Solvent-Free Method for the Copolymerization of Labile Sugar-Derived Building Blocks into Polyamides

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Figure S1 Calculation of the biobased content on an example of PA(12,GalXH)x-co-PA(12,10)_{100-x}, with GalXH composed of 94 wt% bio-based content and 6 wt% fossil content. Figure S2 A scheme representing the internally induced hydrolysis of GalX molecules a. the formation of water during salt polymerization b. generation of protons and c. the formation of Figure S3 ¹H NMR of (a) PA(12,GalXH)x-co-PA(12,10)100-x, (b) PA(6,GalXH)x-co-PA(6,10)100-x and (c) PA(MXD,GalXH)x-co-PA(MXD,12)100-x series of polyamides recorded in a mixture of pentaflurorophenol- d_1 (PFP)/chloroform- d_1 1/4 v/v. subscripts=mol% of each Figure S4 ¹H NMR of (a) $PA(12,GalXMe)_x$ -co- $PA(12,10)_{100-x}$ and (b) $PA(6,GalXMe)_x$ -co-PA(6,10)100-x series of polyamides recorded in a mixture of pentaflurorophenol-Figure S5 Typical DSC plots obtained for a. PA(12,GalXH)x-co-PA(12,10)100-x and b. PA(12,GalXMe)_x-co-PA(12,10)_{100-x}, representing the influence of the GalX content (indicated Figure S6 MALDI-TOF spectrum of PA(12,GalXH)₃₀-co-PA(12,10)₇₀ ($M_{n,GPC}$ =8.1 kg/mol, Figure S7 MALDI-TOF spectrum of PA(12,GalXH)50-co-PA(12,10)50 (M_{n,GPC}=7.4 kg/mol, Figure S8 MALDI-TOF spectrum of PA(12,GalXMe)₃₀-co-PA(12,10)₇₀ ($M_{n,GPC}$ =11.6 kg/mol, Figure S9 MALDI-TOF spectrum of low molecular weight PA(6,GalXMe)₃₀-co-PA(6,12)₇₀ $(M_{n,GPC}=5.5 \text{ kg/mol}, D=5.3).$ 10



Figure S1 Calculation of the biobased content on an example of $PA(12,GalXH)_x$ -*co*- $PA(12,10)_{100-x}$, with GalXH composed of 94 wt% bio-based content and 6 wt% fossil content. x=mol% of GalX salt.



Figure S2 A scheme representing the internally induced hydrolysis of GalX molecules a. the formation of water during salt polymerization b. generation of protons and c. the formation of a stable carbocation from GalXMe.



Figure S3 ¹H NMR of (a) $PA(12,GalXH)_x$ -*co*- $PA(12,10)_{100-x}$, (b) $PA(6,GalXH)_x$ -*co*- $PA(6,10)_{100-x}$ and (c) $PA(MXD,GalXH)_x$ -*co*- $PA(MXD,12)_{100-x}$ series of polyamides recorded in a mixture of pentaflurorophenol-d₁ (PFP)/chloroform-d₁ 1/4 v/v. subscripts=mol% of each salt in the feed.



Figure S4 ¹H NMR of (a) $PA(12,GalXMe)_{x-co-PA(12,10)_{100-x}}$ and (b) $PA(6,GalXMe)_{x-co-PA(6,10)_{100-x}}$ series of polyamides recorded in a mixture of pentaflurorophenold₁(PFP)/chloroform-d₁ 1/4 v/v. subscripts=mol% of each salt in the feed.

Table S1 Melting temperatures (melting point measurement) of the prepared salts.

Salt composition	Tm	Salt composition	Tm	Salt composition	Tm
	[°C]		[°C]		[°C]
C12,C10	160	C12,GalXH	247	C12, GalXMe	221
C6,C12	191	C6, GalXH	272	C6, GalXMe	261
MXD,C12	131	MXD, GalXH	242	MXD, GalXMe	255



Figure S5 Typical DSC plots obtained for a. $PA(12,GalXH)_x$ -*co*- $PA(12,10)_{100-x}$ and b. $PA(12,GalXMe)_x$ -*co*- $PA(12,10)_{100-x}$, representing the influence of the GalX content (indicated as % in the figure above) on the melting point and crystallinity of copolymers.

Table	S2 Lo	w molecu	lar weight	GalX	poly	amides	for	MAL	DI-T	'OF	analy	/sis
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Copolymer	$M_{ m n}^{ m (a)} \ [m kg\cdot mol^{-1}]$	$D^{(a)}$
PA(12,GalXH)30-co-PA(12,10)70	8.1	2.6
PA(12,GalXH)50-co-PA(12,10)50	7.4	2.7
PA(12,GalXMe)30-co-PA(12,10)70	11.6	8.7
PA(6,GalXMe)30-co-PA(6,12)70	5.5	5.3

(a) Molecular weight of the polyamides determined by GPC, D – dispersity



Figure S6 MALDI-TOF spectrum of PA(12,GalXH)₃₀-*co*-PA(12,10)₇₀ (*M_{n,GPC}*=8.1 kg/mol, *D*=2.6).



Figure S7 MALDI-TOF spectrum of PA(12,GalXH)₅₀-*co*-PA(12,10)₅₀ (*M_{n,GPC}*=7.4 kg/mol, *D*=2.7).



Figure S8 MALDI-TOF spectrum of PA(12,GalXMe)30-*co*-PA(12,10)70 (*M_n*,*GPC*=11.6 kg/mol, *D*=8.7).



Figure S9 MALDI-TOF spectrum of low molecular weight PA(6,GalXMe)₃₀-*co*-PA(6,12)₇₀ ($M_{n,GPC}$ =5.5 kg/mol, D=5.3).



Figure S10 Time depended FT-IR spectrum recorded for reaction of (a) C12,C10 salt, (b) C6,C12 salt and (c) MXD,C12 salt. δ – bending (scissoring), v – stretching vibration. Red arrows indicate the development of the signal along the reaction coordinates.



Figure S11 Time depended FT-IR spectrum recorded for reaction of (a) C6,C12 salt with C6,GalXH salt (ratio 50:50) and (b) C6,C12 salt with C6,GalXMe salt (ratio 50:50). δ – bending (scissoring), v – stretching vibration. Red arrows indicate the development of the signal along the reaction coordinates.



Figure S12 Time depended FT-IR spectrum recorded for reaction of (a) MXD,C12 salt with MXD,GalXH salt (ratio 50:50) and (b) MXD,C12 salt with MXD,GalXMe salt (ratio 50:50). δ – bending (scissoring), v – stretching vibration. Red arrows indicate the development of the signal along the reaction coordinates.