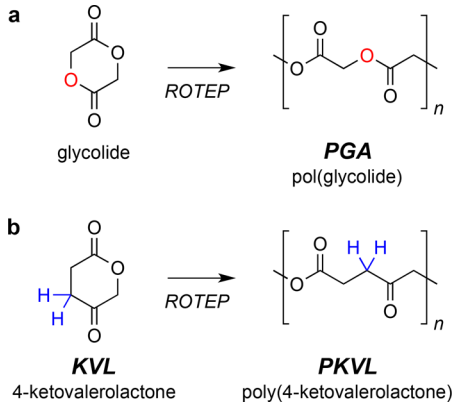

Figure 1. PGA vs PKVL: similar structures, each with a second carbonyl group within each six-atom repeat unit of the polyester.

reduced carbon footprints. Indeed, the development of plant-based polymers is an active area of exploratory research.[13−16] Polylactide (PLA), currently the most successful and widely used bioderived polymer,[17,18] and other renewable polyesters, such as poly(ethylene furanoate) or biosourced poly(ethylene terephthalate), are examples of valuable materials with exploitable and useful properties.

RESULTS AND DISCUSSION

KVL Synthesis. The lactone KVL has been reported twice in the literature—first as a side product formed during a rhodium(II)-catalyzed cycloaddition reaction of certain α-diazo keto amides[19,20] and, later, via a four-step sequence from LA.[21] The latter involved C5-bromination of LA in methanol, acid-catalyzed hydrolysis of the resulting methyl ester, hydrolysis of the primary bromide to give 5-hydroxylevulinic acid (HLA), and Yamaguchi lactone synthesis. The polymerization of HLA by a step-growth polycondensation process gave, nominally, the same polymer as PKVL;[22] however, the NMR spectral data for that condensation polymer is less pure compared to those of the samples prepared and reported here by the more controlled ROTEP of KVL (see the Supporting Information).

The preparation of KVL (Scheme 1a) involves the direct bromination of an enol tautomer of LA. Previous researchers explored rather extensively the impact of solvent on the site selectivity (i.e., 3-Br vs 5-Br) as well as the extent of bromination (i.e., mono- vs di- vs tri-).[23−26] We made qualitatively similar observations but also examined several brominating agents in addition to molecular bromine (Table S1). We eventually discovered that bromination with a Br_2·urea complex in methylene chloride gave ca. 2:1 selectivity for 5-BrLA:3-BrLA (+ ca. 12% of the three known[23−26] dibromination products), including when performed on a scale starting with 50 g of LA. The resulting slurry was then treated directly with triethylamine (2.1 equiv) to induce internal nucleophilic displacement of bromide by the carboxylate. KVL can then be obtained by chromatographic purification in 40% yield or by direct crystallization (from ca. 3:1 vol:vol mixture of hexanes and ethyl acetate, mp 48−51 °C) in 15−20% yield after the two steps (bromination and cyclization).

Polymerization of KVL. Crystalline KVL was used for the polymerization studies. Initial attempts to effect the ROTEP with Sn(II) 2-ethylhexanoate catalyst were, surprisingly, unproductive; the KVL was consumed, but a complex array of resonances was seen in the ^{1}H NMR spectrum of the viscous, crude product. No specific structural information could be discerned with confidence.

We then turned to Brønsted acid catalysis. Trifluoroacetic acid (TFA) in $CDCl_3$ led to slow consumption of the KVL with the appearance of several new entities (discussed later). In contrast, diphenyl phosphate [$(PhO)_2PO_2H$, DPP], known for its advantageous promotion of certain ROTEP reactions,[27−29] proved to be a very effective catalyst for the polymerization of KVL (Scheme 1b). Initial studies in $CDCl_3$ solution, using benzyl alcohol (BnOH) as an initiator, established that high monomer conversion could be achieved. The ROTEP under neat conditions at elevated temperatures (e.g., 70 °C; $T_{m/KVL}$ = 48−51 °C) led to high monomer conversion (up to 96%) and produced PKVL as a semicrystalline substance. The polymer exhibited limited solubility in most solvents; we identified hexafluoroisopropanol (HFIP), TFA, and DMSO/DMF (at elevated temperatures) as good solvents for PKVL. The limited solubility of the polymer in more traditional solvents or in the bulk made it not possible to prepare samples with molar masses over 10 kg mol^{-1} ($M_{n,NMR}$). It also compromised our ability to obtain reliable SEC data. The results from polymerizations performed under a variety of conditions are summarized in Table 1.

The DSC thermogram of the 3.3 kg mol^{-1} sample (Figure 2) showed it to be semicrystalline, with a T_g lower than ambient temperature (T_g = 7 °C) and two T_ms (T_m = 132 and 148 °C). These thermal properties of PKVL can be compared to those of, for example, poly(ε-caprolactone) (T_g = −71 to −60 °C and T_m = 57−63 °C),[30] poly(δ-valerolactone) (PVL) (T_g = −67 °C and T_m = 53−60 °C),[30] poly(β-propiolactone) (P3HP) (T_g = −22 °C and T_m = 76 °C),[31,32] PLA (T_g = 55 °C and T_m = 175 °C),[33] and PGA (T_g = 36 °C and T_m = 225 °C).[34]

Table 1. Reaction Conditions and Selected Properties of PKVL Produced by ROTEP

catalyst	BnOH (mol %)	catalyst (mol %)	temp (°C)	solvent	time (h)	$M_{n,NMR}$ (kDa)	monomer consumption[a] (%)	yield[b] (%)
DPP	5	10	60	neat	17	1.7	98	93
DPP	1	2	90	neat	17	3.3	60	50
DPP	0.2	0.2	90	neat	17	5.5	50	40
DPP	1	1	160	neat	3	3.5	95	60
TBD	5	10	60	neat	17	1.2	56	45
TBD	5	10	60	$CHCl_3$	17	2.0	90	70
$Sn(Oct)_2$	1	1	90	neat	17		97	[c]

[a]Determined by ^{1}H NMR spectroscopy of the crude product. [b]% mass recovery of precipitated material (see the Supporting Information). [c]Precipitation gave 74% mass recovery of a deep-red viscous liquid, the ^{1}H NMR spectrum of which was very complex and showed no discernible resonances for PKVL subunits.

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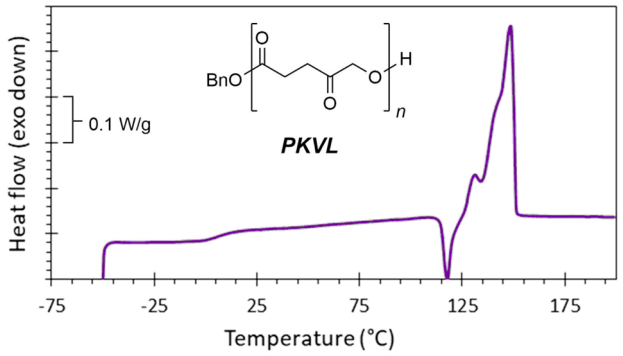


Figure 2. DSC thermogram (with downward exotherm) of PKVL (M_n = 3.3 kg mol^{-1}) taken on the third heating cycle at a heating rate of 5 °C min^{-1}. The thermogram shows a T_g = 7 °C, a T_c = 118 °C, and two T_m's = 132 and 148 °C.

The enthalpy and entropy of polymerization of KVL in a homogeneous solution were determined by using a Van't Hoff analysis (Figure S2).[35] We used starting monomer concentrations of 1.0 M (in chloroform/HFIP = 4:1). The values were $\Delta H_p^0 = -9.0 \pm 0.4$ kJ mol^{-1} and $\Delta S_p^0 = -23 \pm 1$ J mol^{-1} K^{-1}, respectively. For comparison, the analogous reported values for PVL are $\Delta H_p^0 = -10.5$ kJ mol^{-1} and $\Delta S_p^0 = -15$ J mol^{-1} K^{-1}, respectively.[36]

We then studied the relative rates of initiation vs propagation of KVL by NMR monitoring of reaction solutions. When a $CDCl_3$ solution of an *equimolar* mixture of benzyl alcohol and KVL ($[KVL]_0$ = 0.12 M) was allowed to react in the presence of DPP (67 mol %) at ambient temperature, smooth conversion to primarily benzyl 5-hydroxylevulinate was observed (ca. $t_{1/2}$ = 1 h, Figure S3). A similar experiment, this starting with a 5:1 ratio of KVL:BnOH ($[KVL]_0$ = 0.24 M and 50 mol % DPP relative to the BnOH), showed only a trace of oligomer formation at ca. 3 half-lives for the consumption of the BnOH initiator (Figure S4). That is initiation is considerably faster than propagation for the ROTEP reaction of KVL under Brønsted acid catalysis. We suspect that an important contributing factor is that the nucleophilicity of the propagating hydroxyl group at the terminus of the growing polymer chain is deactivated by the adjacent, electron-withdrawing carbonyl carbon.

We also explored the use of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Scheme 1b) as a (basic) ROTEP catalyst for polymerization of KVL (in $CDCl_3$). As expected, a similar extent of monomer consumption was reached [e.g., ca. 90% at 60 °C (Table 1)]. The principal difference was in the rate of polymerization, which was significantly slower with TBD than DPP at the same catalyst loading.

Copolymerization of KVL with δ-Valerolactone (VL). Statistical copolymers of two different lactones are known to alter the thermal properties of either of the corresponding homopolymers. One of the most widely recognizable examples is the family of PLGA materials available from copolymerization of lactide and glycolide.[34] In line with that we briefly examined an array of competitive copolymerizations of KVL and VL, varying the molar ratio of the monomers (Table 2). Starting with equimolar amounts of these two monomers, we observed that the initial rates of consumption were ca. 2:1, the KVL being slightly slower (Figure S1). The statistical copolymerization resulted in high consumptions of both monomers and high yields of the isolated PKVL-*co*-PVL. The fractions of PKVL in the product polymers matched those of the initial charge of monomers. The solid 1,4-benzenedimethanol was used as initiator for the convenience of weighing and transfer into the reaction vessels. It also gives telechelic polymers in which the aromatic resonance in the ^{1}H NMR spectra of the initiator moiety is a singlet.

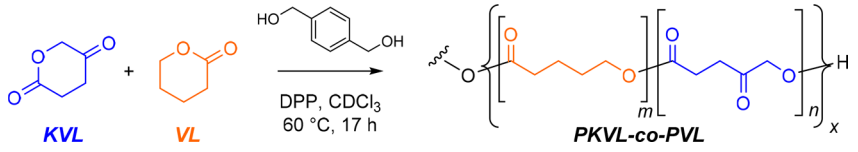
The T_g and T_m of each PKVL-*co*-PVL are shown in Table 3. These increased with a higher fraction of PKVL, the more polar repeat unit. Additionally, the 50% KVL sample was significantly less crystalline than the others, since we observed only a very weak melting phase transition in the DSC thermogram (Figure S10). Therefore, we can modulate the thermal properties of these PKVL-*co*-PVL through changing the monomer composition.

Table 3. Summary of Thermal Properties of PKVL-*co*-PVL

% KVL	T_g (°C)	T_m (°C)
0	−67[30]	53−60[30]
25	−45	30−40
50	−25	90−100
75	1	100−125
90	5	100−120
100	7	132−148

Synthesis and Polymerization of 4-Acetyl-β-propiolactone (APL). APL (Scheme 2a) is a constitutional isomer of KVL. When the bromination of LA is performed in chloroform solution, 3-bromolevulinic acid (3-BrLA) is the major product formed in a 2:1 ratio compared to 5-BrLA. The mixture of these bromoacids could be cyclized by the subsequent direct addition of triethylamine to the bromination reaction mixture to produce

Table 2. Random Copolymerization of KVL and VL with Different Fraction of Monomers



% KVL[a]	consumption of KVL (%)	consumption of VL (%)	PKVL RU[b]	PVL RU[b]	% PKVL[c]	$M_{n,Theo}$ (kDa)	$M_{n,NMR}$ (kDa)	yield[d] (%)
25	98	93	17.2	51.1	25.2	6.8	7.2	87
50	96	97	29.3	30.6	49.0	7.3	6.5	88
75	85	89	59.8	19.0	75.9	9.4	8.9	85
90	72	75	20.4	2.6	89.0	3.2	2.7	57

[a]Molar percentage of KVL in the mixture of initial monomers. [b]Number of repeat units of monomer in the PKVL-*co*-PVL. [c]Percentage of KVL repeat units in the PKVL-*co*-PVL. [d]Percent mass recovery of precipitated material (see the Supporting Information).

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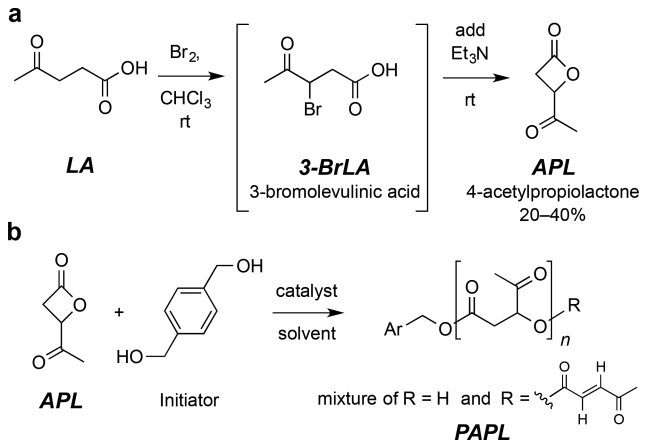
Scheme 2. (a) Two-Step, One-Pot Synthesis of APL from Levulinic Acid; (b) ROTEP of APL to Produce PAPL



APL in 40% yield following chromatographic purification. We observed that when stored at ambient temperature, neat samples of the four-membered lactone APL oligomerized in a matter of hours. Therefore, it was either stored in solution (and in a freezer as an additional precaution) or prepared and purified immediately prior to attempts at catalyzed ROTEP polymerization.

ROTEP of APL was examined by using DPP or TBD as catalyst. The resulting material PAPL, now having an acetyl substituent within each repeat unit in the polymer backbone, was readily soluble in most common organic solvents. However, ^{1}H NMR analysis indicated that this polymerization was not nearly as well-controlled as that leading to PKVL. Most noticeably, a family of alkene resonances (doublets, all with J = ca. 16 Hz) of significant intensity in the δ 6.6−7.2 ppm region was seen (see the Supporting Information). These suggest the presence of *E*-enoyl ester moieties such as that shown in the structure of PAPL. The array of slightly different chemical shifts likely reflects tacticity variation in the penultimate residues. Eliminative chain cleavage over the time course of the polymerization reaction would account for the formation of these terminal enoyl groups. Thermal degradation of PAPL (ca. 200 °C) resulted in quite clean formation of solely the elimination product 3-acetylacrylic acid. Similar phenomena have been reported for the poly(β-butyrolactone)[4] and poly(β-propiolactone) (P3HP, producing, there, acrylic acid).[37,38]

Hydrolytic Degradation Studies. As a prelude to studying the hydrolytic decomposition of PKVL in various basic or acidic media, we examined the hydrolysis of KVL itself (Figure 3a).

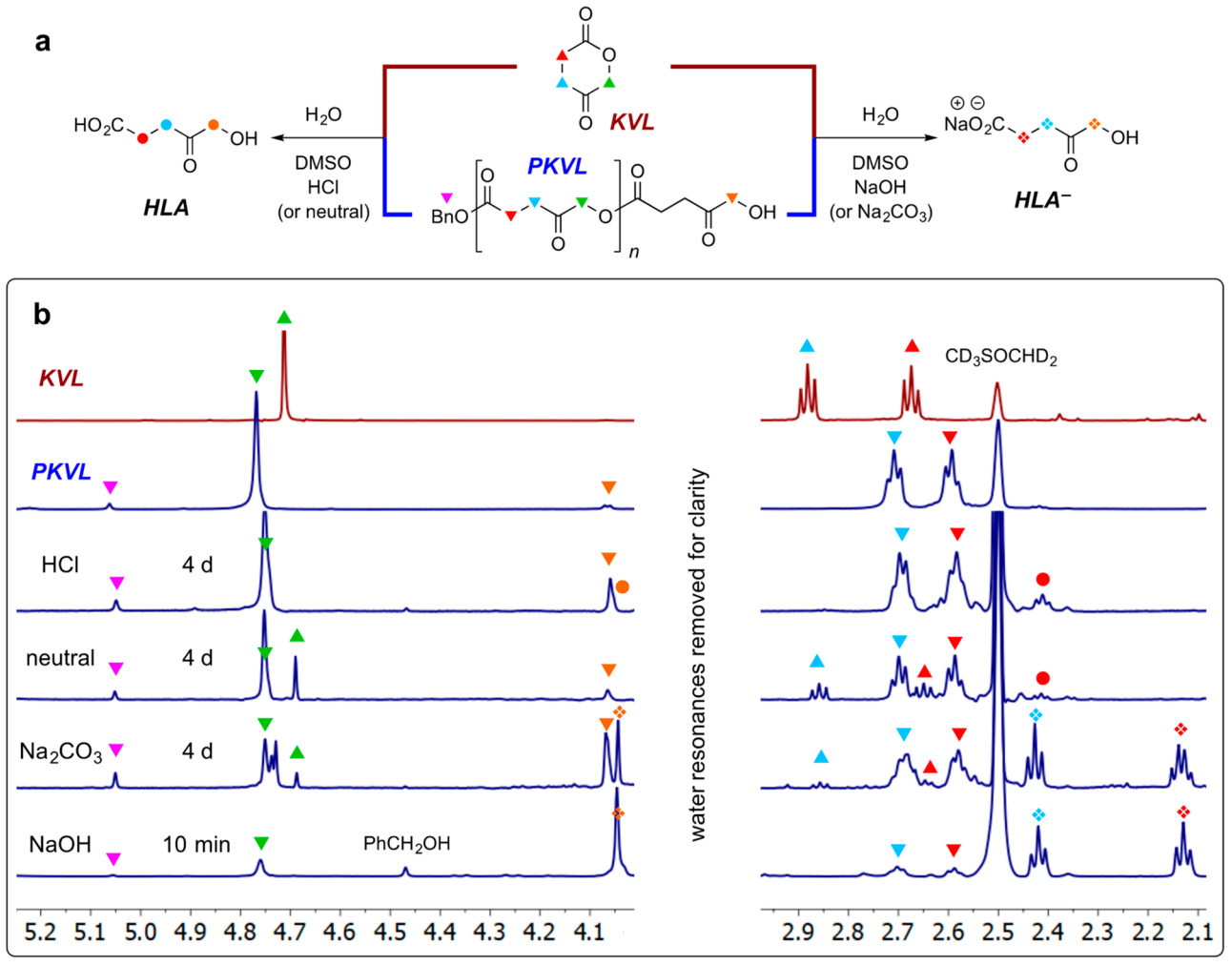


Figure 3. (a) Products of hydrolysis of KVL and of PKVL under acidic or basic conditions. (b) Selected ^{1}H NMR spectra of hydrolysis reaction mixtures (in DMSO-d_6/water) at partial conversion and under different conditions.

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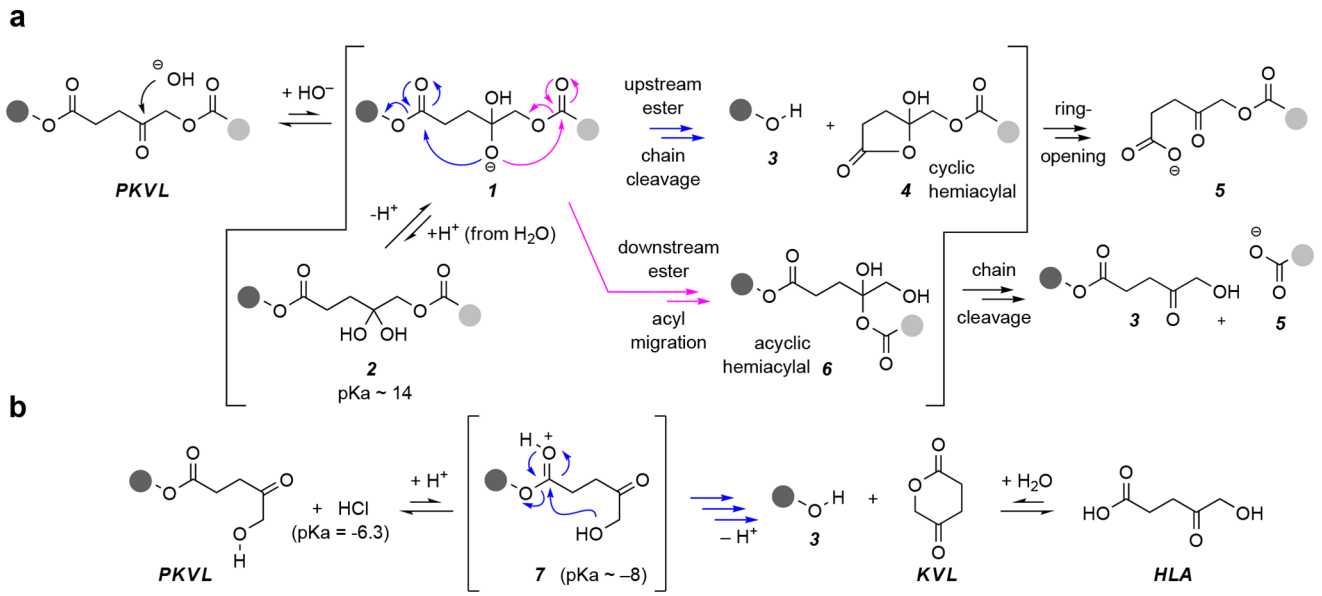
Scheme 3. (a) Hydrolysis of PKVL under Aqueous Basic Conditions via Mid-Chain Cleavage; (b) Hydrolysis of PKVL under Acidic or Neutral Conditions via Backbiting from Chain Ends



Hydrolysis of the KVL monomer at room temperature in the presence of an excess of NaOH (in ca. 10:1 DMSO-d_6:H_2O) led to rapid (<5 min) and full conversion to the ring-opened carboxylate anion of HLA^-. Under acid catalysis (aqueous HCl), the hydrolysis was slower but also reached essentially full conversion to (the neutral) HLA. All hydrolysis degradation studies were performed at ambient temperature (ca. 20 °C).

Under the same conditions, a homogeneous DMSO/H_2O/NaOH solution of the PKVL polymer was also fully hydrolyzed to the HLA carboxylate within ca. 5 min. With the weaker base Na_2CO_3, the hydrolysis of PKVL was significantly slower, reaching 50% conversion after ca. 4 days. In contrast, the DMSO/H_2O/HCl hydrolysis of PKVL only reached ca. 18% conversion after 6 days. Under neutral conditions, the rate of hydrolysis was, surprisingly, quite similar; however, the initial appearance of KVL was more rapid than its subsequent, slower hydrolysis to HLA compared to the ring-opening hydrolysis in the presence of HCl.

Shown in Figure 3b as exemplary are several representative snapshots of ^{1}H NMR spectra of degradation reaction mixtures of PKVL at different time points. These were performed directly in an NMR sample tube and in 10% water in DMSO-d_6 (the spectrum of KVL is also shown at the top for reference). Each spectrum corresponds to an intermediate state of reaction conversion. It is from the more complete time profile gathered during these types of studies (see the Supporting Information) that we can extract the relative reactivities summarized above. For example, it is clear that hydrolytic chain cleavage in the presence of NaOH is much faster than that for when Na_2CO_3 is the basic catalyst. Also, the buildup of resonances for terminal $-CH_2OH$ groups (relative to e.g. the $PhCH_2OC{=}O$ methylene singlet at ca. 5.06 ppm arising from the initiating benzyl alcohol) during the Na_2CO_3 cleavage is indicative of midchain cleavages that give rise to transient oligomeric species of varying chain length en route to full conversion.

Collectively, these observations of PKVL hydrolytic degradation are consistent with the interpretations offered in Scheme 3. In particular, we suggest that under basic conditions (Scheme 3a) hydroxide ion addition can produce the conjugate base **1** of the ketone hydrate **2**. The expected pK_a of the latter[39,40] suggests that **1** should predominate in the **1**/**2** equilibrium in a solution of aqueous NaOH. Rapid intramolecular attack by the anionic oxygen atom in **1** onto either an upstream (blue) or downstream (magenta) backbone ester would lead to either a chain-cleaved cyclic hemiacylal **4** or a backbone migrated acyclic hemiacylal **6**. Regeneration of the ketone carbonyl results in expulsion of the acyloxy (i.e., carboxylate) anion from **4** or **6** to give precisely the same pair of products **3** or **5** (give or take one repeat unit); these are chain-cleaved products are terminated by a primary alcohol and a carboxylate, respectively. Notice that in Scheme 3a **3** is merely a randomly shortened version of PKVL. We also examined the hydrolysis of PVL, which lacks the ketone carbonyl group, under basic conditions. PVL degraded considerably slower than PKVL under the same reaction conditions (DMSO, D_2O, and Na_2CO_3; see the Supporting Information), consistent with this proposal for the involvement of and acceleration by the conjugate base **1** of the ketone hydrate.

The slower degradation of PKVL under the action of aqueous HCl can be explained by assuming that attack by a neutral (and inductively deactivated) hydroxyl group in the ketone hydrate **2** onto one of the flanking (protonated) esters is substantially slower that of the anionic attack within **1**. Instead, we suggest that there is acid-catalyzed, selective depolymerization from the hydroxy-bearing terminus of each chain of PKVL (cf. **7**) that releases KVL monomers one at time. In fact, a small steady-state concentration of KVL was observed by the presence of its resonances in the NMR spectrum of the hydrolysis reaction mixture. The KVL, relatively rapidly, underwent hydrolytic ring-opening to HLA (cf. **7**, Scheme 3b). Results from monitoring this HCl-catalyzed degradation by ^{1}H NMR spectroscopy are consistent with this interpretation; HLA is observed to grow steadily over time without the appearance of significant amounts of the $HOCH_2$ resonances that would arise from mid-chain cleavage events. These interpretations are also consistent, at least qualitatively, with the change in M_n as ester hydrolysis progressed, as judged by ^{1}H NMR analysis. Namely, the increase in the ratio of the number of CH_2OH end-groups vs benzylic

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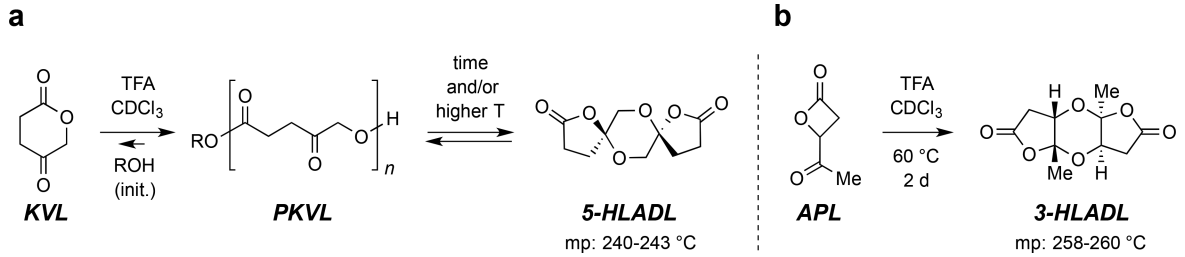
Scheme 4. (a) Equilibrium among KVL, PKVL, and the Bis-Spirocyclic Lactone 5-HLADL under Acidic Conditions; (b) Bis-Spirocyclic Lactone 3-HLADL from APL



ester $PhCH_2O_2C-$ (from the initiator moiety) resonances was large for the hydrolysis under basic conditions but negligible for the acid-catalyzed hydrolysis, consistent with chain cleavage vs chain-end degradation events for the basic vs acidic hydrolyses, respectively.

Additionally, we examined the hydrolysis of the esters ethyl levulinate (as a proxy for PKVL) and *n*-propyl propanoate (as a proxy for PVL), chosen as very simple unimeric models for study of the relative rates of the polymer degradations. Observations from competition experiments under both basic and acidic conditions were consistent with the interpretations presented in Scheme 3. These are discussed in greater detail in the Supporting Information.

Polymer Degradation to a Natural Product. In some initial experiments, briefly mentioned earlier, the ROTEP of KVL was examined (Scheme 4a) in $CHCl_3$ (or $CDCl_3$) by using the Brønsted acid TFA (or *p*-TsOH). Although the appearance of PKVL was observed at early time points, before the equilibrium monomer conversion was reached (ca. 98%, as later measured by the DPP experiments described above), a new set of resonances indicative of a discrete small molecule were seen to emerge. At long reaction times (and or upon further heating) the composition of this system came to a steady state with similar intensities of resonances for the polymer and the new entity (along with a small amount of remaining KVL). A GC-MS analysis indicated that the new product had a molar mass of 228 Da, which corresponds to a dimer of KVL (114 Da). Purification gave a pure sample of this white crystalline substance (mp 240−243 °C, with gas evolution). From analysis of the NMR data, we deduced this to have the structure of the bis-spirocyclic lactone 5-HLADL (5-hydroxylevulinic acid dilactone). We then discovered that this compound is a known material, having been first reported in 1891 (although assigned there with an incorrect constitution) as a product from dehydration of a hydroxylevulinic acid.[41] In 1962 the correct skeletal structure was assigned by Rappe.[42] In 1987, this compound was reported to have been isolated from *Anemone altaica* (C.A. Mey) and given the name altaicadispirolactone.[43] It was subsequently prepared by three chemical syntheses reported in 1996, 2005, and 2016.[44−46] The NMR data for 5-HLADL match well with those in the literature reports from 1987 to 2016.

We then proceeded to study the behavior of APL under treatment with TFA (Scheme 4b). It also formed a dimeric dilactone, assigned structure 3-HLADL. This material had also been described in the early Wolff[41] and Rappe[42] publications, but neither the NMR spectra nor stereochemical assignments have been previously determined and reported.

One note of interest is that based on the melting point data we observe for the isomeric dilactones 5-HLADL and 3-HLADL, we can conclude that the Rappe publication has the two compound structures reversed. That study was accompanied by an infrared spectrum of each substance. Our IR spectra are also more consistent with this reversed assignment.

We further showed that treatment of PKVL with TFA in a homogeneous solution ($CDCl_3$:HFIP; 10:1) also evolved toward the equilibrium ratio of 5-HLADL:PKVL:KVL observed (i.e., ca. 4:5:1) when starting with KVL. Thus, this three-component equilibrium mixture can be accessed starting from either KVL or PKVL via manifold involving only isomerization reactions. Finally, we note that this represents a rare (only?) example of a (one-step) synthesis of a naturally occurring secondary metabolite of at least modest structural complexity (here, tricyclic) wherein a polymer is the starting material.[47]

CONCLUSION

We have synthesized the polyketoester PKVL through ROTEP of the monomeric 4-keto-*δ*-valerolactone (KVL). This monomer was prepared in two steps from levulinic acid. Similarly, 4-acetyl-*β*-propiolactone (APL) could also be prepared. The ROTEP of KVL shows an equilibrium monomer conversion of 96% in bulk at 70 °C. PKVL is a semicrystalline polyester measured to have a T_g = 7 °C, a T_c = 118 °C, and two T_m's = 132 and 148 °C. The thermodynamics and kinetics of the polymerization were studied (ΔH_p° = −9.0 kJ mol^{-1} and ΔS_p° = −23 J mol^{-1} K^{-1}). Hydrolytic degradations of PKVL samples in homogeneous DMSO/H_2O solutions show that under the same basic conditions the hydrolysis of PKVL is faster than that of the parent polyester poly(valerolactone) (PVL). Attempts to carry out ROTEP of APL did not lead to efficient or clean production of a well-characterized polyester. An additional novel feature of this work is that PKVL can be degraded efficiently to the bis-spirocyclic dilactone natural product 5-HLADL (altaicadispirolactone) by using anhydrous Brønsted acids as catalysts. A constitutional isomer, the dilactone 3-HLADL, was also produced from APL under similar conditions.

EXPERIMENTAL SECTION

All experimental information is provided in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00787.

Experimental Section: (I) general experimental protocols; (II) preparation of KVL and APL monomers; (III) preparation and characterization of polymers; (IV) hydrolytic degradations monitored by ^{1}H NMR spectros-

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copy; (V) ^{1}H NMR spectra of PKVL in different solvents; (VI) SI references; (VII) ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

All primary data are available free of charge at the Data Repository for the University of Minnesota (DRUM) at 10.13020/jw1d-a958.

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