Ring-Opening Polymerization of Lactones using Binaphthyl-diyl Hydrogen Phosphate as Organocatalyst and Resulting Monosaccharide Functionalization of Polylactones

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ABSTRACT: Binaphthyl-diyl hydrogen phosphate has been assessed for the first time as a catalyst for the ring-opening polymerization of ε-caprolactone (CL) and δ-valerolactone (VL). In the presence of benzyl alcohol as coinitiator at 40–60 °C, the polymerization is quantitative and controlled both in terms of dispersity and of number-average molecular weight corresponding to the monomer/initiator ratio. The use of a selectively protected D-glucose derivative bearing the primary C6 hydroxyl group as initiator leads to the quantitative end-functionalization of the polyesters in rather short reaction times (ca. 10 min at 60 °C for δ-VL) with dispersities around 1.08–1.10. Methyl-α-D-glucopyranoside has been used as a carbohydrate polyol initiator in bulk. The initiation efficiency is partial, leading to hydrophilic carbohydrates functionalized polylactones in a one-step procedure. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 2279–2287

KEYWORDS: biopolymers; catalysis; cationic polymerization; ring-opening polymerization; polyesters

INTRODUCTION Organocatalyzed ring-opening polymerization of cyclic esters has gained much interest these last years.[1] Numerous catalysts such as organic acids,[2–14] nitrogen bases,[15–17] phosphines,[18] and carbenes[19] among others have been assessed. The polymerization of lactones can be catalyzed by a variety of organic acids, including carboxylic acids,[4,5] naturally occurring acids[5,6] such as citric, lactic, tartaric, and amino acids.[5] High catalyst loadings and high temperatures are required in these latter cases, and hydroxy acids do furthermore initiate the polymerization via the hydroxyl group in addition to their catalytic activities. This leads to poor functionalization efficiencies in the presence of a protic coinitiator. The $H_2O/HCl/Et_2O$ and the *n*-BuOH/HCl/Et_2O systems afford the controlled and living cationic ring-opening polymerizations of ε-caprolactone (CL) and δ-valerolactone (VL) in dichloromethane in mild conditions, with substantial catalyst loadings, however.[2,3] Sulfonic acids including trifluoromethane sulfonic acid present also good potentialities for the controlled cationic ring-opening polymerization of lactones and lactides in combination with protic coinitiators.[7–14] The controlled polymerization of lactones was also reported using a phosphoric acid, diphenylphosphate, in combination with an alcohol in mild conditions in toluene.[20–22]

Biodegradable aliphatic polyesters are widely used in the field of packaging and for biomedical applications. The functionalization of these polymers with carbohydrates derivatives[6,23–39] enables to tailor properties related to biodegradability and drug delivery such as hydrophilicity, crystallinity, and the possibility of form inclusion complexes among other. Monosaccharide end-capped polylactides have been reported as good candidates for excipients in oral sustained release tablets for example.[34] The use of organocatalysts for the carbohydrate functionalization of aliphatic polyesters is of particular interest, as it will lead to polymers that do not contain any residual metal contaminant that can hamper their use for specific applications. Hydroxyl bearing carbohydrate end-capped aliphatic polyesters are are interesting materials in this frame, as

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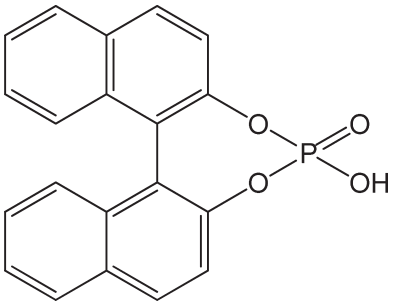


SCHEME 1 Phosphoric acid used as catalyst (BNPH).

the hydrophilic character plays an important role for the solubility and the biodegradation of the resulting polymer. Three-step strategies involving protection/deprotection chemistries are usually used to obtain such hydrophilic carbohydrates functionalized polyesters.[26–33,36] The development of one-step procedures for this purpose is thus of particular interest.[35,37] We envisioned in this frame the use of a bulky and potentially chiral organocatalyst for the ring-opening polymerization of lactones. The bulkiness may indeed hinder sterically the initiation using a carbohydrate polyol. Additionally, carbohydrates such as methyl-α-D-glucopyranoside show stereocenters of well-defined configurations. Using one of the catalyst enantiomers versus the other may afford a certain control over the regioselectivity of the initiation step that may lead to favor or disfavor the initiation of the polymerization by certain hydroxyl groups.

We present in this frame the unprecedented use of a bulky, sterically hindered, and potentially chiral phosphoric acid, 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate (BNPH–Scheme 1) as a catalyst for the ring-opening polymerization of ε-CL and δ-VL. The polymerization in the presence of benzyl alcohol as coinitiator is controlled in mild conditions in bulk, affording a solvent-free well-controlled polymerization. The use of a selectively protected D-glucose derivative as initiator leads to the straightforward end-functionalization of the polyester. The polymerization in bulk enables to use commercial carbohydrate polyols as coinitiators, leading to hydrophilic monosaccharide functionalized polyesters via organocatalysis in a one-step procedure.

EXPERIMENTAL

Materials

Rac-, (*R*)-, and (*S*)-1,1′-BNPH were synthesized from corresponding binols and $POCl_3$ according to a literature procedure.[40] ε-CL and δ-VL were dried over calcium hydride and distilled under reduced pressure before use. Benzyl alcohol (BnOH) was dried with sodium metal for 48 h at room temperature, refluxed over magnesium, and distilled prior to use. Methyl 2,3,4 tri-*O*-benzyl-α-D-glucopyranoside (**Glc-1r,** represented Scheme 4, synthesis described hereafter) and methyl-α-D-glucopyranoside (**Glc-Me**, represented Scheme 4, Aldrich) were purified by 3 distillations over toluene before their use as polymerization initiator.

Carbohydrate Synthesis

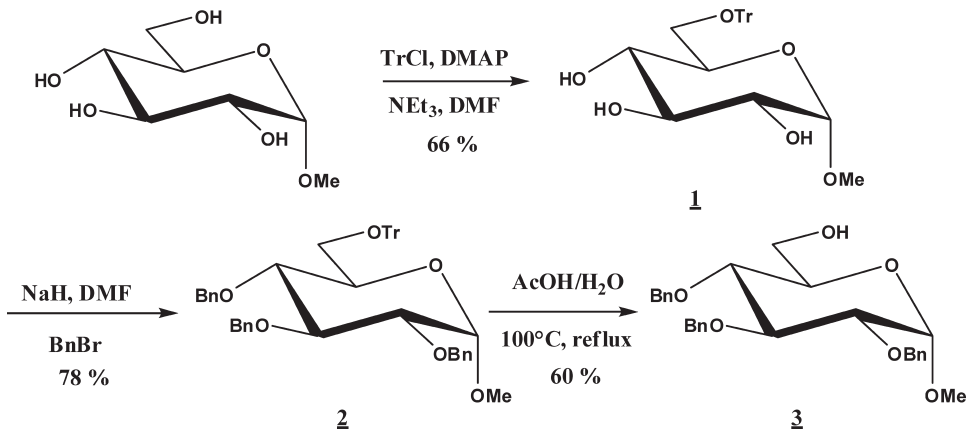
Methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (referred to as **Glc-1r** hereafter) is easily obtained in three steps from the methyl-α-D-glucopyranoside (referred to as **Glc-Me** hereafter) after selective tritylation of the O-6 position and benzylation of the position O-2, O-3, and O-4 in well established conditions in a 66 and 78% yield, respectively (Scheme 2). The trityl group is selectively removed by refluxing in a mixture of acetic acid and water to give **Glc-1r** (Compound **3**) in a 60% yield with the O-6 position differentiated ready to be tested as initiator.

Methyl-6-O-trityl-α-D-glucopyranoside-(1)

A solution of methyl-α-D-glucopyranoside (6.0 g, 0.03 mol), trityl chloride (11 g, 1.2 eq), triethylamine (8 mL), and DMAP (290 mg, 0.5 eq) in DMF (50 mL) was stirred overnight at room temperature under nitrogen. After 12 h stirring, the reaction mixture was poured into ice-water and extracted with dichloromethane. The organic extracts were washed with water, and dried with magnesium sulfate. After removal of the solvents, the solid was recrystallized from ethanol to yield compound 1 (8.9 g, 66%) as a white solid.

Methyl-2,3,4-tri-O-benzyl-6-O-trityl-α-D-glucopyranoside (2)

A solution of **1** (8.9 g, 0.03 mol) in DMF was added at 0 °C NaH (60% in mineral oil, 3.6 g, 4.5 eq). After 30 min BnBr



SCHEME 2 Synthesis of Glc-1r.

TABLE 1 Polymerization of Lactones in Bulk at 60°C using 1 mol % *rac*-BNPH in Combination with Benzylic Alcohol (BnOH)

Entry	M^a	M/BNPH/BnOH	Time (h)	Yield (%)	M_n[b] Calc.	M_n[c] NMR	M_n[d] SEC	D_M[d]	BnO/CH_2OH[e]
1	VL	50/0.5/1	10 min	85	4400	4400	4500	1.08	1.01
2	VL	50/0.5/1	1	96	4900	5300	4600	1.17	1.01
3	CL	50/0.5/1	1	99	5700	5600	6100	1.11	0.99
4	CL	100/1/1	1	80	9200	n.d	10,300	1.13	n.d
5	CL	100/1/1	4	99	11,400	n.d	12,600	1.15	n.d
6[f]	CL	100/1/1	7	100	11,500	n.d	12,200	1.14	n.d
7	CL	100/1/0	4	–	–	–	–	–	–
8	CL	100/0/1	4	–	–	–	–	–	–

[a] Monomer. CL = ε-caprolactone and VL = δ-valerolactone.
[b] Number-average molecular weight calculated considering the growth of one macromolecular chain per OH group and the yield: M_n = M/BnOH*yield%*$M_{monomer}$ + $M_{initiator}$.
[c] Number-average molecular weight determined by ^{1}H NMR (see experimental part).
[d] Number-average molecular weight measured by SEC and corrected by a factor 0.56 and 0.57 for poly(ε-CL) and poly(δ-VL), respectively, and dispersity. Correction factors are applied because the calibration is done using polystyrene standards, see Experimental part.
[e] Ratio between the signals of Ar—CH_2O— polymer (5.1 ppm) and polymer-CH_2OH (3.6 ppm) end-groups.
[f] Reaction conducted at 40 °C.

(10.5 mL, 4.5 eq) was added and the reaction mixture was stirred overnight at room temperature. The reaction was then quenched with water (40 mL) and the aqueous layer was washed with ethyl acetate (4 × 50 mL). The organic extracts were dried with magnesium sulfate. After removal of the solvents, the residue was purified by chromatography (eluent gradient, EtOAc/petroleum ether 1/5 to 1/3), to afford the Compound **2** as a white solid (11 g, 78%).

Methyl-2,3,4-tri-O-benzyl-α-D-glucopyranoside (3 or Glc-1r)

A solution of **2** (11 g, 0.015 mol), in a mixture of acetic acid/water (9/1) was stirred at reflux during 5 h. The solvent was coevaporated with toluene and the residue was purified by chromatography (eluent gradient, EtOAc/ petroleum ether 1/3 to 1/1), to afford the Compound **3** as a white solid (4.2 g, 60%).

Polymerization

In a typical polymerization procedure (Entries 4–6), the protic coinitiator (0.09 mmol), BNPH (0.09 mmol), and the lactone (9 mmol) were added in a flask in a glove-box. The mixture was allowed to react at a given temperature for a given time. The viscous reaction product was dissolved in a small amount of dichloromethane and precipitated into methanol. The resulting polyester was filtered and put under vacuum at room temperature until constant weight.

Analytics

Size exclusion chromatography (SEC) was performed in THF as eluent at 40 °C using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters Styragel columns (HR2, HR3, HR4, and HR5E). The calibration was done using polystyrene standards. Correction factors of 0.56 and 0.57 were applied for the determination of the true number-average molecular weight of poly(ε-CL) and poly(δ-VL), respectively.[41] NMR spectra were recorded on a Bruker Avance 300 spectrometer at room temperature in $CDCl_3$ or DMSO-d6. The number-average molecular weight of the polylactones was determined from the ratio of the signal of the —CH_2OH end groups (3.64 ppm in $CDCl_3$) versus the —CH_2O— groups in the polymer (4.06–4.07 ppm in $CDCl_3$).

MALDI-TOF-MS was performed on a Ultraflex II spectrometer (Bruker). The instrument was operated in either the reflector or linear mode. The spectra were recorded in the positive-ion mode. The samples were prepared by taking 2 μL of a THF solution of the polymer (10 mg/mL) and adding this to 16 μL of 1,8-dihydroxy-9(10H)-anthracenone (dithranol, 10 mg/mL in THF) to which 2 μL of CF_3SO_3Ag (2 mg/mL in THF) had been added. A 1 μL portion of this mixture was applied to the target and 50–100 single shot spectra were accumulated. The given masses represent the average masses of the Ag^+ adducts. The spectrometer was calibrated with an external mixture of angiotensin I, ACTH 18–39, and bovine insulin or PEG 1500.

RESULTS AND DISCUSSION

Polymerization of ε-CL and δ-VL using rac-BNPH and Benzyl Alcohol as Coinitiator

Representative entries of the polymerization of ε-CL and δ-VL using *rac*-BNPH in combination with benzyl alcohol are given in Table 1. The reaction is quantitative in one to several hours using 1 mol % catalyst and 1–2 mol % initiator at 40 and 60 °C (Entries 1–6), with a yield of 85% after 10 min using δ-VL and 2% initiator. The polymerization activity is higher using δ-VL, as reported in the literature for cationic polymerizations.[42] The number-average molecular weight corresponds well with the calculated one considering the growth of 1 macromolecular chain per initiator, and the distribution is narrow (D_M: 1.08–1.17). MALDI-ToF analyses (see Fig. 1 for a representative example) reveal that all polymer chains formed are end-capped with the benzyl alcohol. This is confirmed by NMR analysis (Fig. 2). The ratio between the signal of the Ar—CH_2O—polymer signal around 5.1 ppm and the polymer—CH_2—OH end group at 3.64 ppm is close to 1 (Table 1). It is noteworthy that using *rac*-BNPH

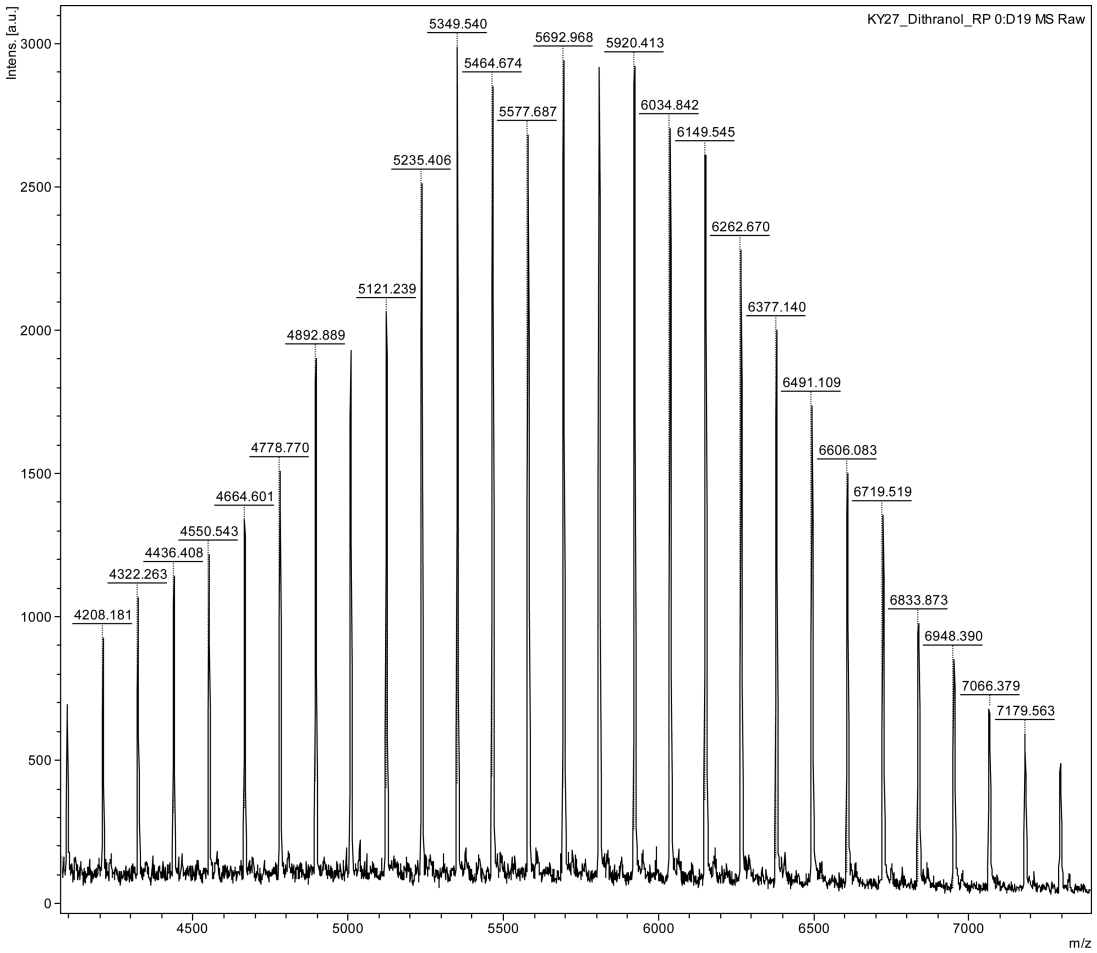


FIGURE 1 MALDI-ToF analysis of Entry 3.

in bulk affords a controlled polymerization with 1 mol % catalyst load, while 2–2.5 mol % are required using diphenylphosphate in toluene.[21,22] Blank reactions conducted in the presence of the catalyst or the initiator alone did not lead to a precipitate under similar experimental conditions (Entries 7–8). Previous studies of the literature on the polymerization of lactones using diphenylphosphate/alcohol combinations[21,22] proposed an activated monomer mechanism.[43] Computational studies suggest a bifunctional mechanism with participation of both the acidic proton and the basic P=O moiety, analogous to that observed for sulfonic acids.[22] A similar mechanism can be proposed for BNPH, as represented in Scheme 3.

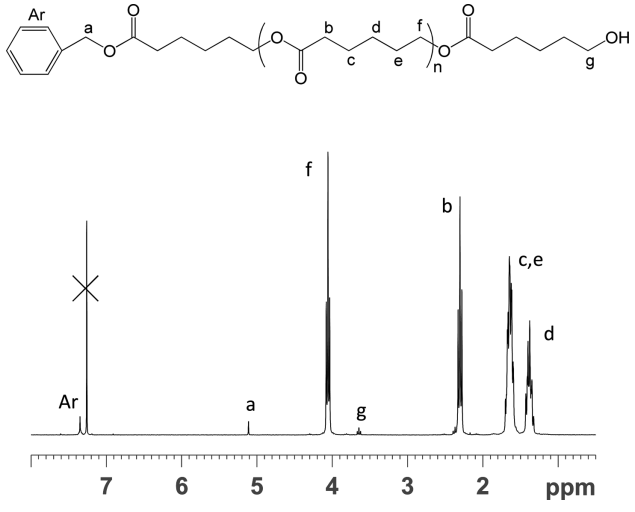
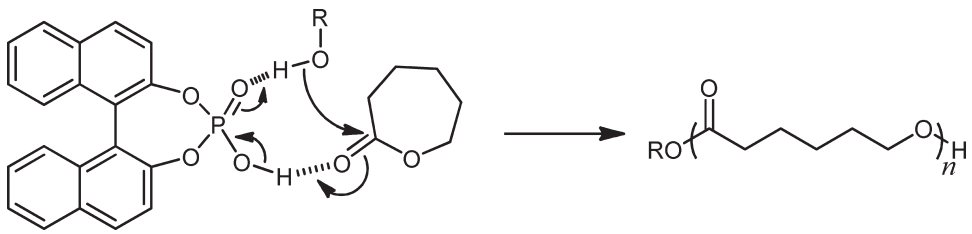


FIGURE 2 ^{1}H NMR analysis of Entry 3 in $CDCl_3$.

Polymerization of ε-CL and δ-VL using BNPH and Monosaccharides as Coinitiators

The selectively protected D-glucose derivative **Glc-1r** bearing a primary hydroxyl group (Scheme 4) was assessed as ring-opening polymerization initiator using *rac*-BNPH as catalyst. The reaction is almost quantitative at 60 °C in 10 and 60 min for δ-VL and ε-CL, respectively (Entries 9 and 10 in Table 2). The reaction is well controlled, with dispersities around 1.08–1.10. The M_n calculated considering the growth of one macromolecular chain per hydroxyl group corresponds well to the M_n measured by NMR or GPC, highlighting quantitative functionalization efficiency.

The ^{1}H NMR spectra of the **Glc-1r** initiator and the corresponding functionalized polylactone (Fig. 3) show the shift of the resonance peaks after the polymerization. The initiator



SCHEME 3 Activated monomer mechanism for the cationic polymerization of ε-CL using 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate and benzyl alcohol.

Glc-1r bears one free OH group, which is able to initiate the polymerization. This free OH group has two neighboring protons, H6. The chemical shift value of protons 6 can be used as indicator, to know whether the polymerization is initiated by the OH group of the monosaccharide, due to the change of the chemical environment of protons 6 after the polymerization. In particular, we found that the resonance peaks at 3.62 ppm, which are assigned to the protons 6 of the methylene group of **Glc-1r** disappeared and new resonance peaks around 4.25 ppm were assigned to the protons 6 of the **Glc-1r** end-capped polyester. Unambiguous assignments of the signals, were done by ^{1}H-^{1}H correlations (COSY) analysis presented in Figure 4. The signal of proton H1 can be easily found, due to its special chemical environment. Two oxygen atoms around makes proton H1 the most unshielded (chemical shift $\delta = 4.58$ ppm) among all the other protons of the monosaccharide. H1 has one neighbor proton H2, so it should have coupling with H2. With the help of COSY spectrum, the coupling between H1 and H2 (H1—H2) can be clearly observed in Figure 4. Similarly, the other protons of the monosaccharide were assigned in this way, with peaks of protons H6 at 4.25 ppm.

Previous studies of the literature reported the monosaccharide functionalization of aliphatic polyesters by ring-opening polymerization using either metal based catalysts[25–29,32,33] or enzymes.[23–25] Lactic acid was reported as an organocatalyst for this purpose, but the functionalization was reported to be only partial due to a side initiation via the hydroxyl group of the hydroxyacid catalyst.[6] It is noteworthy that this drawback is overcome using BNPH as organocatalyst.

The polymerization in bulk enables furthermore to use carbohydrates polyols as initiators as these compounds are not soluble in most organic solvents. Representative examples of the polymerization of δ-VL and ε-CL using *rac*-BNPH combined to methyl α-D-glucopyranoside (**Glc-Me** in Scheme 4) is reported in Table 2, Entries 11–15. For a monomer/OH ratio of 50, the polymerization is quantitative after about 1 and 2.5 h for δ-VL and ε-CL, respectively. It can also be seen from the value of the number-average molecular weight that the initiation efficiency is partial, and increases along the polymerization to reach a maximum of about 55%. The initiation is thus not instantaneous or fast versus the propagation, in contrast to that observed in the presence of benzyl alcohol or **Glc-1r** as initiator. The hydroxyl groups of the monosaccharide polyol present thus a different reactivity for the initiation step. In cationic ring-opening polymerizations, secondary alcohols are usually less reactive than primary

TABLE 2 Polymerization of Lactones in Bulk at 60 °C using 1 mol % BNPH in Combination with 0.5% Carbohydrate Coinitiator (Monomer/OH = 50)

Entry	Cata.	M[a]	I[b]	Time (min)	Yield (%)	M_n[c] per OH Calc.	M_n[d] per OH NMR	Initiation efficiency (%)	M_n[e] SEC	D_M[e]
9	*rac*-BNPH	VL	**Glc-1r**	10	92	4600	4600	100	4500	1.08
10	*rac*-BNPH	CL	**Glc-1r**	60	94	5400	5600	96	6200	1.10
11	*rac*-BNPH	VL	**Glc-Me**	5	27	1400	3500	40	4300	1.13
12	*rac*-BNPH	VL	**Glc-Me**	20	86	4300	8100	53	13,400[f]	1.18
13[g]	*rac*-BNPH	CL	**Glc-Me**	10	84	500	3000	16	5300	1.19
14	*rac*-BNPH	CL	**Glc-Me**	60	33	2100	6800	31	8100	1.14
15	*rac*-BNPH	CL	**Glc-Me**	150	93	5300	9400	56	21,100[f]	1.18
16	(*R*)-BNPH	VL	**Glc-Me**	20	85	4300	8800	49	11,900[f]	1.19
17	(*S*)-BNPH	VL	**Glc-Me**	20	76	3800	7200	53	10,800[f]	1.17

[a] Monomer. CL = ε-caprolactone and VL = δ-valerolactone.
[b] Initiator.
[c] Number-average molecular weight per OH group calculated considering the growth of one macromolecular chain per OH group and the yield: M_n = M/OH*yield%*$M_{monomer}$ (the molecular weight of the carbohydrate initiator is not considered).
[d] Number-average molecular weight per OH group determined by ^{1}H NMR (see Experimental section–the molecular weight of the carbohydrate initiator is not considered).
[e] Number-average molecular weight measured by SEC and corrected by a factor 0.56 and 0.57 for poly(ε-CL) and poly(δ-VL), respectively, and dispersity. Correction factors are applied because the calibration is done using polystyrene standards, see Experimental part.
[f] Distributions showing a slight shoulder.
[g] CL/OH = 5.

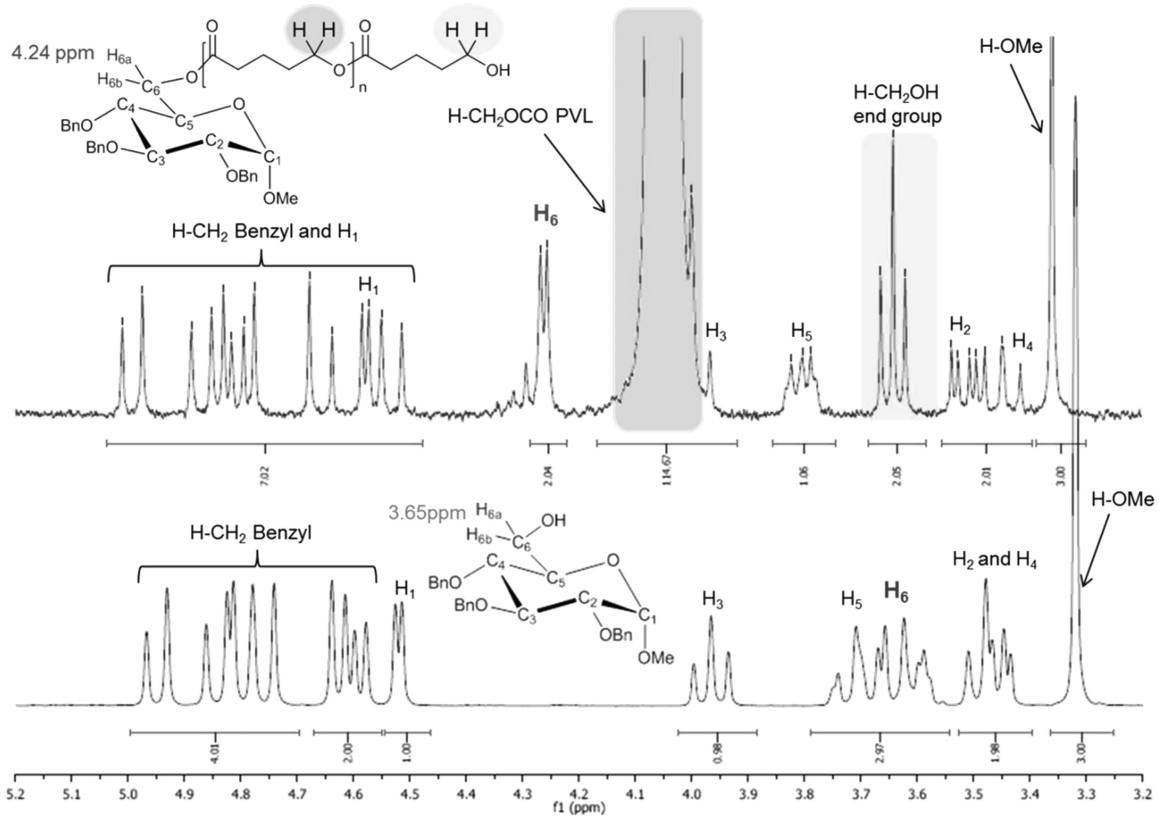


FIGURE 3 ^{1}H NMR spectra of Entry 9 (top) and of the Glc-1r initiator (bottom) in $CDCl_3$. Bn = benzyl.

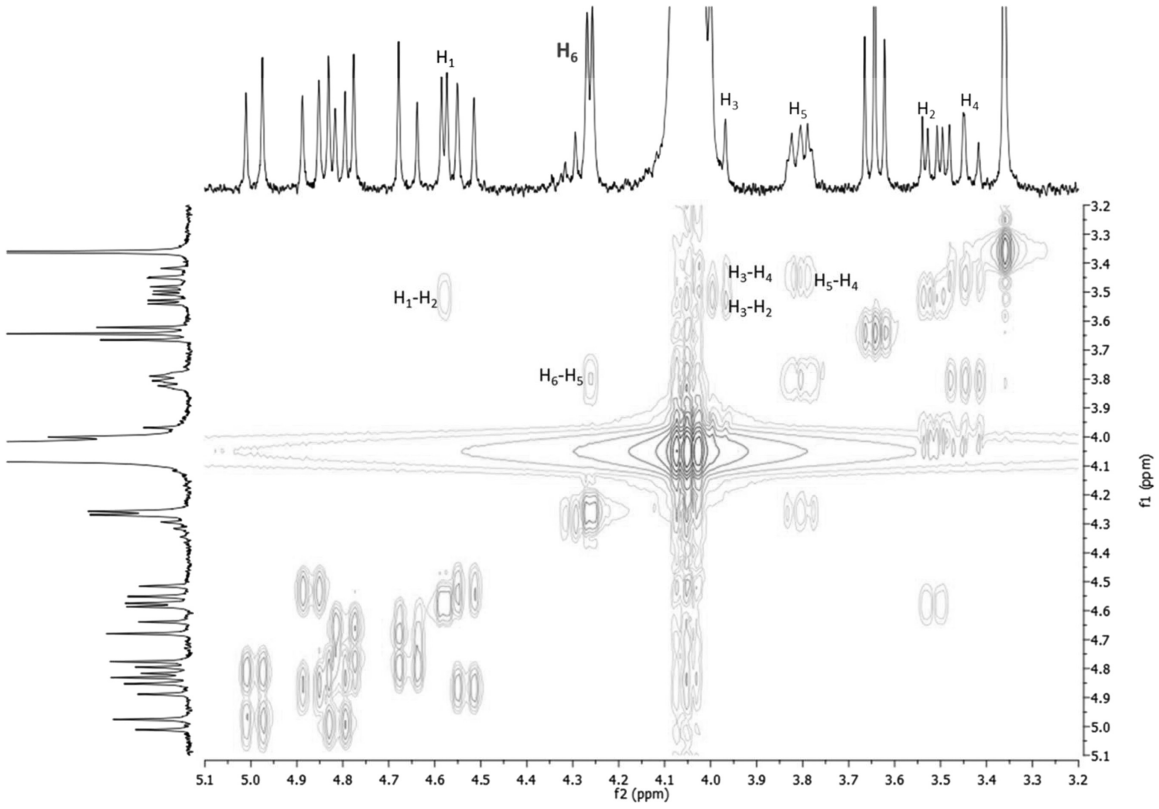
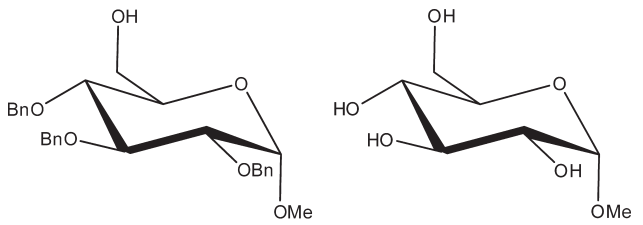


FIGURE 4 COSY analysis of Entry 9 in $CDCl_3$.



Glc-1r Glc-Me

SCHEME 4 Carbohydrates used as polymerization initiators (Bn = benzyl).

alcohols.[42] ^{1}H NMR analysis of Entry 12 is presented in Figure 5. The signal of the methyl group of the carbohydrate [Fig. 5(e)] is split into several peaks, showing that the initiation step is not regioselective. Reactions conducted with the chiral (*R*)-BNPH and (*S*)-BNPH catalysts did not induce a significant effect on the polymerization features (Entries 16–17 vs. 12, and similar signals of the methyl group e on the ^{1}H NMR spectra) highlighting an initiation influenced by steric rather than chiral factors. Unimodal and narrow molecular weight distributions are obtained in the first steps of the polymerization (Entries 11 and 14), and for low monomer/OH ratio (Entry 13). The molecular weight distributions show a slight shoulder at higher conversions for high monomer/OH ratio. This may be attributed to the difference of reactivity of the hydroxyl groups toward the initiation step.

The partial initiation efficiency observed using **Glc-Me** as initiator leads interestingly to hydrophilic monosaccharide functionalized poly(δ-VL) and poly(ε-CL) via organocatalysis in a one-step procedure, as around one half of the hydroxyl functions of the sugar do not initiate the polymerization for a monomer/OH ratio of 50. Experiments with a lower monomer/OH ratio were conducted for NMR analysis of the resulting polymer. A typical example (Entry 14) leads to an initiation efficiency of 16%. The spectrum in the zone 4.4–5.4 ppm recorded in DMSO-D6 is presented in Figure 6. Numerous signals can be seen, mainly doublets. OH protons on carbohydrates can lead to doublets when analyzed by ^{1}H NMR in DMSO-d6, depending on the number of neighboring protons. This can for example be seen on the ^{1}H NMR analysis of methyl-α-D-glucopyranoside. See the spectrum and explanations in the SI. The addition of D_2O was

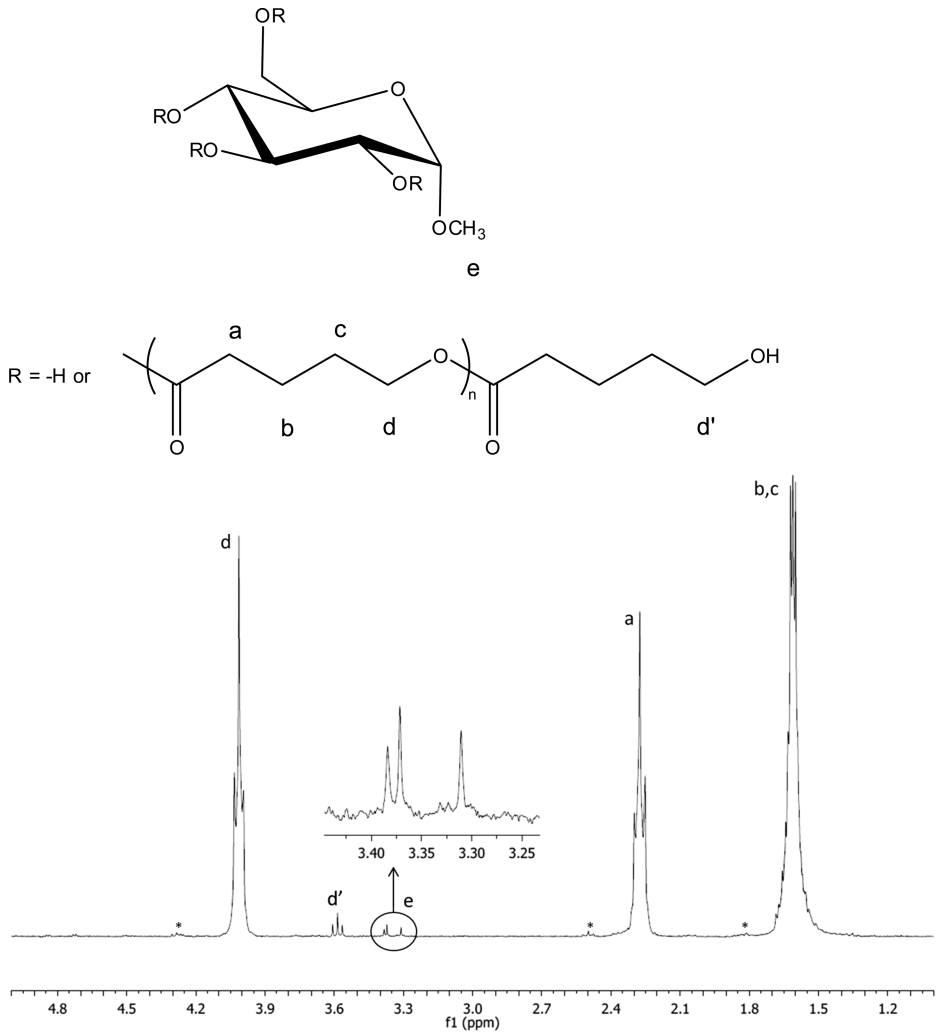


FIGURE 5 NMR spectra of Entry 12 in $CDCl_3$. * traces of monomer.

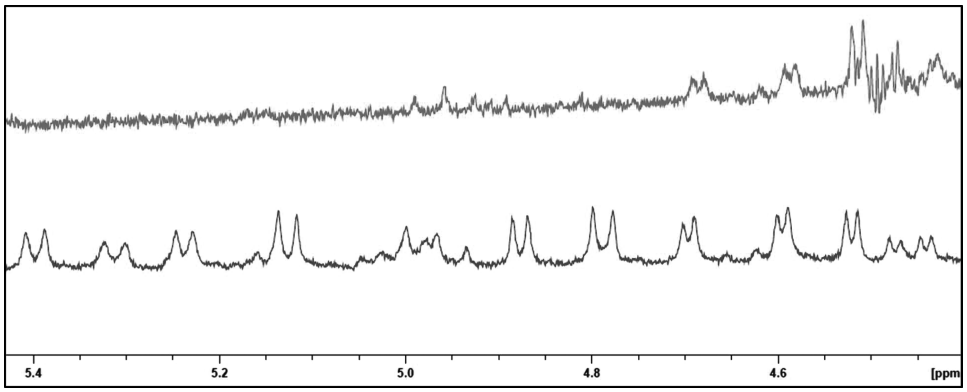


FIGURE 6 ^{1}H NMR spectra of Entry 14 recorded in DMSO-d6 in the zone 4.4–5.4 ppm before (bottom) and after (top) addition of D_2O.

performed to confirm the presence of OH groups. Proton deuterium exchanges efficiently occurred as shown by the disappearance of several doublets. This confirms the presence of unreacted hydroxyl groups on the carbohydrate core of the polymer. Such functionalized polyesters are notably used as precursors for the synthesis of miktoarm polymers[25] or biodegradable gels.[32] Protection/deprotection chemistries are usually used to obtain hydrophilic carbohydrates functionalized polyesters,[26–33,36] one-step procedures being less observed.[35,37] Alkyl glucopyranoside initiated enzymes[23,24] and lactic acid[6] catalyzed ring-opening polymerization of ε-CL were reported for the one-step synthesis of hydroxylated monosaccharide functionalized poly(ε-CL). This work extends the catalytic systems reported for this purpose to the BNPH phosphoric acid.

CONCLUSIONS

The BNPH phosphoric acid is an efficient catalyst for the ring-opening polymerization of lactones in bulk. In combination with benzyl alcohol, the polymerization is quantitative and controlled in mild conditions, with dispersities around 1.08–1.17. Monosaccharides mono- and poly-ols can be used as initiators, affording the organocatalyzed synthesis of carbohydrate-functionalized polyesters. Partial initiation efficiency could be reached using the bulky BNPH, leading to the one-step synthesis of hydrophilic monosaccharide end-capped polyesters. The chirality of the catalyst did in turn not allow to induce a controlled selectivity of the initiation step. The results reported in this work extend the range of applications of phosphoric acids as catalysts for the ring-opening polymerization of lactones to the functionalization of polylactones by monosaccharide derivatives.

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