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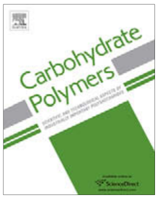

Synthesis of poly-(ε)-caprolactone grafted starch co-polymers by ring-opening polymerisation using silylated starch precursors

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ABSTRACT

Poly-(ε)-caprolactone grafted corn starch co-polymers were synthesized using a hydrophobised silylated starch precursor. The silylation reaction was performed using hexamethyl disilazane (HMDS) as the reagent in DMSO at 70 °C. Silylated starch with a degree of substitution (DS) between 0.45 and 0.7 was obtained. ε-Caprolactone is grafted to silylated starch by a ring-opening polymerisation catalysed by $Al(OiPr)_3$ in THF at 50 °C. The grafting efficiency varies between 28% and 58%, the remainder being homopolymers of ε-caprolactone. The DS of the polycaprolactone graft is between 0.21 and 0.72. The poly-(ε)-caprolactone side chains consist of 40–55 monomer units and is a function of the reagent intakes. Experiments with native starch under similar conditions do not result in the desired poly-(ε)-caprolactone grafted corn starch co-polymers and unreacted starch was recovered after work-up. Removal of the silyl groups of the poly-(ε)-caprolactone grafted starch co-polymers is possible using a mild acid treatment with diluted hydrochloric acid in THF at room temperature.

1. Introduction

Worldwide, 245 million tons of plastics are produced per year, and this value increases with about 10% per year (PlasticsEurope, 2008). These plastics are mainly synthetic polymers from fossil resources, which are known to degrade with difficulty and cause serious environmental problems (Yavuz & Babac, 2003). The development of green biodegradable polymers for e.g. the future generation of packaging materials is highly desirable.

Starch, a natural biopolymer, is one of the potential candidates for future biodegradable polymer products. Starch is abundantly available. Global production of starch is 60 million ton per year in 2004 (International Starch Institute, 2008). Starch is present in the body of many plants (tubers, roots) as granules or cells with typical particle sizes between 1 and 100 μm. The polymeric structure of starch consists of repeating anhydroglucose units. There are two types of biopolymer in starch, amylose (a linear polymer of anhydroglucoses with α-D-1,4-glucosidic bonds) and amylopectin (a branched polymer with α-D-1,6-glucosidic bonds besides α-D-1,4-glucosidic bonds). The content of amylose in starches depends on the plant and typically varies between 18% and 28%. The amylose–amylopectin ratio in native as well as modified starches has a strong impact on the product properties.

Starch films are known to have good oxygen barrier properties. However, as starch is highly hydrophilic, it is water sensitive, and the mechanical properties of starch-based films are generally inferior to those derived from synthetic polymers (Krochta & De Mulder-Johnston, 1997; Tsiapouris & Linke, 2000). Starch modification is therefore needed to meet the product properties in a number of application areas. Various modification strategies have been explored, for instance grafting of monomers (like styrene and methyl methacrylate) to the starch backbone (Bagley, Fanta, Burr, Doane, & Russell, 1977; Beliakova, Aly, & Abdel-Mohdy, 2004). However, in almost all cases, the used monomers and the corresponding grafted chains are not easily biodegradable. Starch has also been thermoplasticized with the help of plasticizers such as glycerol and other polyalcohols (Weber, 2000). However, the product properties are in most cases still not up to standards and blending with other polymers is required (Wang, Yang, & Wang, 2003).

A wide variety of synthetic biodegradable polymers have been prepared. Well known examples are polyesters derived from cyclic lactones (polycaprolactone, polyvalerolactone and polybutyrolactone). Polycaprolactone (PCL) is easily degraded by micro-organisms (Karlsson & Albertsson, 1998). Aerobic soil-burial experiments showed that the mechanical properties of PCL films decreased rapidly in time and were fully degraded after 4 weeks (Goldberg, 1995). PCL has gained much interest for possible applications in the medical field as well as in the area of packaging materials (Chandra & Rustgi, 1998; Chiellini & Solaro, 1996).

Several studies to combine the properties of starch and PCL have been performed to obtain fully biodegradable materials with improved product properties. Blends of thermoplastic starch and PCL are not fully miscible, resulting in undesirable phase separation (Averous, Moro, Dole, & Fringant, 2000). To increase the miscibility of starch and polycaprolactone, it has been proposed to

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chemically graft caprolactone onto the hydroxyl groups of starch using ring-opening polymerisation (Dubois, Krishnan, & Narayan, 1999). Common Ring-Opening Polymerization (ROP) catalysts such as tin octoate or aluminium isopropoxide gave low grafting efficiencies (GE, 0–14%). The highest GE (90%) was achieved using triethylaluminium as catalyst (Dubois et al., 1999). This catalyst is extremely air and water sensitive, therefore difficult to handle and releases ethane, a very flammable by-product, during the reaction. All available data indicate that the presence of water reduces the GE. This is rationalised by assuming that water competes with the hydroxyl groups of starch in the initiation step of the polymerization reaction, thus leading to the formation of PCL homopolymers rather that starch-*g*-PCL (Dubois et al., 1999). Another possible cause for the low grafting efficiencies is the heterogenous nature of the reaction. Starch is insoluble in the typical organic solvents used for ROP (such as toluene or THF), leading to a liquid–solid system. This is expected to lead to reduced reaction rates between starch and CL compared to CL homopolymerisation, thus to a reduction in the GE.

In this paper, an alternative method to synthesize poly-(ε)-caprolactone grafted starch co-polymers (starch-*g*-PCL) is reported. The starch source is made less hydrophilic and thus more soluble in organic solvents by substituting part of the OH groups of starch by a bulky silyl group (Klemm & Einfeldt, 2001; Petzold, Klemm, Stein, & Gunther, 2002; Petzold, Koschella, Klemm, & Heublein, 2003). In this way, the ring-opening polymerisation occurs solely in the liquid phase and this is expected to lead to higher GE values. This approach has also been applied successfully to graft PCL and polylactide on dextran (Nouvel, Dubois, Dellacherie, & Six, 2004; Ydens et al, 2000).

2. Materials and methods

2.1. Materials

Corn starch (Sigma) was dried under high vacuum (∼1 mbar) at 100 °C for one day before use. Hexamethyldisilazane (HMDS, Acros) and methanol (Labscan) were used as received. DMSO (Acros) and toluene (Labscan) were dried overnight over molecular sieves 3 Å (Merck) and stored under a protective nitrogen atmosphere. Dry tetrahydrofuran (THF) and toluene for polymerization experiments were obtained in closed vessels from Aldrich and were used as received. Hydrochloric acid (HCl) 1 N was prepared from Titrisol concentrated hydrochloric acid solution (Merck) and distilled (Milipore) water. ε-caprolactone monomer (Fluka) was dried over Calcium Hydride (CaH_2) for 48 h, distilled under reduced pressure at 100 °C and stored under a protective nitrogen atmosphere. Aluminium triisopropoxide [$Al(OiPr)_3$] (Acros) was used without further purification. A stock solution was prepared by dissolving 1.67 g (8 mmol) $Al(OiPr)_3$ in 50 ml of dry toluene in a glove box.

2.2. Methods

All reactions and manipulations with air-sensitive materials were carried out under a protective nitrogen atmosphere either using standard Schlenk techniques or in a glove box.

2.2.1. Typical example of the starch silylation procedure

The procedure for corn starch silylation was adapted from that published for dextran (Nouvel, Dubois, Dellacherie, & Six, 2003; Nouvel et al., 2002; Nouvel et al., 2004; Rutot, Duquesne, Ydens, Degee, & Dubois, 2001; Ydens et al., 2000). For each experiment, pre-dried corn starch (6 g) and dry DMSO (75 ml) were stirred at 70 °C for about 3 h until a clear solution was formed. The predetermined amount of HMDS (typically 24 ml, 0.111 mol) was added to the gelatinized mixture to initiate the silylation reaction. The reaction was carried out at 70 °C. After 2 and 4 h reaction time, toluene (40 ml) was added to solubilize the precipitated (partially silylated) starch. After 6 h, another portion of toluene (20 ml) was added. After 24 h, the solvents were removed from the silylated starch product under reduced pressure (∼20 mbar) at 70 °C. Traces of DMSO trapped in the product were removed by dissolving the product in a small amount of toluene and re-precipitation in methanol. This procedure was repeated three times. After removal of the solvents under reduced pressure (0.1 mbar, 80 °C), the silylated starch **(1)** product was dried in a vacuum oven (∼5 mbar, 40 °C) until constant weight. The white-to-transparent solid products were stored under vacuum in a desiccator at 6–8 °C. The samples were characterized by ^1H NMR.

Silylated Starch (**1**, before peracetylation, Sample SN-3, DS = 0.60): ^1H NMR ($CDCl_3$, 50 °C): δ 0.12 (m, silyl–CH_3), 3–6 ppm (m, broad peaks, starch).

Silylated Starch (**1**, after peracetylation, Sample SN-3, DS = 0.60): ^1H NMR ($CDCl_3$, 50 °C): δ 0.12 (m, silyl–CH_3), 1.7-2.5 (m, acetate–CH_3), 3–6 ppm (m, broad peaks, starch).

2.2.2. Typical example of in situ polymerization of ε-CL with silylated starch

The silylated product from the first step was dissolved in THF (0.6 mL) at 50 °C (1–2 h). The intake of **1** depended on its DS and was adjusted to obtain a solution with 5×10^{-5} mol free-OH groups/ml of THF. To this homogenous solution, THF (4.5 ml) and a predetermined amount of the stock solution of $Al(OiPr)_3$ in toluene were added. A mol ratio of –OH groups to catalyst of 10:1 was used. The mixture was stirred at 50 °C for 4 h to promote the exchange reaction between the isopropoxide groups of $Al(OiPr)_3$ and the free –OH groups of starch. Subsequently, a predetermined amount of ε-caprolactone monomer (molar ratio of monomer to OH-groups was 13:1 for a standard experiment) was added and the ring-opening polymerization reaction was allowed to proceed for 24 h at 50 °C. The reaction was stopped by cooling down the mixture to room temperature and the addition of 2–3 drops of 1 N HCl to deactivate the catalyst. The silylated starch-*g*-PCL (**2**) product was precipitated from the solution by the addition of heptane (about 250 ml) at −18 °C. The solid precipitate was filtered and dried under vacuum (∼5 mbar) at 40 °C for 48 h. The total isolated yield at this condition (see Table 2) was >99%. The yield was measured gravimetrically and is based on the weight of the product and the total weight of reactants charged to the reactor. The samples were characterized by ^1H NMR.

Silylated Starch-g-PCL (**2**, Sample SN1CL1, $DS_{silylation} = 0.68$, $DS_{PCL} = 0.21$): ^1H NMR (DMSO *d*-6, 60 °C): δ 0.12 (s, silyl–CH_3), 1.16 (d, –CH_3, iPr), 1.31 (m, γ-PCL), 1.54 (m, β and δ-PCL), 2.25 (t, α-PCL), 3.37 (t, ε′-PCL), 3.98 (t, ε-PCL), 3.5–3.75, 4.3–4.5, and 5–5.4 (m, broad peaks, starch), 4.88 ppm (m, –CH, iPr).

2.2.3. De-silylation of poly-(ε)-caprolactone grafted silylated starch co-polymers

Desilylation of **2** was performed using a procedure described by Ydens et al. (2000) for desilylation of silylated dextran-*g*-PCL. The silyl group was removed by adding a slight excess (with respect to the number of the silyl functionalities) of 1 N HCl to a solution of starch-silylated-*g*-PCL in THF (10% w/v). After stirring for 2 h, the desilylated starch-*g*-polycaprolactone product (**3**) was precipitated using heptane, filtrated, and vacuum dried at 40 °C for 24 h. The product was collected as a white solid and characterised by ^1H NMR.

Starch-*g*-PCL (**3**, Deprotection product of Sample SN1CL2, $DS_{silylation} = 0.68$, $DS_{PCL} = 0.34$):

^1H NMR (DMSO, 60 °C): δ 1.16 (d, –CH_3, iPr), 1.31 (m, γ-PCL), 1.54 (m, β and δ-PCL), 2.25 (t, α-PCL), 3.37 (t, ε′-PCL), 3.98 (t, ε-

PCL), 3.5–3.75, 4.3–4.5, and 5–5.4 (m, broad peaks, starch), 4.88 ppm (m, –CH, iPr).

2.2.4. Peracetylation of silylated starch

Characterization of the silylated starch by NMR proved very difficult due to the presence of very broad and overlapping resonances arising from starch. Peracetylation of the remaining OH groups of modified starch is a well established procedure to improve characterization of the products by NMR (Petzold, Einfeldt, Gunther, Stein, & Klemm, 2001) The peracetylation procedure applied in this study was adapted from the literature (Einfeldt et al., 2001; Petzold et al., 2001). Typically, **1** (0.1 g) was suspended in THF (4% w/v) and stirred at 55 °C until it was fully dissolved (typically 3 h). Subsequently, the peracetylating reagents (DMAP, acetic anhydride and pyridine in a DMAP: acetic anhydride: pyridine: AHG molar ratio of 1:10:22:1) were added. The peracetylation reaction was conducted for 7 h at 50 °C. The product was precipitated by the addition of methanol and washed several times with methanol. It was finally dried overnight in a vacuum oven at 70 °C and 5 mbar until constant weight.

2.3. Analytical methods

2.3.1. Nuclear magnetic resonance (NMR)

^{1}H NMR spectra were recorded in $CDCl_3$ at 50 °C or in DMSO *d*-6 at 60 °C on a Varian AMX 400 NMR machine.

2.4. Calculations

The DS of the silylated starch ($DS_{silylation}$) is defined as the average number of silyl groups present on an anhydroglucose unit (AHG) of starch. $DS_{silylation}$ may be calculated using ^{1}H NMR spectra of the products after peracetylation using Eq. (1).

$$\mathrm{DS_{silylation}} = \frac{1}{3} \times \frac{A_{\mathrm{CH_3 silyl}}/9}{A_{\mathrm{starch\ proton}}/7} = \frac{7}{27} \times \frac{A_{-0.6-0.6\ \mathrm{ppm}}}{A_{3-5.8\ \mathrm{ppm}}} \tag{1}$$

where A_{x-y} stands for the ^{1}H NMR peak area in the range δ x−y ppm.

The Average Chain Length (ACL) of the Poly-(ε)-caprolactone chain is defined as the average number of CL repeating units in a grafted polymer chain. The ACL is calculated from ^{1}H NMR spectra by comparing the peak area of protons attached to ε-carbon atoms in a repeating CL unit with that of the characteristic ε′ protons of the last CL unit in a PCL chain (Hamaide, Pantiru, Fessi, & Boullanger, 2001) (see Fig. 3). In this calculation, it is assumed that the average length of the grafted chain is equal to the chain length of the homopolymer. This leads to the following equation:

$$\mathrm{ACL} = \frac{A_{\mathrm{CH_2}-\varepsilon} + A_{\mathrm{CH_2}-\varepsilon'}}{A_{\mathrm{CH_2}-\varepsilon'}} = \frac{A_{3.8-4.2\ ppm}}{A_{3.3-3.4\ ppm}} + 1 \tag{2}$$

The degree of substitution of the PCL graft on **2** (DS_{PCL}) is defined as the average number of PCL polymer chains present on an AHG unit of starch. When assuming that all ε-CL monomer is converted, the DS_{PCL} may be calculated using Eq. (3). The assumption of high conversions (>95%) was correct for all experiments (see Table 2)

$$\mathrm{DS_{PCL}} = \frac{0.5xA_{3.3-3.1} - A_{4.8-4.9}}{\left[\frac{0.5.(A_{3.3-3.4}+A_{3.8-4.2})}{\varepsilon\text{- CL/OHratio}} \times \frac{1}{(3-\mathrm{DS_{silylation}})}\right]} \tag{3}$$

The grafting efficiency (GE) is defined as the percentage of PCL grafted to starch compared to the total amount of polymerized CL (grafted and PCL homopolymer). It is calculated by comparing the area of protons related to the PCL grafted to starch with the area of the protons of all PCL chains present in the product. This leads to the following equation:

$$\begin{aligned}\mathrm{GE} &= \frac{A_{\mathrm{CH_2}-\varepsilon'}/2 - A_{\mathrm{CH-iso}}}{A_{\mathrm{CH_2}-\varepsilon'}/2} \times 100\% \\ &= \left(1 - \frac{A_{\mathrm{CH-iso}}}{A_{\mathrm{CH_2}-\varepsilon'}/2}\right) \times 100\% = \left(1 - \frac{A_{4.8-4.9}}{A_{3.3-3.4}/2}\right) \times 100\%\end{aligned} \tag{4}$$

where A_{x-y} stands for the peak area in the range δ x-y ppm.

The Hildebrand solubility parameter of HMDS and DMSO were calculated using the following equation (Hertz, 1989):

$$\delta = \left(\frac{\Delta H_v - RT}{V_m}\right)^{1/2}$$

where ΔH_v stands for heat of vaporization, *T* stands for absolute temperature, and V_m stands for molar volume. The values of ΔH_v and V_m were obtained from the SciFinder Scholar database (American Chemical Society, 2007).

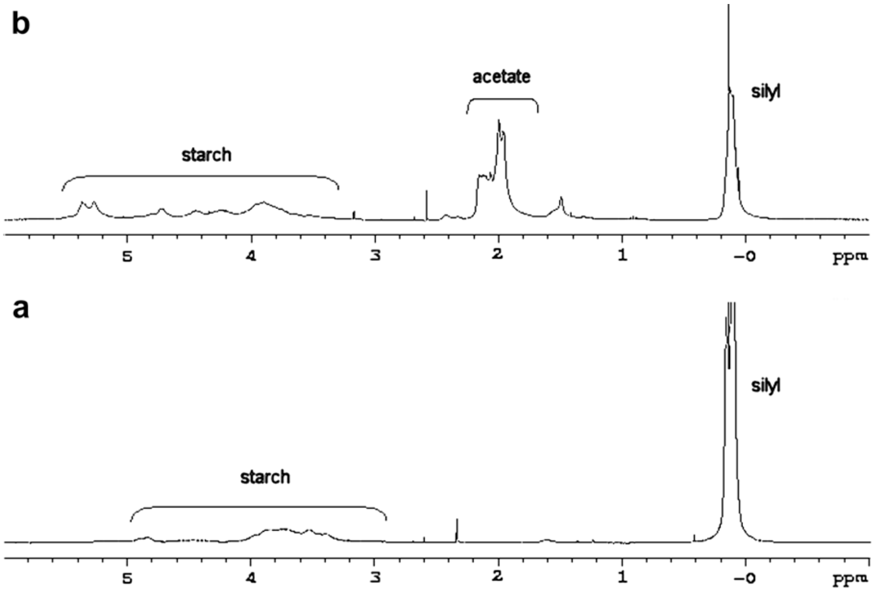


Fig. 1. Typical ^{1}H NMR spectra of silylated starch (sample SN3, $DS_{silylation}$ = 0.60, in $CDCl_3$, 50 °C). (a) not peracetylated; (b) peracetylated.

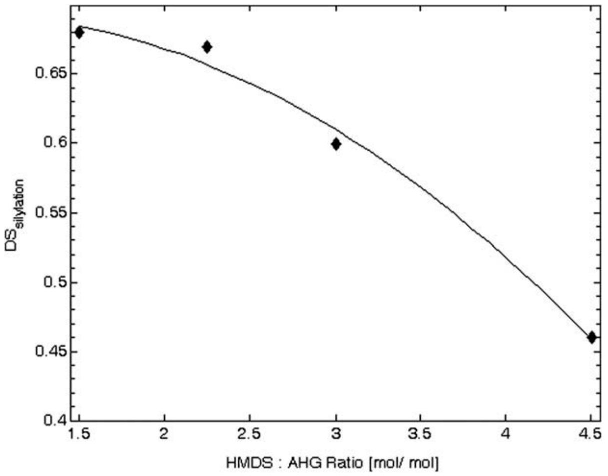


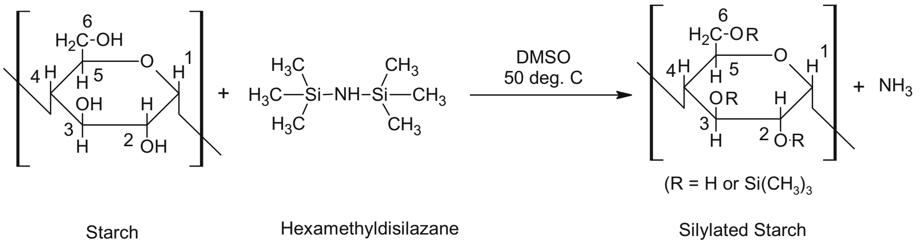
Fig. 2. DS of the silylated products at different HMDS: AHG ratio's (DMSO, 70 °C).

3. Results and discussion

The overall procedure to synthesize poly-(ε)-caprolactone grafted starch co-polymers (**3**) consists of three steps and includes hydrophobization of starch by silylation of part of the hydroxyl groups of starch using hexamethyl disilazane (HMDS), followed by an *in-situ* Ring-Opening Polymerization (ROP) of ε-caprolactone monomer on the hydrophobized starch and subsequent silyl group removal by a mild acid treatment. Although all steps have been investigated, the focus of this paper will be on the first two steps of the procedure.

3.1. Synthesis of silylated starch

The silylation of corn starch was performed with HMDS as the silylating agent Eq. (5). The silylation procedure was adapted from that previously reported for dextran (Nouvel et al., 2002; Nouvel et al., 2003; Nouvel et al., 2004; Rutot et al., 2001; Ydens et al., 2000).



(1)

(5)

Instead of using DMSO as solvent, mixtures of toluene and DMSO were applied to avoid precipitation of the silylated starch during the reaction. In this way, a homogeneous reaction mixture was maintained throughout the reaction. The silylated products were characterised by NMR. Very broad peaks of starch protons at δ 3–5 ppm and a sharp peak of the methyl substituents of the silyl group at about δ 0 ppm were observed (see Fig. 1a).

The degree of substitution of the silyl groups ($DS_{silylation}$) was determined by ^1H NMR. It is defined as the average number of silyl substituted OH groups on the anhydroglucose (AHG) unit of starch. The ^1H NMR spectrum of silylated starch (Fig. 1a) shows the presence of silyl groups at about δ 0 ppm. However, the starch peaks are very broad and this feature hampers accurate determination of the $DS_{silylation}$. An additional peracetylation procedure to substitute the free hydroxyl groups with acetate groups was performed to improve the quality of the NMR spectra, as suggested by Einfeldt et al. (2001). The ^1H NMR peaks from the AHG unit after peracetylation were indeed considerably sharper and allowed more accurate DS calculations (Fig. 1b). Using standard conditions (HMDS: AHG molar ratio of 3, 70 °C, 24 h), a product with a DS of 0.60 was obtained.

The effect of the HMDS to starch molar ratio (1.5–4.5) on the product DS was investigated by performing experiments with a constant starch and a variable HMDS intake. The results are given in Table 1 and Fig. 2.

Surprisingly, the $DS_{silylation}$ decreases for higher intakes of HMDS. For reactions with an order higher than zero, a positive effect of higher reagent intake on the reaction rate and thus the DS is expected. The experimentally observed lowering at higher HMDS intakes is likely due to a decrease in the polarity of the reaction mixture. HMDS is an rather apolar compound (Hildebrand solubility parameter of 6.25 $cal^{1/2}\,cm^{-3/2}$) due to the presence of the bulky apolar $SiMe_3$ groups. Its presence will reduce the polarity of the reaction medium (DMSO, solubility parameter = 11.36 $cal^{1/2}\,cm^{-3/2}$) considerably. At a mol ratio of HMDS to AHG of 4.5:1, the volumetric HMDS intake is about half of the DMSO intake. The silylation reaction involves charged-ionic species (Ydens et al., 2000) and a reduction in the polarity of the reaction medium is expected to lead to a lowering of the silylation reaction rates. Similar reductions in the reaction rates when working at higher reactant intakes were observed for the esterification of starch with vinyl laurate and stearate (Junistia et al., 2008).

To the best of our knowledge, the silylation of starch in pure DMSO using HMDS as the reagent has not been reported to date. The $DS_{silylation}$ (0.45–0.7) of the products is in the range of those published for other starch silylation systems. Petzold et al. (2003) reported that silylation of starch with trimethylsilylchloride (TMSCl) in pyridine yielded trimethyl-silyl substituted starch with DS values between 0.3 and 2.2. Silylation of starch with HMDS in formamide, DMF, DMA/LiCl, pyridine, liquid ammonia, and DMSO/pyridine mixtures yielded silylated starch with DS values ranging between 0.7 and 3.0 (Horton & Lehmann, 1978; Petzold et al., 2003). The use of HMDS to silylate dextran (Mw = 6000–40000) in DMSO (HMDS to OH molar ratio of 0.25–5.0) gave silylated dextran with DS values between 1.1 and 3.0 (Nouvel et al., 2002). The much higher DS values obtained for dextran compared to starch may be related to differences in molecular weights between starch and dextran and the type of AHG linkages (mainly α-1,6-glucosidic for dextran).

3.2. In situ ring-opening polymerization of ε-caprolactone with silylated starch

A number of *in situ* ROP experiments with ε-caprolactone (CL) were carried out using a typical silylated starch sample (DS = 0.68, sample SN-1) in THF at 50 °C for 24 h using $Al(OiPr)_3$

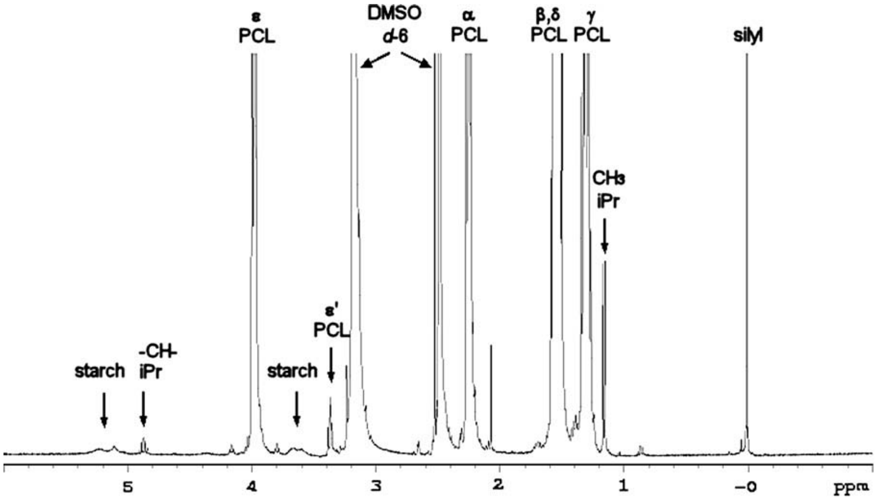


Fig. 3. Typical ^{1}H NMR spectrum of a silylated starch-*g*-PCL sample. (Sample SN1CL1, $DS_{silylation}$ = 0.68, DS_{PCL} = 0.21) in DMSO-d_6 at 60 °C. Coding of the peaks is given in Fig. 4.

Table 1
Effect of HMDS: AHG mol ratio on DS of the silylation product.[a]

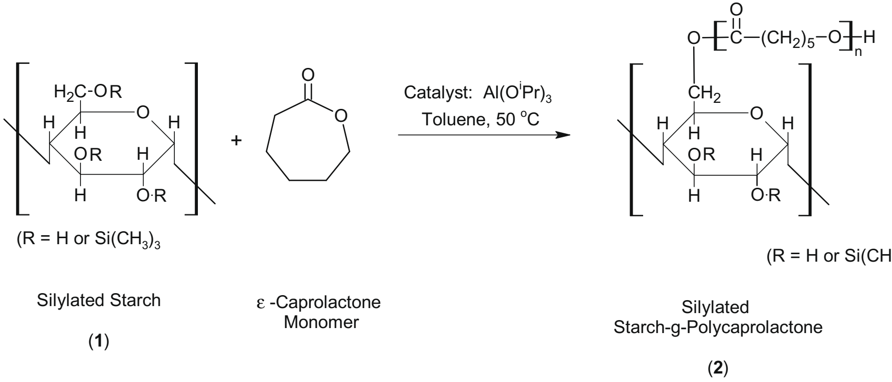
Experiment	HMDS intake (ml, mmol)	HMDS: AHG mol ratio	Product DS ($DS_{silylation}$)
SN1	12 (56)	1.5	0.68
SN2	18 (83)	2.25	0.67
SN3	24 (111)	3	0.60
SN4	36 (167)	4.5	0.46

[a] Experiments were performed in DMSO at 70 °C. For all experiments, a fixed starch intake of 6 g (37 mmol AHG) starch was applied.

as catalyst. A schematic representation of the reaction is provided in Eq. (6). After precipitation with heptane and vacuum drying, white solid products with isolated yield >96% were obtained. The products are soluble in DMSO as well as in less-polar solvent such as chloroform and THF.

The products were characterized using ^{1}H NMR analysis in DMSO-*d*-6 as the solvent. A typical spectrum is shown in Fig. 3.

The peaks from the polycaprolactone units are clearly present in the range of δ 1.2–4 ppm and imply that the ring-opening polymerisation reaction of CL indeed occurred. Resonances from the starch peaks are observable as small, broad peaks in the region δ 3.4–3.8 and 5.0–5.4 ppm. However, not all of the caprolactone is grafted to starch and large amounts of PCL homopolymers (up to 72%) were formed. This is clearly indicated by resonances of the iPr end-group of the PCL homopolymer at δ 4.9 and 1.2 ppm. Further process optimization studies allowed the synthesis of products with less than 42% of homopolymers (*vide infra*). The homopolymers are formed by direct polymerization of ε-CL initiated on isoproproxide moieties attached to the Al catalyst, as is shown in Fig. 4. Apparently, the exchange reaction between $Al(OiPr)_3$ and the OH groups of silylated starch is not quantitative under the conditions applied in this study. The formation of CL homopolymers for this type of reactions



(6)

Table 2
Overview of results for the grafting of ε-CL on silylated starch.[a]

Experiment	ε-CL/OH (mol/mol)	Total yield[b] (%)	Avg. chain length (mon. units)	DS_{PCL}	Grafting efficiency (%)
SN1CL1	13.0	>99	40	0.21	28
SN1CL2	15.0	>99	43	0.34	43
SN1CL3	18.9	>99	44	0.47	48
SN1CL4	22.5	99	49	0.58	55
SN1CL5	29.2	96.5	54	0.72	58

[a] All reactions were performed using the same intake of SN1 silylated starch (DS = 0.68) in THF at 50 °C with $Al(OiPr)_3$ as the catalyst (1 mol $Al(OiPr)_3$ per 10 mol-starch-OH groups).

[b] Determined gravimetrically and defined as the total weight of the isolated product divided by the total intake of reactants (silylated starch and CL).

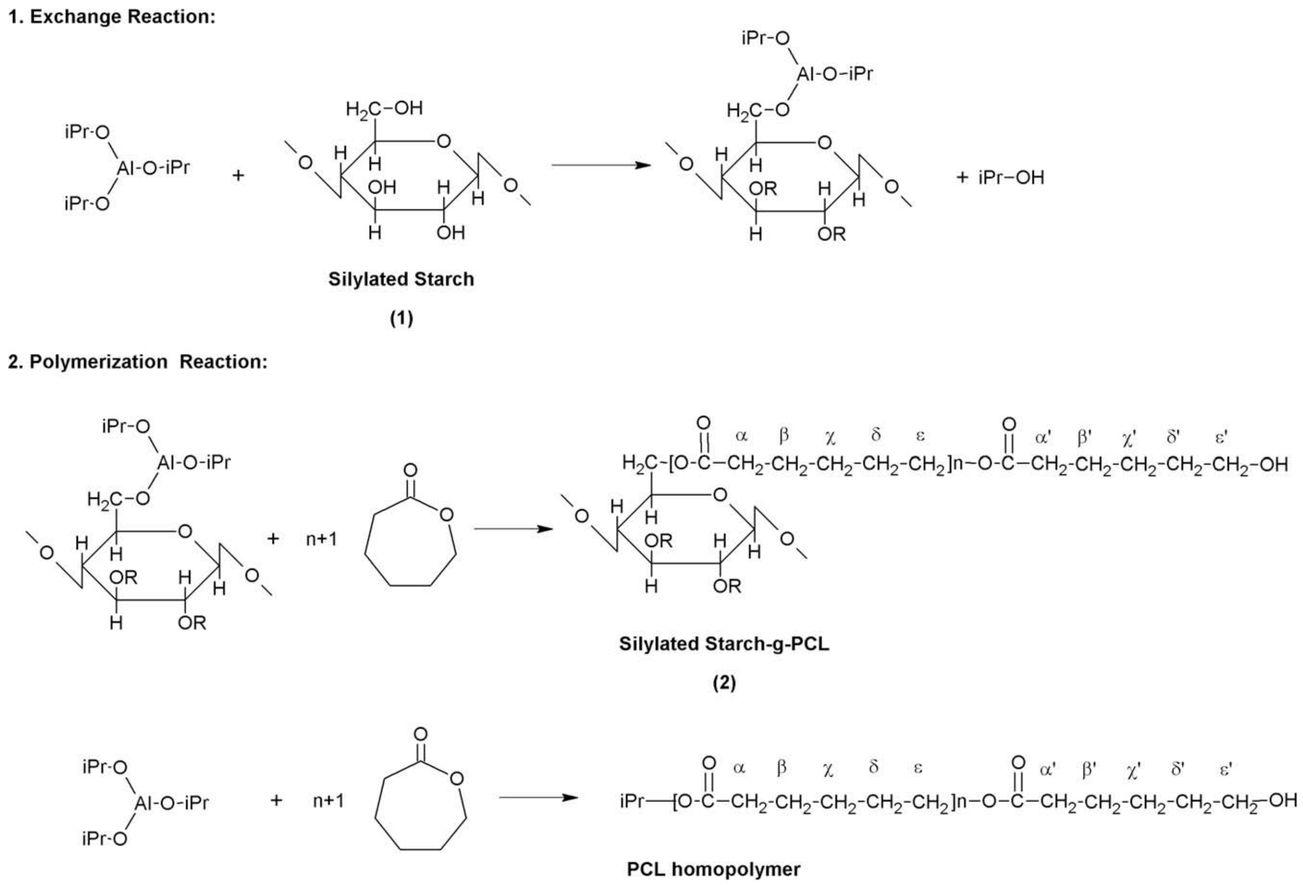
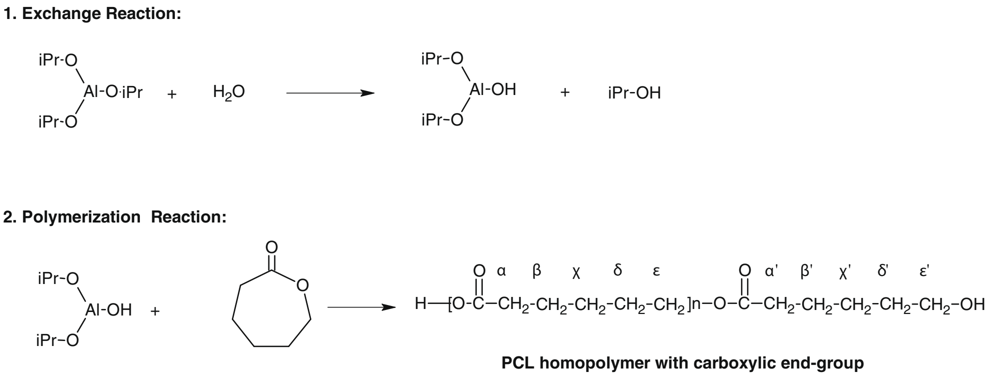


Fig. 4. Product formation for the reaction between silylated starch and ε-caprolactone.

has been observed before (Dubois et al., 1999; Hamaide et al., 2001).

Besides the –OH group of starch, residual water may also initiate the polymerisation reaction. This leads to the formation of carboxylic end groups (see Eq. (7)). However, peaks arising from a –COOH unit could not be detected in ^{13}C NMR spectra (δ 175–180 ppm).



(7)

The ratio of homopolymerisation versus grafting on starch may be obtained by comparing the integrals of selected peaks in ^{1}H NMR spectra. In the case of only homopolymerisation, the intensity of the peak from the $–CH_2–$ end group of the homopolymer (ε′ at δ 3.3 ppm) should be twice the intensity of the –CH– proton of the isopropoxide end group (δ 4.9 ppm). However, in all samples, the intensity of the resonance ε′ was considerably higher than that of the –CH– iPr peak. This implies that grafting of caprolactone to starch also occurs to a significant extent. The grafting efficiency (GE) for the sample given in Fig. 3 (SN1CL1) is 28%.

Five experiments were performed to study the effect of different ε-CL to silylated starch ratio's. The results are given in Table 2 and Fig. 5. The yield of the products was measured gravimetrically and varies between 96.5% and 100%. This implies that the ε-CL conversion is essentially quantitative in all cases. The GE increases with higher ε-CL intakes, and reaches 58% for a ε-CL to starch–OH ratio of 29.2.

The ACL of the polymer and the DS_{PCL} increase almost linearly with the ε-caprolactone intake (Fig. 5). This indicates that higher ε-CL concentrations during the reaction lead to longer PCL grafts as well as to higher levels of initiation of the grafting reaction on free hydroxyl group of silylated starch.

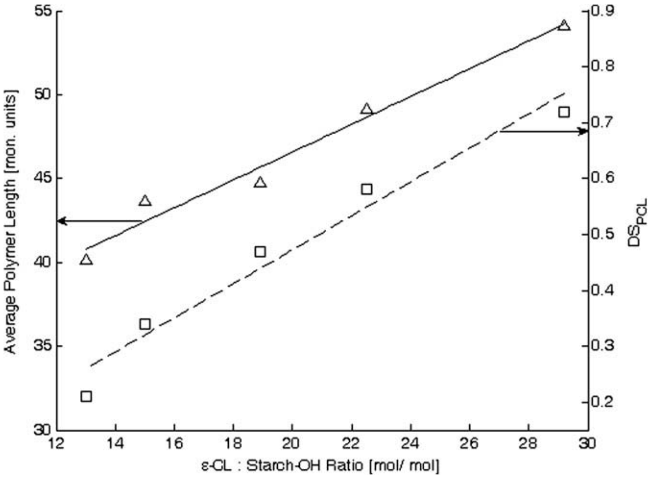


Fig. 5. Average Chain Length (ACL) and the DS for as a function of the CL-starch intake. —Δ—: Average Chain Length (ACL); – ⊟ –: DS_{PCL}.

The mechanism of ROP of cyclic esters such as caprolactone in the presence of an alcohol (ROH, silylated starch in our case) is provided in Scheme 1 (Duda, 1996; Penczek, Biela, & Duda, 2000). Higher monomer intakes are expected to lead to higher polymerization rates as shown in Scheme 1b. This will result in longer PCL chains in the final product, in line with the experimental observations (see Table 2 and Fig. 5).

At higher ε-caprolactone intakes not only the ACL of the grafted chain increases but also higher values for the DS_{PCL} are observed. This finding may be rationalised by assuming that the rate of chain transfer (Scheme 1c) with starch is increased at higher ε-caprolactone intakes. The rate of this reaction is expected to be a function of both the starch and the concentrations of Al-species with a growing PCL chain. The starch intake for all experiments was equal, meaning that the concentration of Al-species with a growing PCL chain should be higher at higher ε-CL intakes. This is indeed predicted by the mechanism given in Scheme 1b; higher caprolactone intakes will increase the rate of this reaction and lead to higher concentration of Al-species with a growing PCL chain.

The observation that a higher monomer to alcohol ratio leads to higher amounts of PCL chains with an alcohol end group and thus a higher DS was also reported for the polymerization of *p*-dioxanone with Zn-lactate as catalyst and α-tocopherol as the alcohol (Kricheldorf & Damrau, 1998).

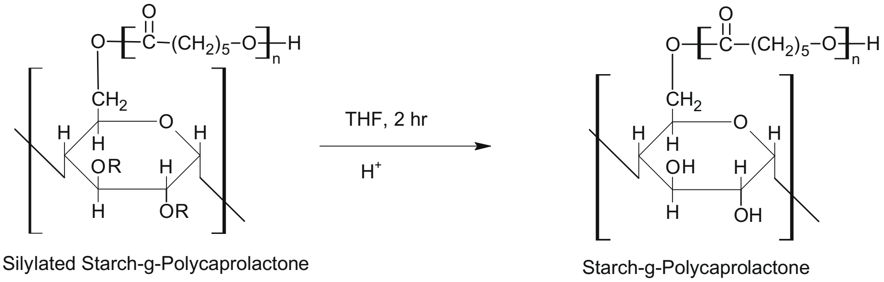
To show the potential of our approach to use hydrophobised starch instead of native starch for the ring-opening polymerisation of cyclic esters, several ring-openings polymerisation of native starch with ε-CL monomer were performed either in pure ε-CL or in a mixture of ε-CL and toluene (80–100 °C, 24 h). At the start of the reaction, the starch was always insoluble in the reaction medium. After reaction the product was isolated, washed thoroughly with toluene and dried. The weight of the product, however, was very close to the initial starch intake. Examination of the products by FT-IR does not show the presence of caprolactone vibrations. Thus, it may be concluded that solubilisation of starch is of key importance to obtain poly-(ε)-caprolactone grafted starch co-polymers.

These findings are in line with earlier studies on the ROP of ε-caprolactone on native granular starch using $Al(OiPr)_3$ as catalyst (Dubois et al., 1999) Here, caprolactone polymerization did not occur after 18–24 h reaction time and only liquid ε-CL was recovered. Only when performing the reaction with high concentrations of the aluminium catalyst, a product with a GE of about 13% was obtained. This low GE was explained by assuming that the reaction between starch and $Al(OiPr)_3$ is slow and due to the heterogeneous nature of the reaction mixture.

Our study, together with the result of Dubois et al. (1999) indicate that homogenous reaction conditions are required for the successful ROP of ε-CL to obtain poly-(ε)-caprolactone grafted starch co-polymers when using $Al(OiPr)_3$ as the catalyst. When performing the reaction under heterogenous conditions, a high grafting efficiency is only achievable when using triethylaluminium as the catalyst (Dubois et al., 1999).

3.3. Deprotection of silylated-starch-g-PCL

A preliminary experiment was performed to remove the silylated groups of the silylated starch-g-PCL Eq. (8) using a mild acid treatment with diluted hydrochloric acid in THF at room temperature. All silyl groups were removed successfully, as is clearly seen from an NMR spectrum given in Fig. 6.



(**2**) (**3**) (8)

4. Conclusions

The successful synthesis of poly-(ε)-caprolactone grafted corn starch co-polymers using a three step approach is reported. The key feature is the use of a homogeneous reaction mixture for the ROP of starch with ε-CL. This was achieved by making the starch more hydrophobic by partial substitution of the OH groups by trimethylsilyl groups. Silylated starch with a low-medium DS (0.46–0.68) was obtained using a DMSO/toluene mixture as the solvent and HMDS as the silylating agent. The ROP with ε-CL was performed using $Al(OiPr)_3$ as catalyst in THF as the solvent. Poly-(ε)-caprolactone grafted silylated starch co-polymers with average chain length of 40–55 monomer units (polymer molecular weight

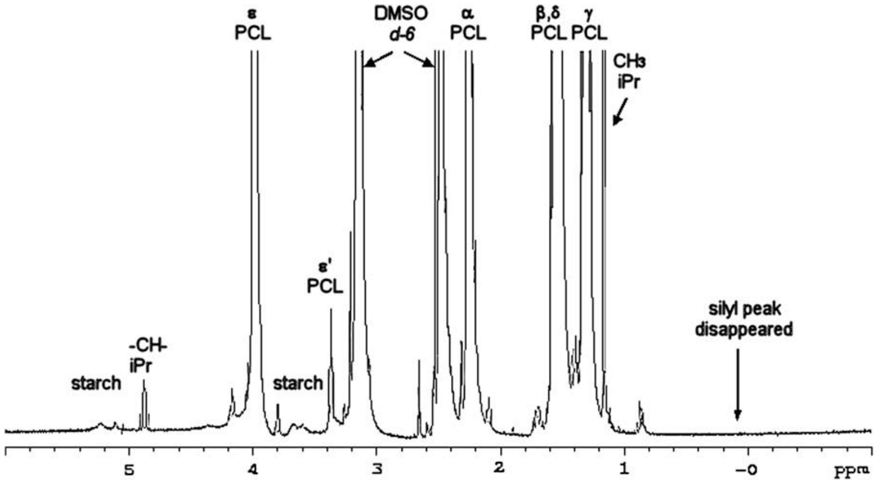
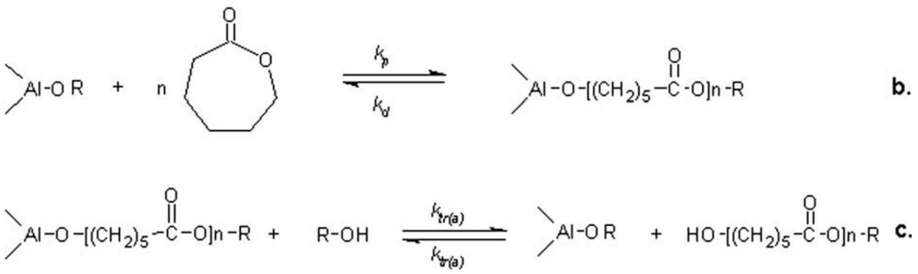


Fig. 6. ^{1}H NMR Spectrum of Starch-*g*-PCL (reaction product after desilylation of sample SN1CL2, $DS_{silylation} = 0.68$, $DS_{PCL} = 0.34$), in DMSO-d_6.



Scheme 1. Proposed mechanism of the Ring-Opening Polymerization (ROP) of ε-caprolactone in the presence of an alcohol ROH.

of 4500–6300) were obtained. The DS of the PCL chains was between 0.21 and 0.72, depending on the ε-CL-starch ratio. Considerable amounts of ε-CL homopolymers with isopropyl end-groups were also formed. The grafting efficiency varied between 28% and 58%, the highest value was obtained with a ε-CL-AHG ratio of 29.2. Control ROP experiments of ε-CL with native starch under similar conditions did not produce the desired poly-(ε)-caprolactone grafted corn starch co-polymers, indicating that homogeneous reaction conditions are favorable for the grafting reaction. Further systematic studies on process conditions (temperature, catalyst and caprolactone to starch ratio) and type of catalyst are in progress to optimize the grafting efficiencies and reduce homopolymer formation. The products may have interesting applications as compatibilizers for starch-polymer blends.

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