Poly(ε-caprolactone)-Grafted Acetylated Anhydroglucose Oligomer by Ring-opening Polymerization –Synthesis and Characterization

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ABSTRACT: A novel acetylated anhydroglucose oligomer (AGU-oligomer), prepared by acid catalyzed transglycosidation of potato starch triacetate and ethylene glycol, was used as a multifunctional coinitiator for the ring-opening polymerization of ε-caprolactone (ε-CL). The polymers were synthesized using different weight ratios of the starting materials and were characterized by NMR, SEC, and MALLS. The results confirmed the expected P(AGU/CL) polymer structure, namely a 'comb-like' graft-copolymer having the AGU oligomer as backbone with PCL grafts of variable chain lengths (L_{CL} = 4–21). Thermal and mechanical properties of graft-copolymers with different ε-CL block lengths were examined. By changing the graft length, crystallinity was controlled and amorphous polymers were obtained with AGU-oligomer contents higher than 50 wt %. The tensile properties varied with the composition and a copolymer having 40 wt % of AGU-oligomer behaved like soft elastomer, showing high elongation at break. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1633–1641, 2006

Key words: biopolymers; graft copolymers; polyesters; ring-opening polymerization; polysaccharides

INTRODUCTION

Polyesters and polysaccharides are arguably the most important examples of hydrophobic and hydrophilic biodegradable polymers, respectively.[1,2] Polysaccharides, such as starch, chitosan, and pullulan, are typical examples of natural hydrophilic biopolymers. Starch has long been considered as a valuable material for biodegradable materials because of its large natural abundance, renewability, and low cost.[1,3,4] Starch based materials may also be of interest in biomedical applications, as they show enzymatic degradation behavior and relatively good biocompatibility.[5–7] For certain applications, starch-based materials have some limitations in their physical properties, including a lack of long-term stability due to high water absorption, poor mechanical properties, and limited processability.[3] To overcome these weaknesses, various physical (blending, plasticization) and chemical modifications of the starch molecule, as well as copolymerization, have been considered and studied.[4]

Polyesters such as poly(lactic acids) (PLA), poly(glycolide), and poly(ε-caprolactone) (PCL) play important roles in the design of biodegradable and biocompatible polymers as both homopolymers and copolymers. These materials have hydrolysable backbones that lead to good biodegradability. PCL is a semicrystalline polymer with a $T_g = -60$°C and a melting point T_m = 59–64°C. In general, PCL crystallizes readily to an approximate degree of crystallinity of 40–50%.[8] High molecular weight PCL is a strong, ductile polymer with excellent mechanical properties, while PCL of lower molecular weight form viscous liquids or more frequently hard waxes. The repeating unit of PCL consists of five nonpolar methylene groups and a single relatively polar ester group. This molecular structure gives PCL some unique properties. The high olefinic content of PCL contributes to the mechanical properties similar to polyolefins and makes it highly compatible with many polymers. The methylene groups also impart the hydrophobic nature to the polymer and make PCL one of the most hydrophobic of the commercially available biodegradable polymers.[9,10] At present, PCL is regarded as a soft and hard-tissue compatible material, which has found use in resorbable sutures, drug-delivery systems, and bone graft substitutes.[11] The properties of PCL, especially its biodegradation rate and mechanical properties, may be tailored by controlling its crystallinity. However, applications of PCL may eventually be limited due to its slower degradation and resorption ki-

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netics when compared with that of other aliphatic polyesters.

The ability to synthesize hydrophobic-hydrophilic biodegradable polymers containing polyesters and polysaccharides provides a way to materials with novel physical properties and applications.[12,13] Particularly, biodegradable polyester graft-copolymers with polysaccharide units, i.e., PLA-grafted pullulan,[6] PCL-grafted cellulose[14] and hydroxyethylcellulose,[5] PCL- and PLA-grafted dextran,[15–17] PCL-grafted starch through diisocyanate reactions[18,19] and through ring-opening polymerization,[20–23] and also PLA-grafted amylose,[7] have been reported. In addition, the versatile macromolecular architectures allows the preparation of block and graft copolymers, comb-, star-, hyperbranched-, and dendrimer-shaped structures, with all the consequent variations in properties one can predict from such differences.[24–27] Linear and star-shaped poly(ethylene oxide)-PCL and PEO-PLA block copolymers with different molar compositions have been investigated to alter hydrophilicity of the copolymer.[28–33]

Starch, its derivatives, and its hydrolysis products are well-established in the food and technical industries. Destructurized starch has been used as a component in biodegradable plastics. More advanced starch-based products are manufactured by biotechnical and chemical processes. They comprise a variety of monomeric compounds like polyols, glucosides, and their derivatives obtained by esterification, etherification, and amination. Manufacture of alkyl oligopolyglucosides and glycol glucosides by transglycosidation of starch and alcohol is well known process in the literature.[34] Alkyl glucosides may be used as raw material for manufacture of biodegradable and nonirritant emulsifiers for use in cosmetic, pharmaceuticals, and food industries. Glycol glucosides are also potential raw materials for the preparation of alkyd resins and polyurethanes.[35]

Herein, we present the preparation of a PCL grafted acetylated anhydroglucose oligomer [P(AGU/CL)] by ring-opening polymerization of ε-caprolactone coinitiated by a low molecular weight starch acetate based anhydroglucose oligomer (AGU-oligomer). Our goal was to conduct solvent-free reactions with a wide range of monomer compositions to obtain a graft copolymer containing PCL chains grafted on the AGU-oligomer backbone. The effects of changes in the polymer structure on its thermal properties and mechanical performance are presented. Evidence for the possibility of an accelerated degradation rate due to an increased hydrophilicity of PCL are shown.

EXPERIMENTAL

Materials

ε-Caprolactone (CL, >99%, Fluka) was dried over 3 Å molecular sieves for two days before use. The initiator of the ring-opening polymerization, tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, Sigma), was used as received. The AGU oligomer was prepared from potato starch triacetate, which was transglycosylated with ethylene glycol by acid catalysis at 100°C in a 50 dm^3 Lödige contact dryer (Gebr. Lödige Maschinenbau GmbH, Paderborn, Germany).[36,37] The product was precipitated into cold water, filtered, and washed several times with water. The filtered crude product was then dried and milled. Further purification of AGU-oligomer was accomplished by extraction with isopropanol. Before polymerization, oligomers were vacuum dried in an oven at room temperature for two days. The properties of the AGU-oligomer are presented in Table I.

TABLE I
Properties of AGU-Oligomer

M_n (g/mol)[a]	6,400
M_w (g/mol)[a]	12,600
M_n (g/mol)[b]	12,600
DS (tot)[b]	2.43
DS C-6[b]	0.54
DS C-2[b]	0.88
DS C-3[b]	1.00
T_g (°C)	156

[a] Determined by SEC.[38]
[b] Determined by NMR.

Polymerization

P(AGU/CL) copolymers were prepared in a 2.5 dm^3 batch reactor (DIT: Design Integrated Technology) equipped with an inlet and outlet tube for nitrogen. CL monomer was fed to the reactor with the appropriate amount of AGU-oligomer. The AGU/CL weight ratio in the feed was varied between 20/80 and 80/20 as presented in Table II. The reaction mixture was agitated at 100°C for 1 h to ensure that the AGU oligomer was completely dissolved in the CL monomer. $Sn(Oct)_2$ (0.03 mol %) was then added to the homogenous reaction mixture. The reaction was carried out at 140°C for 18 h under nitrogen atmosphere. The extent of the polymerization was followed by taking samples from the reactor and for analysis by size exclusion chromatography (SEC).

Characterization

Molecular weights of P(AGU/CL) were determined by room temperature SEC (Waters System Interface module, Waters 510 HPLC Pump, Waters 410 Differential Refractometer, Waters 717plus Autosampler, Waters Styragel® guard column and four gel columns: 10^4Å, 10^5Å, 10^3Å, and 100 Å connected in series). Chloroform (Riedel-de Haën) was used as the eluent at flow rate of 1 mL/min. The samples were filtered

TABLE II
Molecular Weights of Copolymers Obtained and Conversions

P(AGU/CL) (wt %/wt %)	M_n[a] (calc.)	SEC			^{1}H NMR		SEC-MALLS	
		M_w (g/mol)	M_n (g/mol)	MWD	M_n[b] (g/mol)	Conversion (%)	M_w (g/mol)	M_n (g/mol)
20/80	62,900	70,300	20,500	3.3	62,200	98.6	101,500	35,200
40/60	31,500	38,300	11,700	3.3	31,000	97.8	74,100	24,300
50/50	25,200	33,500	10,300	3.3	25,100	99.2	63,300	22,100
60/40	21,000	30,700	10,200	3.0	20,500	93.9	50,600	12,300
80/20	15,700	23,400	8,400	2.8	15,500	90.8	20,500	10,100

[a] M_n(calc) = M_n(AGU-oligomer) + n(CL)·M(CL)/n(AGU-oligomer)
M_n = M_n(AGU-oligomer) + Conversion·(number of initiating OH)·L_{CL}·M(CL); see eq. (1) and (2).

through a 0.5 μm Millex SR filter prior to injection. Monodisperse polystyrene standards were used for primary calibration without further correction. Molecular weights of the AGU-oligomer was determined as described in the literature.[38] Multiangle laser light scattering (SEC-MALLS) data and absolute molecular weights were obtained using a Wyatt Technologies Dawn DSP Laser photometer connected to Waters 510 HPLC pump, two PLgel Mixed C columns and a Perkin-Elmer LC-RI detector. Data was analyzed using ASTRA software (Wyatt Technologies) assuming 100% mass recovery and a known dn/dc. THF (1 mL/min) was used as solvent through out SEC-MALLS experiments. Dn/dc values were determined by injecting a series of copolymer solutions of known concentrations into a Wyatt Technologies Optilab® RI detector using a syringe pump. The Optilab® RI detector operated at the same wavelength as the Dawn DSP detector (690 nm). The dn/dc values were calculated using the Wyatt Technologies dn/dc software.

Thermal analysis of the copolymers was performed on a Mettler Toledo Star DSC821 differential scanning calorimeter (DSC). The samples were cooled to -100°C and heated to 180°C at a rate of 10°C/min. Values were recorded from the second heating cycle. In separate melt-quench experiments, each sample was heated to 180°C and rapidly cooled (quenched) to –100°C. The cooling rate during the quench was -25°C/min. Data from these experiments were recorded from the first heating scan (10°C/min). In addition, a third set of experiments were carried out to determine changes in degrees of crystallinities as a function of time. In these experiments, samples were placed in an oven at 130°C for 15 min, after which the temperature of the oven was lowered to 35°C. Samples were held at this temperature for a predetermined time period and then withdrawn from the oven for DSC analysis. Samples were withdrawn from the oven after 1, 2, 3, 7, 14, 22, and 49 days. The melting point of PCL crystals ($T_{m,PCL}$) and the measured enthalpy of fusion of PCL ($\Delta H_{m,PCL}$) of these samples were determined from the first heating scan between 0 and 180°C, using cooling and heating rates of 10°C/min. The crystallinities of PCL grafts ($X_{c,PCL}$) in copolymers were calculated via $X_{c,PCL} = (\Delta H_{m,PCL} - \Delta H_{c,PCL})/\Delta H_{ref,PCL}$, in which $\Delta H_{c,PCL}$ is the measured enthalpy of cold crystallization and $\Delta H_{ref,PCL}$ is the theoretical enthalpy of fusion (139.5 J/g) for completely crystalline PCL.[39]

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AMX-500MHz spectrometer. ^{1}H-NMR spectra were run on 5% w/v chloroform-*d* solutions. Broad-band proton decoupled ^{13}C NMR spectra with a delay time of 15 s between pulses were obtained from 40% w/v chloroform-*d* solutions. Relaxation time for methylene carbons was maximized through a series of measurements to make calculations as accurate as possible. A delay time longer than 15 s did not result in larger integration values for the methylene carbons.

The mechanical properties of the copolymers were measured with parallel air-conditioned specimens that had been left for 72 h at 23°C and 50% relative humidity. The specimens were prepared with a mini-injection molding machine (DSM) and as well by compression molding (Fontijne). The melt temperature during molding was 60°C, except for P(AGU80/CL20) (120°C) due to its high melt viscosity. The mold was kept at room temperature except for P(AGU80/CL20) the mold temperature was held at 60°C. Mechanical properties were measured with an Instron 4204 tensile testing machine. Crosshead speed was 10 mm/min and specimen type was 1BA according to the ISO/R 527-1993(E) standard.

Contact angle measurements were performed with a CAM 200 (KSV Instruments, USA) apparatus. An 8 μL water droplet was placed on the surface of the sample. A CCD video camera was used to visualize a magnified image of the specimen and droplet on a monitor. Image analysis software evaluated the static contact angle θ between the droplet and the surface. A mean value of θ was determined from 5 runs on various parts of the specimen.

RESULTS AND DISCUSSION

Polymerization and characterization of P(AGU/CL) structure

In this work, a novel anhydroglucose oligomer (AGU-oligomer) prepared by acid catalyzed transglycosida-

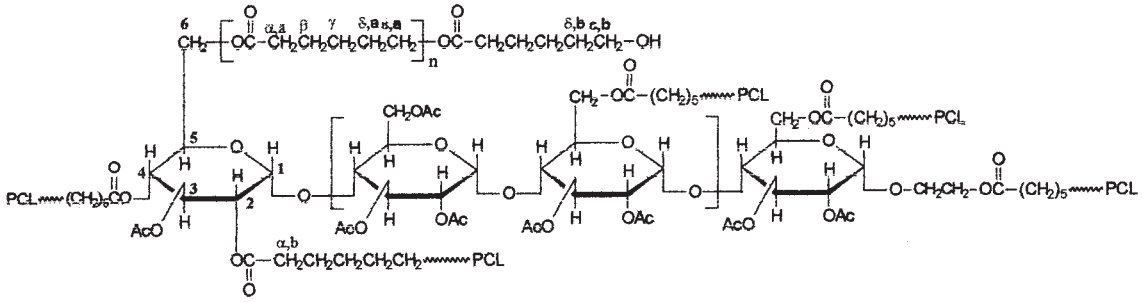

Figure 1 Structure of P(AGU/CL).

tion of potato starch triacetate and ethylene glycol was used as the multifunctional coinitiator for ε-CL ring-opening polymerizations.[37] The AGU-oligomers synthesized by this method are white, odorless powders with excellent solubility in common organic solvents as well as in cyclic carboxylic acid anhydrides and lactones. The molecular weight of the oligomer as well as the degree of acetylation may be controlled by changing the mole ratio of reactants and reaction conditions in the transglycosidation reaction.[37] The acetyl groups of starch acetate were found to be quite stable during the acid catalyzed exchange reaction with the diol. The following stability order was observed: C-3 > C-2 > C-6 (numbers denotes the carbons in the glucose unit, see Fig. 1). The distribution and degree of acetyl substitution (DS) of the AGU-oligomer was determined by quantitative ^{13}C NMR. The starting material was an almost completely acetylated starch acetate (DS = 2.6), while the AGU-oligomer had a DS = 2.43. The oligomer had retained its complete acetyl substitution at C-3. Remaining free hydroxyl groups were found to be located mainly at position C-6 (DS = 0.56) and residual hydroxyl groups at C-2 (DS = 0.88). As a result of the transglycosidation reaction, the reducing end group of the oligomer is hydroxyethylated. The degree of polymerization (DP) of the AGU-oligomer was determined to be 47, resulting in a molecular weight of ~12,600 g/mol. This is in reasonable agreement with SEC results (Table I and II). The number of hydroxy groups and their distribution in the AGU-oligomer can be calculated by using the degree of acetyl substitution, acetyl group distribution, and the DP values. Thus, each AGU-oligomer has an average of 26.8 hydroxy groups of which ~21 are located at C-6 position and ~6 in C-2 position. Additionally, there are two hydroxyl groups remaining at C-4 (non reducing end) and glycol end-groups at C-1 as a result of the hydrolysis of the glucose linkages. Thus, the average number of hydroxyl groups per AGU-oligomer is 28.8, which equals the theoretical maximum amount of PCL-grafts in P(AGU/CL) copolymers. In addition, any C-6 carbons at possible branch points of amylopectin do not have hydroxyl groups. Determined by ^{13}C NMR, only 1.0% of the total glucose linkages were found to be 1,6-linkages. This suggests that the AGU-oligomer is mostly found as a linear molecule. As the majority of the free hydroxyl groups are located at the C-6 position, a "comb-shaped" molecular structure may be expected.

Five different AGU/CL weight ratios were copolymerized to cover the whole composition range of possible copolymers (Table II). The molecular weight was predetermined by the relative molar amount of ε-CL monomer used with respect to the coinitiator. A variable amount of coinitiators is frequently used to regulate the MW, i.e., chain lengths.[40,41] Also, the structure of the resultant polymer depends on the structure of the alcohols used as coinitiators.[17,22,42–45] Mono- and difunctional alcohols yield linear polymers, while alcohols with higher functionality give star-like polymer structures. Hence, the free hydroxyl groups of the AGU-oligomer act as coinitiators in the polymerization of ε-CL initiated by a complex of $Sn(Oct)_2$ and the AGU-oligomer. The molecular weights of the P(AGU/CL) polymers determined by SEC, ^1H-NMR, and MALLS showed a clear dependence related to the amount of AGU-oligomer in the feed, indicating that AGU was directly involved in the polymerization (Table II). Number average molecular weights determined by SEC, ^1H-NMR, and MALLS were in reasonable agreement with theoretical values.

Conversions of the ring-opening polymerizations of ε-caprolactone were determined by comparing the intensities of the monomeric and polymeric α-methylene protons. Because of the nature of the polymerization, the ring-opening polymerization of CL should reach very high conversions. The ring-opening polymerization of cyclic lactones such as lactide, glycolide, and ε-caprolactone using Lewis acids as catalysts has been thoroughly investigated by several research groups.[24,46–49] $Sn(Oct)_2$ is probably the most widely used initiator in these polymerizations. $Sn(Oct)_2$ first reacts with compounds containing hydroxyl groups to form a tin alkoxide that acts as the actual initiating species for the polymerization. After formation of the tin alkoxides, propagation proceeds via a 'coordination-insertion'-type mechanism. The coordination of the carbonyl group of the cyclic monomer to the tin

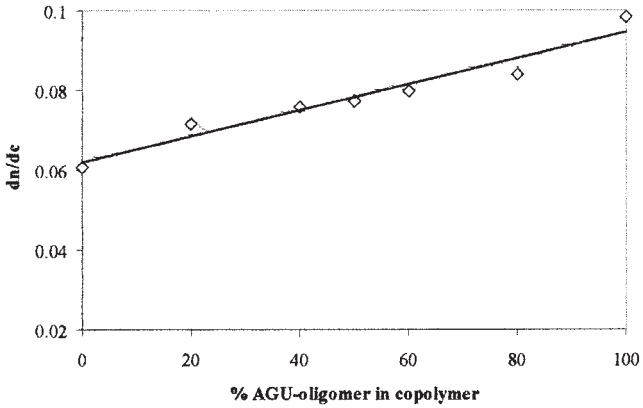

Figure 2 dn/dc values as a function of AGU-oligomer content in P(AGU/CL) copolymers.

alkoxide is followed by the cleavage of acyl-oxygen bond. The growing chain remains attached to the tin center, thus reforming the catalytic active species for the ring opening of the next coordinated cyclic monomer. CL monomer conversions of 98% or higher were observed for P(AGU/CL) graft-copolymers having lower amounts of AGU-oligomer (20 to 50 wt % of AGU). However, an increased AGU-oligomer content (> 60 wt %) was found to prevent high conversions from being reached despite reaction times of 18 h. This fact is not fully understood as the rate of the polymerization typically increases with an increasing amount of chain transferring OH-groups.[45] The decreased rate of polymerization may be explained by interference of the acetyl groups in the reaction. It may be that the $Sn(Oct)_2$ initiatior coordinates to acetyl groups in the AGU-oligomer and possibly promotes their cleavage. Such an effect would be most pronounced especially at the beginning of the polymerization, when the acetyl groups of the AGU-oligomer are not sterically protected by growing PCL chains. The presence of acetic acid, liberated during the catalyst cycle, would decrease the rate of polymerization significantly as shown in previous studies.[46–49] However, a notable loss of acetyl groups or a change in the DS of the AGU-oligomer could not be determined by NMR.

The molecular weights were also determined by SEC equipped with a MALLS detector. Laser light scattering measurements have been shown to be reliable with oligomeric molecules although problems may occur while determining the molecular weights of smaller molecules because of their limitations in the actual scattering of light.[42] The dn/dc values for P(AGU/CL) copolymers, required for calculation of their molecular weights, were determined and displayed a nearly linear dependence (Fig. 2). Random copolymers frequently show a weighed average of dn/dc values based on the weight fractions of the components in the copolymer. Also, copolymers usually require a fairly narrow molecular weight distribution to provide completely accurate data as the composition of the copolymers and thus their dn/dc values may vary with different molecular weights. Despite rather broad polydispersities, the molecular weights of P(AGU/CL) copolymers obtained by SEC/MALLS are still in agreement with theoretical values as well as with SEC and NMR results (Table II).

Data obtained from ^1H and ^{13}C NMR spectra were used in calculations of molar composition, average chain length of PCL graft, number of initiating OH-groups (i.e., number of the PCL grafts), and the average efficiency of initiation of the OH-groups in an AGU-oligomer. The composition of P(AGU/CL) was determined from the intensities of C-6 in the AGU-unit at 96.8 ppm and from ε-carbon in the CL-unit at 64.4 and 62.2 ppm. It is seen from the composition data presented in Table III, that the molar fraction of the CL units (F_{CL}) in the graft-copolymer is in close agreement to the feed values (f_{CL}).

The average chain length of PCL-graft (L_{CL}) was calculated according to

$$L_{CL} = \frac{I_{\varepsilon,a} + I_{\varepsilon,b}}{I_{\varepsilon,a}} \quad (1)$$

where $I_{\varepsilon,a}$ and $I_{\varepsilon,b}$ represent the intensities of ε methylene proton signals for CL chain repeating units at 4.02 ppm and for CL termini units at 3.61 ppm, respectively, (Fig. 1). The number of initiating hydroxyl groups of AGU-oligomer is given by

$$\text{initiating OH—groups} = \frac{F_{CL}}{F_{AGU} \cdot L_{CL}} \quad (2)$$

TABLE III
Chain Lengths of Grafted PCL and Initiating Efficiency of Non-Acetylated OH-Groups in AGU Measured by ^1H NMR

AGU/CL (wt%/wt%)	Composition (mole fraction)		L_{CL} (theor. calc.)	L_{CL} (NMR)	Initiating OH-groups (OH/AGU-molecule)	Efficiency of initiation (% OH-groups)
	f_{AGU}/f_{CL} (in feed)	F_{AGU}/F_{CL} (NMR)				
20/80	0.002/0.998	0.001/0.999	15.6	21.2	20.9	72.4
40/60	0.006/0.994	0.006/0.994	5.8	10.1	16.3	56.7
50/50	0.009/0.991	0.008/0.992	3.9	7.4	14.9	51.9
60/40	0.013/0.987	0.012/0.988	2.6	5.7	12.8	44.5
80/20	0.035/0.965	0.034/0.966	0.97	4.0	6.9	23.9

TABLE IV
Thermal Properties of P(AGU/CL) Copolymers

AGU/CL (wt%/wt%)	Melt-quenched			Annealed[a]		
	$T_{g,PCL}$ (°C)	$T_{m,PCL}$ (°C)	$X^{b}_{c,PCL}$ (%)	$T_{m,PCL}$ (°C)	$X^{b}_{c,PCL}$ (%)	$X^{b,c}_{c,PCL}$ (%)
20/80	−59.2	44.6	27.7	55.6	43.4	54.2
40/60	−50.7	43.6	1.8	54.8	13.3	22.2
50/50	−41.7	44.3	<1	53.4	3.3	6.7
60/40	—	44.9	<1	54.1	1.5	3.7
80/20	—	—	0	—	0	0

[a] Measured by DSC, annealed (48 d) samples.
[b] The degree of crystallinity was calculated using the theoretical heat of fusion value (139.5 J/g) of PCL at 100% crystallinity.[47]
[c] The enthalpies of crystallization are normalized to the amount of CL.

The initiating efficiency can then be obtained from the ratio of the number of initiating hydroxyl groups to all hydroxyl groups in AGU oligomer (28.8 in each AGU-oligomer). As presented in Table III, the L_{CL} of the graft varied from a maximum of 21 caprolactone repeating units of P(AGU20/CL80), to as short as 4 units in the case of P(AGU80/CL20). The measured chain length was found to be longer than the theoretical value for all copolymer compositions. This may suggest that all available OH-groups do not initiate the ring-opening polymerization. In fact, it was observed that the number of OH-groups participating in the initiation process decreased as the AGU-oligomer content increased in the polymer. In other words, a decreased CL content increases the length of the PCL-chain compared to the theoretical value and affects the initiation of the grafting reaction. This may be due to differences in reactivities of various OH-groups attached to the AGU-oligomer backbone. It may be expected that it is more feasible for a monomer to add to the growing chain end than for the $Sn(Oct)_2$ catalyst to transfer to an increasingly sterically crowded OH group on the AGU-oligomer.

A problem sometimes encountered in graft copolymerizations of polysaccharides is the simultaneous formation of homopolymer. The possibility of PCL homopolymerization, initiated by impurities in monomer or possibly by residues of ethylene glycol from the transglycolysation process, was investigated by fractionation. A fractionation of P(AGU/CL) copolymer with 50 wt % AGU-oligomer in the feed was carried out according to the procedure found in the literature.[50] By using a solvent combination of methanol and dichloromethane, two main fractions were collected and analyzed by ^{1}H-NMR. Both fractions were found to contain PCL grafts with increasing chain length (i.e., increasing molecular weight) as the solvent ratio CH_2Cl_2:MeOH increased in value. A presence of PCL homopolymer could neither be found in smaller fractions collected in the fractionation process.

Thermal properties of P(AGU/CL)

The thermal properties of the copolymers were determined by DSC. The results of melt-quenched and annealed samples are shown in Table IV. The DSC thermograms of PCL-grafted anhydroglucose copolymers showed thermal transitions characteristic to those of PCL (Fig. 3). The amorphous AGU-oligomer displayed a $T_{g,AGU}$ at 156°C. However, this $T_{g,AGU}$ was not observed in any of the P(AGU/CL) copolymers prepared. The glass transition temperature of PCL chains ($T_{g,PCL}$), on the other hand, increased with an increasing AGU content. Correspondingly, the width of these transitions were observed to increase from 14°C for copolymer P(AGU20/CL80) to 36°C for copolymer P(AGU50/CL50). This may be associated with the presence PCL segments of various chain lengths, suggesting that with higher AGU content there are more PCL grafts of different chain length. No glass transitions were detected with CL contents lower than 50 wt %. This is most likely a result of average chain lengths being too short.

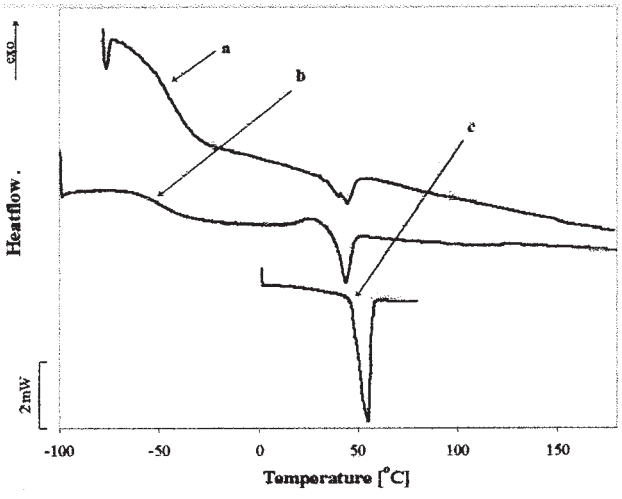

Figure 3 DSC thermograms of P(AGU40/CL60) (a) from the second heating scan, (b) from the melt-quench experiment, and (c) after 49 days of thermal treatment at 35°C.

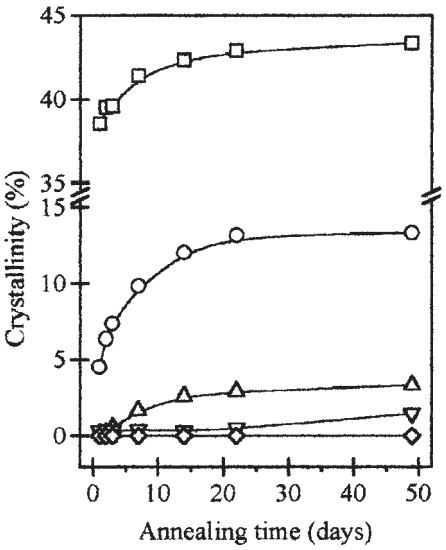

Figure 4 Crystallinity of P(AGU/CL) that developed during thermal treatment; (□)AGU20/CL80, (○)AGU40/CL60, (△) AGU50/CL50, (----) AGU60/CL40, and (◇)AGU80/CL20.

Initial DSC measurements were performed under helium atmosphere, using standard heating and cooling rates of 10°C/min. However, upon storage of samples at room temperature, the physical appearance of the polymers was observed to change with time. In particular, copolymers P(AGU40/CL60) and P(AGU50/CL50) displayed this hardening phenomenon over time. This prompted us to further investigate the cause of this phenomenon. We assumed this observation to be associated with a continuous crystallization of PCL segments. Similar behavior has been previously observed for copolymers of lactide and ε-caprolactone.[51] DSC measurements confirmed the hypothesis of an increasing degree of crystallinity with time (Figs. 3 and 4). In general, crystallinities of polymers depend on their molecular weights. For molecular weights higher than 100,000 g/mol the crystallinity of PCL is ~40%, while it increases to 80% as the molecular weight decreases to 5000 g/mol.[52] Only the crystallinity of P(AGU20/CL80) of all P(AGU/CL) copolymers was within this range. The other copolymers exhibited significantly lower values of crystallinity. In general, a gradual decrease in copolymer crystallinity was observed with a decreasing PCL chain length in the P(AGU/CL) copolymers.

The effect of time and temperature on the crystallinity of the samples was monitored by heating samples to 130°C and subsequent storage at 35°C for predetermined periods of time. Figure 4 shows the increase of crystallinity in the copolymers during this thermal treatment. The initial values were obtained by melt-quench experiments. These experiments also demonstrated that even rapid cooling (-25°C) did not completely prevent crystallization of PCL grafts, although the degree of crystallization was remarkably lower when compared to values obtained after 7 weeks of storage at 35°C. In addition, during the melt-quench experiments, a cold crystallization exotherm was observed for P(AGU20/CL80) and P(AGU40/CL60) copolymers. These transitions occurred from −35 to 25°C and from 10 to 35°C, respectively. The value of the cold crystallization exotherm was measured to be 7.5 J/g for P(AGU20/CL80) and 2.0 J/g for P(AGU40/CL60). No other cold crystallization exotherms was observed. The crystallinity values, X_c, were observed to plateau after about 20 days of thermal treatment.

The initial melting points of PCL crystals were observed to be significantly lower than that of high molecular weight PCL.[8,52] Crystalline imperfections may have caused the observed decrease in the PCL melting points, which were determined to occur at ~44°C for all samples except P(AGU80/CL20). P(AGU80/CL20) did not show any transitions in DSC experiments. The presence of an amorphous AGU component may strongly influence the rate and the crystallization behavior of PCL. The diffusion of PCL chains towards the growing front of the crystallites may be restricted by the amorphous AGU-oligomer component which has a higher T_g than the onset temperature of PCL crystallization. This would expectedly lead to a decrease of the overall rate of crystallization, especially when the content of amorphous AGU-oligomer increases.[53] Thus, the crystallization that occurs within the PCL micro domain structure, may not be similar to that which occurs in a homopolymer.[54] Finally, the crystallinity disappears when the concentration of the CL decreases under 40 wt %. Thus, P(AGU80/CL20) failed to display any PCL melting endotherms and it appears that the PCL chains are unable to crystallize when the average PCL chain length is below 5. This may be due to a result of a substantially increased disturbance from a larger number of end groups and a decrease in segmental length.

Surface and mechanical properties

As stated earlier, the PCL homopolymer is rather hydrophobic. Moreover, acetylation of OH-groups in glucose molecule decreases the hydrophilic character of starch. In AGU-oligomer the degree of substitution is quite high (2.43) which will affect the surface properties of P(AGU/CL) copolymers. Static contact angle measurements were carried out to examine how the surface hydrophobicity varied in the copolymers as a function of the AGU-oligomer content. Decreasing contact angles indicate an increasing hydrophilic nature of the copolymer. Figure 5 shows that contact angles decrease when AGU-oligomer content increases, suggesting a decreasing hydrophobicity of copolymer as AGU-oligomer content increase. This

may be explained by an increased amount of hydroxyl groups per polymer molecule compared to a PCL homopolymer. However, the effect of the hydrophobic nature of the AGU-oligomer can be seen with the highest content of AGU-oligomer. In this case, the average chain length of PCL-graft is very short, only 3.5 CL-units, and the number of grafts per molecule is only one quarter of all OH-groups. As a result, the hydrophobic nature of the acetyl groups becomes predominant.

Results of the tensile testing are summarized in Table V. PCL is a relatively ductile polymer, able to undergo large deformations. P(AGU/CL) graft-copolymers with composition of (20/80) behave more like a brittle material. The tensile modulus remains approximately at the same level as for PCL, but the strength and especially elongation at break were relatively low (PCL homopolymer ≈ 200–300%). Typically, higher contents of starch-based materials are responsible for the increased brittleness. This was observed with P(AGU60/CL40). It behaves like a brittle material and a decreased tensile modulus was observed compared to P(AGU20/CL80). Specimens with the highest AGU content (80/20) were too brittle to be measured. Copolymers P(AGU50/CL50) and P(AGU40/CL60) behaved like typical soft elastomers, showing poor tensile strength and high elongation at break. In these copolymers, the decrease in tensile modulus and strength, and increase in elongation at break was caused by the length and the amount of PCL-grafts, which may act as internal plasticizers for the copolymer. Side-chain crystallinity affected the mechanical properties by stiffening the structure,[55] which can be seen in the compositions where crystallinity appears, i.e., where the average chain length of PCL-graft is more than 10. Below this length, the grafts could not crystallize and act as an efficient plasticizer. In addition, free volume made by side-chain hydroxyl groups was also responsible for the change of mechanical properties.

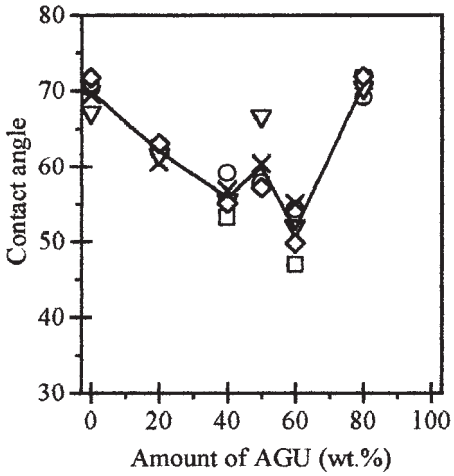

Figure 5 Contact angles for P(AGU/CL) copolymers. The line represents the weighed average of the experiments.

TABLE V
Mechanical Properties of P(AGU/CL) Copolymers

AGU/CL (wt%/wt%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
20/80	290 ± 40	2.1 ± 0.4	3.3 ± 3.6
40/60	33 ± 4	1.0 ± 0.1	56 ± 10
50/50	25 ± 3	0.6 ± 0.0	240 ± 16
60/40	160 ± 10	2.6 ± 0.7	2.5 ± 0.8
80/20[a]	—	—	—

[a] Not measured; specimens were too brittle.

CONCLUSIONS

We have described a new type of biocompatible polyester graft-copolymers with polysaccharide units. The grafting reactions were conducted in the bulk using different amounts of the acetylated anhydroglucose oligomer, which was prepared by transglycosidation of potato starch triacetate with ethylene glycol. This oligomer acted as a multifunctional coinitiator for ring-opening polymerization of ε-caprolactone. This reaction pathway holds further potential for tailoring the properties of starch-based graft-copolymers by controlling the molecular weight and the acetyl substitution of the AGU-oligomer.

Introduction of glucose units may overcome some of the disadvantages of PCL, such as slow degradation rate, by increasing the hydrophilicity of the polymer and by reducing its crystallinity. The observed mechanical properties are explained on the basis of its graft-length and crystallinity. P(AGU50/CL50) showed especially interesting elastic properties. The obtained materials could be useful in various biomedical applications, such as drug delivery systems and as a tissue engineering material.

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