Isocyanate-Free Fully Biobased Star Polyester-Urethanes: Synthesis and Thermal Properties

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ABSTRACT: A green strategy for the synthesis of nonisocyanate polyester-urethanes (NIPHEUs) was developed. These NIPHEUs were synthesized by step growth polymerization combining sugar-derived dimethyl-2,5-furan dicarboxylate (DMFD) with polyhydroxylurethanes (PHUs) adducts bearing four hydroxyl groups. The later hydroxyl urethane tetraols (HU-tetraols) building blocks were prepared by aminolysis of glycerol carbonate with two different aliphatic diamines having different chain lengths, 8 and 12 carbons. Qualitative and quantitative NMR analyses of the HU-tetraols showed the presence of primary and secondary hydroxyl moieties at different ratios. Hence, in the polycondensation stage, the stoichiometry of the diester was varied from 1 to 6 equiv in order to tailor the structural features of the prepared NIPHEUs. The success of the chain extension through polycondensation was confirmed by FTIR and NMR analyses. Thermal analyses of these new polymers demonstrated satisfactory thermal stability, with onset degradation temperatures ranging from 170 to 220 °C where the main first degradation stage occurs. Their melting temperatures ranged between 93 and 110 °C and seem to be driven by the thermal behavior of HU-tetraol monomers. Surprisingly, preliminary results from thermal analyses revealed the occurrence of a striking thermal change in the NIPHEUs upon repetitive heating cycles. This behavior may be related to a thermal-induced bond exchange probably driven by transcarbamoylation reaction. Such interesting vitrimer-like behavior for this new type of NIPHEUs would be unique and should be confirmed by a deeper study before leading to a new range of functional green materials.

INTRODUCTION

Polyurethanes (PU) are used in a broad range of highly demanding applications, which rank them as the sixth most produced polymers in the world with 18 Mt of global production in 2016.1,2 Based on their structure–property relationships, PUs are used in both thermoplastics and thermosets and are known for specific mechanical, physical, biological, and chemical properties.1,3,4 These properties allow their use in many applications ranging from coatings, sealants, adhesives, medical implants and devices, textiles, insulation foams, and so on. From a structural stand point, PUs are segmented in hard and soft segments that determine their final properties. Therefore, significant research attention is directed toward tailoring PUs structures in order to endow additional properties and enlarge their application domains. Design of new PUs can be achieved through design of new architectures mainly through combination with other types of polymers, development of new synthesis routes and processing technologies, and finally, the use of new raw materials such as biobased ones.1

Typically, PUs are obtained by the reaction between a polyfunctional isocyanate and a polyl. However, isocyanates are harmful for human and environment, therefore their substitution has become a major concern.5,6 Research about nonisocyanate polyurethanes (NIPUs) has been intensively carried out by academic and industry communities during the last years.7−10 Among the promising and practical solution...
developed is the synthesis of polyhydroxyurethanes (PHUs), which are obtained by the aminolysis reaction of cyclic carbonates.11 Their final structure is thus composed of urethane linkage with an additional pendant hydroxyl group. Five-membered cyclic carbonates are easily synthesized by carbon dioxide carbonation of epoxides, which makes this pathway one of the most eco-friendly and the least toxic ones for the synthesis of PHUs.12−15 Indeed, the valorization of carbon dioxide which is a renewable, cheap and nontoxic resource, is a strong advantage of the PHU synthesis. Nevertheless, the low reactivity and conversion of carbonate/amine reaction are the main drawbacks of PHUs synthesis.16

To overcome this issue, recent works from our team and others on hybrid-polyhydroxyurethanes (H-PHU) allowed to obtain new properties and to improve system reactivity. Hybrid epoxy-polyhydroxyurethanes are the most described in the literature and can be obtained by two different routes. The first one consists in aminolysis of a mixture of multifunctional epoxides and cyclic carbonates in a single step.17,18 On the other hand, amine-terminated PHU prepolymers are first synthesized with an amine excess and are then cross-linked by reacting with polyfunctional epoxy monomers in a second step.19−21 PHUs with acrylate end groups have been cross-linked by aza-Michael addition with di- or triamines,22 whereas PHUs with methacrylate end groups have been cross-linked by conventional radical chain growth polymerization.23 Hybrid siloxane-polyhydroxyurethanes thermosets have been obtained from siloxane-based cyclic carbonate monomers.24 The low viscosity of these monomers allowed to reach high conversion and to combine flexibility of siloxanes with high mechanical properties of urethanes. However, despite these interesting reported works on end-functionalized PHUs with various functions, the use of hydroxyl groups that are easily obtained by aminolysis was never exploited to synthesize polyester-urethane type polymers. Therefore, the aim of this study was to synthesize fully biobased nonisocyanate poly(ester-urethane)s, more specifically polyhydroxy(ester-urethane)s (NIPHEUs) with thermoplastic behavior. Polymers lack excellent physical and mechanical properties, and the addition of urethane linkages in their backbone is a good way to increase their properties.10 To obtain NIPHEUs, glycerol carbonate (GC) was reacted with two different aliphatic diamines, 1,8-diaminooctane and 1,12-diaminododecane, that can be obtained from renewable feedstock through biotechnological pathways,15 making thus the two HU-tetraols potentially fully biobased. Therefore, a second step consisted to react all hydroxyl groups of these HU-tetraols (two from GC and two from hydroxyurethane linkages) with the dimethyl ester of 2,5-furandicarboxylic acid to obtain NIPHEUs. The polycondensation of this new type of polyester linkages was optimized and the thermal properties of the resulting NIPHEUs were investigated. This study could interestingly lead to a new range of hybrid-NIPUs.

## MATERIALS AND METHODS

### Materials

2,5-Furan dicarboxylic acid (FDCA; purum 97%), tetrabutyl titanate (TBT) catalyst, 1,8-diaminooctane, and 1,12-diaminododecane were purchased from Sigma-Aldrich Merck (Darmstadt, Germany). FDCA was used to prepare dimethyl-2,5-furan dicarboxylate (DMFD) as previously reported in our literature.26 Glycerol carbonate was purchased from Huntsman (the Woodlands, TX, U.S.A.). All materials were used as received. Deuterated solvent DMSO-\text{d}_6 was obtained from Eurisotop for NMR study.

### Synthesis of HU-tetraol-C8 and HU-tetraol-C12. In a round-bottom flask, glycerol carbonate (2.4 equiv, 9.8 g) and 1,8-diaminoocctane (2.0 equiv, 5.0 g) were dissolved in 35 mL of methanol. The solution was heated at 65 °C under stirring for 5 h. Once the solution was cooled down, the final product was precipitated in 350 mL of ethyl acetate at −18 °C to remove the excess of glycerol carbonate. The powder was then washed several times with cold ethyl acetate and dried under vacuum. The pure product HU-tetraol-C8 was obtained as a white powder (yield = 98%). The same procedure was applied for the synthesis of HU-tetraol-C12.

Assignments of HU-tetraol-C8 as determined by 600 MHz 1H and 13C NMR. 1H NMR δ 1.23 (s, 8H), 1.36 (m, 4H), 2.94 (m, 4H), 3.33 (m, 2H), 3.39−3.54 (m, 4H), 3.59 (m, 1H), 3.79−3.96 (m, 2H), 4.54 (m, 1H). 13C NMR δ 26.2 (CH−CH=CH), 29.0 (CH−CH=CH−NH), 39.5 (CH2−NH), 60.1 (CH=N−O−H), 62.8 (HO−CH=CH−OH), 65.4 (O−CH=CH−OH), 69.8 (CH−OH), 75.3 (HOCH2−CH=CH−OH), 156.4 (C=O).

### Polymer Synthesis

The novel NIPHEUs were successfully synthesized via a step growth polymerization method in solution as follows: the predetermined amount of HU-tetraol-C8 or HU-tetraol-C12 and DMFD with different molar ratios of tetraol/diester of 1:1, 1:3, and 1:6 were introduced in a round-bottom flask with 400 ppm of TBT catalyst. The polystyirenication was carried out in DMF under a mild nitrogen flow and heated at 90 or 120 °C. At last, the reaction mixture with the reagents cooled down at room temperature and then it was precipitated in 10 volume of cold diethyl ether. The resulting polymers were again dissolved in a small amount of DMF and reprecipitated again in cold diethyl ether to ensure the elimination of unreacted compounds. The resulting polymers are coined hereafter as follows CXX-Yeq-T. For example, C8−1eq-90 refers, where C8 stands for the tetraol-C8 monomer used in the polymer synthesis; 1 equiv denotes the molar amount of DMFD, and 90 refers to the reaction temperature of the polycondensation.

### Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was conducted on a Bruker TENSOR 27 (Ettlingen, Germany) in the attenuated total reflection (ATR) mode using a diamond crystal. The background and sample spectra were recorded at 4 cm$^{-1}$ spectral resolution across the 4000−400 cm$^{-1}$ range.

### Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded using an AVANCE III HD Bruker spectrometer operating at a proton frequency of 600 MHz and equipped with a 5 mm BBO probe. HU-tetraol adducts and different NIPHEU polymers were dissolved in deuterated dimethyl sulfoxide (DMSO-\text{d}_6). The spectra were referenced relative to tetramethylsilane (TMS). Assignments were performed using a combination of COSY, HSQC, and HMBC spectra.

### Differential Scanning Calorimetry (DSC)

DSC thermograms were recorded using a Mettler Toledo apparatus operating at an inert atmosphere (nitrogen) for the analysis of the thermal behavior of the HU-tetraol adducts and the corresponding NIPHEU polymers. Approximately 5−7 mg of sample, sealed in an aluminum pan, was heated under nitrogen from room temperature to 180 °C at a heating rate of 10 °C/min then it was cooled down to 0 °C at 10 °C/min and held at this temperature for 10 min to erase any thermal history and heated again for the second heating scan from 0 to 350 °C with a heating rate of 10 °C/min.

### Thermogravimetric Analysis (TGA)

Thermogravimetric analysis measurements were performed using a Mettler Toledo instrument for the analysis of the thermal degradation of the HU-tetraol adducts and the corresponding NIPHEU polymers. Approximately 10 mg of the sample were heated under a nitrogen flow from room temperature to 800 °C (heating rate 10 °C/min).

## RESULTS

### Synthesis and Characterization of HU-Tetraols

The synthesis of HU-tetraol was performed in methanol at 65 °C without catalyst during 5 h under stirring. Two different aliphatic amines 1,8-diaminoocctane and 1,12-diaminododecane...
were reacted with glycerol carbonate (GC) to yield respectively to HU-tetraol-C8 and HU-tetraol-C12 (Figure 1). An excess of GC (2.4 equiv) was reacted with diamines (2 equiv) to ensure a complete functionalization. A quantitative yield of HU-tetraol adducts was achieved. The success of the reaction was confirmed by NMR analyses and the full assignments of the peaks was done by 2D $^1$H–$^1$H and $^1$H–$^{13}$C NMR which confirm the expected molecular structure of the resulting HU-tetraol adducts. The protons c at 2.9 ppm confirm the formation of the urethane linkage. Moreover, in the FTIR spectra (Figure SI-1), the band in the region of 3380–3440 cm$^{-1}$ is characteristic to the NH groups of the urethane bonds. The band at 1725 cm$^{-1}$ is attributed of the C=O group of the urethane bond. The region around 1530 cm$^{-1}$ shows characteristic bands for CN and NH bonds of the urethane groups. The group C=O–C can be identified by the presence of a band in 1235 cm$^{-1}$. Additionally, the wave numbers of 3330, 2920, and 2850 cm$^{-1}$ are assigned to asymmetrical and symmetrical stretching modes of the CH2-groups of the diamine backbone.

Quantitative NMR analyses confirmed that the ring opening aminolysis of cyclic carbonate leads predominately to the creation of secondary pendant hydroxyl groups (∼80%; proton at 3.6 ppm labeled e in Figure 2) that are thermodynamically more stable compared to primary ones.$^{27}$ The protons h at 4.5 ppm correspond to the primary alcohols that are minors. The ratio between secondary and primary alcohols was estimated by $^1$H NMR analyses. With the integration of the peaks d and h, the secondary/primary alcohol ratio were determined at 85/15 and 80/20 for HU-tetraol-C8 and HU-tetraol-C12, respectively. These values are in accordance with the values already reported in the literature for the aminolysis of five-
membered cyclic carbonate with amines.\textsuperscript{28} Considering the primary hydroxyl groups originally present in the carbonate (at 3.33 ppm, labeled as $f$), the overall ratio of primary and secondary hydroxyl groups present in the HU-tetraol is estimated to be around 60 and 40% respectively.

This ratio is an important parameter for the synthesis polyesters using these HU-tetraols as building blocks with diacids. Indeed, primary alcohols are more reactive than secondary ones. In view of using these HU-tetraols with diacids for the chain extension in polyester synthesis, special attention was given to the adjustment of the ratio of alcohol to acid in order to optimize polymerization step.

The thermal properties and stability of the above synthesized HU-tetraol was determined by DSC and TGA respectively (see DSC and TGA profiles depicted in Figure SI-2). HU-tetraol-C8 exhibited a melting temperature around 97 °C while the melting temperature of HU-tetraol-C12 was higher (122 °C). The (semi)crystalline structure of PHUs was largely investigated and it is accepted that the hydrogen bonding network induces such crystalline organization. No large difference in the thermal stability as well as the thermal degradation behavior was observed between the two adducts; both showed to be thermally stable up to 210 °C. The degradation temperature at 5% weight loss was 211 °C for HU-tetraol-C8 and 221 °C for HU-tetraol-C12 and the remained residual weight above 500 °C ranged between 0.35 and 0.47%.

The HU-tetraol building blocks were used as polyols in combination with DMFD for the synthesis of polyesters using solution step growth polymerization. Giving the chemical structure differences between the hydroxyl groups present in the HU-tetraol and their respective amount, the required feeding equivalent of the DMFD is vital to ensure the occurrence of the esterification. The effect of the temperature reaction is also an important factor. Both parameters will also influence the structural features of the resulting polymers, thus they were investigated in order to optimize the polymerization.

The ratio of hydroxyl:diester was varied from 1:1 up to 1:6 and the reaction was performed at 90 and 120 °C. The occurrence of the polycondensation was followed by FTIR and NMR analyses. The recorded FTIR spectra for the polymers obtained at different conditions are depicted in Figure 3. In addition to characteristic bands attributed to the different moieties of HU-tetraol adducts previously detailed (particularly urethane moieties and CH$_2$ groups), additional bands typical of the double bond and ester linkage of the furan moiety that appeared at around 1585 and 1710 cm$^{-1}$, respectively. The later overlapped with the band attributed to the urethane, but it appeared clearly at higher molar ratio of DMFD (6 equiv).

These observations were further confirmed by $^1$H and $^{13}$C NMR analyses (Figure 4). From a structural standpoint, both analyses confirmed the occurrence of the polycondensation by the presence of the characteristic peaks of the furan moieties and ester linkages. Precisely, in $^1$H NMR spectra one peak at 7.4 ppm and in $^{13}$C NMR two peaks at 121 and 147 ppm are characteristics of the furan. In $^{13}$C NMR spectra, the presence of the peak at 165 ppm confirms the creation of an ester linkage and, hence, the success of the polycondensation reaction. Furthermore, the deshielding of the peaks of the protons $f$ and $h$ of HU-tetraols, attributed to primary hydroxyls, from 3.33 and 4.55 ppm, respectively, to 3.79–3.96 ppm, where the proton $d$ (also engaged in ester bond) of the HU-tetraol is located confirms that the esterification-driven chain extension occurs mainly on primary hydroxyl groups.

Figure 3. FTIR spectra of NIPHEUs synthesized in different conditions (top with HU-tetraol-C8 and bottom with HU-tetraol-C12).

The continuous decrease of the intensities of these peaks (e.g., $h$ and $f$, their respective integrals are gathered in Table 1 in the SI) as well as those of the peaks related to the related OH located between 4.4 and 5.2 ppm with the increase of the temperature and, more particularly, the increase of molar ratio of DMFD demonstrates the chain growth. Noting that the peak attributed to proton $e$ remained unchanged, confirming that under the used conditions this secondary hydroxyl group did not engage in the polycondensation reaction. It is most likely that it has been esterified once, but the chain extension from this hydroxyl was not prolonged further.

Based on the previous observations, we can conclude that the three hydroxyl groups involved in the polycondensation at distinct kinetics led to branched NIPHEUs most probably with low branching degree. Following the bimolecular nonlinear polymerization concept (BMNLP), one can predict the structural features particularly the end groups of the synthesized polyesters.\textsuperscript{29} This method developed by Flory and Stockmayer allows the prediction of a number of properties of the branching reaction in a [aA$_b$ + bB$_c$] system,
where $x \geq 3$ and $y \geq 2$, in terms of the molar ratios of the reactive groups with multiple reactive sites (3 hydroxyls and 2 acids in our case).

The critical conditions to accommodate arbitrary functionalities of the reactive monomers in an $[aA_x + bB_y]$ system are generalized in the following equation:

$$r_p A^2 \geq \frac{1}{(x-1)(y-1)},$$

with $r$ as the ratio of the number of A and B groups initially present in the system and $p_A$ and $p_B$ are the probability that groups A and B, respectively, have reacted at any stage of the reaction between them. Hence, a soluble branched polymer can be obtained if A is the minor component when $r_p A^2 > (x-1)(y-1)$ and if B is the minor component when $p_B^2/r < 1/(x-1)(y-1)$. For example, if all B groups present in the $aA_x + bB_y$ system reacts, a soluble branched polymer having A end-groups will be formed without gelation if $r > (x-1)(y-1)$, with $r = ax/by$ and if all A groups react, a soluble branched polymer with B end-groups will be formed if $r < 1/(1-x)(1-y)$.

In our case, one can presume that below or even up to 3 equiv of diesters, the synthesized NIPHEUs bear most likely hydroxyl moieties at their end groups while, with 6 equiv of diesters, the end groups are predominately carboxylic acid (in ester form). The signals of the end groups in both cases (hydroxyl or carboxylic groups) overlapped with the existing functionalities making the confirmation of these assumptions very challenging. To this end, in-depth NMR characterization using labeled molecules and advanced sequences are ongoing to identify and quantify these end groups.

The assessment of the thermal properties of polymeric materials is of high importance in order to evaluate their application domains. Therefore, the thermal properties of all resulting NIPHEUs were investigated by TGA and DSC analyses. These properties were related to their composition (ratio HU-tetraol and DMFD). Figure 5 presents the recorded TGA thermograms, and all collected data are gathered in Table 2 in the SI. The data of the HU-tetraol monomers are also provided as reference.

All polymers exhibited similar degradation behaviors as they underwent three degradation stages occurring between 245 and 260 °C, 325−335 °C, and 445−450 °C for HU-tetraol-C8 and 235−264, 330−338, and 450−455 °C for HU-tetraol-C12. These degradations are typical of dehydration, decarboxylation and the scission of the different bonds present in polymers (C−H, C−C, C=O, C−N). Some of these bonds, such as C−N, are more heat resistant than the others. It was observed that the second stage degradation of all HU-tetraol-C8-based polymers occurred at higher temperatures than the corresponding HU-tetraol monomers (for HU-tetraol-C8: 293 °C). The opposite trend was observed for the HU-tetraol-C12 based polymers where the degradation of the HU-tetraol was at 355 °C versus 330−338 °C for the polymers. This might be related to the chain length of the used diamine containing more carbon than the previous one.

The degradation temperatures at 5% weight loss of the polymers were slightly lower than those of the corresponding HU-tetraols and they decreased with the amount of DMFD monomers. In the case of HU-tetraol-C8, $T_{d,5\%}$ decreased from 211 to 200.6 °C, while for HU-tetraol-C12-based polymers $T_{d,5\%}$ decreased from 221 to 215.5 °C. The sublimation of end-group furan moieties is suspected to occur between 150 and 210 °C, as it has been reported, which may cause this decrease of the temperature of first event degradation.
The thermal properties of the prepared polymer were further analyzed by DSC. The recorded thermograms at the first heating rate of the obtained materials derived from HU-tetraol-C8 and HU-tetraol-C12, combined with different ratios of DMFD are presented in Figure 6, and the melting temperatures ($T_m$) measured are gathered in Table 2. All synthesized polymers exhibited clear melting temperatures showing their semicrystalline structures. Like the monomers, these crystalline structures were believed to be induced by the hydrogen bond networks formed mainly between the HU-tetraols monomers. For HU-tetraol-C8 based polymers, the melting temperature decreased from 106 to 93 °C with the increase of the DMFD content and also the temperature. The same trend was observed for HU-tetraol-C12-based polymers (from 110 to 101 °C), but in this case, the melting temperature of all obtained polymers were clearly lower than those of the corresponding monomer HU-tetraol-C12 (122 °C). This behavior could be explained by the flexibility of the long chain of the used diamine in this case, which can reduce the hydrogen bonding network, while the chain growth of the NIPHEUs is progressing.

Unlike traditional polyurethanes, neat PHUs are known to undergo dynamic bonding exchanges through transcarbamoylation reactions providing them the capability to be recycled and reprocessed.31 Few studies demonstrated that this behavior is mainly induced upon heating,32,33 but a recent study has shown that it can also be mechanically activated under given conditions for some particular molecular architectures.34 Although very interesting, this behavior, along with the hydrogen bonding networks, are considered as limiting factors for achieving higher molecular weights for polymerization. Therefore, the development of polymerization strategies to overcome this drawback while preserving this vitrimer-like character is highly sought. In our case, particular attention was given to check the occurrence of this bonding exchange in the new synthesized polymers. Hence, after an isothermal ramp at room temperature, a second heating cycle was conducted for all polymers as well as for the monomers in the DSC. Noting that, as described in Materials and Methods, the first heating ramp was stopped at 180 °C to prevent any thermal degradation and hence molecular changes to avoid any
misinterpretation. The recorded DSC of the polymers are depicted in Figure 7 (those of the HU-tetraol monomers are in Figure SI-2). For HU-tetraol, a clear endothermic peak appeared at 62 °C, followed by an exothermic peak at 65 °C, before reaching the final melting temperature of 86 °C. The presence of such peaks revealed the occurrence of an association−dissociation of bonds that are related to transcarbamoylation reactions already reported for PHUs in the same temperature ranges. In the case of HU-tetraol-C12, an additional small peak was observed at 106 °C near to the melting temperature (111 °C), confirming the effect of the length of the spacer molecules on the thermal properties of PHUs as previously discussed. In regard to the resulting NIPHEUs, similar thermal behavior was observed for all polymers prepared with up to 3 equiv of DMFD, regardless of the temperature. Endothermic and exothermic peaks were detected prior to the melting temperature. However, for the polymers synthesized with 6 equiv of furan diesters for C8-based HU-tetraols, this behavior was not observed because no peak was detected, including the peak associated with the melting. In this case, the complete dissociation of the hydrogen bond network, which was originally weak, was not reformed, most probably hindered by the long chain of spacer and also the expected high molecular weight. Regarding the structural features determined by NMR, one can speculate that the end groups of the NIPHEUs, particularly the presence of free hydroxyl groups, play a key role in the bond exchange phenomenon observed. Indeed, for polymers synthesized with up to 3 equiv furan diesters that bear hydroxyl moieties at their end groups are most likely to undergo bond exchanges. The presence of esterified carboxylic moieties at the end groups of the polymers prepared NIPHEUs impede the bond exchanges. The anticipated high molecular weight of these polymers prepared with 6 equiv of furan diesters may also play a role in the restriction of occurrence of bond exchange by limiting the chain mobility. Further in-depth examination is absolutely needed to shed more light on this striking behavior revealed for the first time for such new polyester-urethanes with particular architectures.

■ CONCLUSIONS

Here, we reported for the first time to our knowledge the chain extension through polycondensation of fully biobased polyhydroxylurethanes, used as polyols in combination of sugar-derived 2,5-furandicarboxylic acid. The reported consecutive synthetic paths allowed formation of covalent cross-linked isocyanate-free polyester-urethane networks with various furanic molar ratios. The resulting networks exhibited striking thermal behavior upon repetitive heating cycles. Already reported for polyhydroxylurethanes, this behavior, reported herein for the first time for polyester-hydroxyurethanes, is associated with thermal induced bond exchange driven by transcarbamoylation reaction and at less extent to hydrogen bonding network. Such vitrimer-like behavior of this new type of NIPHEUs is unique, which can pave the way toward the design of a new range of functional green materials. In-depth investigations of this behavior using in situ NMR analyses, rheological characterization, in addition to further thermomechanical scrutiny to provide more insights to better understand this behavior are ongoing.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.biomac.0c00156.

Supporting figures and tables (PDF)

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Funding
The authors are grateful to the Luxembourg National Research Fund (FNR) for the financial support under CatBiose Project INTER-ANR-FNR No. 14/990334.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors are grateful to the Luxembourg National Research Fund (FNR) for the financial support under CatBiose Project INTER-ANR-FNR No. 14/990334.

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