Macromolecules

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Hydrogen Borrowing Catalysis for the Modification, Depolymerization, and Synthesis of Polyesters

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Cite This: *Macromolecules* 2025, 58, 2366−2378

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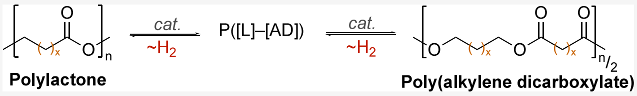


ABSTRACT: A ruthenium-catalyzed hydrogen transfer ester metathesis (HTEM) is reported that allows for the isomerization of different types of linear polyesters such as polylactones without the need for any stoichiometric reagent, forming novel types of copolyesters containing additional alkylene dicarboxylate (AD) repeating units. Depending on the thermodynamic boundary conditions given by the polyester, the cocatalyst, and the potential resting state, the reported HTEM reaction equilibrates toward a thermodynamic minimum, which is otherwise not accessible by a regular transesterification or hydrolysis. It is for example demonstrated that poly(butylene succinate) (PBS) is depolymerized to cyclic butyrolactone (BL_c) with high yield and high selectivity, whereas cyclic valero- (VL_c) and caprolactone (CL_c) can be polymerized by HTEM to poly(lactone-alkylene dicarboxylate) copolyesters. Mechanistic investigations show that the formation of the chemically modified polyester relies on a two-fold catalytic reaction: a HTEM via a hydrogen borrowing process and a concomitant transesterification catalyzed by the base cocatalyst. Evidence is provided that hydrogen transfer ester metathesis proceeds via a reversible aldehyde formation. The described HTEM represents an unprecedented, catalyzed hydrogen borrowing process within polymers and bears significant importance regarding a dynamic postsynthetic modification of polyesters.

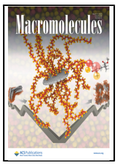
■ INTRODUCTION

Metal−ligand cooperativity has been a key concept for the development of homogeneous catalysts for novel atom-economic and sustainable reactions with molecular substrates in the past two decades. Recent advancements of such metal−ligand cooperative catalysis particularly involve hydrogenation, dehydrogenation, and dehydrogenative coupling reactions as well as hydrogen borrowing-type reactions.[1−13] These important developments were also applied for the synthesis of polyesters[14−16] and polyamides[17−20] by dehydrogenative coupling, as well as for alternative strategies for the recycling of polyesters,[21−24] polyamides,[25,26] and polyurethanes[26] by hydrogenation (Figure 1A), but the huge number of catalytic hydrogen borrowing-type protocols in organic synthesis have never been applied to polymers (Figure 1B),[27] although this can provide access to new types of polymeric materials and can be also used to tune the chemophysical properties of the material.

Polyesters are of increasing importance as they can function as substitutes for other bulk and commodity polymers due to their high potential with respect to the embedding into closed loops, but methodologies to achieve their recycling, degradation, and valorization, as well as the optimization of their properties, still require significant improvement. Important milestones have been the introduction of covalent adaptive networks (CANs) and vitrimers, which both rely on a catalytic transesterification reaction at elevated temperatures,[28,29] as well as the discovery that aliphatic long-chain polyesters, which can be produced from renewable feedstocks and recycled by transesterification, exhibit properties similar to high-density polyethylene (HDPE).[30,31] In this context, the postmodification of polymers exhibits great potential and can produce unusual properties, such as enormous electro-[32] and barocaloric effects,[33] but methods for the postsynthetic modification of polyesters, yielding functionalized polymers with tuned properties, are often limited to blending, curing, grafting, or derivatization with reagents,[32−39] whereas the modification of the main chain or backbone often involves specifically designed polymers.[40,41] In particular for statistic copolyesters, formed by random incorporation of a second minor monomer in polyesters, it has been demonstrated that biodegradation can be facilitated, while important properties of the original polyester are maintained.[42]

In the current paper, we report a novel type of transesterification reaction for polyesters that relies on a hydrogen transfer ester metathesis (HTEM) sequence (Figure 1C), which represents the first example of a catalytic hydrogen

Received: December 14, 2024
Revised: February 12, 2025
Accepted: February 12, 2025
Published: February 26, 2025



https://doi.org/10.1021/acs.macromol.4c03132

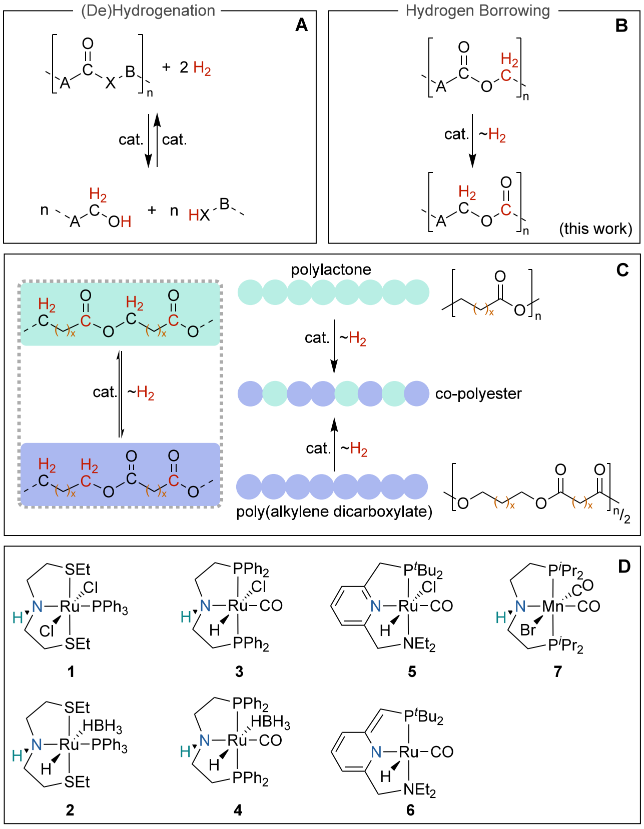


Figure 1. Previously reported dehydrogenative polymer synthesis and hydrogenative depolymerization (A) and the novel hydrogen borrowing reaction introduced in this work (B). Concept of the hydrogen transfer ester metathesis of polyesters (C) as well as potential precatalysts (D).

borrowing reaction with polymers as substrates. The combination of the latter with a concurrent catalytic transesterification allows for a dual catalytic system, which gives rise to the efficient main-chain modification and conversion of a homopolyester into a randomly sequenced copolyester in the presence of a suitable cooperative catalyst system and in the absence of any stoichiometric reagent. It is demonstrated that with the formation of constitutional isomers, the properties of the utilized polyester can be modified in an atom-economic reaction. Depending on the repeating unit in the utilized polyesters, in some cases, selective depolymerization of poly(alkylene dicarboxylate) to the corresponding cyclic, monomeric lactone is observed.

■ RESULTS AND DISCUSSION

HTEM of Model Polyesters. Aliphatic linear polyesters of different chain lengths are ideal model substrates to transfer the reactivity from molecular esters[43] to polyesters, as their morphology and the role of entanglements are well-understood. Using the previously optimized conditions for molecular esters, we utilized 1 mol % of Gusev's catalyst **1** with respect to the average number of ester groups (M) together with 5 mol % KO^{t}Bu cocatalyst (B) in the reaction of different aliphatic polyesters and cyclic lactones in toluene-d_8. The resulting reaction mixtures were analyzed by gel permeation chromatography (GPC), as well as by NMR spectroscopy. Further, we investigated some physical properties, e.g., crystallinity by solid-state NMR spectroscopy or thermal behavior by differential scanning calorimetry (DSC) for one selected reaction product to acquire deeper insights in the material behaviors.

The reaction of PCL (M_n = 5 kDa) at 80 °C yields a polyester with reduced molecular weight of M_n = 3 kDa (entry 1, Table 1) after 16 h. The ^{1}H NMR spectrum of the reaction did not show any diagnostic changes due to superimposed resonances. However, by comparison of the ^{13}C{^{1}H} NMR spectra of reference samples, including PCL + KO^{t}Bu, poly(hexylene adipate) (PHA), and PHA + KO^{t}Bu, we identified hexylene adipate (HA) as a major new repeating unit in the formed polyester (Figure 2) with a characteristic chemical shift of 173.42 ppm (Figure 3A) for the carbonyl carbon atom, which is the exact value, reported for HA segments in block copolymers.[44] As the resonances of the $\underline{C}H_2COO$ carbon atoms in CL and HA repeating units exhibit similar relaxation times in the ^{13}C{^{1}H} NMR spectrum (Figures S8 and S9), we used the integrals of these resonances to estimate the overall fraction of CL and HA units in the formed copolymers and to monitor the progress of the reaction. This analysis revealed that the resulting polyester contains 61% CL monomer units and 39% HA monomer units after the catalytic reaction (16 h) in the presence of 1 mol % catalyst **1** and 5 mol % KO^{t}Bu (entry 1, Table 1; two CL units are converted to one HA unit and are weighted accordingly). The catalyst system in this mixture remains active, and continuous heating for overall 88 h yields a copolyester with 55% CL and 45% HA monomers. High-molecular-weight PCL (M_n = 49 kDa) displays a similar reactivity with 1 mol % complex **1** and 5 mol % KO^{t}Bu, yielding 35% HA units after 16 h at 80 °C, but with significantly reduced molecular weights (M_n = 5 kDa, entry 3, Table 1). Continuous heating yields an HA fraction of 40% after 88 h showing reduced reaction speed compared to low-molecular-weight PCL suggesting the influence by hindered diffusion due to longer chains in the beginning. The catalytic HTEM of PCL takes place at ambient temperature as well (entry 4, Table 1). With complex **1** and KO^{t}Bu as a cocatalyst, the reaction is significantly slower after 4 h at ambient temperature but shows similar conversions after 16 h and finally yields a similar fraction of 43% HA after 88 h (Figure 3B), suggesting that catalyst deactivation is more facile at elevated temperatures.

The employment of the ruthenium-based precatalyst **3**, containing the amine-based MACHO ligand, as a precatalyst (1 mol %) with 2.5 mol % KO^{t}Bu (instead of 5 mol % since **3** has only one chloride ligand) for the HTEM of PCL (M_n = 49 kDa) yields a polyester containing 24% HA units at 80 °C after 16 h (entry 6, Table 1). The conversion is comparable to the utilization of 0.5 mol % **1** with 2.5 mol % KO^{t}Bu under identical conditions (entry 5, Table 1). The utilization of 1 mol % Milstein's precatalyst **5** with 2.5 mol % KO^{t}Bu (since **5** also has only one chloride ligand) shows the lowest conversion after 16 h under equal conditions with a resulting HA content of 3%, but the molecular weight drop is less drastic with the resulting M_n value of 20 kDa (entry 8, Table 1). These findings indicate that ruthenium SNS-type catalysts are more active than ruthenium PNP- and PNN-type catalysts for HTEM of polyesters, whereas for low-molecular-weight PCL, **1** and **3** give rise to similar conversions and product compositions after 88 h (entries 1 and 2, Table 1), indicating that catalyst diffusion is hindered to a different extent for **1** and **3** with a polyester substrate. To evaluate the influence of the base, we synthesized the new hydrido borohydrido precatalyst **2** (Figure

Table 1. Catalytic Hydrogen Transfer Ester Metathesis (HTEM) of Polycaprolactone (PCL) and the Corresponding Poly(hexylene adipate) (PHA) of Different Molecular Weight, Using Different Precatalysts and Different Reaction Conditions

educt entry	M_n[a] [kDa]	PD[a]	C	M/B/C[b]	T [°C]	t [h]	polymer composition[c] [%]		polymer/lactone[d] [%]	M_n[a] [kDa]	PD[a]	TON[e]
PCL							PCL	PHA	P(CL-HA)/CL_c			
1	5	1.2	1	100/5/1	80	16(88)	61(55)	39(45)	100/0	3	1.5	39(45)
2	5	1.2	3	200/5/2	80	88	55	45	100/0	3	1.5	45
3	49	1.7	1	100/5/1	80	4(16)	72(65)	28(35)	100/0	5	1.4	28(35)
4	49	1.7	1	100/5/1	23	4(16)	86(64)	14(36)	100/0	7	1.4	14(36)
5	50	1.8	1	200/5/1	80	16	79	21	100/0	8	1.7	42
6	49	1.7	3	200/5/2	80	16(88)	76(74)	24(26)	100/0	13	1.6	24(26)
7	50	1.8	3	100/5/1	80	16(88)	60(56)	40(44)	100/0	9	1.6	40(44)
8	50	1.8	5	200/5/2	80	16(88)	97(95)	3(5)	100/0	20	1.5	3(5)
9	50	1.8	5	100/5/1	80	16(88)	62(58)	38(42)	100/0	8	1.4	38(42)
10	49	1.7	2	100/0/1	80	16(160)	92(85)	8(15)	100/0	10	1.8	8(15)
11	49	1.7	4	100/0/1	80	16(160)	92(89)	8(11)	100/0	14	1.7	8(11)
12	50	1.8	6	100/0/1	80	16(160)	99(99)	1(1)	100/0	30	1.9	1(1)
13	50	1.8	7	100/5/1	80	16	100	0	100/0			0
14	50	1.8		100/5/0	80	16	100	0	100/0	11	2.6	0
15	50	1.8		100/0/0	80	16	100	0	100/0	49	1.8	0
PHA												
16	8	1.5	1	50/5/1	80	40	55	45	100/0	4	1.5	27

[a]Determined by gel permeation chromatography (GPC) in THF. The oligomer formation was neglected. [b]M/C/B is the utilized number of ester groups (M) to base (B) and precatalyst (C) ratio. The reactions were performed with 100 mg of the starting material dissolved in 3 mL of toluene-d_8 in a 4 mL screw cap vial. [c]Obtained by integration of selected resonances in the $^{13}C\{^1H\}$ NMR spectra, for which the relaxation times are determined by inversion recovery experiments to be sufficiently similar. This approach was further validated by ^{13}C NMR measurements with different relaxation delays, which gave almost identical integral ratios. For more details, see the SI. [d]Determined by comparison of $^{13}C\{^1H\}$ NMR measurements of cyclic lactone with the product of hydrogen transfer ester metathesis. Oligomers with resonances different from the polymer resonances are neglected. [e]Refers to the conversion of the starting material repeating units to the corresponding HTEM product. One alkylene dicarboxylate unit is converted into two lactone units and vice versa and is weighted accordingly.

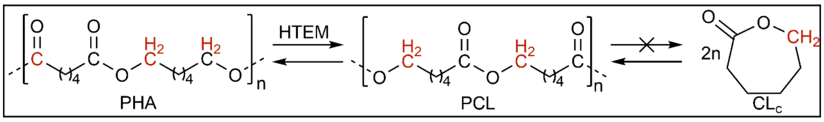


Figure 2. Equilibration of polycaprolactone and poly(hexylene adipate) units as a consequence of hydrogen transfer ester metathesis.

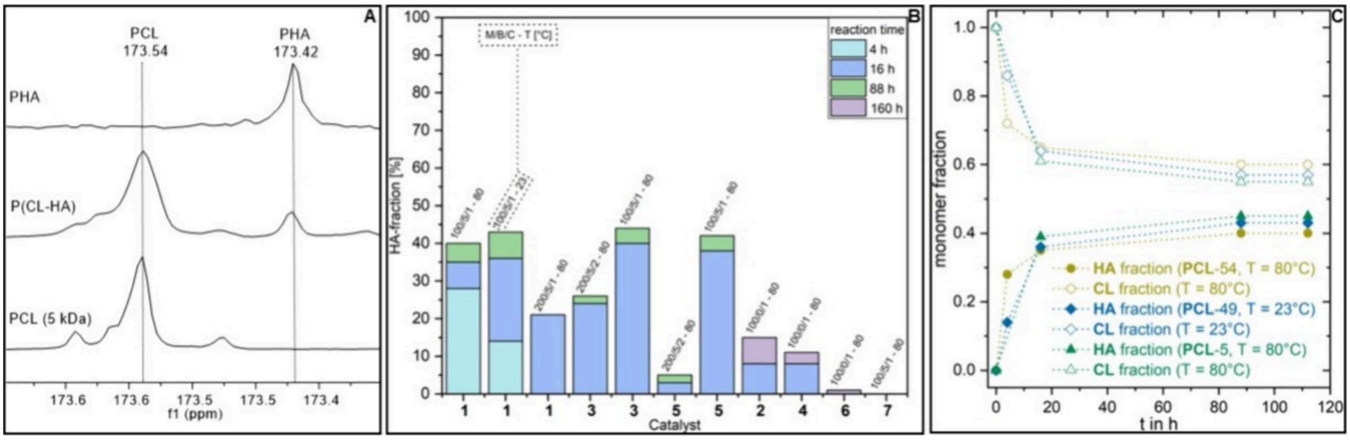


Figure 3. Carbonyl regions in the $^{13}C\{^1H\}$ NMR spectra (125 MHz, $CDCl_3$, 300 K) of PCL and PHA and from HTEM of PCL obtained P(CL-HA) in a stacked plot (A), fraction of hexylene adipate (HA) units formed by catalytic conversion of high-molecular-weight PCL (M_n = 49−50 kDa) at different reaction conditions with different precatalysts (B), and conversion of CL to HA units for different-sized PCL and reaction conditions (C).

1D). This complex is isolable and was fully characterized.[45] Catalyst **2** does not require the presence of a base cocatalyst for precatalyst activation and represents an alternative to Gusev's commercially available catalyst, which can be utilized in the absence of base. Interestingly, complex **2** as a precatalyst in the absence of KO^{t}Bu as a cocatalyst exhibits significantly reduced activity and yields only 15% HA at 80 °C after 160 h (entry 10, Table 1). Utilizing the hydrido borohydrido precatalyst **4** with a MACHO ligand yields 11% of HA units (entry 11, Table 1) under identical conditions. Since for both catalysts, **2** and **4**, conversion of the tetrahydridoborate ligand is necessary, we utilized Milstein's catalyst **6**, which does not require a base cocatalyst or a dissociative step for activation. Even after 160 h of reaction time at 80 °C, only 1% HA units are formed (entry 12, Table 1). These results again indicate a reduced activity of PNP- and PNN-type precatalysts for HTEM of polyesters (Figure 3B). Notably, the reactions with **2**, **4**, or **6** as a precatalyst lead to reduced molecular weight as well, but the resulting M_n values are with 10, 14, and 30 kDa significantly higher than with **1**/KO^{t}Bu, respectively. Recently, manganese pincer-type complexes have been demonstrated to exhibit comparable or even better catalytic activities in reactions involving dihydrogen than corresponding ruthenium complexes.[12,18,46−60] For this reason, we tested [(^{i}Pr-PN^{H}P)-MnBr(CO)$_2$][61−67] (**7**) as a potentially more sustainable precatalyst under the same conditions (entry 13, Table 1). To our surprise, no formation of HA units was observed by NMR spectroscopy, although ^{1}H and ^{31}P{^{1}H} NMR spectra clearly indicated activation of **7**.

The utilization of **2** and **4** for the HTEM of high-molecular-weight PCL in the absence of KO^{t}Bu results in the formation of smaller amounts of HA at 80 °C (entries 10 and 11, Table 1), indicating that KO^{t}Bu is crucial to achieve high activity in this reaction. For this reason, control experiments were performed, in which PCL was heated in the absence (entry 15, Table 1) and in the presence of 5 mol % KO^{t}Bu (entry 14, Table 1) for 16 h in toluene. In the absence of base, no conversion and no significant change in the molecular weight distribution are observed, whereas the presence of KO^{t}Bu reduced the average molecular weight from M_n = 50 kDa to M_n = 11 kDa. Notably, the employment of a non-nucleophilic base like 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) did not result in any conversion and the ^{31}P{^{1}H} NMR spectrum of the reaction mixture confirmed that activation of precatalyst **1** does not take place with DBU. To confirm the necessity of KO^{t}Bu for an increased activity, we utilized catalysts **3** and **5** with 5 mol % KO^{t}Bu each as well, resulting in significantly higher conversion rates. The reaction of **3** (1 mol %) and 5 mol % KO^{t}Bu with PCL (M_n = 50 kDa) results in the formation of 40% HA units after 16 h (entry 7, Table 1) and 44% after 88 h, which is almost twice as fast as **3**/KO^{t}Bu with 1 and 2.5 mol % (Figure 3B). Catalyst **5** (1 mol %) with 5 mol % KO^{t}Bu (entry 9, Table 1) show slightly reduced reactivity than **3**/KOtBu (1 and 5 mol %), but compared to **5**/KO^{t}Bu (1 and 2.5 mol %) (entry 8, Table 1), the conversion of CL into HA units is about 10 times faster (Figure 3B). In summary, the speed of the HTEM clearly depends on the amount of the base cocatalyst. An increased amount of KO^{t}Bu accelerates the reaction, but concurrently, the molecular weight drops more significantly (compare, e.g., entries 6/7 or 8/9). In the presence of the 5 mol % KO^{t}Bu, catalyst **3** exhibits similar activity like catalyst **1** (Figure 3B), but with lower catalyst loadings, **1** shows the highest turnover number after 16 h, which is in line with the previous report on molecular esters.[43] In the following, we focused on catalysts **1** and **2** as in the absence of KO^{t}Bu, the SNS-type catalyst (**2**) performs the best in the hydrogen transfer ester metathesis and the catalyst conversion rates of **1**, **3**, and **5** after 88 h in the presence of 5 mol % KO^{t}Bu are comparable (Figure 3B).

Overall, for different molecular weights and different reaction conditions, the formation of 40−45% HA seems to be thermodynamically favorable (Figure 3C), indicating that there is a thermodynamic minimum P(CL-HA) composition, which is different from 50%. To verify this hypothesis of a thermodynamic minimum with a well-defined HA content, we utilized PHA with a different molecular weight of M_n = 8 kDa. With 1 mol % complex **1** as a precatalyst and 5 mol % KO^{t}Bu cocatalyst, however, only a small conversion of PHA is observed after 16 h, but further addition of complex **1** (1 mol %) along with an additional 5 mol % KO^{t}Bu resulted in the formation of an identical HA content of 45% after 40 h (entry 16) in a copolyester with a molecular weight M_n = 4 kDa. These findings indicate that the reaction with PHA is significantly slower than with PCL, however, strongly suggesting the presence of a thermodynamically favored constitution of approximately 45% HA and 55% CL units.

Physical and Chemical Properties. In line with the reduced molecular weight of PCL after the catalytic reaction, a lower melting temperature (T_m) is observed by differential scanning calorimetry (DSC) in the second heating run with respect to the starting material (Figure S24 and Table S17). The identity of the resulting copolyesters was further investigated by mass spectrometric investigations using matrix-assisted laser desorption ionization (MALDI), which confirm the findings observed by NMR spectroscopy and GPC. We evaluated the exact composition of the low-molecular-weight PCL (M_n = 5 kDa) and the resulting HTEM product. As the molecular mass of an HA unit is the same as that of two CL units, tandem mass spectrometry experiments were performed using MALDI TOF-TOF MS to distinguish the different repeating units after the catalytic reaction. By comparison of the fragmentation mass spectrum (Figure S21) of the PCL starting material and the formed P(CL-HA) copolymer for selected mass peaks (e.g., 1513 m/z), several additional ion peaks were identified in the P(CL-HA) copolymer (e.g., $[C_6H_8O_3+H]^+$ at 129 m/z or $[C_{12}H_{18}O_4+H]^+$ at 227 m/z), which clearly indicate the presence of adipic acid ester units together with CL units. MALDI TOF MS investigations of PHA and the resulting P(CL-HA) copolyester (Figure S22) prove the existence of both repeating units, through additional peaks with $\Delta m/z$ = 114, whereas for PHA, only peak differences of $\Delta m/z$ = 228 are observed. The utilized PHA predominantly exists as macrocycles without any end groups, whereas the resulting P(CL-HA) copolyester is available as macrocycles and chains with hydroxy end groups on both sides, whereas carboxylic end groups are not observable. The observation of P(CL-HA) macrocycles and chains with hydroxy end groups after HTEM indicates that the modification via HTEM occurs in the whole polyester chain without a preference for a mid- or end-chain reaction. The utilized PCL and the resulting HTEM product P(CL-HA) copolyester have only hydroxy end groups on both sides of the polymer chains. As the HTEM is applicable for hydroxy-terminated polyesters as well as macrocyclic polyesters, a possible participation of the end groups on the HTEM seems improbable.

As the starting material used for HTEM optimization, polycaprolactone (PCL) is a semicrystalline polyester; different methods were used to investigate the change in crystallinity after the catalytic reaction. The IR spectrum of the resulting polyester after HTEM of PCL (M_n = 5 kDa) displays bands that are unique for crystalline PHA (Figure S23), indicating that longer sequences with HA units are formed during HTEM. ^{1}H static solid-state NMR spectroscopic experiments[45,68] show an overall decrease in the crystalline fraction (Figure S25) by 10−15% (e.g., from 60.3 to 45.1 at 20 °C)

Table 2. Catalytic Conversion of Different Polyesters Using Hydrogen Transfer Ester Metathesis (HTEM)

educt entry	M_n[a] [kDa]	PD[a]	C	M/B/C[b]	T [°C]	t [h]	polymer composition[c] [%]			polymer/lactone[d] [%]	M_n[a] [kDa]	PD[a]	TON[e]
PBS							BS	BL		P(BS-BL)/BL_c			
1	40	2.1	1	100/5/1	80	40(88)	92(0)	(8)0		31/69(0/100)	2(0)	1.5	8(0)
PPeG							PeG	VL		P(PeG-VL)/VL_c			
2	15	1.8	1	100/5/1	80	16(184)	88(72)	12(28)		98/2(92/8)	5	1.5	12(28)
PVL													
3	10	2.1	1	100/5/1	80	16	5	95		54/46	5	2.6	5
4	10	2.1		100/5/0	80	16	0	100		88/12	8	3.0	0
PCL										P(CL-HA)/CL_c			
5	49	1.7	1	100/5/1	80	4(16)	72(65)	28(35)		100/0	5	1.4	28(35)
PHA													
6	8	1.5	1	50/5/1	80	40	55	45		100/0	4	1.5	27
PHeP										P(HeP-HL)/HL_c			
7	14	1.8	1	100/5/1	80	16(160)	70(60)	30(40)			14	1.6	30(40)
PHexP							HexP/HeA	CL/HA	HL/HeP				
8	18	1.7	1	100/5/1	80	136	38.5/4.5	24/4.5	24/4.5		12	1.5	61
PHeA													
9	21	1.8	1	50/5/1	80	136	1.5/69.5	13/1.5	13/1.5		12	1.6	15
PTGS							TGS/DeD	DL/DeS	TNL/TGD				
10	8	1.8	1	50/5/1	80	136	66/6	8/6	8/6		6	1.5	17
PEG-*b*-PCL							CL	HA		PEG-*b*-P(CL-HA)/CL_c			
11	18	2.0	1	100/5/1	80	16(160)	84(78)	16(22)		100/0	12	1.5	16(22)

[a] Determined by gel permeation chromatography (GPC) in THF (in HFIP for PBS and P(BS-BL)). Monomer and oligomer formation was neglected. [b] M/C/B is the utilized number of ester groups (M) to base (B) and precatalyst (C) ratio. The reactions were performed with 100 mg of the starting material dissolved in 3 mL of toluene-d_8 in a 4 mL screw cap vial. [c] Obtained by integration of selected resonances in the $^{13}C\{^1H\}$ NMR spectra, for which the relaxation times are determined by inversion recovery experiments to be sufficiently similar. This approach was further validated by ^{13}C NMR measurements with different relaxation delays, which gave almost identical integral ratios. For more details, see the SI. [d] Determined by comparison of $^{13}C\{^1H\}$ NMR measurements of cyclic lactone with the product of hydrogen transfer ester metathesis. Oligomers with resonances different from the polymer resonances are neglected. [e] Refers to the conversion of the starting material repeating units to the corresponding HTEM product. One alkylene dicarboxylate unit is converted into two lactone units and vice versa and is weighted accordingly.

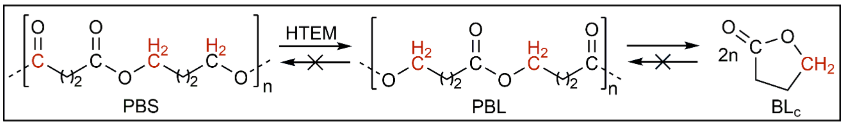


Figure 4. Depolymerization of poly(butylene succinate) as a consequence of the hydrogen transfer ester metathesis by forming polybutyrolactone, which fast depolymerizes.

with a concomitant increase of the amorphous fraction (Figure S26) after HTEM with respect to the utilized PCL starting material. In addition to the overall increase in the amorphous fraction, a decreasing interphase fraction (Figure S27) indicates the presence of thicker amorphous and crystalline domains after the catalytic reaction. ^{13}C MAS NMR spectroscopy with spin−lattice relaxation filtering[42,68] can be used to detect and distinguish resonances of the crystalline, intermediate, and highly mobile amorphous phases of the utilized PCL before and after the catalytic reaction in comparison to PHA. New resonances assignable to HA units were identified after HTEM of PCL in the ^{13}C MAS NMR spectra, which are observed in spectra showing exclusively resonances of crystalline as well as in spectra showing the amorphous phase (Figure S30). These findings suggest that the newly formed HA units become part of the (co)crystal and that the semicrystalline nature of PCL is not disturbed by incorporation of HA units. As PCL and PHA as well as blends of both polymers give rise to similar characteristic reflections by wide-angle X-ray diffraction (WAXD), almost identical diffractograms were obtained before and after HTEM of PCL (Figure S31), indicating the absence of new crystalline domains after HTEM. The absence of these reflexes at 110 °C indicates melting of the investigated polyesters.

Hydrogen Transfer Depolymerization. As the crystallinity of the modified materials is only slightly reduced, we assume that mechanically attractive materials can be prepared by HTEM. To extend the scope of chemical modification by HTEM, we investigated different types of polyesters with the precatalyst/base combination of 1 mol % **1** and 5 mol % KO^{t}Bu (Table 2). With poly(butylene succinate) (PBS) as the starting material, complete depolymerization and formation of cyclic butyrolactone (BL_c) take place after 88 h (entry 1). The formation of small amounts of the corresponding HTEM product polybutyrolactone (PBL) can be observed in the $^{13}C\{^1H\}$ NMR spectrum after 40 h (Figure S13), indicating that the depolymerization runs through the short-lived PBL intermediate (Figure 4).

HTEM Modification of Different Types of Polyesters. Considering that polyesters like PBS are intensively studied as a sustainable polyester alternative in recent years that can be derived from renewable feedstocks,[69] the observed reactivity represents an atom-economic pathway for the revalorization of PBS to BL_c in the absence of any stoichiometric reagent, which takes place under mild conditions (even at ambient temper-

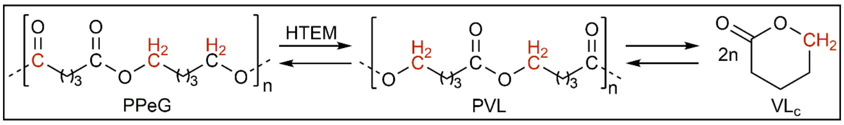


Figure 5. Equilibration of poly(pentylene glutarate) and polyvalerolactone units with partial monomer formation as a consequence of the hydrogen transfer ester metathesis.

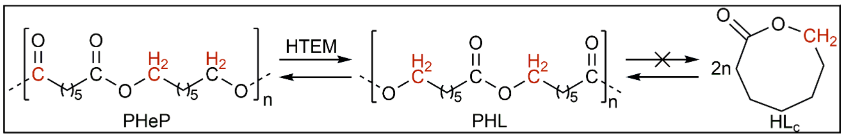


Figure 6. Equilibration of poly(heptylene pimelate) and polyheptanolactone units as a consequence of the hydrogen transfer ester metathesis.

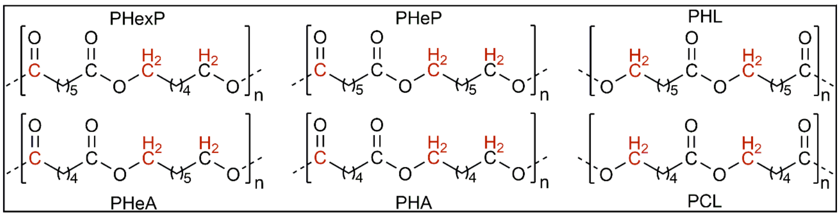


Figure 7. Monomeric units formed by hydrogen transfer ester metathesis of the asymmetrical polyesters poly(hexylene pimelate) and poly(heptylene adipate).

ature). In a recent report, the formation of BL_c from PBS could only be detected at an elevated temperature of 185 °C.[70] As the thermodynamically favorable formation of a five-membered lactone leads to depolymerization in the presence of **1**, polyvalerolactone (PVL) and its potential HTEM product poly(pentylene glutarate) (PPeG) were investigated, which both would give rise to the formation of the six-membered cyclic valerolactone in the case of depolymerization (Figure 5). The reaction of PVL (M_n = 10 kDa) with **1**/KO^{t}Bu results in the formation of a P(PeG-VL) copolyester with a composition of 5% PeG units and 95% VL units (entry 3, Table 2), whereas the HTEM on PPeG (M_n = 15 kDa) yields a copolyester containing 88% PeG and 12% VL units (entry 2, Table 2) under identical conditions. However, partial depolymerization to cyclic valerolactone VL_c occurs with PVL and PPeG as starting materials according to the NMR spectra. As δ-valerolactone (VL_c) formation from PPeG requires the generation of PVL units via HTEM prior to the actual depolymerization (Figure 5), the observed lactone to polyester ratio, P(PeG-VL):VL_c, is 98:2 (entry 2) significantly higher than with PVL as the starting material (entry 3), where a P(PeG-VL):VL_c ratio of 54:46 was detected. The resulting P(PeG-VL) copolyesters give rise to reduced molecular weights of M_n = 5 kDa independent of the composition and starting material. In the presence of KO^{t}Bu without an HTEM catalyst, the molecular weight of PVL (M_n = 10 kDa) reduces to M_n = 8 k and mixed-sized oligomers as well as cyclic valerolactone monomers arise. The polymer/cyclic lactone ratio is PVL:VL_c = 88:12 (entry 4).

As the extent of molecular weight reduction and depolymerization seems to depend on the number of carbon atoms in the repeating unit and in the monomeric lactones, we synthesized poly(heptylene pimelate) (PHeP) to evaluate the influence of the increased number of carbon atoms per repeating unit within this series (Figure 6). Utilization of 1 mol % **1** with 5 mol % KO^{t}Bu in the HTEM of PHeP (M_n = 14 kDa) results in the formation of a heptanolactone (HL)/heptylene pimelate (HeP) copolyester P(HL-HeP) containing 70% HeP and 30% HL units after 16 h at 80 °C (entry 7, Table 2). The molecular weight of the resulting copolyester is unchanged (M_n = 14 kDa) even after 160 h of reaction time, although the HTEM continued to a 40% HL fraction, clearly indicating that the resulting molecular weight depends on the substrate and the underlying thermodynamics for depolymerization, monomer formation, and the isomerization in HTEM. In this context, the employed catalysts simply equilibrate the different reactions for the respective polyesters under the reaction conditions.

Moreover, we investigated polyesters with mixed numbers of carbon atoms in the repeating unit, such as poly(hexylene pimelate) (PHexP) and poly(heptylene adipate) (PHeA), containing a diol with a different number of carbon atoms than the diacid in the repeating unit. The reaction in the presence of **1**/KO^{t}Bu (entries 8 and 9) enables the formation of a copolyester containing six different repeating units P(HexP-HeA-CL-HA-HL-HeP) (Figure 7). The molecular weight decreases during the copolyester formation but not that drastically compared to PCL or PHA, which must be the influence of the HeP and HL units, as the number of carbon atoms for the HeA and HexP units lies in between HA and HeP. The molecular weight of the created copolyesters is determined to M_n = 12 kDa, irrespective of the starting material (PHexP or PHeA), the utilized catalyst/base amounts, or the resulting composition.

Poly(triglycol sebacate) (PTGS), a linear aliphatic polyester from triglycol and sebacic acid containing additional ether bonds, is suitable for HTEM as well. As the diol and diacid part in PTGS differs, the number of possible monomers in the resulting copolyester after HTEM has to be six (Figure S3), analogous to the HTEM on PHexP and PHeA. The reaction with **1**/KO^{t}Bu (entry 10) with PTGS (M_n = 8 kDa) yields a copolyester P(TGS-DeD-DL-DeS-TNL-TGD) (Figure 8) with a reduced molecular weight of M_n = 6 kDa. By comparing the resulting $^{13}C\{^1H\}$ NMR spectrum with the literature, it reveals

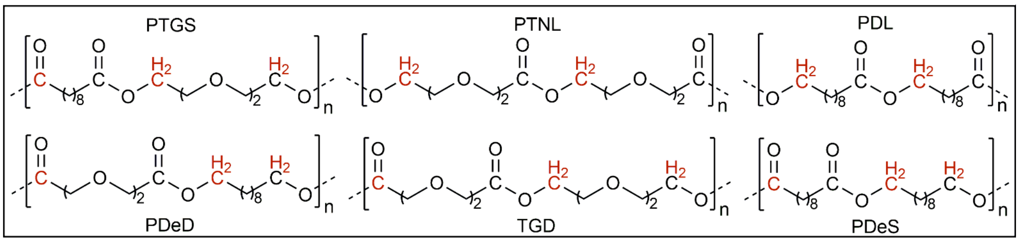


Figure 8. Monomeric units formed by hydrogen transfer ester metathesis on poly(triglycol sebacate).

Table 3. Catalytic Ring Opening Polymerization (ROP) of Different Cyclic Lactones Using Hydrogen Transfer Ester Metathesis (HTEM)

educt entry	M_n[a] [kDa]	C	M/B/C[b]	T [°C]	t [h]	polymer composition[c] [%]		polymer/lactone[d] [%]	M_n[a] [kDa]	PD[a]	TON[e]
BL_c						BS	BL	P(BS-BL)/BL_c			
1		1	100/5/1	80	88	0	0	0/100			0
2			100/5/0	80	88	0	0	0/100			0
VL_c						PeG	VL	P(PeG-VL)/VL_c			
3		1	100/5/1	80	16(64)	14(36)	86(64)	83/17(76/24)	5	1.3	14(36)
4			100/5/0	80	16(64)	0(0)	100(100)	88/12(88/12)	9	1.7	0(0)
CL_c						CL	HA	P(CL-HA)/CL_c			
5		1	100/5/1	80	112	61	39	100/0	4	1.6	39
6			100/5/0	80	88	100	0	100/0	6	2.7	0
7		2	100/0/1	80	40	87	13	100/0	28	1.7	13

[a] Determined by gel permeation chromatography (GPC) in THF. Monomer and oligomer formation was neglected. [b] M/C/B is the utilized number of ester groups (M) to base (B) and precatalyst (C) ratio. The reactions were performed with 100 mg of the starting material dissolved in 3 mL of toluene-d_8 in a 4 mL screw cap vial. [c] Obtained by integration of selected resonances in the $^{13}C\{^1H\}$ NMR spectra, for which the relaxation times are determined by inversion recovery experiments to be sufficiently similar. This approach was further validated by ^{13}C NMR measurements with different relaxation delays, which gave almost identical integral ratios. For more details, see the SI. [d] Determined by comparison of $^{13}C\{^1H\}$ NMR measurements of cyclic lactone with the product of hydrogen transfer ester metathesis. Oligomers with resonances different from the polymer resonances are neglected. [e] Refers to the conversion of the starting material repeating units to the corresponding HTEM product. One alkylene dicarboxylate unit is converted into two lactone units and vice versa and is weighted accordingly.

diagnostic peaks for decalactone (DL) and decylene sebacate (DeS) repeating units, which have isochronous chemical shifts (Figure S17 and Table S14). As sebacate units reduce, on one and both sides, the triglycol units need to undergo oxidation during HTEM. Specific ^{13}C NMR resonances for the mono-oxidized triglycol units, more precisely trioxanonalactone units (TNL) are assigned in the $^{13}C\{^1H\}$ NMR spectrum as well (Figure S17 and Table S15). ^{13}C NMR resonances for decylene dioxasuberate (DeD) and triglycol dioxasuberate (TGD) repeating units, which contain the formal dioxidized HTEM product of triglycol, are not reported in the literature. Only the ^1H NMR chemical shifts for PDeD are reported, and a specific singlet at 3.76 matches by comparison with the ^1H NMR spectrum of the copolyester resulting from HTEM on PTGS (Figure S18). The other reported resonances for PDeD cannot be assigned due to superimposition (Table S16).

Investigations with a block copolymer containing 71.8 mol % PCL and 28.2 mol % poly(ethylene glycol) (PEG), as determined by ^1H NMR spectroscopy, reveals that the additional ether bonds are not affected by HTEM (Figure S11, PEG ^{13}C chemical shift at 71 ppm) and the molecular weight reduction is limited. The reaction of PEG-*b*-PCL (M_n = 18 kDa) in the presence of 1 mol % **1** and 5 mol % KO^{t}Bu (entry 11) yields a polymer with molecular weight of M_n = 12 kDa, containing 16% HA units after 16 h at 80 °C. The rate of conversion seems to be reduced with respect to pure PCL, supporting the assumption of a hindered diffusion and therewith lower catalyst activity with an increasing molecular weight.

HTEM Polymerization of Lactones. As thermodynamics for HTEM and depolymerization are strongly substrate-dependent, which is reflected in different molecular weight and product distributions after the catalytic reaction in the presence of **1**/KO^{t}Bu, it should be possible to polymerize certain lactones, such as BL_c, VL_c, and CL_c by ring opening polymerization (ROP) using HTEM in the presence of KO^{t}Bu (Table 3). The reaction of BL_c gives neither PBL nor PBS in the presence of ROP catalysts (Figure 4), no matter whether it is **1**/KO^{t}Bu (entry 1) or just the base (entry 2). These results are supported by the literature, as the synthesis of PBL is difficult[71,72] due to the high stability of BL_c,[73−75] and correspond to the observed depolymerization of PBS during HTEM. VL_c polymerizes in the presence of 5 mol % KO^{t}Bu to PVL with a molecular weight of M_n = 9 kDa (entry 4, Table 3), which is similar to the molecular weight measured for the reaction of PVL with KO^{t}Bu (M_n = 8 kDa; entry 4, Table 2). The residual amount of 12% VL_c is in line with the results from the reaction of PVL, which indicates a thermodynamical equilibrium between polymerization and depolymerization (Figure 5). The ROP of VL_c with **1**/KO^{t}Bu results in a copolyester P(VL-PeG) containing 86% VL and 14% PeG units with a P(PeG-VL):VL_c ratio of 83:17 (entry 3, Table 3). As the reaction progresses, the amount of free VL_c has increased (P(PeG-VL):VL_c = 76:24) and the residual copolyester contains 64% VL and 36% PeG units after 64 h. Apparently, KO^{t}Bu catalyzes rapidly the ROP to the equilibrium mentioned before (PVL:VL_c = 88:12) and the relatively slow HTEM gradually shifts it. The molecular weight

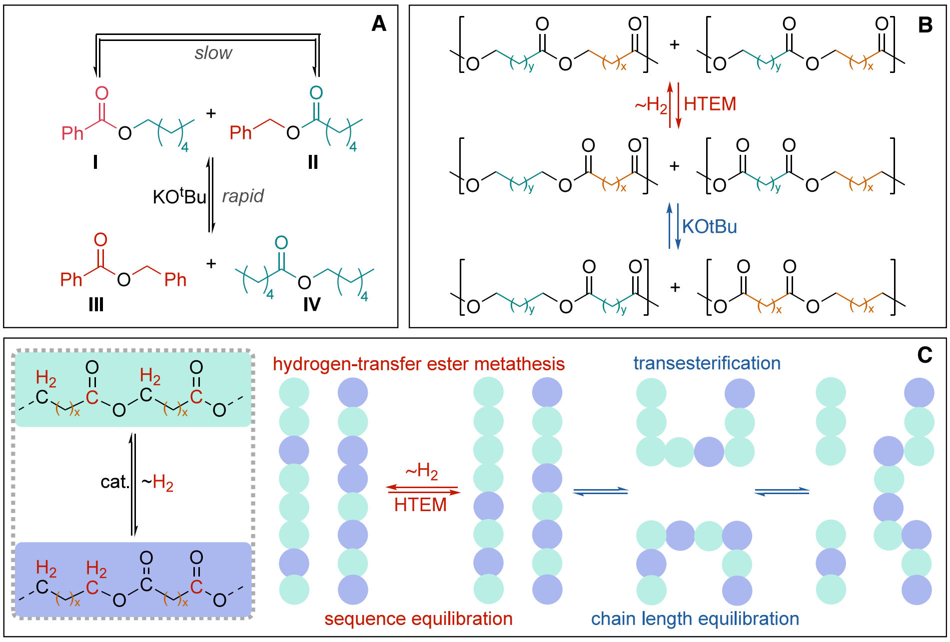


Figure 9. Observed catalytic reactions for molecular esters (A). Product formation for asymmetric polyesters through the combination of hydrogen transfer ester metathesis and transesterification (B) as well as the illustration of sequence and chain length equilibration (C).

is, as well as for the reactions of PVL and PPeG, determined to be M_n = 5 kDa (entry 3, Table 3; entries 2/3, Table 2). In the presence of an HTEM catalyst, an additional isomerization between VL and PeG units takes place that seems to shift the initial molecular weight equilibrium obtained after base-catalyzed ROP.

The ROP of CL_c with 5 mol % KO^{t}Bu leads to PCL with a molecular weight of M_n = 6 kDa (entry 6, Table 3), which is the exact value reported in the literature[76] and similar to the product from PCL with KO^{t}Bu (M_n = 11 kDa; entry 14, Table 1). By utilization of 1 mol % **1** with 5 mol % KO^{t}Bu, the ROP results in a P(CL-HA) copolyester with 39% HA units (entry 5, Table 3). The molecular weight of M_n = 4 kDa is similar to the molecular weight of M_n = 3−5 kDa resulting from the conversion of high- and low-molecular-weight PCL under identical conditions (entries 1/3, Table 1). These findings suggest a favored molecular weight range of M_n = 3−5 kDa for the resulting P(CL-HA) copolyester, which seems independent of the starting material (PCL or PHA), the initial molecular weight, and the utilized amount of the precatalyst and KO^{t}Bu (compare for example M_n in entries 1/3/16, Table 1).

To eliminate the equilibration and the resulting drop in molecular weight in the presence of base, the hydrido tetrahydridoborate complex **2** was used as a precatalyst for the ROP of CL_c, yielding a polyester with 13% HA units (entry 7). Although the HA content after ROP of CL_c is similar to the HTEM of PCL in the presence of **2** (entry 10, Table 1), the copolyester resulting from ROP exhibits a significantly higher molecular weight of M_n = 28 kDa after 40 h. Molecular CL_c is not observable anymore in the $^{13}C\{^1H\}$ NMR spectra of all ROP products, but the chromatograms reveal the formation of small oligomers as well. The ring opening polymerization seems to proceed quickly with a subsequent equilibration of the chain length (and therefore the molecular weight M_n).

Mechanistic Investigations. As the ester groups in the polyesters formed by HTEM are very similar, it can be assumed that the main driving force for the observed catalytic HTEM reaction is entropy and possibly the preferential stability of certain sequences. To gain further insights into the possible driving force for the reported HTEM, we performed quantum chemical investigations of small oligomers for the PCL−PHA system with three to five lactone repeating units to identify potentially more stable sequences. Following a protocol that involves conformational preoptimization using the Materials Studio program package, we performed density functional theory (DFT) calculations of the preoptimized structures on the B97D3/def2-TZVP level of theory with a solvent correction, using the polarizable continuum model (PCM) for toluene, for all 2^n possible constitutional isomers that can be formed by the hydrogen transfer ester metathesis, where n is the number of linking ester groups (n = 2−4). It turns out that the calculated difference in Gibbs energy of certain sequences with respect to PCL varies over a range of −11 to +33 kJ/mol, indicating that a number of sequences are of comparable stability to the sequence in PCL, whereas the formation of several sequences seems thermodynamically less favorable (Table S18). As the catalytic reactions with PCL and PHA result in almost identical PCL/PHA ratios after long reaction times, the existence of a thermodynamically favorable composition is likely, although the difference in the Gibbs energy might be small. Considering that the utilized catalysts are active for the conversion of molecular esters, a small difference in Gibbs energy for different polyester sequences suggests a high reversibility of each HTEM step and a significant competition with side reactions, such as depolymerization, depending on the thermodynamic circumstances for each substrate. As hydrogen liberation needs to be avoided for the reaction to proceed, the HTEM has to be conducted in closed vessels, which in the case of polyesters means that the utilized catalysts (**1**−**6**) will simply equilibrate the PCL or PHA on a quite flat potential energy surface.

To gain better insights into the catalytic process, we investigated the underlying catalytic reaction with molecular ester in more detail (Table S3). Applying identical reaction

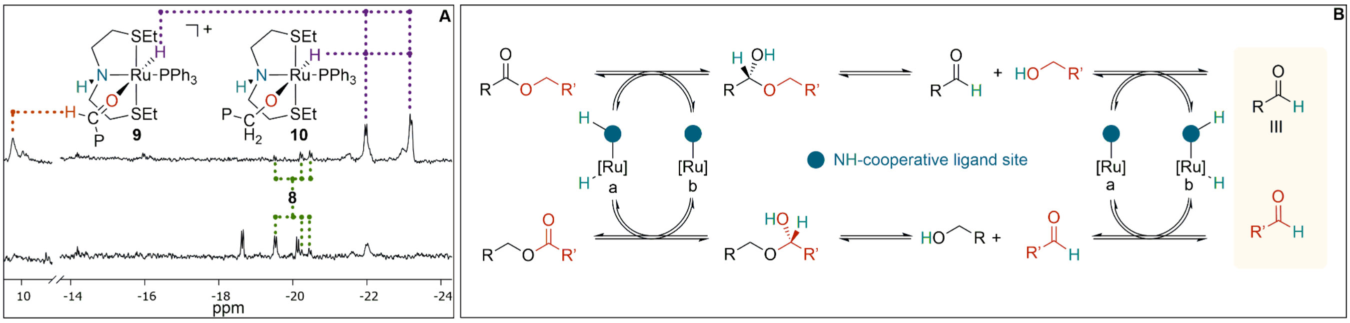


Figure 10. Selected regions of the ^{1}H NMR spectra of the catalytic reaction with PCL after 16 h of reaction at 80 °C in toluene-d_8 (top) and with reduced pressure for the last hour of the reaction (bottom) (A) as well as the anticipated, simplified mechanism for the hydrogen transfer ester metathesis (B).

conditions as for the polyesters (toluene, 80 °C, 16 h, closed vessel), the reaction with hexyl benzoate (**I**) is in principle expected to result in the formation of four esters (**I**–**IV**, Figure 9A). Benzyl hexanoate (**II**) is directly formed by HTEM, whereas esters **III** and **IV** are formed by a regular transesterification of a mixture of **I** and **II**. It is demonstrated that neither complex **1** in the absence of KO^{t}Bu nor pure KO^{t}Bu is catalytically active in the hydrogen transfer ester metathesis reaction. As bases such as KO^{t}Bu are known to catalyze transesterification reactions without hydrogen transfer,[77] a mixture of the symmetric esters **III** and **IV** was used as the substrate to investigate the influence of base-catalyzed transesterification in the investigated reaction. It turns out that in the presence of **1**/KO^{t}Bu, the formation of equimolar amounts of **I**–**IV** is observed at ambient temperature in less than 1 h. An identical observation is made with KO^{t}Bu as a catalyst, suggesting that with the utilized combination of a precatalyst and a base cocatalyst, two catalytic reactions are involved: a comparably slow HTEM and a rapid, base-catalyzed transesterification. With respect to the reported polyester reaction, the KO^{t}Bu catalyzes a rapid regular transesterification of polyester chains, which might be responsible for the formation of sequences of blocks after the actual hydrogen transfer steps. The significance of the transesterification in this process is supported by the utilization of complex **2**, which can transform hexyl benzoate into the four esters and therefore catalyzes transesterification as well but with a clearly reduced conversion rate.

In view of the observations made for nonsymmetric molecular esters, such as hexyl benzoate (**I**), the transesterification is directly involved in the formation of up to six different repeating units after HTEM of polyesters (Figure 9B), such as poly(hexylene pimelate) (PHexP) or poly(heptylene adipate) (PHeA). In this scenario, the caprolactone (CL) and heptanolactone (HL) units are both formed by one initial HTEM step, while a second HTEM step yields the corresponding asymmetric (alkylene dicarboxylate) units (HeA from HexP units and vice versa). The transesterification between the HeA and HexP units provides the symmetric hexylene adipate (HA) and heptylene pimelate (HeP) units. The identical behavior is observable for the HTEM on poly(triglycol sebacate) (PTGS), where decalactone (DL) and trioxanonalactone (TNL) units both are formed by the first HTEM step, decylene dioxasuberate (DeD) units by the second one, and the transesterification rearranges TGS and DeD units into the symmetric decylene sebacate (DeS) and triglycol dioxasuberate (TGD) units.

Therefore, the dual catalytic process, including HTEM and transesterification, for lactone–polyester systems can be described with two general equilibration steps (Figure 9C). The equilibration between the monomer, oligomer, and polymer (chain length equilibration) characterizes the amounts of the mixed-sized species and the molecular weight of the resulting copolyester. The chain length equilibrium results from dynamic bond rearrangements through the transesterification reactions. For symmetric lactone–polyester systems, HTEM facilitates two, for asymmetric polyesters six, possible constitutional isomers of poly(lactone/alkylene dicarboxylate) copolyesters. The amounts of the different repeating units can be described through a sequence equilibrium. The combination of precatalyst **1** (1 or 2 mol %) and KO^{t}Bu (5 or 10 mol %) rapidly equilibrates the chain length. For the application of **1** (0.5 mol %) or **3** (1 mol %) with KO^{t}Bu (2.5 mol %), the equilibration is decelerated as well as for the utilization of the base-free catalysts **2** and **4**, which are active for HTEM but almost inactive for regular transesterification. The different chain length behaviors of various aliphatic polyesters were previously studied in detail. PCL and PVL have a high tendency of spontaneous and random chain scission as well as inter- and intramolecular reactions, forming mixed-sized oligomers. These processes are even accelerated at elevated temperatures and in the presence of transesterification catalysts, such as KO^{t}Bu.[76,78−83] The main difference between both polyesters is the generation of cyclic valerolactone (VL$_c$), whereas the formation cyclic caprolactone (CL$_c$) is not favored.[79−83] These tendencies are reflected in the observations with HTEM catalysts in this work, as the molecular weight of the resulting P(CL-HA) and P(PeG-VL) copolymers is reduced, and smaller, mixed-sized oligomers are observable in the gel permeation chromatograms. As mentioned, cyclic VL$_c$ could be assigned in the ^{13}C{^{1}H} NMR spectra, whereas CL$_c$ is not traceable. The Gibbs free energies for polymerization ΔG_P provide an explanation as $\Delta G_{P,CL} < \Delta G_{P,VL} < 0 < \Delta G_{P,BL}$, which also explains the complete depolymerization of PBS and selective BL$_c$ formation.[74,75,84,85] The constant molecular weight of the P(HL-HeP) copolyester can be rationalized by the ring tension, although smaller oligomers are observable in the gel permeation chromatogram after HTEM on PHeP, as well. Cyclic heptanolactone (HL$_c$) is described to have the highest ring strain compared with BL$_c$, VL$_c$, CL$_c$, and larger cyclic lactones.[86] In line with this trend, HL$_c$ is reported to have a high polymerization tendency[87] and rapidly forms high-molecular-weight polyheptanolactone (PHL) in the presence of ROP catalysts.[88,89]

Precatalyst **1** is known for its high catalytic activity in the hydrogenation of esters and the acceptorless dehydrogenation of primary alcohols. For these reactions, the two active species *fac*-[(SNS)Ru(H)$_2$(PPh$_3$)] and *mer*-[(SNS)Ru(H)(OEt)-(PPh$_3$)]·EtOH that are involved in the catalytic cycle could be isolated and partially characterized (SNS = {EtSCH$_2$CH$_2$}-NH).[90] As the reported HTEM is conducted in a closed system, whereas acceptorless dehydrogenations are typically conducted in an open system or a stream of inert gas and hydrogenations typically require hydrogen pressure, ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixtures after HTEM were acquired to identify decomposition products as well as potential resting states or active species (Figure 10A). The ^{1}H NMR spectra of the reaction mixtures with PCL of different lengths in toluene-d_8 after 16 h display two doublet resonances in the hydride region of similar intensity at −21.97 ppm ($^2J_{PH}$ = 23.5 Hz) and −23.19 ppm ($^2J_{PH}$ = 25.6 Hz) as well as three small resonances for the diastereomers of *mer*-[(SNS)Ru(H)-Cl(PPh$_3$)]·(**8**).[91] In addition, a broadened resonance at 10.23 ppm with an integral associated with one proton with respect to one of the hydride resonances indicates the presence of an aldehyde or a coordinated aldehyde. The utilized SNS ligand usually gives rise to different diastereomers in meridional coordination mode, differing in the orientation of the thioether groups.[90,91] The observed hydride species may therefore either originate from two diastereomeric hydrido aldehyde complexes or from two species with a similar chemical environment (Figure 10A), such as a hydrido aldehyde complex (**9**) and a hydrido alkoxide complex (**10**). Notably, when the reaction conditions after 15 h at 80 °C of the HTEM are changed to an open system with reduced pressure, which are conditions that typically favor acceptorless dehydrogenation, the resonance corresponding to an aldehyde disappeared and three new hydride isomers are formed. These findings provide further support for our hypothesis that the ester groups are partially reduced to aldehydes, which are reconnected by the catalyst.

Overall, these findings indicate that two catalytic reactions are involved in the formation of the novel type of polyester reported herein (Figure 9C): (i) the ruthenium-catalyzed hydrogen transfer ester metathesis that results in chemically modified ester groups and (ii) the base-catalyzed transesterification that facilitates a rapid chain exchange and equilibrates the system toward the most stable sequences as well as the thermodynamically more favorable molecular weight range. Both reactions involve an initial cleavage of an ester group and lead in the case of (i) to a cleaved (aldehyde) resting state, which disappears under reduced pressure.

Based on our mechanistic investigations, as well as the previously reported mechanistic work for molecular systems,[92−96] a possible mechanism involves a number of hydrogenation and dehydrogenation steps resulting in a temporary cleavage of the ester group linkage via hemiacetal formation and its subsequent dissociation (Figure 10B). Dehydrogenation of the resulting alcohol group, followed by hydrogenation of the initial aldehyde, yields a new hemiacetal, whose dehydrogenation finalizes the HTEM sequence.

CONCLUSIONS

In conclusion, we reported for the first time a catalytic hydrogen borrowing reaction that transfers linear polyesters into novel copolyesters, consisting of additional repeating units without the need for any stochiometric reagent. The developed HTEM protocol can convert alkylene dicarboxylate into lactone repeating units and vice versa, which, depending on the thermodynamic stability of the corresponding cyclic lactone, can lead to selective depolymerization. This allows for selective depolymerization of poly(butylene succinate) (PBS) to cyclic butyrolactone in the absence of any stochiometric reagent. The formation of butyrolactone (BL$_c$) from PBS represents a true revalorization with respect to hydrolysis products. In turn, cyclic lactones with increased ring tension can be polymerized using HTEM to the described copolyester with alkylene dicarboxylate and lactone units. In the case of polycaprolactone (PCL), it was demonstrated that the crystallinity is only slightly reduced after HTEM and that the newly formed ester units seem to become part of a (co)crystal, which suggests that mechanically attractive materials are formed. The mechanistic investigations show that two catalytic reactions are operative under the employed conditions: a hydrogen transfer ester metathesis (HTEM), resulting in truly chemically modified ester groups via a hydrogen transfer reaction, and a (common) base-catalyzed transesterification. For different polyesters as starting materials, the HTEM was found to equilibrate the possible sequences, whereas the transesterification gives rise to a chain length equilibration. We further provide evidence that hydrogen transfer ester metathesis (HTEM) proceeds via a reversible aldehyde formation. Therefore, we are currently focusing our efforts on the application of the reported postsynthetic modification to tune properties and facilitate chemical recycling.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c03132.

Experimental and computational details, spectra, and more detailed discussion for some analytical methods (PDF)

Crystallographic information for complex **2** (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

R.L. is grateful to the Deutsche Forschungsgemeinschaft (DFG) for funding within the Heisenberg program (LA 2830/9-1). F.H. gratefully acknowledges the Fonds der Chemischen Industrie (FCI) for their support through the Liebig Fellowship.

Notes

The authors declare no competing financial interest.

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