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ORIGINAL PAPER

Chemical vapor deposition of carbohydrate-based polymers: a proof of concept study

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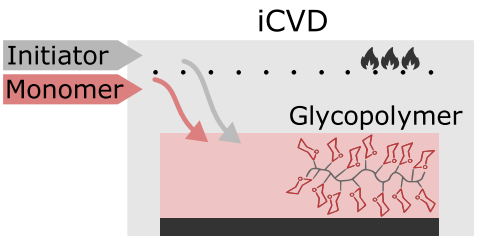
Abstract

The aim of this work is to investigate if vinyl-modified carbohydrate compounds are suitable monomers for thin film polymerization via chemical vapor deposition in a proof-of-concept study. Synthetic carbohydrate-based polymers are explored as biodegradable, biocompatible, and biorenewable materials. A thin film of synthetic polymers bearing sugar residues can also offer a good surface for cell attachment, and thus might be applied in biomaterials and tissue engineering. The possibility of having such thin film deposited from the vapor phase would ease the implementation in complex device architectures. For a proof-of-concept study, sugar vinyl compound monomers are synthesized starting from methyl α-D-glucopyranoside and polymerized by initiated chemical vapor deposition (iCVD) leading to a thin polymer layer on a Si-substrate. Thus, a successful vapor polymerization of the sugar compounds could be demonstrated. Infrared spectroscopy shows that no unwanted crosslinking reactions take place during the vapor deposition. The solubility of the polymers in water was observed in situ by spectroscopic ellipsometry.

Graphical abstract



Keywords Carbohydrates · Chemical vapor deposition · iCVD · Thin polymer film · Carbohydrate-based monomer · Polymerization

Introduction

Chemical vapor deposition (CVD) polymers have been successfully integrated into prototypes for applications including, but not limited to, membranes, microfluidics, sensors, controlled release, and flexible optoelectronics, due to the easy tunability of the surface chemistry and properties [1, 2]. While most CVD techniques fail at retaining the monomer functional groups at elevated deposition rates, initiated chemical vapor deposition (iCVD) has demonstrated to produce polymers with conventional structure made of repeating units without unwanted loss of functionality or crosslinking [3]. This deposition method is gaining more and

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more industrial significance due to its versatility in polymerizing a large variety of vinyl monomers, the easy thin film processability and scalability [4]. iCVD can lead to interesting molecular aggregation patterns in the deposited polymer films, because the lack of solvents influences how the monomer molecules adsorb on the substrate and get incorporated into the polymer structure.

The mechanism of polymerization by iCVD is shown in Fig. 1a [5]. It consists of the same steps as a classical radical polymerization: initiation, propagation, and termination with the difference that the propagation and termination take place heterogeneously between the vapors and the solid substrate surface. The radical initiator (I_2) and the monomer (M) enter the vacuum chamber as vapors. Most common initiators used in this process are peroxides, such as di-*tert*-butyl peroxide, since they can be easily thermally decomposed already at temperatures in the range 150–300 °C. The decomposition of the initiator ($I_2 \rightarrow 2\ I^{\cdot}$) takes place at a filament array, suspended above the plate where the substrate is placed. The substrate is kept at temperatures below 60 °C, enhancing the adsorption of the monomer. The radicals of the initiator react with the monomer units adsorbed on the substrate surface, initiating the polymerization. The polymerization reaction propagates by addition of other monomer (M) molecules and forms the polymer.

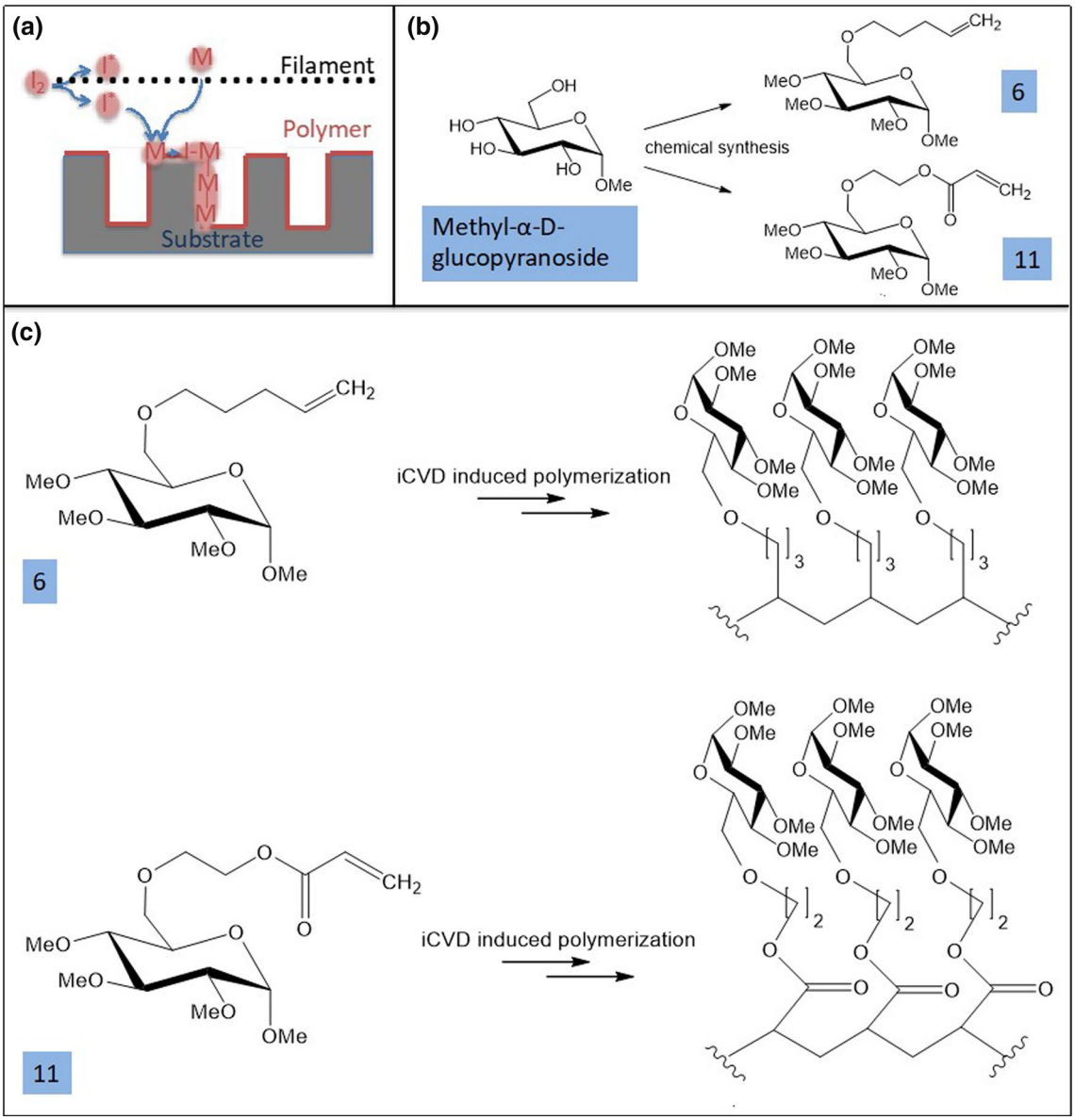
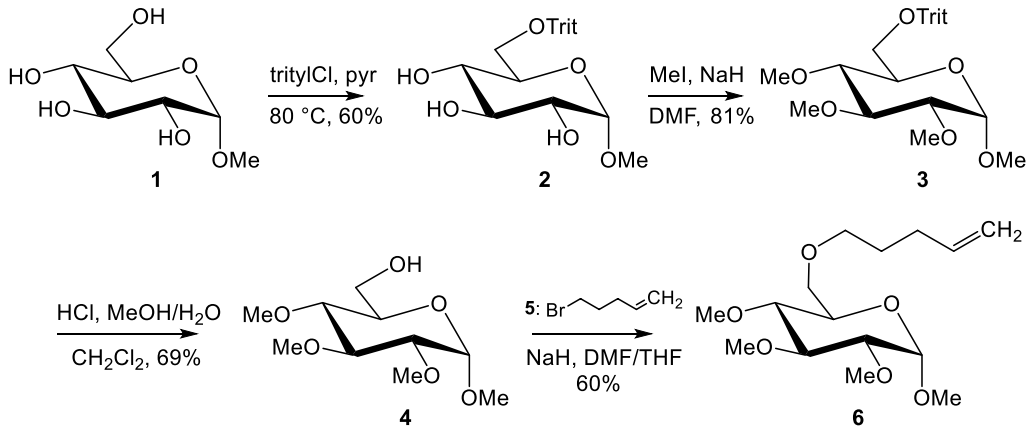


Fig. 1 Schematic of **a** the iCVD process, **b** the synthesis of the monomer units, and **c** of the polymer films obtained in this study upon iCVD. M and I_2 indicate the monomer and the initiator molecules, respectively

Scheme 1



The synthesis of carbohydrate-based polymers is of high interest since they derive from mostly environmentally friendly raw materials, in addition to the benefit of preparing a physiologically active material that mimics carbohydrate-based surfaces for different applications [6, 7]. Even though the synthesis of such polymers has been demonstrated in several ways [8, 9], they were never obtained in a thin film form by vapor synthesis. In particular, free-radical polymerization of carbohydrate-based monomers has been achieved by coupling an unsaturated component to a carbohydrate derivative through an ether, ester, or amido linkage [10]. The synthesis of pure vinylogous-sugar monomers is the key step in polymer synthesis. Subsequently, the vinylogous monomers are polymerized in organic or aqueous media using a radical initiator.

Vapor phase-based radical polymerization methods, such as iCVD, completely circumvent the use of solvent, because they are performed under vacuum [3]. The related advantages are that uniform over large areas, ultra-thin films (< 100 nm) can be obtained on virtually any substrate. In addition, vapor deposition methods are nowadays largely scaled up and integrated into industrial production lines. Therefore, expanding the portfolio of vapor-based syntheses to such polymers could be beneficial for their implementation into, e.g., microfluidic and sensor devices.

In this work, we synthetize the vinylogous-sugar monomers methyl 2,3,4-tri-*O*-methyl-6-*O*-(pent-4-en-1-yl)-α-D-glucopyranoside (pentenylOMeGlu, **6**) and methyl 2,3,4-tri-*O*-methyl-6-*O*-ethylacrylate-α-D-glucopyranoside (acrylateOMeGlu, **11**), and describe the fabrication of sugar-based polymer thin films by solvent-free iCVD (Fig. 1b, c).

Results and discussion

Monomer synthesis and characterization

To obtain a compound that could be polymerized by iCVD, two main requirements have to be fulfilled: (1) the compound needs to present a double bond feature, (2) the compound needs to have a vapor pressure optimally between 1 and 10^{-3} Torr at 25 °C. Therefore, a terminal double bond has been introduced, most suitably at position O-6 of methyl α,D-glucopyranoside and the secondary hydroxyl groups have been methylated to increase the vapor pressure and fulfill the requirements for iCVD (Fig. 1b). Two different vinylogous groups have been investigated, one in the form of 1-alkene (compound **6**) and the other one in the form of acrylate (compound **11**).

Synthesis of the vinylogous-sugar monomers

First, a simple pentenyl group was introduced at position O-6 (Scheme 1). Therefore, in methyl α-D-glucopyranoside (**1**), position O-6 was blocked temporarily with a trityl group, the reaction occurred employing tritylchlorid in pyridine, which led to 6-*O*-trityl-D-glucose derivative **2** in a yield of 60%. Next, methylation of positions O-2, O-3 as well as O-4 was achieved by reaction of compound **2** with methyl iodide (MeI) in dimethylformamide (DMF) and sodium hydride (NaH) as base, which led to

per-*O*-methylated compound **3** in 81% yield after purification by silica gel chromatography. Detritylation was carried out conventionally under acidic conditions liberating position O-6 in compound **4** for further derivatizations. For the introduction of a terminal double bond, compound **4** was reacted with 5-bromopent-1-ene (**5**) and sodium hydride as base in a solvent mixture of dimethylformamide (DMF)/tetrahydrofuran (THF) (v/v 1/4) which led to final methyl 2,3,4-tri-*O*-methyl-6-(pent-4-ene-1-yl)-α-D-glycopyranoside (**6**, pentenylOMeGlu) (Scheme 1).

The second vinylogous carbohydrate-based monomer contains an acrylate entity at position O-6, compound **11** (Scheme 2). Therefore, compound **4** was reacted with *O*-tetrahydropyran (THP) protected 2-bromoethanol **7** in DMF employing NaH as base to give compound **8** in 68%. Next, the THP protecting group was cleaved off which was conducted in a methanolic solution of HCl to yield alcohol **9** in 74% yield. The final step had been the introduction of the acrylate group. Therefore, compound **9** was reacted with acryloyl chloride **10** in a solution of CH_2Cl_2 and Et_3N as base. The final compound, methyl 2,3,4-tri-*O*-methyl-6-*O*-ethylacrylate-α-D-glucopyranoside (**11**, acrylateOMeGlu) was obtained in a yield of 48% after purification.

Monomer characterization

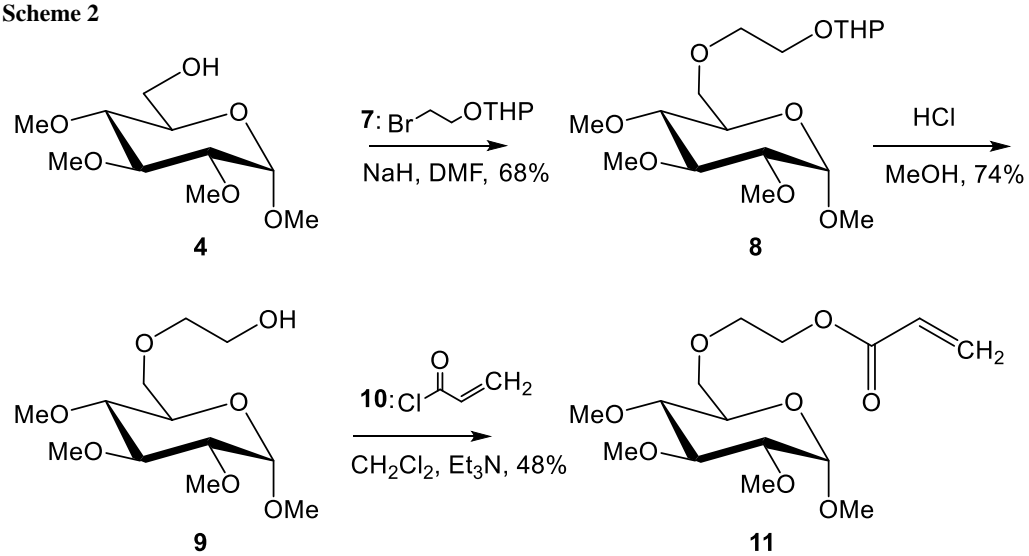
Compounds **6** and **11** have been characterized using standard methods such as NMR spectroscopy, IR spectroscopy, mass spectrometry as well as optical rotation (data are shown in the supporting info). Both monomers were obtained as syrups at room temperature and soluble in organic solvents. To investigate if the monomers **6** and **11** were stable during the vaporization in the iCVD process, a representative sample was heated to 100 °C and analyzed by NMR spectroscopy before as well as after heating. The ^{1}H NMR spectra turned out to be identical, proofing that the monomer is stable during the heating process (data shown in Supporting Info).

iCVD polymerization

The pentenylOMeGlu **6** was polymerized by iCVD and yielded to a deposition rate of 0.12 ± 0.01 nm/min averaged over several substrates placed in the same deposition and several runs. The small standard deviation demonstrates that the deposition was uniform over a 10×10 cm^2 area and repeatable. Such low deposition rate could be the consequence of two factors (1) 1-alkenes are not very reactive for radical polymerization (reaction-limited kinetics), (2) the transport of the monomer vapors inside the reactor is not effective; therefore, a small fraction of monomer vapors reaches the substrate and polymerizes (mass-transport-limited kinetics). To overcome the second limitation, an attempt to increase the deposition rate was made by inserting a silicon wafer with 200 mm^3 of the liquid monomer spin coated on top in the deposition chamber and exposing it to vapors of the initiator radicals, instead of flowing it in through external heated pipes. Due to the low vapor pressure of the monomer **6** (lower than the pressure at which iCVD was run), it did not vaporize under vacuum and could be polymerized with a rate of 0.92 ± 0.01 nm/min. Nevertheless, in this case, the deposition was largely inhomogeneous and presented pinholes and large features already visible by optical microscopy (Fig. 2).

The polymerization of acrylateOMeGlu **11** was slightly faster, with a rate of 0.16 ± 0.01 nm/min. A faster polymerization rate was expected with the acrylic derivative instead of the vinyl derivative of the sugar, since its chemical nature makes the double bond in **11** more active toward the radical polymerization. Considering instead that the polymerization

Scheme 2



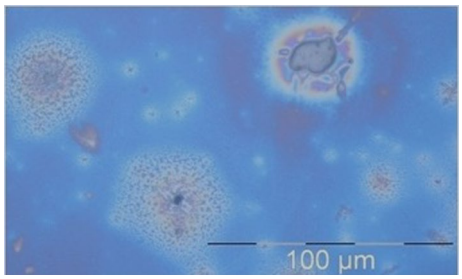


Fig. 2 Optical micrograph of the surface of the vinyl sugar **6** first spin coated on a silicon wafer and then polymerized by iCVD

rates obtained with the two monomers are not very different, it is plausible to assume that the rate-limiting factor was the mass transfer of the monomers rather than the reaction kinetics [11]. The low volatility of the monomers probably prevented in both cases to obtain high monomer vapor concentrations in the reactor, therefore limiting the achievable rate.

The chemical characterization of the polymers obtained was performed by FT-IR. Figure 3 shows a comparison between the IR spectra of the monomers and of the polymers.

Both monomer spectra show defined absorption peaks related to the double bonds at 3095–3010 cm^{-1} (C^{sp2}–H stretching), 1640 cm^{-1} (C=C stretching), 990 and 910 cm^{-1} (C^{sp2}–H out of plane bending). Furthermore, the band at 2950–2850 cm^{-1} can be assigned to C^{sp3}–H stretching typical of methyl and methylene groups. The CH_2 and CH_3 bending modes are visible at 1465 and 1375 cm^{-1}, respectively. Finally, evident are also the absorptions of the C–O stretch in the region 1300–1000 cm^{-1}. In the spectrum of the monomer **11**, the adsorption at 1750 cm^{-1} typical of the carbonyl group is also visible.

The spectrum of polymer from pentenylOMeGlu **6** appears noisier due to the low polymer thickness and the absorptions of the adsorbed water overlap strongly with the polymer signals, especially in the region 1550–1700 cm^{-1}. Nevertheless, it can be seen that the typical bands of the

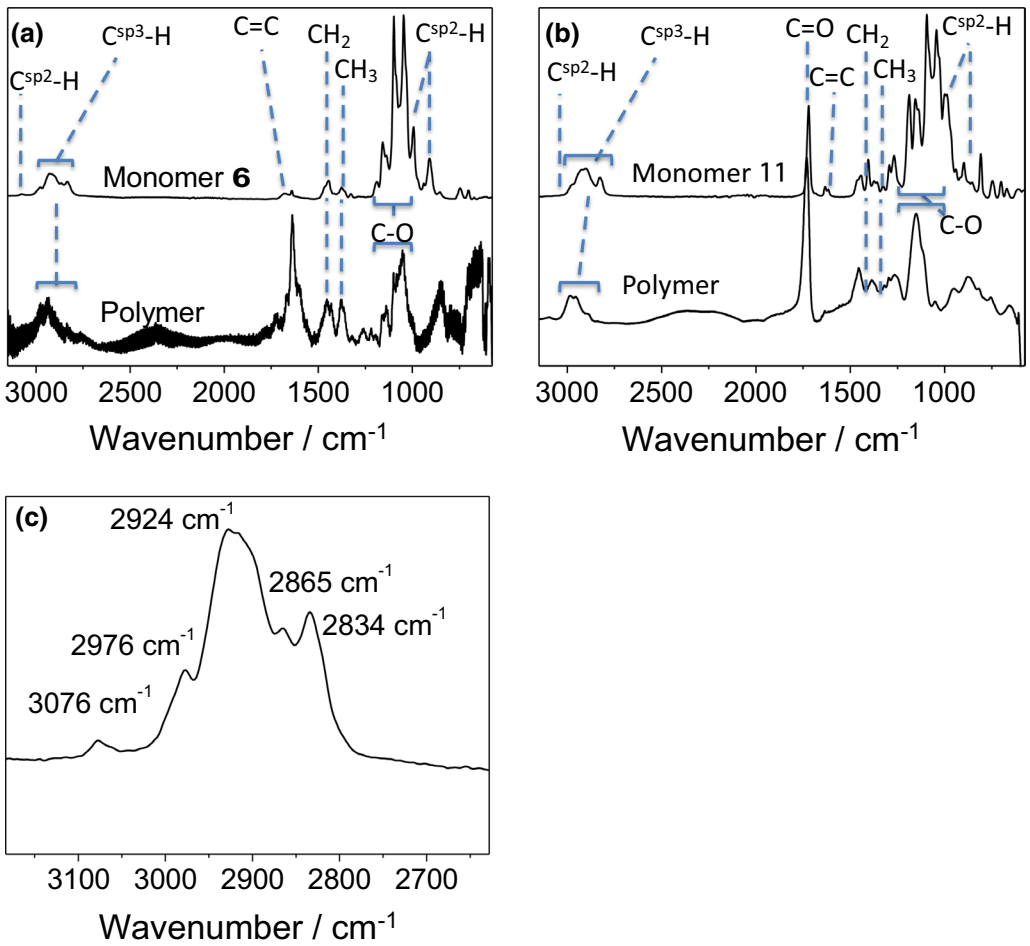


Fig. 3 FT-IR spectra of the monomers **6** (**a**) and **11** (**b**) and of their corresponding polymers obtained by iCVD. (**C**) Zoom into the C–H stretching band of monomer **6**

monomer are retained, while the absorptions of the double bond are reduced. A broad and very noisy band can be observed in the range 2000–2500 cm^{-1}. We believe this band is a mathematical artifact due to the background correction. No other additional absorptions are visible, confirming that the iCVD process allows a complete retention of the monomer structure without unwanted side reactions. The same conclusion can be drawn by comparing the spectra of the acrylateOMeGlu **11** and of its polymer.

The obtained polymers were exposed to water to further characterize them. As the OH groups in the carbohydrate-based monomers as well as produced polymeric films are modified with methyl groups, it was expected that both sugar entities will not be soluble in water, as shown in the experiment. The in situ measurements of thickness of the polymer thin films upon water exposure is shown in Fig. 4. The thickness of the polymer from pentenylOMeGlu **6** decreases when exposed to water. Different slopes can be observed during the dissolution process, indicating that this starts immediately but at different rates. The lower initial rate could be due to some surface rearrangements taking place before the water can fully penetrate and dissolve the polymer structure. Such behavior was already evidenced with other polymers and was explained with the formation of a hydrophobic skin at the interface polymer–air to minimize the surface energy [12]. After 20 min, the polymer is mostly dissolved, probably due to the presence of oligomer chains that easily dissolve in water.

Figure 4b shows the thickness variation of the polymer from acrylateOMeGlu **11** upon water exposure. In this case, the polymer thickness slightly increases from 269 to 272 nm and to then stabilizes at around 270 nm. The lack of dissolution could be due to a higher molecular weight of the polymer.

Conclusion

In this proof-of-concept study, the successful vapor polymerization of the sugar-based monomers pentenylOMeGlu **6** and acrylateOMeGlu **11** was demonstrated. The FT-IR spectra provide evidence that the polymers obtained have the expected chemical structure, typical of sugar-based radical polymer; however, the deposition rate obtained was rather low. In situ ellipsometry shows that upon water exposure, the polymer derived from the acrylateOMeGlu **11** did not dissolve.

The advantage of solvent-free and surfactant-free processing, as initiated chemical vapor deposition, eliminates the environmental, safety, and health considerations associated with these components and can reduce waste disposal. In addition, it would facilitate the implementation of synthetic sugar-based thin polymer films into functional devices, where the use of solvents for the deposition of the synthetic polymer thin film would be detrimental.

The versatility of the approach demonstrated is such that further improvements on the process are possible, in perspective. For example, the volatility of the monomers can be increased by trimethylsilyl ether groups at the secondary hydroxyl functions of the carbohydrate backbone. Investigations in this respect are currently conducted. In addition, more efforts will be devoted to improving the scalability of the whole process.

Experimental

NMR spectra were recorded on a Bruker Ultrashield spectrometer at 300.36 MHz (^{1}H) and 75.53 (^{13}C) MHz, respectively. Methanol-d_4 was used as solvent, chemical shifts are listed in ppm employing residual, non-deuterated solvent as

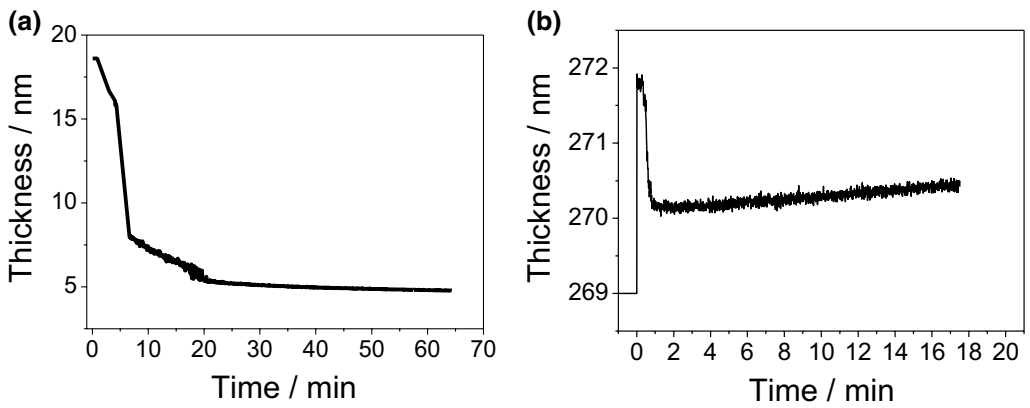


Fig. 4 Solubility curves of the iCVD polymer thin films, measured by ellipsometry upon exposure of the polymer of pentenylOMeGlu **6** (**a**) and of acrylateOMeGlu **11** (**b**) to water (at time = 0 (min))

the internal standard and $CDCl_3$. Signals were unambiguously assigned by COSY and HSQC experiments. MALDI-TOF mass spectrometry of compound **4** was performed on a Micromass TofSpec 2E time-of-flight mass spectrometer. Analytical TLC was performed on pre-coated aluminum plates Silica Gel 60 F254 (E. Merck 5554), detected with UV light (254 nm). For staining, a solution of 9 g vanillin in a mixture of 950 cm^3 H_2O/750 cm^3 EtOH/120 cm^3 H_2SO_4 or ceric ammonium molybdate (100 g ammonium molybdate/8 g ceric sulfate in 1 dm^3 10% H_2SO_4) were employed followed by heating on a hotplate. For column chromatography, silica gel 60 (230–400 mesh, E. Merck 9385) or silica gel 60 (Acros Organics, AC 24036) were used. Unless otherwise specified, all starting materials, reagents, and solvents are commercially available and were used without further purification.

Methyl 6-*O*-(triphenylmethyl)-α-D-glucopyranoside (2, $C_{26}H_{28}O_6$) To a solution of 5.02 g methyl α-D-glucopyranoside (**1**, 30.9 mmol) in 50 cm^3 pyridine, 8.62 g triphenylmethylchloride (30.9 mmol) was added and the reaction mixture stirred at 60 °C for 24 h until thin layer chromatography (TLC) (cyclohexane (C)/ethyl acetate (EE) 2/1 v/v) indicated complete consumption of the starting material. Methanol (10 cm^3) was added and the solvent was removed under reduced pressure. The residue was diluted with ethyl acetate (EE), washed consecutively with HCl (6%) and $NaHCO_3$ satd, dried over Na_2SO_4 and the filtrate was concentrated under reduced pressure. The crude material was purified by silica gel chromatography (C/EE 10/1→1/3 v/v) to give compound **2** in a yield of 60.3% (6.80 g, 15.6 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.57–7.44$, 7.37–7.15 (15H, aromat), 4.78 (d, 1H, $J_{1,2} = 3.5$ Hz, H-1), 3.83–3.71 (bm, 1H, H-5), 3.64 (dd, 1H, $J = 9.2$ Hz, H-3(4)), 3.53 (s, 3H, OCH_3), 3.50–3.40 (bm, 2H, H-2, H-6), 3.36–3.22 (bm, 2H, H-6'), H-3(4)) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 145.6$, 130.0, 128.8, 128.1 (18C, aromat), 101.2 (C-1), 87.7 (C-7), 75.5, 72.4 (2C, C-3, C-4), 73.6 (C-2), 72.6 (C-5), 65.0 (C-6), 61.6 (OCH_3) ppm.

Methyl 2,3,4-tri-*O*-methyl-6-*O*-(triphenylmethyl)-α-D-glucopyranoside (3, $C_{29}H_{34}O_6$) To a solution of 0.99 g compound **2** (2.3 mmol) in 50 cm^3 DMF, 430 mg NaH (60%, washed with C) was added and the reaction mixture was stirred at room temperature. After 30 min, 1.68 g MeI (11.9 mmol) was added. When TLC (C/EE 2/1 v/v) showed full consumption of the starting material, 7 cm^3 MeOH was added and the solvents were removed under reduced pressure. The residue was diluted with CH_2Cl_2, washed consecutively with HCl (6%) and $NaHCO_3$ satd., dried over Na_2SO_4 and the filtrate was concentrated under reduced pressure. The crude product was purified employing silica gel chromatography (C/EE 4/1 v/v) to give compound **3** in a yield of 80.6% (0.88 g). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50–7.37$, 7.29–7.11 (15H, aromat), 4.84 (d, 1H, $J_{1,2} = 3.3$ Hz, H-1), 3.59–3.51 (bm, 4H, H-5, OCH_3), 3.49 (s, 3H, OCH_3) 3.45–3.35 (bm, 4H, OCH_3, H-3(4)), 3.32 (dd, 1H, $J_{6,6'} = 10.0$ Hz, H-6), 3.27–3.17 (bm, 5H, OCH_3, H-2, H-3(4)), 3.04 (dd, 1H, $J_{6',5} = 4.3$ Hz, H-6′) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 144.09$, 128.8, 127.7, 126.9 (18C, aromat), 97.4 (C-1), 86.3 (C-7), 83.8, 81.9, 80.0 (3C, C-2, C-3, C-4), 70.1 (C-5), 62.5 (C-6), 61.0, 60.4, 59.0, 55.0 (4C, 4xOCH_3) ppm.

Methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside (4, $C_{10}H_{20}O_6$) Compound **3** (0.88 g, 1.8 mmol) was dissolved in a solvent mixture containing 13 cm^3 MeOH, 2 cm^3 H_2O, and 20 cm^3 CH_2Cl_2, and the pH was adjusted to 1 by adding HCl concentrated dropwise. The reaction mixture was stirred at 40 °C for 3 h until TLC (C/EE 1/4 v/v) indicated full consumption of the starting material. CH_2Cl_2 (20 cm^3) was added and the organic layer was washed with HCl (6%) and $NaHCO_3$ satd, dried over Na_2SO_4 and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel chromatographic (C/EE 10/1 → EE) to give compound **4** (0.3 g) in a yield of 69%. ^{1}H NMR (300 MHz, MeOH-d_4): $\delta = 4.86$ (bs, H-1), 3.78 (dd, 1H, $J_{6,6'} = 11.7$ Hz, $J_{6,5} = 1.6$ Hz, H-6), 3.68 (dd, 1H, $J_{6',5} = 4.7$ Hz, H-6'), 3.60 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.47–3.38 (m, 5H, OCH_3, H-5, H-3(4)), 3.20 (dd, 1H, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 9.6$ Hz, H-2), 3.15 (dd, 1H, $J = 9.7$ Hz, H-3(4)) ppm; ^{13}C NMR (75.5 MHz, MeOH-d_4): $\delta = 98.5$ (1C, C-1), 84.8, 83.0, 80.7 (3C, C-2, C-3, C-4), 72.6 (1C, C-5), 62.0 (1C, C-6), 61.1, 60.8, 58.8 55.4 (4C, 4xOCH_3) ppm.

Methyl 2,3,4-tri-*O*-methyl-6-*O*-(pent-4-ene-1-yl)-α-D-glucopyranoside (6, $C_{15}H_{28}O_6$) To a solution of 1.34 g compound **4** [13] (10.2 mmol) in 50 cm^3 THF/DMF (4/1 v/v), 1.34 g NaH (60%, washed with C) was added and the reaction was stirred at room temperature. After 40 min, 2.11 cm^3 5-bromopent-1-ene (**5**, 17.8 mmol) was added and the reaction mixture was stirred at room temperature until TLC (C/EE 1/3 v/v) indicated quantitative consumption of the starting material. The solvent was removed under reduced pressure; the residue was diluted in CH_2Cl_2, washed with HCl (6%) and $NaHCO_3$ satd. and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel chromatography (C/EE 1/2). Compound **6** (1.87 g) was obtained in a yield of 60.3%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.75$ (m, 1H, H-10), 5.02–4.84 (m, 2H, H-11), 4.76 (d, 1H, $J_{1,2} = 3.3$ Hz, H-1), 3.63–3.28 (m, 20H, H-4(3), H-5, 2xH-6, 2xH-7, 3xOCH_3), 3.21–3.09 (m, 2H, H-2, H-3(4)), 2.17–1.95 (m, 2H, H-9), 1.75–1.57 (m, 2H, H-8) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 138.3$ (1C, C-10), 114.7 (1C, C-11), 97.5 (1C, C-1), 83.6, 81.8, 79.5 (3C, C-2, C-3, C-4), 71.0 (1C, C-6), 70.0 (1C, C-5), 69.3

(1C, C-7), 60.9, 60.5, 59.0, 55.1 (4C, 4xOCH$_3$), 30.3 (1C, C-9), 28.9 (1C, C-8) ppm; MS: *m/z* calcd. for [$C_{15}H_{28}O_6Na$] 327.1798, found 327.1782; $[a]_D^{20} = +119.5$ ($c = 1.4$, $CHCl_3$).

Methyl 2,3,4-tri-*O*-methyl-6-*O*-(tetrahydro-2*H*-pyran-2-yl-oxyethyl)-α-D-glucopyranoside (8, $C_{17}H_{32}O_8$) Compound **4** (4.1 g, 17.3 mmol) was dissolved in 200 cm^3 DMF, and 720 mg NaH (60% suspension in paraffin oil, 18.0 mmol was washed with C) was added in portions and stirred at RT for 0.5 h. Next, 4.8 g 2-(2-bromoethoxy)tetrahydro-2H-pyran (**7**, 3.5 cm^3, 23.2 mmol) was added and the reaction mixture was stirred at RT for 3 days. After TLC (C/EE 2:1, UV + CAM $R_{f(\text{product})} = 0.36$) showed complete conversion, the reaction was quenched by addition of 25 cm^3 MeOH. The solvents were removed under reduced pressure, the crude product (colorless oil) was dissolved in 20 cm^3 DCM, washed with HCl (6%) followed by $NaHCO_3$ satd. The combined organic phase was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The crude product was chromatographed by column normal phase chromatography (start: C/EE 3:1, End:1:2) to give compound **8** (4.3 g, 11.8 mmol) in a yield of 68%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.75$ (d, 1H, $J_{1,2} = 3.4$ Hz, H-1), 4.57 (s, 1H, THP), 3.81 (d, 2H, $J_{1,2} = 5.1$ Hz, H-2, H-3), 3.64 (s, 3H, H-5, 2 × H-6), 3.56 (s, 4H, 2 × H-1′, 2 × H-2′), 3.44 (s, 8H, 3 × OCH_3), 3.33 (s, 3H, OCH_3), 3.15 (dd, 2H, $J_{1,2;\,3,4} = 5.2$, 3.4 Hz, 1H, OCH_3, H-4), 1.66 (d, 2H, $J_{1,2} = 12.4$ Hz, THP), 1.47 (d, 4H, $J_{1,2} = 2.4$ Hz, THP) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 99.01$–98.78 (1C, C-1 diastereomers), 97.52 (THP C-1), 83.61 (C-3), 81.75 (C-2), 79.43 (C-4), 70.92 (C-2′), 70.10 (C-1′), 69.83 (C-5), 69.77 (THP C-5), 62.01 (C-6), 60.89–55.11 (4C, 4 × OCH_3), 30.60 (THP C-2), 25.45 (THP C-4), 19.38 (THP C-3) ppm; MS: *m/z* calcd. for [$C_{17}H_{32}O_8Na$] 387.1995, found 387.1995.

Methyl 2,3,4-tri-*O*-methyl-6-*O*-(2-hydroxyethyl)-α-D-glucopyranoside (9, $C_{12}H_{24}O_7$) Compound **5** (7.5 g, 20.6 mmol) was dissolved in 200 cm^3 MeOH, the solution was cooled to 0 °C with an ice bath, and 23 cm^3 methanolic HCl was added and the reaction mixture stirred at RT for 1 h. After TLC (C/EE 1:2, UV + CAM $R_{f(\text{product})} = 0.09$; EE/MeOH 10:1 $R_{f(\text{product})} = 0.49$) showed complete conversion of the starting material, 30 cm^3 DCM was added and the organic layer was washed with $NaHCO_3$ satd. The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The crude product (yellowish oil) was purified by column chromatography (C/EE 1:1 → C/EE 1:5) to yield alcohol **9** (7.4 g, 26.3 mmol) in a yield of 74%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.75$ (s, 1H, H-1), 3.65 (d, 4H, $J_{1,2} = 2.8$ Hz, H-2, H-3, H-4, OH), 3.56 (s, 6H, H-1', H-2', H-6), 3.48 (s, 7H, OCH_3), 3.34–3.33 (m, 3H, OCH_3), 3.13 (dd, 2H, $J_{1,2;\,3,4} = 6.2$, 1.6 Hz, OCH_3), 2.08–2.06 (m, 1H, H-5) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 97.55$ (C-1), 83.49 (C-3), 81.78 (C-2), 79.53 (C-4), 72.75 (C-2'), 70.04 (C-1'), 69.90 (C-5), 61.84 (C-6), 60.88–55.22 (4C, 4 × OCH_3) ppm; MS: *m/z* calcd. for [$C_{12}H_{24}O_7Na$] 303.1420, found 303.1420; $[a]_D^{20} = +112.7$ ($c = 0.79$ $CHCl_3$).

Methyl 2,3,4-tri-*O*-methyl-6-*O*-(2-acryloylethyl)-α-D-glucopyranoside (11, $C_{15}H_{26}O_8$) Compound **9** (68.5 mg, 0.3 mmol) was dissolved in 10 cm^3 CH_2Cl_2, and 74.5 mg Et_3N (102 mm^3, 0.7 mmol) was added and the reaction mixture was cooled to 0 °C using an ice bath and sealed with a dry tube filled with $CaCl_2$. After 10 min, 26.6 mg acryloyl chloride (**10**, 24 mm^3, 0.3 mmol) was added and the reaction was stirred for 0.5 h at 0 °C. The solution turned yellow. As TLC (EE, UV + CAM, $R_{f(\text{product})} = 0.69$) showed incomplete conversion, additional acryloyl chloride (0.6 equivalents, 11 mm^3) was added. The reaction was stirred overnight at room temperature. The reaction was quenched by addition of 10 cm^3 MeOH. The solvents were removed under reduced pressure, the crude product (yellow oil) was dissolved in 10 cm^3 EE, washed with HCl solution (6%) and $NaHCO_3$ satd. The organic layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography (C/EE 7:1 → 2:1) to give desired compound **11** (39 mg, 0.1 mmol) in a yield of 47.6%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.36$ (d, 1H, $J_{1,2} = 15.5$ Hz, H-5′), 6.06 (d, 1H, $J_{1,2} = 5.0$ Hz, H-4′), 5.76 (s, 1H, H-5′), 4.74 (s, 1H, H-1), 4.27 (d, 2H, $J_{1,2} = 3.8$ Hz, H-2′), 3.73 (d, 1H, $J_{1,2} = 3.4$ Hz, H-5), 3.63 (d, 3H, $J_{1,2} = 2.1$ Hz, H-3, 2 × H-6), 3.55 (s, 4H, H-2, H-3, 2 × H-1′), 3.44 (s, 7H, OCH_3), 3.33 (s, 3H, OCH_3), 3.14 (d, 2H, $J_{1,2} = 1.7$ Hz, OCH_3) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 166.07$ (C = O), 130.97 (C5′), 128.26 (C-4′), 97.55 (C-1), 83.59 (C-3), 81.74 (C-2), 79.31 (C-4), 70.04 (C-2'), 69.78 (C-1′), 69.39 (C-5), 63.70 (C-6), 60.96–55.14 (4C, 4 × OCH_3) ppm; MS: *m/z* calcd. for [$C_{15}H_{26}O_8Na$] 357.1525, found 357.1525; $[a]_D^{20} = +109.0$ ($c = 1.05$ $CHCl_3$).

iCVD polymerization

Radical polymerization of pentenylOMeGlu **6** and acrylateOMeGlu **11** was performed via initiated chemical vapor deposition (iCVD) in a custom build reactor, using di-*tert*-butyl peroxide (TBPO, Sigma Aldrich, purity 98%) as initiator. A detailed description of the experimental setup can be found in a recent publication [14]. As substrates, silicon wafers with a native oxide layer (SIEGERT WAFER, Germany) were used. The monomers were vaporized at 100 °C. All the depositions were performed at a working pressure of 800 mTorr and initiator flow rate of 1 sccm. The filament was heated to 210 °C while the substrate temperature was held at 20 °C.

Transmission mode Fourier transform infrared spectroscopy (FT-IR) was performed on a Bruker IFS 66v/s

spectrometer. All the data were converted to absorption spectra in the OPUS software.

The film thickness and the solubility in water were measured by spectroscopic ellipsometry with an M-2000 ellipsometer (J.A. Woollam Co., USA) in reflection at an incident angle of 75°, recording optical data in the wavelength range of 370–1000 nm. A liquid cell (J. A. Woollam) was used to hold the pure water in a tight seal. In the dry state, the measured data were modeled with a three-layers system containing silicon and native silicon dioxide (2.1 nm) as substrate and a Cauchy layer for the thin film polymer. In water, the polymer layer was modeled with the effective medium approximation (EMA), which models the material as a mixture of two components with defined optical parameters. The thickness and the materials ratio were the fitting parameters. This is a typical procedure for transparent swollen hydrogels [15].

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Data availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form a part of an ongoing study.

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