



Mechanistic Considerations of Efficient Esterification of Starch with Propionic Anhydride/Lauric Acid in the Green Solvent Imidazole

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Starch esters have become increasingly attractive as sustainable materials. Instead of carboxylic acid chlorides, mixtures of carboxylic acid anhydrides and carboxylic acids are used to synthesize highly substituted starch esters efficiently applying the new starch solvent imidazole. The reaction is a promising alternative to the existing protocols and leads to thermoplastic mixed starch esters. The mechanism for the reaction path is elucidated by the conversion of starch with propionic anhydride/lauric acid in molten imidazole and various model reactions applying Fourier transform infrared spectroscopy and NMR spectroscopic measurements. Mixed starch esters are obtained bearing not only propionate groups introduced by the reactive anhydride but also moieties originating from the lauric acid. The propionic anhydride is shown to react with imidazole to form the corresponding imidazolide. Moreover, the imidazolide is in equilibrium with the lauric acid to form the corresponding imidazolide as well.

1. Introduction

Plastic materials are applied in various fields and usually produced from fossil resources. They are light, cheap, and both mechanically and chemically stable. Due to this stability, plastic materials accumulate in the environment if they are not disposed of properly, recycled, or burned.^[1] Furthermore, the amount of available fossil resources is limited. Thus, it is necessary to replace those materials in the future.^[2] As a consequence, the use of renewable resources is highly desirable.

Starch, one of the most important renewable resources, is available in unlimited amounts because it is produced in many plants (e.g., rice, maize, potatoes) as an energy storage material. Furthermore, it is not only bio-based but also biodegradable.

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Unfortunately, it has poor mechanical properties and is hydrophilic.^[3] Water uptake impairs the mechanical properties further. Therefore, the conversion of starch into hydrophobic materials is preferable, especially as it also improves its thermal properties. The synthesis of starch esters is an appropriate approach to get hydrophobic products with good thermal characteristics. While starch decomposes under heating up to 300 °C without melting, starch esters may exhibit thermoplastic behavior, which is also desirable for use as plastic material.^[4] Especially mixed esters of starch are attractive due to the opportunity of adjusting the properties as needed.^[5] Starch esters, even with high degrees of substitution (DS) up to 3, are considered as biodegradable.^[6]

In industrial applications, starch is chemically modified to products of low DS exclusively. A rather higher DS is needed to get starch esters with thermoplastic properties. High DS values can be obtained by the reaction of the biopolymer with carboxylic acid chlorides in pyridine.^[7–13] Carboxylic acid chlorides have the advantage to be highly reactive. However, they are also difficult to handle, may undergo undesirable hydrolysis, and lead to the formation of corrosive hydrogen chloride during the reaction with hydroxyl groups. Mixed starch esters with thermoplastic behavior could be obtained in a one-step synthesis applying carboxylic acid chlorides as reagents.^[14] Another appropriate path to obtain starch esters is the conversion of the biopolymer with carboxylic acids activated in situ with agents like 4-toluenesulfonyl chloride, *N,N'*-dicyclohexylcarbodiimide/4-(1-pyrrolidinyl)pyridine, 1,1'-carbonyldiimidazole, and *N,N*-dimethylformamide (DMF) combined with oxalyl chloride.^[15] The products are thermoplastics. Up to now, pyridine is the most common solvent for achieving starch esters of high DS. Pyridine exhibits a high vapor pressure (20.5 hPa, 20 °C), toxicity (LD₅₀, rat oral is 891 mg kg⁻¹), and can be easily taken up via inhalation and skin contact.^[16] On the contrary, imidazole is less toxic (LD₅₀, rat oral is 970 mg kg⁻¹), exhibits a significant lower vapor pressure (0.00327 hPa, 25 °C), and its uptake via skin contact is very slow. Furthermore, it is readily biodegradable.^[17] Recently, it was found that imidazole dissolves starch at about 100 °C and may act as reaction medium, base, and catalyst for homogeneous esterification of starch and may be

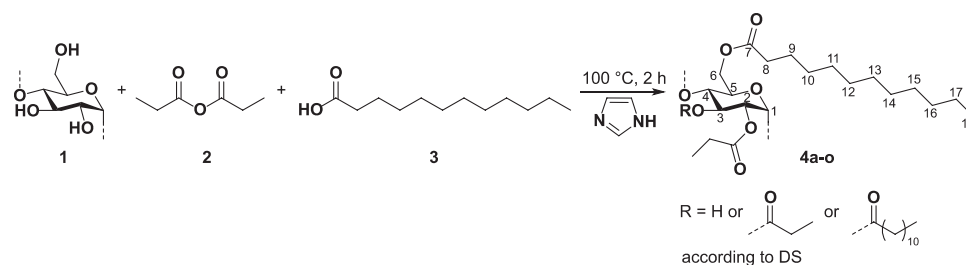


Figure 1. Reaction scheme of the conversion of starch with propionic anhydride and lauric acid in molten imidazole.

recycled.^[18,19] Although 1-methylimidazole dissolves starch like dextrin or amylopectin-rich starch at 100 °C as well,^[20] imidazole is more appropriate due to the fact that carboxylic acids form the corresponding imidazolide, which is reactive.

The studies presented aim at the homogeneous esterification of starch to get mixed starch esters by a reaction of the biopolymer with carboxylic acid anhydride/carboxylic acid in molten imidazole as the solvent. It was studied whether mixed starch esters of high DS could be produced using propionic anhydride and lauric acid in order to replace carboxylic acid chlorides and pyridine—the usual and problematic reagent and medium. Mechanistic investigations were undertaken to understand the reaction system.

2. Results and Discussion

Mixed starch esters could be prepared by a homogeneous conversion of the biopolymer with a mixture of a reactive carboxylic acid anhydride in the presence of a carboxylic acid applying molten imidazole as the solvent. This reaction has not been investigated up to now but the reaction of starch with carboxylic acid chlorides in molten imidazole was studied.^[18]

2.1. Synthesis and Characterization of Starch Laurate Propionate

To investigate the new reaction system in detail, starch dissolved in molten imidazole was allowed to react with propionic anhydride and lauric acid homogeneously (**Figure 1**).

Mixed starch laurates propionates of different DS were obtained (**Table 1**). No nitrogen was found by elemental analysis; hence, the products obtained did not contain any remaining imidazole after a usual work-up procedure. The ¹³C-NMR spectra showed typical signals for highly substituted starch esters. Exemplarily, the signals of sample 4n (**Figure S1**, Supporting Information) with a DS of 3 will be discussed. The signal at 95.71 ppm can be assigned to C-1 of the anhydroglucose unit (AGU) with an esterified position 2. Position 2 was completely converted into the ester group because of the absence of the signal corresponding to C-1 with position 2 containing OH moiety. The completely esterified hydroxyl group at position 3 of the AGU causes the signal at 72.03 ppm. The signals at 70.38 and 69.23 ppm can be assigned to the positions 2 (esterified) and 5 of the AGU, respectively. The completely converted position 6 of the AGU causes the signal at 61.46 ppm compared to a non-esterified C-6 that would lead to a signal at 60.00 ppm. A set of signals in the range from 174 to

Table 1. Molar ratio of AGU to lauric acid (LA) to propionic anhydride (PA) and characteristics of starch laurate propionates obtained after 2 h at 100 °C in molten imidazole as the solvent.

Molar ratio of AGU/ LA/PA	Starch laurate propionates					
	Number	Yield [%]	DS _{laurate}	DS _{propionate}	DS _{tot}	Melting area [°C]
1.0:1.0:1.0	4a	6	0.50	0.92	1.42	160–190
1.0:1.0:3.0	4b	78	0.48	2.52	3.00	120–145
1.0:1.0:5.0	4c	70	0.74	2.26	3.00	160–180
1.0:1.5:1.5	4d	82	0.51	1.16	1.67	150–180
1.0:2.0:2.0	4e	82	1.02	1.35	2.37	90–105
1.0:2.5:2.5	4f	69	0.90	2.05	2.95	95–110
1.0:2.5:5.0	4g	69	0.62	2.37	2.99	105–120
1.0:3.0:1.0	4h	5	0.06	0.14	0.20	No melting
1.0:3.0:3.0	4i	69	1.02	1.98	3.00	105–120
1.0:3.0:5.0	4k	84	0.69	2.31	3.00	130–150
1.0:5.0:1.0	4l	37	0.40	0.40	0.80	No melting
1.0:5.0:2.5	4m	63	1.29	1.61	2.90	75–95
1.0:5.0:3.0	4n	76	1.48	1.52	3.00	100–120
1.0:5.0:5.0	4o	79	1.10	1.90	3.00	105–120

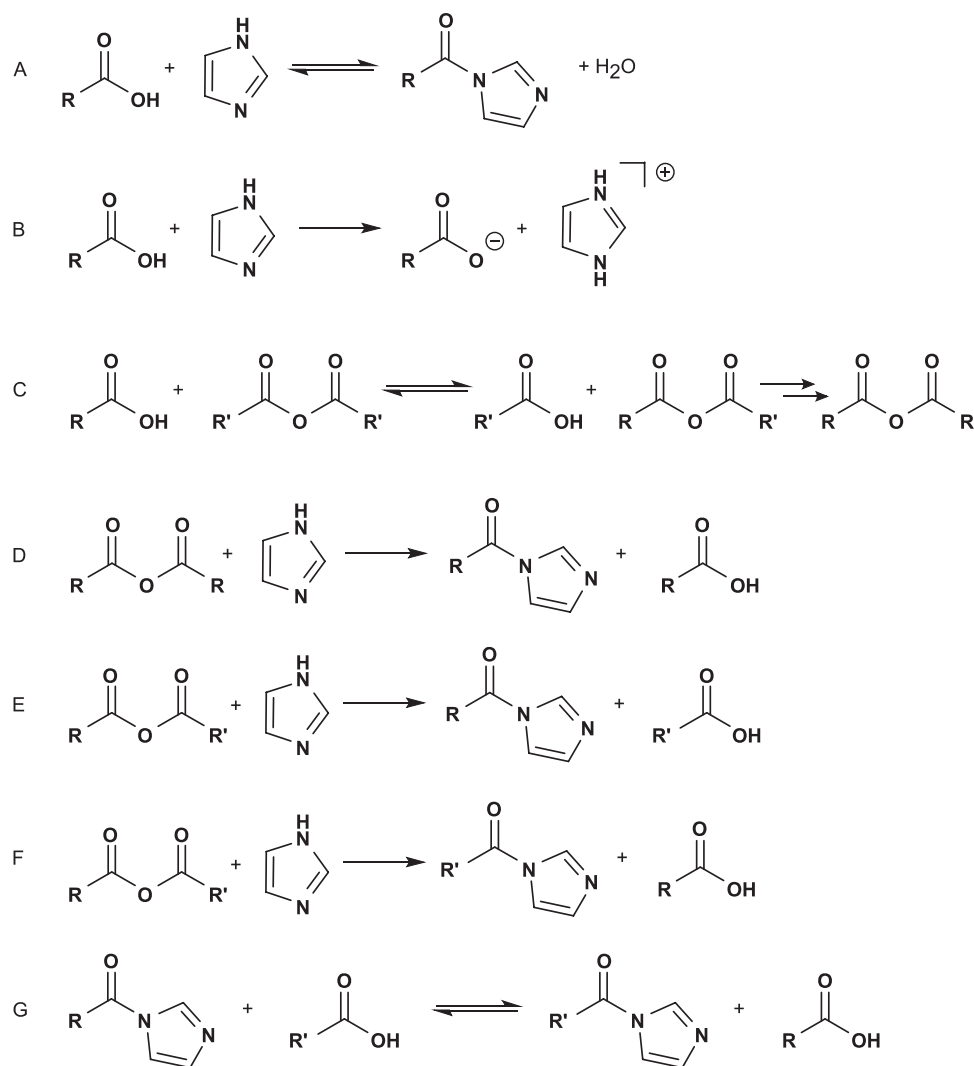


Figure 2. Possible reactions in the system of imidazole, propionic anhydride, and lauric acid.

172 ppm is caused by the carbonyl carbons of the propionate and laurate moieties. The signals of the aliphatic groups can be found in the range from 35 to 8 ppm. The ^{13}C -NMR spectrum of 4l (Figure S2, Supporting Information) that possesses a DS of 0.80 appeared to be more complex due to the distribution of the ester moieties within the repeating unit. Generally, the spectrum contains signals for carbonyl moieties and aliphatic groups in the same areas as already described for the highly substituted ester, confirming the presence of ester moieties. Additionally, there are signals at 100.61 and 61.02 ppm, indicating no substitution in position 2 of the AGU and only partial substitution in position 6.

NMR spectroscopy was used to calculate the partial DS values of laurate and propionate moieties using ^1H -NMR spectra that were measured in the presence of trifluoroacetic acid (TFA) to obtain the DS of laurate ($\text{DS}_{\text{laurate}}$). The $\text{DS}_{\text{laurate}}$ was calculated by integrating the signals of the modified AGU and the methyl group of the laurate according to Equation (2). Knowing the $\text{DS}_{\text{laurate}}$, the $\text{DS}_{\text{propionate}}$ could be figured out by comparing the integrals of the signals of the two α -methylene

groups of the substituents in the ^{13}C -NMR spectrum knowing that no difference in the NOE exists. The calculation was carried out based on Equation (3).

The values of the $\text{DS}_{\text{laurate}}$ and $\text{DS}_{\text{propionate}}$ are dependent on the molar ratio of the AGU to lauric acid and propionic anhydride applied (Table 1). The total DS (DS_{tot}) ascends with increasing molar ratio of propionic anhydride as expected. The propionic anhydride is reactive and may activate the lauric acid. The total DS_{tot} reaches a maximum of 3.00, if three equivalents of propionic anhydride are applied. Moreover, the DS_{tot} exceeds the molar ratio of propionic anhydride in some cases when less than three equivalents of propionic anhydride were applied (see samples 4a, 4d, 4e, 4f, and 4m, Table 1). It is assumed that lauric acid and propionic anhydride may form the corresponding mixed anhydride. Thus, laurate moieties could be incorporated in the product. However, there would be a limitation of DS_{tot} , which is determined by the amount of propionic anhydride because it was needed to form this mixed anhydride. Thus, questions about the detailed mechanism of the synthesis path have to be answered.

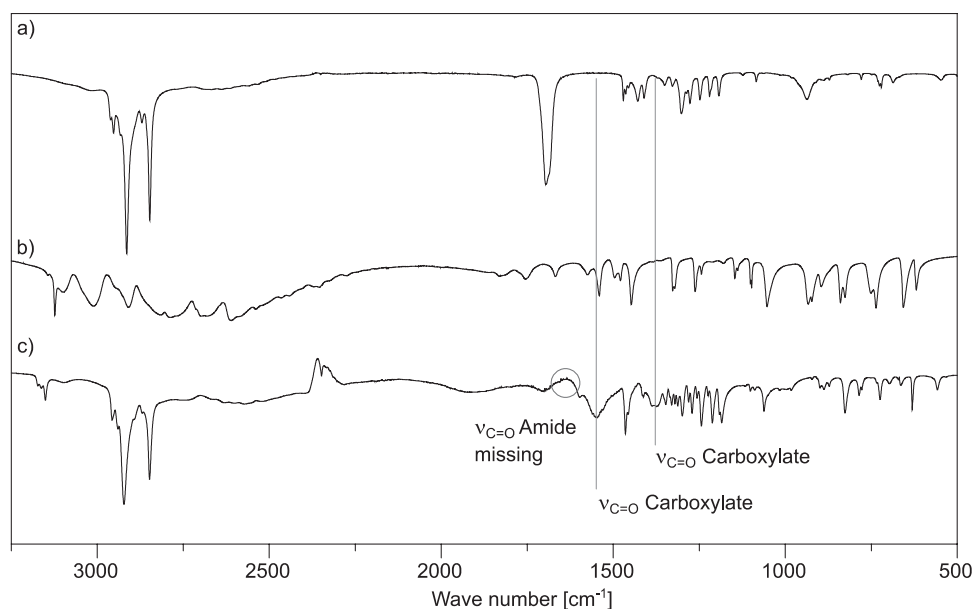


Figure 3. ATR-FTIR spectra (resolution: 2 cm^{-1} , 64 scans) of a) lauric acid, b) imidazole, and c) a mixture of lauric acid and imidazole after treatment for 2 h at $100\text{ }^{\circ}\text{C}$. The signal assignment was made according to the literature.^[21]

The products obtained are soluble in nonpolar solvents as chloroform or toluene. Moreover, melting could be expected in agreement with other studies about fatty acid esters of starch.^[18,19] As summarized in Table 1, there is a DS_{tot} that needs to be exceeded to obtain thermoplastic materials. The threshold of DS_{tot} seems to be about a value of 1.0. The melting area is dependent on both the DS_{tot} and the DS_{laurate} . In general, higher DS_{tot} leads to lower melting temperature. Comparing samples with similar DS_{tot} , higher content of laurate moieties decreases the melting area further. The DS values and, hence, the thermoplastic properties, can be adjusted by changing the

molar ratio of lauric acid and propionic anhydride in the synthesis path.

2.2. Mechanistic Considerations

Apart from starch, the reaction mixture consists of propionic anhydride, lauric acid, and imidazole that may undergo various reactions (Figure 2). The formation of a carboxylic acid imidazolide through a reaction of imidazole with a carboxylic acid may occur (reaction A). Considering the pKa values of

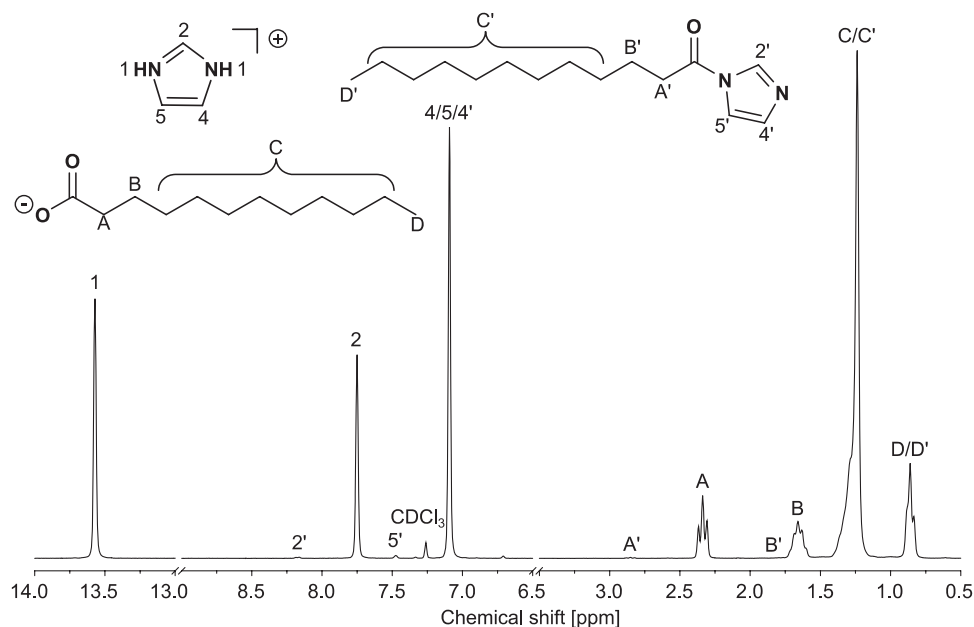


Figure 4. ^1H -NMR spectrum (250.13 MHz, 297 K, CDCl_3) of a mixture of lauric acid and imidazole after treatment for 2 h at $100\text{ }^{\circ}\text{C}$.

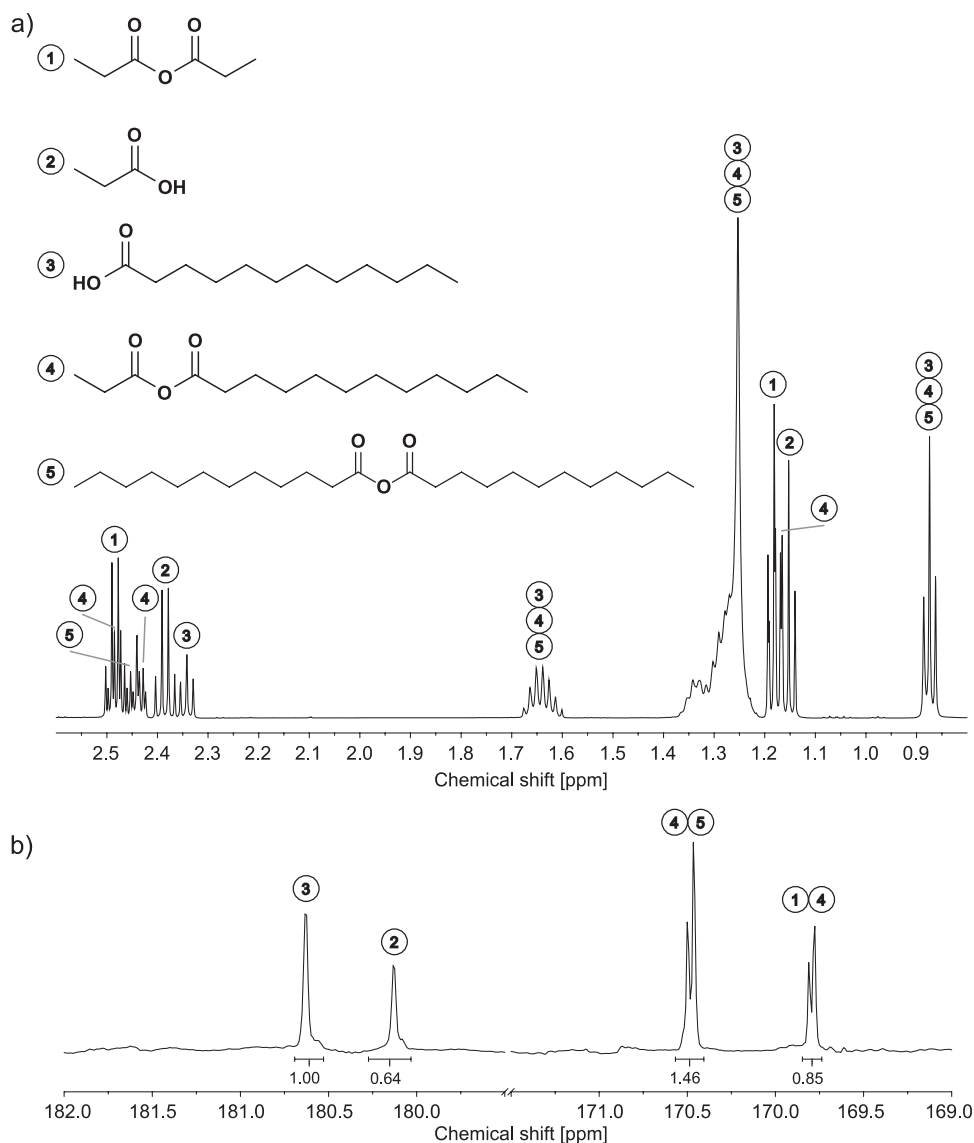


Figure 5. a) $^1\text{H-NMR}$ (600.15 MHz, 297 K, CDCl_3) and b) quantitative $^{13}\text{C-NMR}$ spectra (100.63 MHz, 297 K, CDCl_3) of a mixture of propionic anhydride and lauric acid after treatment for 2 h at 100 °C. Spectrum of b) the integrals are reported below the signals. Numbers in circles designate peaks caused by the particular molecules.

imidazole (pKa about 7) and the carboxylic acids (pKa below 5), imidazolium carboxylate is formed from imidazole and the carboxylic acid (reaction B), i.e., lauric acid or propionic acid resulting from the reaction of propionic anhydride and imidazole or with lauric acid. Further, a carboxylic acid could react with a carboxylic acid anhydride to give the mixed anhydride. The mixed anhydride could react with lauric acid yielding the symmetric anhydride (reaction C). Carboxylic acid imidazolides can be formed by the reaction of imidazole with any anhydride (reactions D, E, and F). Finally, there could be an equilibrium between carboxylic acid imidazolides and carboxylic acids or probably their carboxylates (reaction G). Thus, various reactions need to be investigated to get a reasonable image of the processes that may occur.

To investigate the possible reactions, lauric acid and imidazole were mixed and heated to 100 °C for 2 h (to mimic the

original reaction conditions with starch). The products were inspected utilizing Fourier transform infrared spectroscopy (FTIR) and $^1\text{H-NMR}$ spectroscopy. In the FTIR spectrum, the signal at 1696 cm^{-1} attributed to the $\nu_{\text{C}=\text{O}}$ vibration of lauric acid disappears completely (Figure 3). Moreover, no signal could be observed in the region around 1635 cm^{-1} caused by the $\nu_{\text{C}=\text{O}}$ vibrations of amides whereas signals arise at 1548 and 1375 cm^{-1} . These signals result from $\nu_{\text{C}=\text{O}}$ vibrations of carboxylates. Thus, it can be concluded that no lauric acid imidazolide but imidazolium laurate is formed (reaction B, Figure 3). In the $^1\text{H-NMR}$ spectrum, only tiny signals corresponding to lauric acid imidazolide could be seen (Figure 4), i.e., this reaction can be neglected. In summary, the components lauric acid and imidazole form the imidazolium laurate only.

Heating a mixture of propionic anhydride and lauric acid to 100 °C for 2 h results in the formation of the mixed anhydride

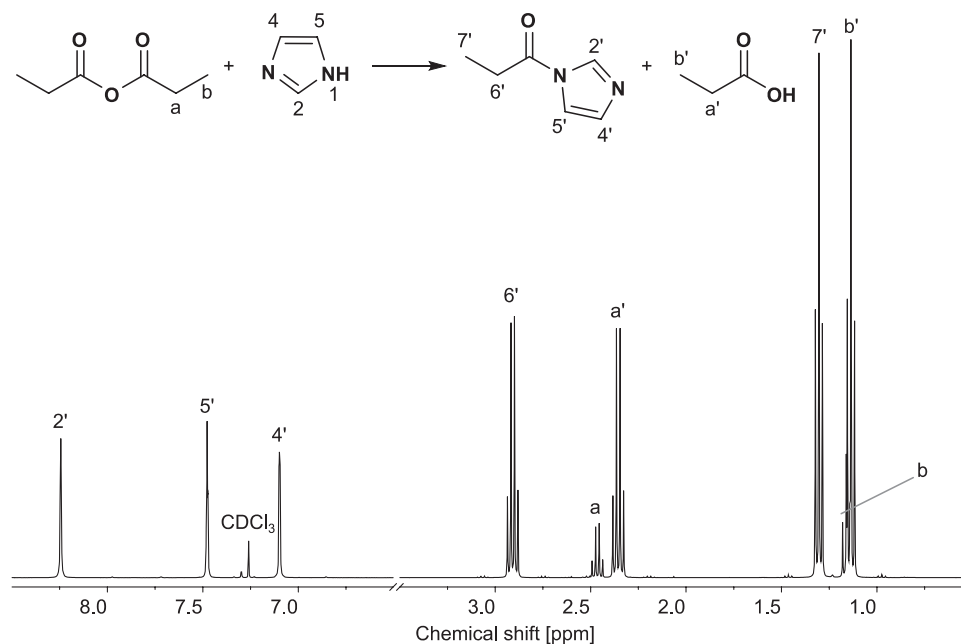


Figure 6. $^1\text{H-NMR}$ spectrum (400.20 MHz, 233 K, CDCl_3) of a mixture of propionic anhydride and imidazole in CDCl_3 after treatment for 2 min at -40°C .

as well as the symmetric lauric anhydride (reaction C, Figure 2). The $^1\text{H-NMR}$ spectrum of this mixture contains signals that can be assigned to propionic anhydride and lauric acid (Figure 5a). Besides, it shows signals caused by propionic acid, the mixed anhydride, and the symmetric lauric anhydride. Integration of the signal area from 2.6 to 2.3 ppm reveals a conversion of 59% of lauric acid into both anhydride species. Almost the same value is calculated for the conversion of propionic anhydride to propionic acid (56%), which confirms the result. Furthermore, integration of the carbonyl signals of a quantitatively measured $^{13}\text{C-NMR}$ spectrum leads to comparable result of 59% conversion of lauric acid (Figure 5b). Thus, around 60% conversion of the educts took place after 2 h at 100°C .

To check the kinetic aspects of this reaction as well, propionic anhydride and lauric acid were mixed in equimolar amount in CDCl_3 and $^1\text{H-NMR}$ spectra were recorded frequently. Initially, no conversion could be detected at room temperature. Heating to 50°C resulted in a conversion of <5%, <12%, and <19% after 5, 45, and 95 min, respectively. Thus, the reaction of propionic anhydride with lauric acid proceeds slowly.

$^1\text{H-NMR}$ spectroscopic measurements of a mixture of propionic anhydride and imidazole indicated that propionic acid imidazolide was formed after heating them to 100°C for 2 h (Figure 2, reaction D). The signals of imidazole completely disappeared. Moreover, the spectrum contains signals of propionic acid imidazolide (8.25, 7.48, 7.10, 2.91, and 1.31 ppm), propionic acid (2.36 and 1.15 ppm), and propionic anhydride (2.47 and 1.17 ppm). Thus, the complete conversion of imidazole to propionic acid imidazolide could be concluded.

To get information about the kinetics, an experiment was performed by cooling propionic anhydride and imidazole, separately dissolved in CDCl_3 , to -32°C and mixing them right before the NMR measurement at -40°C (spectrometer temperature). Figure 6 shows the $^1\text{H-NMR}$ spectrum acquired after ≈ 2 min after mixing the components. The imidazole signals

vanished and, apart from the propionic acid imidazolide signals, only propionic acid signals and signals of the not consumed propionic anhydride can be observed. Thus, it can be concluded that this reaction proceeds rapidly, on the one hand. On the other hand, no lauric anhydride species and, thus, no lauric acid imidazolide would be formed via this reaction path (Figure 2, reactions E and F). The formation of a mixed anhydride is slow compared with the reaction of propionic anhydride with imidazole to the corresponding propionic acid imidazolide.

In a further experiment, propionic acid was mixed with imidazole and heated to 100°C for 2 h to form imidazolium propionate. Subsequently, lauric acid imidazolide was added and the reaction was allowed to continue for another 2 h. In the $^1\text{H-NMR}$ spectrum of the resulting mixture, signals for the solvent imidazole can be observed at 7.83 and 7.10 ppm (Figure 7a). Moreover, signals assigned to propionic acid or its carboxylate and lauric acid imidazolide can be seen at 2.35 and 1.15 ppm as well as 8.20, 7.48, 7.10, 2.85, and 1.79 ppm, respectively. Additionally, signals at 2.91 and 1.31 ppm appeared that can be assigned to propionic acid imidazolide. Aromatic imidazolide signals in the range from 8.20 to 7.00 ppm could not be distinguished. Thus, the same sample was recorded in acetone- d_6 (Figure 7b). The signals, caused by the methylene groups in α - and β -position to the carbonyl groups, are not as well separated as in the chloroform spectrum, on one hand. On the other hand, set of signals appear in the range of 8.30–7.00 ppm that can be assigned to the two different imidazolide species. Thus, carboxylates can react with carboxylic acid imidazolides to form other imidazolides. It may be assumed that the formation of a mixed anhydride under elimination of imidazole is the first step on this reaction path, followed by nucleophilic attack of imidazole to one of both carbonyl carbon atoms of the anhydride, resulting in a chemical equilibrium and both imidazolides could be formed.

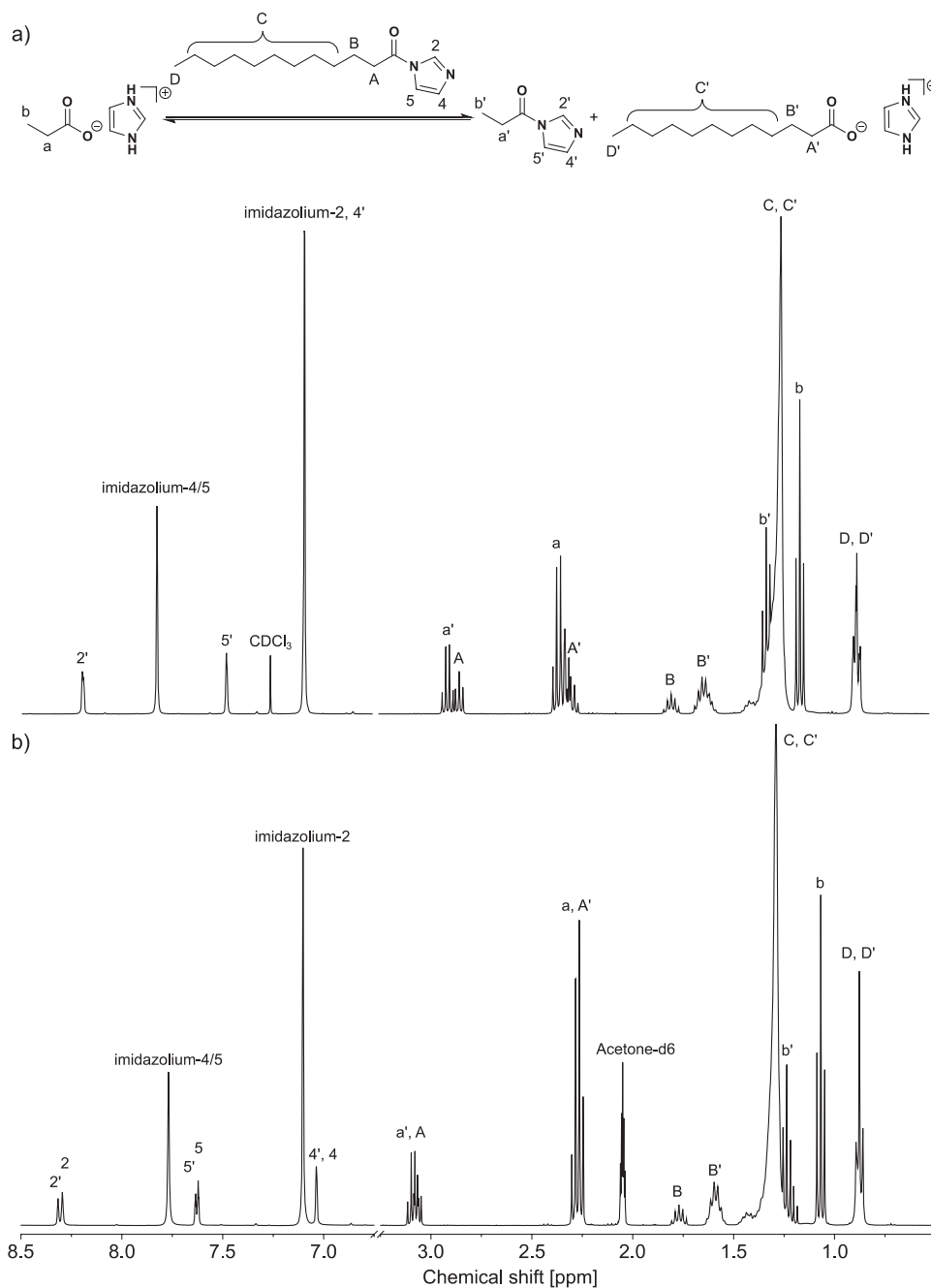


Figure 7. $^1\text{H-NMR}$ spectra (400.13 MHz, 297 K) of a mixture of propionic acid, imidazole, and lauric acid imidazolide after treatment for 2 h at 100 °C in a) CDCl_3 and b) acetone- d_6 .

A comparable investigation, however, without the inclusion of the salt formation, led to the same result, i.e., the carboxylic acid is capable to react with the imidazole, too. The results from the mechanistic investigations explain the incorporation of laurate moieties into the starch backbone in the starch-containing reaction.

Lauric acid imidazolide is formed during the reaction of propionic anhydride, lauric acid, and imidazole. Propionic anhydride was allowed to react with lauric acid in molten imidazole for 2 h at 100 °C. In the $^1\text{H-NMR}$ spectrum, lauric acid can still

be detected based on the signals at 2.34 and 1.66 ppm, which can be assigned to the methylene groups in α - and β -position to the carbonyl group (Figure 8). Besides, signals at 2.85 and 1.79 ppm appear, which can be assigned to the methylene groups of the lauric acid imidazolide. No signals were visible in the range from 2.50 to 2.40 ppm, evidencing the absence of any anhydride species.

The investigations conducted to unravel the reaction pathway in the experiments containing starch led to some assumptions that can be summarized as follows:

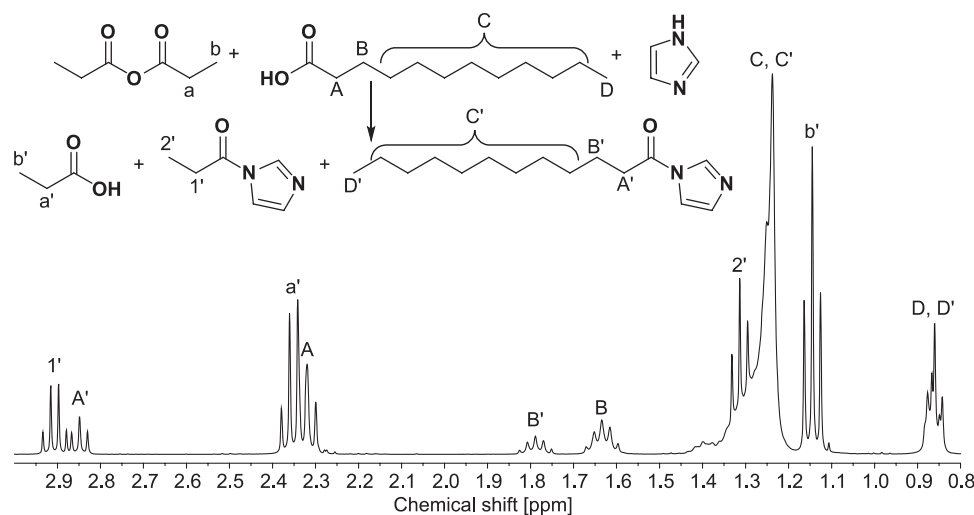


Figure 8. Section of the ^1H -NMR spectrum (400.21 MHz, 297 K, CDCl_3) of a mixture of lauric acid, propionic anhydride, and imidazole after treatment at 100 °C for 2 h.

1. Anhydrides are completely consumed to form carboxylic acid imidazolides in a rapidly proceeding reaction.
2. Carboxylic acid imidazolides can be transformed into each other due to a chemical equilibrium between carboxylic acids or their carboxylates and the imidazolides.
3. Reactive carboxylic acid derivatives are formed from the anhydrides only, i.e., the molar ratio of propionic anhydride should limit the DS_{tot} .

As a consequence, the DS_{tot} of the product should not exceed a value determined by the amount of carboxylic anhydride used in relation to the AGU. However, as can be seen at the DS values summarized in Table 1, higher values can be reached. Thus, it may be assumed that the esterification of the starch backbone causes an activation of the remaining hydroxyl groups for further reaction, i.e., the hydroxyl groups react with carboxylic acids. To investigate this possibility, starch was allowed to react with propionic acid chloride in the presence of pyridine in DMAC in a first step to yield starch propionate with a DS of 2.10. In a second step, the starch propionate was dissolved in molten imidazole and allowed to react with lauric acid. It turned out that the resulting product showed a slightly lower $\text{DS}_{\text{propionate}}$ (1.90), on one hand. On the other hand, a $\text{DS}_{\text{laurate}}$ of 0.66 could be detected. This experiment is the evidence for the theory mentioned above. Furthermore, the DS_{tot} exceeds the $\text{DS}_{\text{propionate}}$ of the educt, precluding a simple transesterification.

To understand the partial DS values of the different acids depending on the molar ratio AGU/carboxylic anhydride/carboxylic acid, a set of experiments was carried out; lauric acid and propionic anhydride were allowed to react in molten imidazole for 2 h at 100 °C (Table 2). The molar ratio of both components was adjusted to the same ratio applied for the starch reaction. The resulting molar ratio of the reactive species could be calculated applying Equations (5)–(8) based on the three assumptions mentioned above. Thus, the ratio of lauric acid imidazolide of total imidazolides could be determined and compared with the ratio of the laurate moieties of total ester groups

at the starch backbone. It turned out that the ratio of laurate moieties of total ester groups can roughly be correlated to the ratio of lauric acid imidazolide of total imidazolides. Due to the decrease in the ratio of lauric acid imidazolide with increasing amount of propionic anhydride, one would expect the ratio of $\text{DS}_{\text{laurate}}$ to behave in the same way. This can be observed within the limits of the method's precision.

3. Conclusion

Starch can be transformed into thermoplastic materials by the homogeneous reaction of the biopolymer with lauric acid and propionic acid anhydride in molten imidazole as a solvent. The melting temperatures can be adjusted by the total DS and partial DS values that can be controlled by the use of different molar ratios of the reagents. The formation of carboxylic acid imidazolides from the carboxylic anhydride and imidazole proceeds

Table 2. Calculated values of conversion of lauric acid into lauric acid imidazolide (C_{LAIm}), actual molar ratio of imidazolides, ratio of lauric acid imidazolide of total amount of imidazolides ($\text{LAIm}/\text{Im}_{\text{tot}}$), and ratio of $\text{DS}_{\text{laurate}}$ of DS_{tot} ($\text{DS}_{\text{laurate}}/\text{DS}_{\text{tot}}$) within the reaction mixture of starch, lauric acid, propionic anhydride, and imidazole.

Molar ratio of LA/PA	C_{LAIm}	Actual molar ratio of AGU/LAIm/PAIm	$\text{LAIm}/\text{Im}_{\text{tot}}$	$\text{DS}_{\text{laurate}}/\text{DS}_{\text{tot}}$
1:1	0.43	1:0.43:0.57	0.43	0.35
1:3	0.39	1:0.39:2.61	0.31	0.16
1:5	0.43	1:0.43:4.57	0.09	0.25
3:1	0.19	1:0.57:0.43	0.57	0.30
3:3	0.30	1:0.90:2.10	0.30	0.34
3:5	0.50	1:1.50:3.50	0.30	0.23
5:1	0.16	1:0.80:0.20	0.80	0.50
5:3	0.27	1:1.35:1.65	0.45	0.49
5:5	0.21	1:1.05:3.95	0.21	0.37

rapidly and afterwards there is an equilibrium between carboxylic acid imidazolides and carboxylic acids. Additionally, starch esters are found to be more reactive than starch regarding further esterification. Thus, the total DS can exceed the molar ratio of carboxylic acid anhydride applied, which makes the reaction very efficient. The esterification system containing a short-chain carboxylic acid anhydride and a long-chain fatty acid seems to be a universal path for efficient esterification of polysaccharides that is studied at present. It was also found that the reaction of starch with a fatty acid anhydride only yields starch fatty acid esters. The conversion of starch with three moles of lauric acid anhydride per mole AGU led to starch laurate with a DS_{laurate} of 2.83 and a melting temperature in the range from 70 to 90 °C. This chemistry will be investigated in more detail in further studies. The biodegradability of the mixed starch esters, as well as the recyclability of imidazole used as solvent, base, and catalyst, is under investigation.

4. Experimental Section

Materials: Lauric acid (Acros Organics), propionic anhydride (Fluka), and imidazole (abcr) were commercially available and used without further purification. Acetone- d_6 and chloroform- d were purchased from Aldrich and Deutero, respectively. Maize starch ($\bar{M}_n = 60\,572\text{ g mol}^{-1}$, $D = 2.96$) was obtained from Ingredion and dried at 110 °C for 8 h in vacuum before use.

Methods: The melting temperatures were measured using a hot stage microscope.

The ATR-FTIR spectra were recorded with a Shimadzu IRAffinity-1. Sixty-four scans with a resolution of 2 cm^{-1} were averaged.

The NMR spectra were recorded on Bruker devices. The solvents, temperatures, and frequencies are given in the figure captions. Chemical shifts are stated in parts per million normalized to tetramethylsilane.

The DS values were calculated from the NMR spectra recorded in the presence of TFA according to Equations (2)–(4).

Equations:

$$\text{Yield (\%)} = \frac{m_{\text{sample}}}{\frac{M_{\text{AGU}} - (DS_{\text{tot}} \times M_{\text{H}}) + (DS_{\text{propionate}} \times M_{\text{propionate}}) + (DS_{\text{laurate}} \times M_{\text{laurate}})}{\frac{m_{\text{starch}}}{M_{\text{AGU}}}}} \times 100\% \quad (1)$$

m_{sample} —mass of a sample (g), M_{AGU} —molar mass of the AGU (g mol^{-1}), M_{H} —molar mass of hydrogen (g mol^{-1}), $M_{\text{propionate}}$ —molar mass of propionyl substituent (g mol^{-1}), M_{laurate} —molar mass of lauroyl substituent (g mol^{-1}), m_{starch} —mass of starch that was used in the reaction (g)

$$DS_{\text{laurate}} = \frac{I_{0.84} \times 7}{I_{5.75-3.50} \times 3} \quad (2)$$

$I_{0.84}$ —integral of the signal located at 0.84 ppm in the $^1\text{H-NMR}$ spectrum after addition of TFA, $I_{5.75-3.50}$ —integral of all signals in the range from 5.75 to 3.50 ppm in the $^1\text{H-NMR}$ spectrum after addition of TFA

$$DS_{\text{propionate}} = DS_{\text{laurate}} \times \frac{I_{27}}{I_{34}} \quad (3)$$

I_{27} —integral of the signal located at 27 ppm in the $^{13}\text{C-NMR}$ spectrum, I_{34} —integral of the signal located at 34 ppm in the $^{13}\text{C-NMR}$ spectrum

$$DS_{\text{tot}} = DS_{\text{laurate}} + DS_{\text{propionate}} \quad (4)$$

$$C_{\text{LAIm}} = \frac{I_{1.79}}{I_{1.79} + I_{1.65}} \quad (5)$$

C_{LAIm} —conversion of lauric acid into lauric acid imidazolide, $I_{1.79}$ —integral of the signal located at 1.79 ppm in the $^1\text{H-NMR}$ spectrum, $I_{1.65}$ —integral of the signal located at 1.65 ppm in the $^1\text{H-NMR}$ spectrum

$$n_{\text{LAIm}} = n_{\text{LA, initial}} \times C_{\text{LAIm}} \quad (6)$$

n_{LAIm} —moles of lauric acid imidazolide (mol), $n_{\text{LA, initial}}$ —moles of lauric acid applied (mol)

$$n_{\text{PAIm}} = n_{\text{PA, initial}} - n_{\text{LAIm}} \quad (7)$$

n_{PAIm} —moles of propionic acid imidazolide (mol), $n_{\text{PA, initial}}$ —moles of propionic anhydride applied (mol)

$$L\text{AIm}/I_{m_{\text{tot}}} = \frac{n_{\text{LAIm}}}{n_{\text{LAIm}} + n_{\text{PAIm}}} \quad (8)$$

$L\text{AIm}/I_{m_{\text{tot}}}$ —share of lauric acid imidazolide of total imidazolides.

Syntheses—Starch Laurate Propionates (4i, Representative Example): Starch (2.00 g; 12.34 mmol) and finely powdered imidazole (8.00 g; 117.51 mmol) were heated to 120 °C for 2 h under stirring to obtain a clear solution, which was allowed to cool to 100 °C. Lauric acid (7.41 g; 37.01 mmol) and propionic anhydride (4.74 mL; 37.01 mmol) were added and allowed to react for 2 h at 100 °C under mechanical stirring. After cooling the mixture to ambient temperature, it was poured into 200 mL methanol, filtered off, and washed four times with 100 mL methanol. The product was dried at 40 °C in vacuum to give a beige powder.

Yield: 3.93 g (8.56 mmol; 69%); $DS_{\text{laurate}} = 1.02$; $DS_{\text{propionate}} = 1.98$.

$^{13}\text{C-NMR}$ (62.90 MHz, 297 K, CDCl_3): $\delta = 174.50\text{--}173.70$ (C-7), 173.50–172.50 (C-7_{propionate}), 95.68 (C-1'), 72.12 (C-3_s), 70.43 (C-2_s), 69.27 (C-5), 61.53 (C-6_s), 34.28 (C-8), 32.02 (C-16), 29.80–29.40 (C-10–C-15), 27.49 (C-8_{propionate}), 25.06–24.77 (C-9), 22.79 (C-17), 14.21 (C-18), 9.21–8.82 (C-9_{propionate}). mp: 105–120 °C.

Syntheses—Model Reactions for NMR Investigations:

1. Imidazole (8.00 g; 117.51 mmol) and lauric acid (7.41 g; 37.01 mmol) were magnetically stirred for 2 h at 100 °C. A sample of 20 mg was dissolved in CDCl_3 and the $^1\text{H-NMR}$ spectrum was recorded.
2. Propionic anhydride (5.94 mg; 0.0456 mmol) and lauric acid (9.16 mg; 0.0457 mmol), dissolved in 250 μL CDCl_3 each, were mixed. Immediately, $^1\text{H-NMR}$ spectra were recorded every 5 min.
3. Propionic anhydride (9.84 mg; 0.0734 mmol) and imidazole (5.00 mg; 0.0734 mmol), dissolved in 250 μL CDCl_3 each, were cooled to -32 °C. The solutions were mixed in the NMR tube and instantly transferred to the spectrometer that was pre-cooled to -40 °C and $^1\text{H-NMR}$ spectra were recorded every 2 min.
4. Finely powdered imidazole (0.84 g; 12.34 mmol) and propionic acid (0.915 mL; 12.34 mmol) were stirred at 100 °C for 2 h. Lauric acid imidazolide (3.09 g; 12.34 mmol) was added and stirred at 100 °C for 2 h. A sample of 20 mg was dissolved in CDCl_3 (or acetone- d_6) and the $^1\text{H-NMR}$ spectrum was recorded. The procedure was repeated without imidazole and without the first heating cycle to check if propionic acid could react with lauric acid imidazolide, too.

5. Finely powdered imidazole (8.00 g; 117.51 mmol) and lauric acid (7.41 g; 37.01 mmol) were molten and propionic anhydride (4.74 mL; 37.01 mmol) was added. The reaction mixture was magnetically stirred for 2 h at 100 °C. A sample of 20 mg was dissolved in CDCl₃ and a ¹H-NMR spectrum was recorded.

Syntheses—Synthesis of Starch Propionate: Starch (2.00 g; 12.34 mmol) was suspended in 50 mL *N,N*-dimethylacetamide and heated to 120 °C for 2 h. After cooling to 80 °C, pyridine (2.5 mL; 30.84 mmol; 2.50 equiv.) and propionyl chloride (2.5 mL, 28.37 mmol; 2.30 equiv.) were added and the mixture was stirred at 80 °C for 2 h. It was cooled to room temperature, poured into 400 mL deionized water, filtered off, and washed twice with 200 mL water each. The product was dried at 40 °C in vacuum to yield a colorless solid.

Yield: 2.44 g (8.72 mmol; 71%), DS_{propionate} = 2.10 (91%).
¹³C-NMR (62.90 MHz, 297 K, CDCl₃): δ = 174.34 (C-7), 97.71 (C-1'), 78.19 (C-4), 73.51 (C-3_s), 71.69 (C-2_s), 69.75 (C-5), 63.92 (C-6_s), 27.77 (C-8), 9.50–9.19 (C-9).

Syntheses—Conversion of Starch Propionate with Lauric Acid in Imidazole: Starch propionate (DS = 2.10, 2.00 g, 7.15 mmol) was dissolved in imidazole during stirring for 2 h at 120 °C. Lauric acid (2.86 g, 14.30 mmol, 2.0 equiv.) was added and the mixture was stirred for 2 h at 120 °C. After cooling to room temperature, it was poured into 200 mL ethanol and dialyzed against ethanol in a cellulose membrane (MWCO = 3.5 kDa). The solvent was removed under reduced pressure to obtain the product.

Yield: 660 mg, DS_{propionate} = 1.90, DS_{laurate} = 0.66, DS_{tot} = 2.56.
¹³C-NMR (62.90 MHz, 297 K, CDCl₃): δ = 174.11–172.43 (C-7_{laurate} and C-7_{propionate}), 100.66 (C-1), 98.17–95.40 (C-1'), 72.08–69.51 (C-4, C-3_s, C-2_s, and C-5), 62.26 (C-6_s), 34.42 (C-8_{laurate}), 32.02 (C-16), 29.74–29.46 (C-10–C-15), 27.42 (C-8_{propionate}), 24.79 (C-9_{laurate}), 22.80 (C-17), 14.23 (C-18), 9.14 (C-9_{propionate}).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

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