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β-Pinene-Based Polyester from Renewable Feedstock with Elastomeric Behavior

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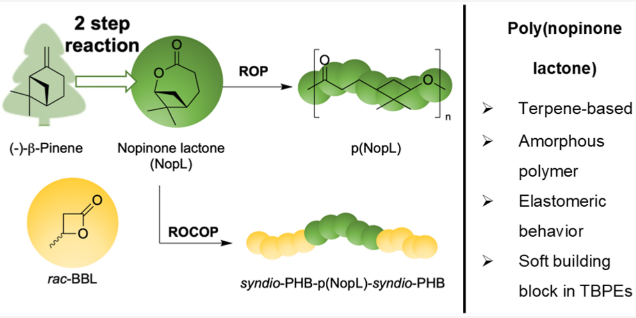

ABSTRACT: The utilization of biobased feedstocks in the production of polyesters is a promising opportunity as the industry focuses more and more on sustainability. Terpenes are naturally derived and inexpensive feedstocks that do not compete with agricultural land and can be transformed into a variety of biobased polymers. In particular, the bicyclic monoterpenes *α*-pinene, *β*-pinene, and 3-carene are promising candidates for high-value polymer materials when incorporating their cyclic unit in the backbone of polymers. In this work, we propose a straightforward synthesis, transforming *β*-pinene into nopinone lactone (NopL) via ozonolysis followed by a Baeyer−Villiger reaction without further skeletal rearrangement. Ring-opening polymerization of the lactone monomer was achieved using yttrium-bis(phenolate) and indium-salan complexes as catalysts at different monomer-to-catalyst ratios, yielding tunable molecular weights up to 105 kg·mol^{-1} and maintaining narrow polydispersities. The cyclobutane ring introduced in the polymer main chain induces higher rigidity in the resulting poly(nopinone lactone) (pNopL), yielding a thermally highly stable amorphous polymer with a glass transition temperature above room temperature (T_g = 23 °C). Mechanical studies show elastomeric behavior with a high elongation at break of 559 ± 46%. Incorporation of p(NopL) as a soft building block in triblock polymers (TBPE) with *syndio*-polyhydroxybutyrate (PHB) was successful, and stress−strain measurements showed the beneficial influence of the terpene-based polyester on the elasticity of ABA-type polymers.

■ INTRODUCTION

Polymers have a major influence on modern life and can contribute to a more sustainable environment by improving the efficiency of cars through lightweight materials or acting as insulators to increase energy savings. More than 350 million tonnes[1] of polymers are produced annually, corresponding to a market value of USD 624.8 billion in 2023[2] with an annual growth rate of around 4.2%. Currently, biobased polymers cover only 1% of the global production, which corresponds to 2.11 million tonnes, showing a huge growth potential, since they can be considered a major stepping stone toward achieving some of the United Nations Sustainable Development Goals.[1,3] In order to establish a circular economy, not only renewable feedstocks but also alternative end-of-live scenarios such as biodegradation or chemical recyclability need to be accounted for, which can help to reduce the carbon footprint.[1,4]

Biobased polymers can be divided into three categories depending on the origin of the feedstock. Sugars and lipids[5−7] as well as natural polymers such as lignin, cellulose, or polysaccharides[6,8] are the two categories already widely used on an industrial scale. The third category includes small molecular biomass obtained from forestry or agricultural products or by microorganism fermentation, which can be functionalized and further polymerized. Poly(lactic acid) (PLA) is an example of a commercially widely applied sustainable polymer derived from lactic acid produced from starch.[9] Other raw materials are for example vegetable oils or terpenes, which can either be polymerized directly[10−12] or can be functionalized by oxidative transformations and polymerized to yield polyesters similar to conventional petroleum-derived polymers.[6,13,14]

Two major problems of sustainable resources for polyesters are high prices in comparison to fossil-based monomers and the risk of diverting agricultural land for commodities. The class of terpenes and terpenoids is addressing both aspects, being cheap and valuable biomass derived as waste feed from many industrial processes like pulp production and is an upcoming topic in research for polymers replacing commodity materials.[6,15−17] The structural feature of a double bond makes the feedstock a versatile precursor for either cationic or radical polymerization, resulting in various poly(hydrocarbons);[18−20]

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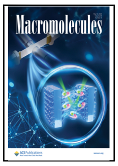

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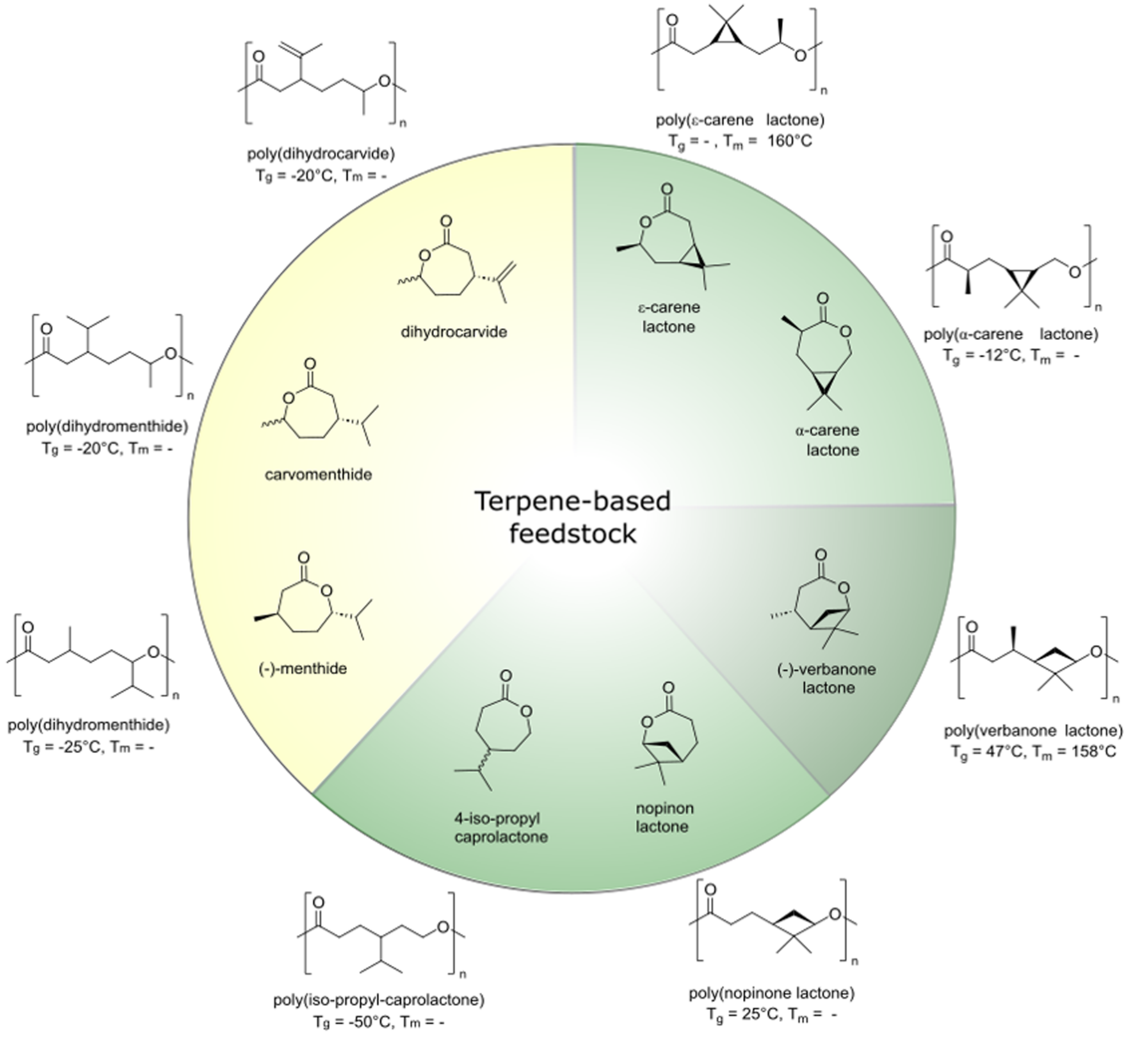
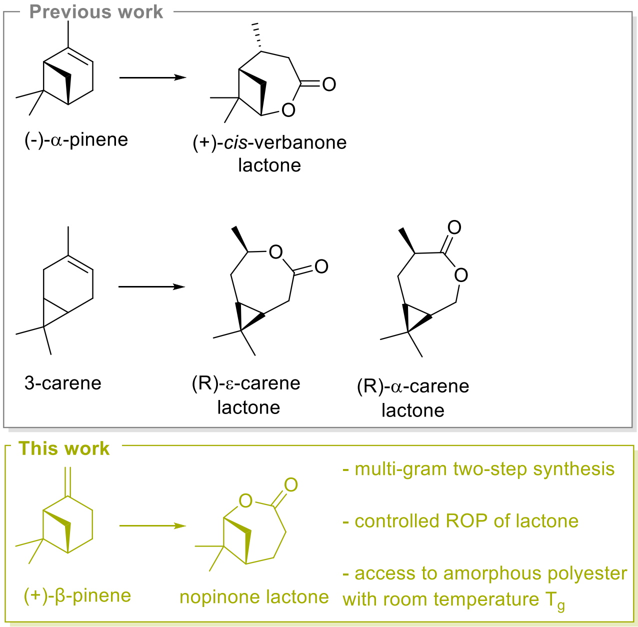


Figure 1. Overview of terpene-based monomers for catalytic ring-opening polymerization sorted after raw materials limonene (yellow), 3-carene (light green, upper right), *α*-pinene (green, middle), and *β*-pinene (dark green, lower right) and the resulting polyesters with their thermal properties.[13,14,21−23,25,−29]

however, their cyclic structure leaves also the possibility for ring-opening polymerization (ROP) to polyesters as a promising opportunity.[16] Regarding the ROP of terpenes, two major feedstock classes are prominently featured, either the limonene-based terpenoids carvone and menthol or the bicyclic monoterpenes *α*-pinene, *β*-pinene, and 3-carene, which are the main components of turpentine oil.[13,14,21]

In order to convert terpenes into polyesters, different oxidative transformations are necessary where the key reaction is always the ring expansion of the respective terpene ketones to the corresponding lactones. An overview of previously reported limonene- and turpentine-based polyesters is shown in Figure 1. Hillmyer and co-workers were the first to successfully transform (−)-menthol via Baeyer−Villiger ring expansion with *m*CPBA into (−)-menthide. Catalytic ROP with Zn-alkoxide catalysts resulted in polyesters with molecular weights up to 91 kg·mol^{-1} ($Đ$ = 1.1) and amorphous behavior, possessing a glass transition temperature T_g of around −25 °C.[22] Derived from (−)-carvone, the three possible lactones carvomenthide, dihydrocarvide, and epoxidized dihydrocarvide oxide are reported. Poly(dihydromenthide) obtained from the anionic ROP of the respective lactone exhibits molecular weights of around 62 kg·mol^{-1} ($Đ$ = 1.2) and an amorphous behavior with a T_g of −20 °C just like poly(menthide) due to the similarity of the *iso*-propyl and methyl side chain.[23] Replacing the *iso*-propyl group of poly(dihydromenthide) to an *iso*-propenyl side chain is making it a versatile candidate for postpolymerization functionalization.[24] Concerning the bicyclic monoterpenes, *β*-pinene was transformed into 4-*iso*-propylcaprolactone in a multistep synthesis route involving skeletal rearrangement and various oxidation steps. Molecular weights of up to 23 kg·mol^{-1} ($Đ$ = 1.3) could be obtained; however, the T_g of the aliphatic polyester was at −50 °C.[14] Comparison of the already mentioned polymers poly(verbanone lactone)[25,26] based on *α*-pinene and poly(*ε*-carene lactone),[27] based on 3-carene, led to the conclusion that retaining the bicyclic character in the lactone and introducing a cycloaliphatic ring in the polymer backbone enhance thermal and mechanical properties. Both are semicrystalline materials with a melting point of around 160 °C, indicating the higher rigidity of the polymer main chain.[25,27] Herein, we report the synthesis and catalytic ROP of nopinone lactone (NopL) derived from *β*-pinene, retaining its bicyclic structure during the oxidative transformation and successfully incorporating a cyclobutene moiety into the main chain of the resulting polyester (Scheme 1).

Scheme 1. Bicyclic Lactones Derived from Monoterpenes Applied in Ring-Opening Polymerization for Polyesters[25,27]



■ METHODS AND MATERIALS

General Experiments. Nopinone was synthesized according to a literature-known procedure with slight modifications; for a detailed synthesis procedure and analysis, see the Supporting Information. The catalyst $Sn(Oct)_2$ was purchased from Sigma-Aldrich and distilled prior to use; $(ONOO)^{tBu}Y(X)(thf)$(X = *sym*-col, bdsa),[2,30] $[(ONOO)^{tBu}Y]_2(TMPy)$,[31] and $(ONNO)^{tBu}In(O^tBu)$[32] were prepared according to literature procedures. NopL was dried over CaH for 1 week prior to distillation. Additional details on measurement protocols and further characterization of polymers are given in the Supporting Information.

Baeyer–Villiger Oxidation of Nopinone. 20.0 g of (+)-nopinone (144 mmol, 1.0 equiv) and 60.0 g of *m*CPBA (348 mmol, 2.4 equiv) were added to a 250 mL round-bottom flask and were stirred for 12 days at rt. After completion of the reaction, 60.0 g of K_2CO_3 (434 mmol, 3.0 equiv) and 200 mL of DCM were added, and the mixture was stirred for 1 h. The resulting suspension was filtered and washed with 50 mL of DCM. Afterward, 200 mL of H_2O was added to the filtrate, and the resulting phases were separated. The organic phase was washed with brine (1 × 150 mL) and dried with magnesium sulfate. The solvent was removed in vacuo, resulting in 13.1 g of the crude product. Lactone was distilled under reduced pressure (bp. 55 °C, 0.04 mbar), resulting in 10.5 g (+)-nopinone lactone (68 mmol, 47%) as a colorless oil.

Ring-Opening Polymerization. The ring-opening polymerization in bulk was performed by adding 100 mg (0.65 mmol) of lactone into a crimp vial, adding the corresponding amount of the catalyst, and heating the sealed vial to 110 °C for 24 h. For solution polymerizations, 100 mg (0.65 mmol) of lactone was dissolved in 0.5 mL of dry toluene and added to the respective amount of the catalyst solved in 0.5 mL of dry toluene. The mixture was stirred at 110 °C or room temperature for the indicated time. After polymerization, an aliquot for conversion determination was withdrawn and quenched in 0.5 mL of wet chloroform-d_1 before the mixture was precipitated in 10 mL of pentane/Et_2O. The residue was dried in vacuo at 60 °C overnight and analyzed using $^1H/^{13}C$ NMR, SEC, TGA, and DSC.

■ RESULTS AND DISCUSSION

Monomer Synthesis and Polymerization of Nopinone Lactone (NopL). The synthesis of the monomer based on *β*-pinene was achieved by ozonolysis, yielding nopinone, followed by a Baeyer–Villiger oxidation (BVO) using *m*CPBA (Scheme 2). While the synthesis of lactone was already reported in the literature,[33,34] yields and scale-up of the reactions always hampered the polymerization of *β*-pinene-based bicyclic lactones. By simply using solvent-free conditions, we were able to selectively isolate one regioisomer of the corresponding lactone, thus establishing a monomer synthesis with isolated yields of 45%. Usually, BVO yields two regioisomers; however, under our updated conditions, selectively, 7,7-dimethyl-2-oxa-bicyclo[4.1.1]octan-3-one (nopinone lactone, NopL) was obtained. The selective synthesis can be explained by the migration ability of the substituents on one side, as insertion into the higher substituted position is favored. Additionally, under these conditions, the minor lactone is less stable and hydrolysis takes places, lowering the overall yield.[35,36] In summary, a facile two-step reaction sequence on a multigram scale could be established, resulting in monomer-grade lactone.

Scheme 2. Synthesis of Nopinone Lactone (NopL) via Ozonolysis of *β*-Pinene (Isolated Yield 74%, 50 g Scale) and Subsequent Baeyer–Villiger Oxidation of Nopinone (Isolated Yield 43%, 20 g Scale), Followed by Ring-Opening Polymerization with Various Organometallic Catalysts[14,30,32,34,37]

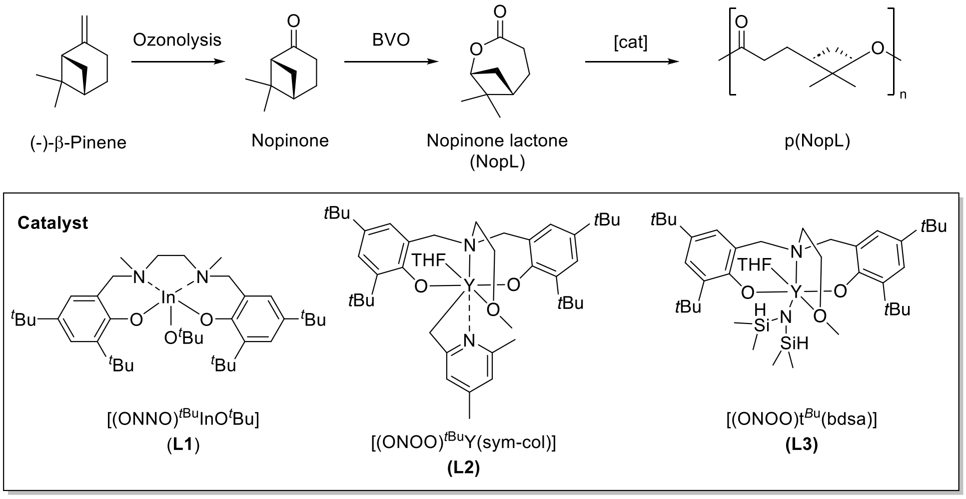


Table 1. Ring-Opening Polymerization of NopL Using Catalysts L1−L3

entry	catalyst	solvent	[M]/[cat][a]	T (°C)	t_R[b] (h)	X_m[c] (%)	$M_{n,theo}$[d] (kg·mol^{-1})	$M_{n,rel}$[e] (kg·mol^{-1})	$Đ$[e]
1	$Sn(Oct)_2$	toluene	1:100	110	24	n.d.	n.d.	n.d.	n.d.
2	$Sn(Oct)_2$	bulk	1:100	110	24	n.d.	n.d.	n.d.	n.d.
3	**L1**	toluene	1:100	RT	24	80	12	42	1.3
4	**L1**	toluene	1:200	RT	24	53	16	52	1.3
5	**L2**	toluene	1:50	RT	8	99	8	25	1.8
6	**L2**	toluene	1:100	RT	8	95	15	37	1.9
7	**L2**	toluene	1:200	RT	24	99	30	48	1.3
8	**L2**	toluene	1:400	RT	24	94	58	105	1.7
9	**L2**	DCM	1:100	RT	27	72	11	25	1.7
10	**L3**	toluene	1:100	RT	5	93	14	44	1.7
11[f]	**L3**	toluene	1:200	RT	20	96	30	61	1.7

[a] Monomer−catalyst ratio as weighed, 1.0 mmol of the monomer. [b] Reactions were performed under solution conditions $[M]$ = 1.0 M. [c] Conversion of the monomer calculated from aliquot ^{1}H NMR (detailed calculation in Figure S11). [d] Theoretical molecular weight $M_{n,theo}$ = [M]/[cat] × X_m × 152.21 g·mol^{-1}. [e] Relative molecular weight $M_{n,rel}$ and polydispersity $Đ$ determined via SEC in THF at 40 °C relative to polystyrene. [f] Reaction was performed with 6.5 mmol of the monomer and under solution conditions $[M]$ = 1.5 M. n.d. = not determined.

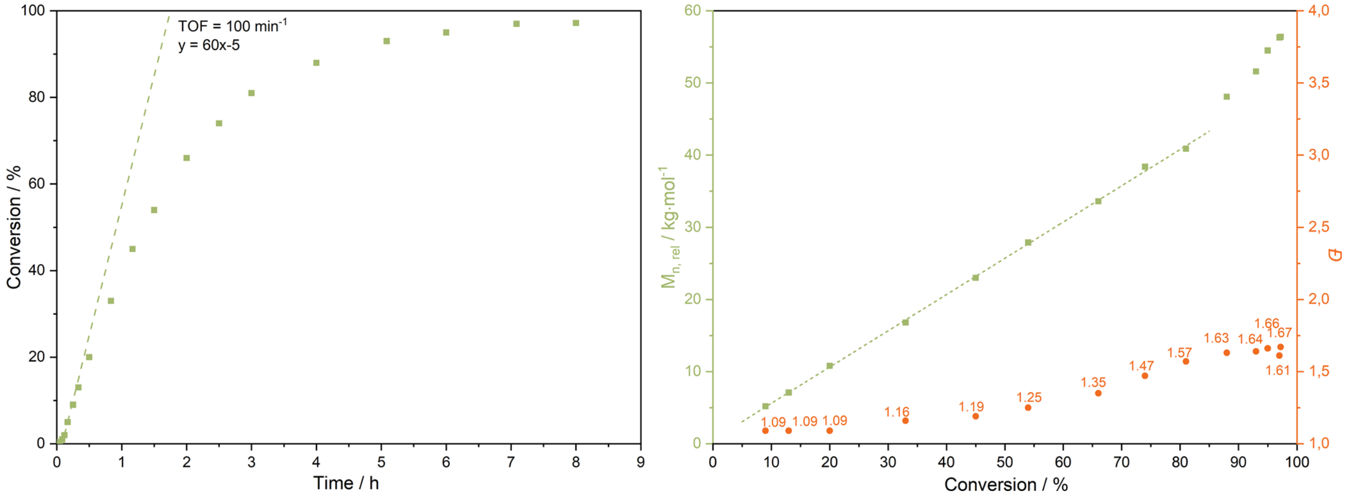


Figure 2. Catalytic activity of **L3** in the ROP of NopL (left); dependency of $M_{n,rel}$ and polydispersity over the conversion of NopL in toluene at room temperature (right); $[NopL]_0$ = 1 mmol, $[NopL]_0$:$[L3]_0$ = 100:1.

Several organometallic catalysts were investigated in the ring-opening polymerization of NopL; however, by using industrially applied tin(II) 2-ethylhexanoate ($Sn(Oct_2)$), no conversion could be obtained at 110 °C (Table 1, entries 1 and 2). Switching to more complex organometallic catalysts, salan-type indium *tert*-butoxide **L1**, yttrium-*bis*(phenolate) catalyst **L2**, and CH-activated 2-methoxyethylamino-*bis*(phenolate) yttrium catalyst **L3** were tested in the polymerization of NopL to poly(nopinone lactone) (p(NopL)). Salan-type catalyst **L1** is known to be active in the polymerization of different lactones[32] and yielded p(NopL) with good conversion at room temperature after 24 h in ratios of 1:100 and 1:200 (Table 1, entries 3 and 4). The obtained polyester reached high molecular weights ($M_{n,rel}$ = 42−52 kg·mol^{-1}) with a narrow and monomodal distribution ($Đ$ = 1.3; Figures S22 and S23). Switching to yttrium-*bis*(phenolate) catalysts **L2**, full conversion was reached after 24 h for the ratio of 1:200; however, the obtained molecular weight of 28 kg·mol^{-1} was lower but maintained a narrow monomodal dispersity ($Đ$ = 1.3; Table 1, entry 8). Variation of the ratio catalyst to monomer from 1:50 to 1:400 led to increased molecular weights ranging from 25 to 105 kg·mol^{-1} depending on the ratio, indicating a controlled polymerization featuring tunable molecular weights. However, a broadening of the molecular weight distribution was observed ($Đ$ = 1.7−1.9). Switching the solvent from toluene to DCM led to a decreased conversion of 72% after 27 h and a decreased $M_{n,rel}$ of 11 kg·mol^{-1} while still obtaining a broad dispersity (Table 1, entries 7 vs 9). End-group analysis via ESI-MS measurements of the respective polymer with **L2** indicates a catalytic ring-opening polymerization via nucleophilic attack of the initiator, as expected for this kind of catalyst and monomer (Figure S12).[38,39]

In order to investigate the mechanistic details of the ROP further, kinetic measurements were performed using **L3** as the catalyst, a literature-known complex in the ROP of multiple cyclic esters.[30,40] The turnover frequency was determined to be 6000 h^{-1} with a linear increase in the first 2 h, indicating at the beginning a first-order kinetic (Figure 2 left). Conversion over molecular weight and dispersity reveals a linear correlation of $M_{n,rel}$, confirming a living-type catalytic ROP. At high conversion, transesterification side reactions are the reason for the deviation of the linear character, associated with increased dispersity (Figure 2 right).

Thermodynamic analysis of the ring-opening polymerization of NopL was conducted by measuring the equilibrium concentration of the polymerization with $(ONOO)^{tBu}Y(bdsa)$ **L3** (1:200) at a reaction temperature between 25 and 80 °C and a starting monomer concentration $[M]_0$ of 0.2 M in

Scheme 3. Copolymerization of NopL and *rac*-BBL to Obtain the Polymer Architecture of AB-Type and ABA-Type Polymers Using L2 and L4

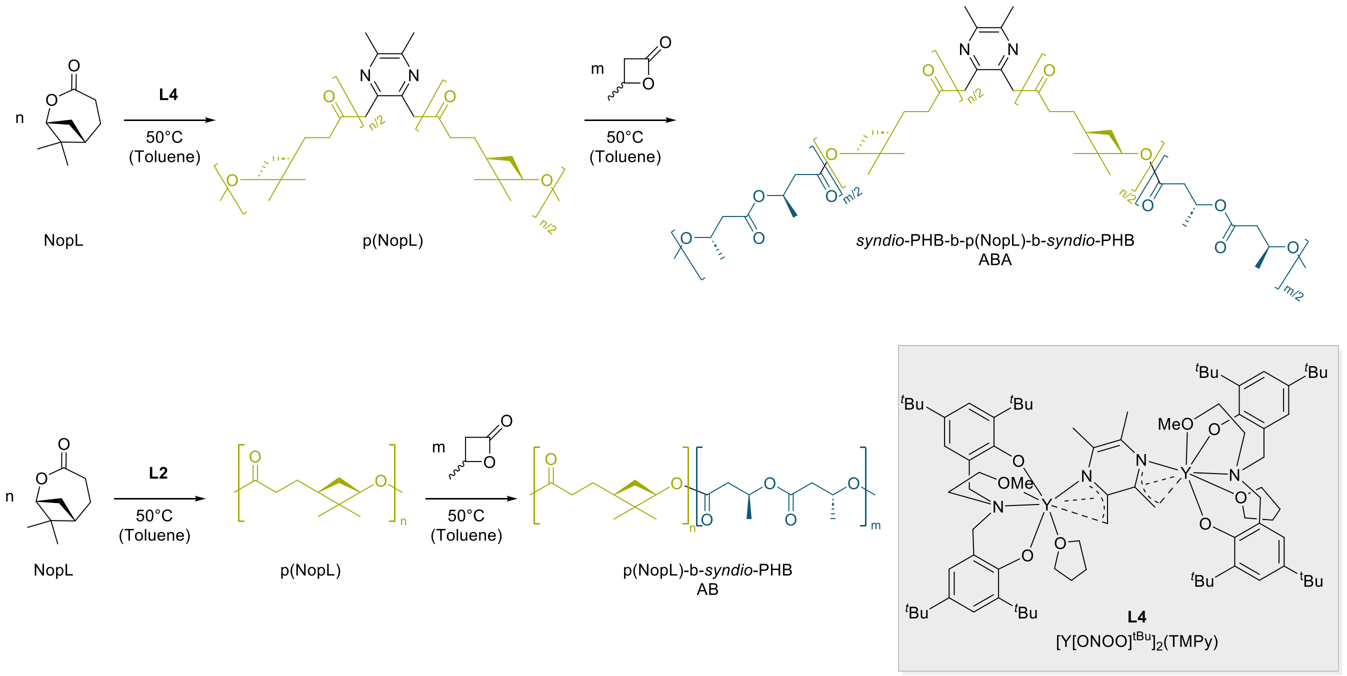


Table 2. Ring-Opening Copolymerization of NopL and *rac*-BBL Using Catalysts L2 and L4[a]

entry	cat.	NopL/BBL	t^A (h)	X_A[b] (%)	$M_{n,rel}^{A}$[c] (kg·mol^{-1})	t^B (h)	X_B[b] (%)	$M_{n,rel}^{A,B}$[c] (kg·mol^{-1})	$Đ$[c]	PHB/pNopL[d] (%)	P_r
1[e]	**L4**	1/200/0	6	96	40	n.d.	n.d.	n.d.	1.8	n.d.	n.d.
2	**L4**	1/100/100	2	82	31	2	99	36.0	1.4	60/40	0.83
3[f]	**L4**	1/100/200	2	80	28	2	95	35.9	1.4	73/27	0.74
4	**L2**	1/100/100	3	80	38	2.5	85	42.3	1.5	51/49	0.74

[a] Monomer−catalyst ratio as weighed, 0.65 mmol of NopL, and reactions were performed under solution conditions [NopL] = 0.5 M at 50 °C. [b] Conversion of the monomer calculated from aliquot ^{1}H NMR. [c] Relative molecular weight $M_{n,rel}$ and polydispersity $Đ$ determined via SEC in THF at 40 °C relative to polystyrene. [d] Calculated via ^{1}H NMR spectroscopy (Figure S13). [e] Polymerization was conducted at room temperature. [f] Reaction was performed with 2.1 mmol of NopL. n.d. = not determined.

toluene. The standard state thermodynamic parameters were then calculated by using a van't Hoff plot (Figure S35), resulting in a standard state enthalpy of $\Delta H_p^0 = -16.6 \pm 1.9$ kJ·mol^{-1} and a standard state entropy of $\Delta S_p^0 = -23.9 \pm 5.9$ J·mol^{-1}·K^{-1}. Comparing the thermodynamic values with menthide ($\Delta H_p^0 = -16.8 \pm 4.6$ kJ·mol^{-1}, $\Delta S_p^0 = -27.4 \pm 4.6$ J·mol^{-1}·K^{-1} at 0.2 M) in toluene polymerization of NopL has a similar exothermicity.[22,41,42] As the enthalpy is determined by the ring strain of monomers in the ring-opening polymerization, similar values of ΔH_p^0 indicate only a minor influence of the cyclopropane unit on the ring strain.[42,43] Besides the slightly lower ring strain, NopL also has a high ceiling temperature T_c at $[M]_{eq}$ = 1 M of 419 °C compared to menthide or valerolactone, indicating lower depolymerizability (Table S2).

Block Copolymerization of NopL and *rac*-BBL. Besides the investigation of homopolymerization, copolymerization and thus the synthesis of different polymer architectures were investigated. Since yttrium-*bis*(phenolate) catalysts **L2** and **L3** were active in the homopolymerization, we also tested the activity of bifunctional yttrium-*bis*(phenolate) 2,3,5,6-tetramethylpyrazine (TMPy) catalyst **L4**[31,39] (Scheme 3). While monometallic catalysts can lead to AB-type polymers, the bimetallic option opens the possibility of an A-B-(TMPy)-B-A type polymer. For the second polymer block, racemic *β*-butyrolactone (BBL) was chosen, as the monomer is commercially available, and additionally can be derived from CO_2 as a starting material, complementing the idea of a biobased polymer.[44] All yttrium amino-alkoxy catalysts are known to polymerize BBL syndioselective, which leads to semicrystalline polyhydroxybutyrate (PHB) with a T_m ranging between 120 and 170 °C depending on syndiotacticity (P_r is the probability of racemic linkages) and can therefore be used as a hard building block in triblock polymers (TBPE).[39,40]

The activity of **L4** in the polymerization of nopinone lactone was initially tested at room temperature and resulted in polyesters with narrow dispersity and a $M_{n,rel}$ of 40 kg·mol^{-1} after 6 h (Table 2, entry 1). In order to decrease the gelation of p(NopL), which occurs at higher conversions, we conducted all copolymerization at 50 °C. Additionally, *rac*-BBL has a higher coordination strength than NopL. Therefore, polymerization of the terpene-based monomer is to be conducted first, followed by the addition of *rac*-BBL, and by varying the monomer feed, control over the ratios within the polymer is possible.

Both copolymerization attempts for an ABA (A = PHB; B = p(NopL)) polymer were successful, with a NopL conversion of 80% after 2 h and a further complete conversion of *rac*-BBL after another 2 h (Table 2, entries 2−4). ^{1}H NMR shows the formation of an AB and ABA polymer with a composition of

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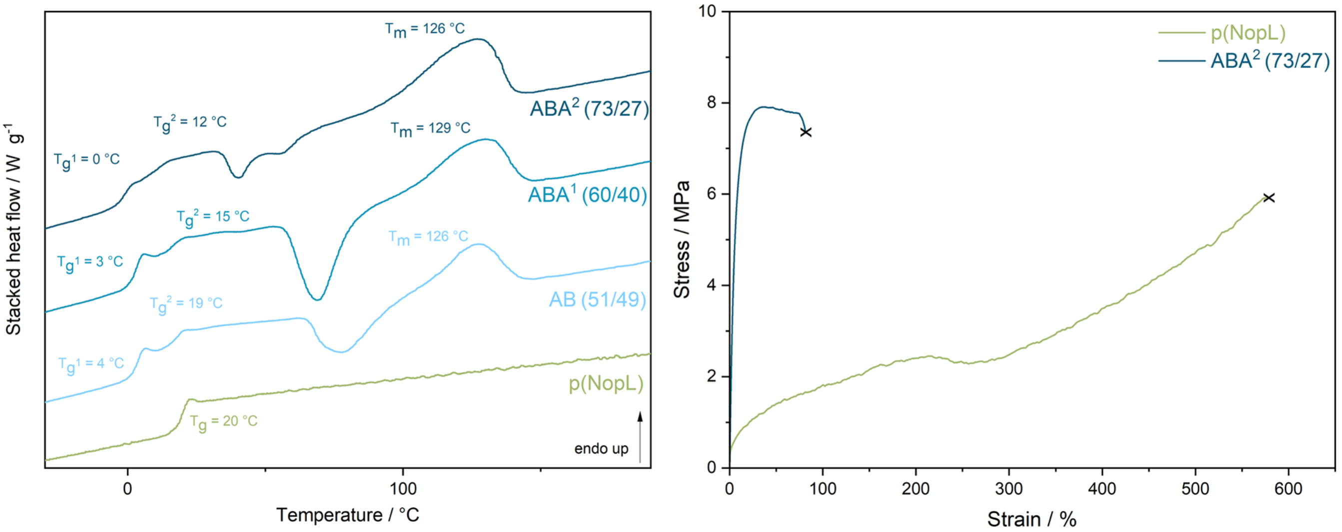

Figure 3. Differential scanning calorimetry of p(NopL) with $M_{n,rel}$ = 48 kg·mol^{-1} (Table 1, entry 6), ABA^1 with $M_{n,rel}$ = 36 kg·mol^{-1} (Table 2, entry 2), ABA^2 with $M_{n,rel}$ = 40 kg·mol^{-1} (Table 2, entry 3), and AB with $M_{n,rel}$ = 42 kg·mol^{-1} (Table 2, entry 4) (left); stress−strain curves of p(NopL) ($M_{n,rel}$ = 61 kg·mol^{-1}) and ABA^2 ($M_{n,rel}$ = 36 kg·mol^{-1}); break points indicated by "X" (right).

51/49 (AB), 60/40 (ABA^1), and 73/27 (ABA^2) of PHB to p(NopL) (Figures S15−S17). Analysis of the carbonyl signals in ^{13}C NMR spectra shows only the respective signals for p(NopL) at 173.1 and 169.2 ppm for PHB, consistent with the formation of distinct blocks (Figure S18). To further verify the formation of a successful triblock polymer, DOSY-NMR studies and SEC analysis were conducted. Both DOSY spectra show only one set of signals, corresponding to one diffusion coefficient (Figures S19−S21), which is consistent with joined p(NopL) and PHB blocks. Additionally, the increase in polymer molar mass while obtaining a narrow dispersity ($Đ$ = 1.4) supports the successful formation of TPEs (Figures S32−S34).

Thermal Properties and Mechanical Properties. Application of sustainable polyesters in engineering areas is of particular industrial interest if the materials exhibit distinguished thermal and mechanical properties. Thermogravimetric analysis (TGA) was applied to assess the polyester thermal stability, showing a 5% weight loss ($T_{d,5\%}$) at 350 °C (Figure S36). The decomposition temperature is much higher in comparison with already industrially relevant sustainable polyesters like bacterial PHB ($T_{d,5\%}$ = 239 °C).[45] Bicyclic monoterpene-based polyesters bearing a cyclic unit in the backbone are usually semicrystalline polymers with high melting points due to the more rigid structure of the cyclic backbone.[25,27] Contrary to this observation, differential scanning calorimetry of p(NopL) indicates an amorphous polymer with a glass transition temperature T_g at 23 °C (Figure 3, left).

The mechanical properties were analyzed by uniaxial tensile testing of dog-bone-shaped specimens. For this purpose, polymerization was carried out on a 1 g scale (Table 1, entry 10), yielding a polyester with $M_{n,rel}$ = 61 kg·mol^{-1} and $Đ$ = 1.7, from which three samples were prepared by hot compression molding at 80 °C, resulting in clear, elastic specimens (Figure S40). The stress−strain curves showed ductile behavior with a high elongation at break ε_B of 559 ± 46%, an ultimate tensile strength σ_B of 5.6 ± 0.3 MPa, and a Young's modulus E of 9.7 ± 1.7 MPa (Figure 3, right). At a strain of ~200%, strain hardening[46] can be seen due to a small maximum; however, samples are regaining their previous structure and clarity after resting for 1 day at room temperature, indicating an elastomeric behavior due to the low glass transition temperature (Figure S41).

Due to the high elasticity of p(NopL), it is well suited to be incorporated in a brittle thermoplastic to enhance the elongation at break. The copolymers of PHB and p(NopL) were therefore investigated in terms of their thermal and mechanical properties via DSC, TGA, and stress−strain measurements. The TGA analysis shows a $T_{d,5\%}$, corresponding to the PHB block as well as a $T_{d,5\%}$ at 330 °C assigned to the decomposition temperature of the p(NopL) block (Figure S37). DSC analysis was performed to obtain further information on the miscibility of the TBPEs, since microphase separation is necessary to obtain beneficial mechanical properties. The AB, as well as the ABA-type polymers, show two T_gs, which correspond to the PHB (0−4 °C) and p(NopL) (12−15 °C) and additionally exhibit the melting point corresponding to PHB. All copolymers have, therefore, some crystalline domains, while the precrystallization corresponding to PHB is not equally distinctive.

In order to see the influence of p(NopL) in the sydiotactic PHB on the mechanical properties, stress−strain measurements were performed for ABA^2 (P_r = 0.79). Dog-bone-shaped specimens were produced by hot compression molding at 140 °C, resulting in clear, elastic specimens. The beneficial influence of p(NopL) can be seen if the stress−strain behavior is compared with that of the homopolymers of p(NopL) and PHB (Figure 3, right). *Syndio*-PHB is a thermoplastic with a Young's modulus of 195 MPa but is a rather stiff material with an ε_B of 18% (P_r = 0.74).[39] Incorporation of p(NopL) led to a 4 times higher elongation (ε_B = 77 ± 3%) while still obtaining a high Young's modulus of 113 ± 11 MPa. Compared to the homopolymer of p(NopL), an increased ultimate tensile strength of 7.5 ± 0.6 MPa leads to a more stable specimen. The TPBE contributes thus from the thermoplastic behavior of PHB and its semicrystalline behavior and, however, also has higher elasticity due to the soft building block.

CONCLUSIONS

This work highlights the opportunities of using biobased feedstocks such as turpentine, specifically β-pinene, as a starting material for the synthesis of sustainable polyesters. A simple two-step reaction sequence leads to the monomer nopinone lactone (NopL), which can be easily polymerized by using commonly reported catalysts at room temperature. Kinetic studies show a living character when applying yttrium-*bis*(phenolate) catalysts, allowing precise molecular weight control while maintaining narrow polydispersities. Thermodynamic studies indicate a similar enthalpy as that of menthide; thus, the bicyclic character of the monomer has only a minor influence on the polymerization behavior. Thermal and mechanical properties show a thermally stable, fully amorphous polyester with a glass transition temperature at room temperature and a high elongation at break value of 559 ± 46%. The incorporation as a soft building block in TBPEs with *syndio*-PHB as the hard block was successful, and a tensile test could show the beneficial influence of p(NopL) as the elongation at break increases up to 77 ± 3% while maintaining a high Young's modulus and ultimate tensile strength, making p(NopL) an excellent candidate for a soft block in thermoplastic elastomers, broadening the application profile of terpene-based polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02663.

> General experimental details; ESI-MS measurements; full SEC characterization and SEC traces; additional $^1H/^{13}C$ NMR spectra; and TGA measurements. (PDF)

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ABBREVIATIONS

BVO;Baeyer−Villiger oxidation; DSC;differential scanning calorimetry; NopL;nopinone lactone; pNopL;poly(nopinone lactone); ROP;ring-opening polymerization; SEC;size exclusion chromatography; TGA;thermogravimetric analysis

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