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Hydrophobicities of poly(ϵ -caprolactone) oligomers functionalized with different succinic anhydrides

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ARTICLE INFO

Article history:

Received 7 August 2008

Received in revised form 10 November 2008

Accepted 10 November 2008

Available online 18 November 2008

Keywords:

Poly(ϵ -caprolactone)

Alkenylsuccinic anhydride

Oligomer

Hydrophobicity

Contact angle

ABSTRACT

Different succinic anhydrides were used for modification of hydrophobicities of linear and star-shaped poly(ϵ -caprolactone) oligomers with different molecular weights. Hydroxyl-terminated poly(ϵ -caprolactone) oligomers were acid-functionalized either with succinic anhydride (SAH) or with alkenylsuccinic anhydrides (ASAs) containing 8 or 18 carbons in their alkenyl chains. Hydrophobicities of the linear and corresponding star-shaped oligomers were investigated by immersion studies and by water contact angle measurements. In comparison with SAH functionalized oligomers, alkenyl chain containing oligomers showed lower thermal transitions and higher hydrophobicities. In addition, oligomers with 18 carbons alkenyl chain showed considerably higher hydrophobicities than corresponding oligomers with 8 carbon alkenyl chain.

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1. Introduction

The bioresorbability, nontoxicity and biocompatibility of synthetic biodegradable polyesters, such as polyglycolide acids (PGAs), polylactides (PLAs) and poly(ϵ -caprolactones) (PCLs) with hydrolyzable ester bond structure, make them highly attractive biomaterials for pharmaceutical and medical applications [1–3]. In addition to the high molecular weight polyesters prepared by ring-opening polymerization (ROP), chain-linked and crosslinked polymers have been prepared from oligomeric polyester precursors [4]. Chain extending and crosslinking can be exploited to improve the physical and mechanical properties and increase control over the rate of biodegradation of the resulting polymers [5].

The biodegradation rate of polyesters can be controlled by introducing hydrophilic or hydrophobic components into the polyester chain. Poly(ethylene glycol) (PEG), for example, is a biocompatible nontoxic polymer that is commonly

included as a hydrophilic block in polyester copolymers [6]. Various linear PLA–PEG and PCL–PEG block copolymers are reported in the literature, where PLA or PCL chains are introduced into PEG blocks by ring opening polymerization [7,8] or polycondensation [9,10]. Wide variations in water uptake and degradation rate have been achieved by varying the ratio of hydrophilic to hydrophobic units [11–13]. As in thermoplastic linear block copolymers, PEG has been used in crosslinked polyester networks to take advantage of its hydrophilicity. Park et al. [14] used diacrylated forms of PEG and PCL as building blocks for the synthesis of networks to be used as biodegradable polymer scaffolds in tissue engineering, and Sawhney et al. [15] prepared hydrogels from diacrylated PLA–PEG–PLA and PGA–PEG–PGA macromers. Proper selection of the copolymer ratio allowed control over the degradation rate, degree of crosslinking and hydrophobicity/hydrophilicity of the networks.

In most studies on polyesters containing hydrophilic or hydrophobic components, the aim is to increase the hydrophilicity; attempts are more rarely made to increase the hydrophobicity. Vogt et al. [16] slowed the degradation

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of lactide-based networks by crosslinking dimethacrylated lactide macromers with more hydrophobic methyl methacrylate monomer. Storey et al. [17] lowered the degradation rate of crosslinked networks by copolymerizing lactide with more hydrophobic trimethylene carbonate and applying methacrylation and thermal curing. Kim et al. [18] increased the hydrophobicity of lactide-based diacrylated macromers by changing the hydrophilic PEG co-initiator to more hydrophobic poly(propylene glycol) (PPG) or poly(tetramethylene glycol) (PTMG). The water uptakes were lower and water contact angles higher for the PPG- and PTMG-based crosslinked networks than for the PEG-based networks. Recently, Kurokawa et al. [19] increased the hydrophobicity of PLLA films by end-capping the PLLA with hydrophobic dodecyl and dodecanyol groups. Xu et al. [20] increased the hydrophobicity of lactide- and glycolide-based thermoplastic polymers in two distinct steps. In the first step, oligomers with different hydrophobicities were prepared by polymerization of ϵ -lactide with alkanediols containing carbon chains of different length as co-initiators. In the second step, macromer diols were coupled with diacid dichlorides of various carbon chain lengths. The authors stated that surface erosion can be achieved in poly(ϵ -lactide) copolymers by tuning the hydrophobicity of the polymer backbone.

Alkenylsuccinic anhydrides (ASAs) contain alkenyl chains of various lengths and have been found useful for tailoring the hydrophobicities of biomaterials. ASAs are reported to increase the hydrophobicity of soy protein and gelatin surfactants and to improve the hydrophobicity performance of chitosan and starch surfaces [21–24]. In earlier work, we used ASAs to modify the degradation of thermoplastic poly(ester anhydrides) based on polylactone oligomers [25]. Although the alkenyl chains decreased the degradation rate of the poly(ester anhydrides) they also lowered thermal transitions of the oligomers. This complicated the estimation of the extent of the increase of hydrophobicity via mass loss and water absorption analyses. The specific purpose of this study was to establish the value of water contact angle measurements as a method to differentiate changes in the hydrophobicity of these oligomers. The materials used in this study were linear and star-shaped PCL oligomers functionalized with succinic anhydride or with alkenylsuccinic anhydrides containing alkenyl chains of 8 or 18 carbons.

2. Experimental

2.1. Materials

Oligomers were polymerized from ϵ -caprolactone (CL, Solvay Interlox) in the presence of stannous octoate (SnOct_2 , Sigma–Aldrich) and 1,4-butanediol (BD, Acros Organics) or pentaerythritol (PERYT, Acros Organics). The ϵ -caprolactone was dried over molecular sieves and stannous octoate, 1,4-butanediol and pentaerythritol were used as received. Succinic anhydride (SAH, Acros Organics), (+/-)-2-octen-1-ylsuccinic anhydride (8-ASA, Sigma–Aldrich) and *n*-octadecenylsuccinic anhydride (18-ASA, Tokyo Kasei Organic Chemicals) were used in the functionalization without further treatment.

2.2. Preparation of oligomers

1,4-Butanediol- and pentaerythritol-initiated oligomers were synthesized by a similar method to that used earlier [25–28]. In brief, ϵ -caprolactone was fed to the reactor with an appropriate amount of (2.5–10 mol%) co-initiator and 0.02 mol% of SnOct_2 as initiator, and polymerization was carried out at 160 °C for 4 h under nitrogen atmosphere. After the polymerization, the hydroxyl telechelic oligomers were functionalized in a reaction of hydroxyl groups with SAH or ASAs (3 h at 160 °C) to obtain oligomers with carboxylic acid end groups. SAH, 8-ASA and 18-ASA were used in 1.3 excess of the stoichiometric amount. Functionalized oligomers are denoted in the form LIN-1000-8 or STAR-1000-8, where LIN and STAR indicates linear and star-shaped molecular architecture, 1000 indicates molecular weight and 8 indicates alkenyl chain lengths of 8 carbons. After the functionalization the oligomers were purified by dissolving them in dichloromethane (CH_2Cl_2) and precipitating them in *n*-hexane or isooctane. Finally, the acid-terminated oligomers were dried overnight under vacuum at room temperature.

2.3. Characterization

The molecular weights and molecular weight distributions (MWD) were determined with respect to polystyrene standards by size exclusion chromatography (SEC). A Waters Associates system was equipped with a Waters 717plus autosampler, a Waters 510 HPLC solvent pump, four linear PL gel columns (10^4 , 10^5 , 10^3 and 100 \AA) connected in series, and a Waters 2414 differential refractometer. All samples were analyzed at room temperature. Chloroform (Riedel-de Haën Ag, stabilized with 1% ethanol) was used as the eluent at a flow rate of 1.0 ml min^{-1} . The samples were dissolved in chloroform at a concentration of 0.1% (w/v). The injection volume was 200 μl .

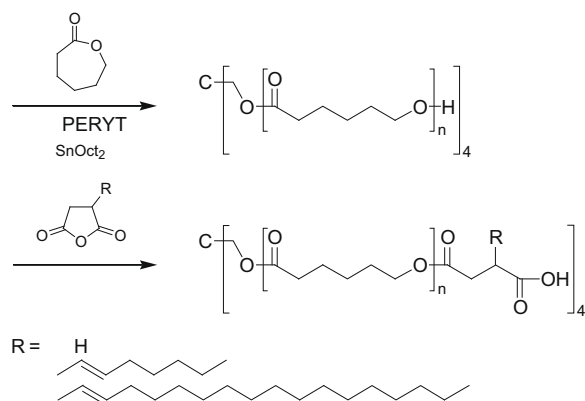
NMR spectra were recorded on a Varian Gemini 2000 300 MHz spectrometer. For ^1H NMR measurements, the samples were dissolved in chloroform- d_1 (Fluka Chemical) with deuteration degree not less than 99.8%, in 5 mm NMR tubes, at room temperature. The sample concentration was about 1.0% by weight. ^{13}C NMR was performed with 10% sample concentration in 10 mm tubes. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet Magna FTIR 750 spectrometer with 2 cm^{-1} resolution. The oligomer samples were dissolved in chloroform at a concentration of 0.1% (w/v) and film-cast onto a NaCl slide.

Differential scanning calorimetric (DSC) measurements were carried out on a Mettler Toledo Star^c DSC 821^e with measurements run from –100 to 200 °C. Heating and cooling rates were 10 °C min^{-1} . The glass transition temperatures (T_g), melting temperatures (T_m) and melting endotherms (ΔH) of the samples were measured during the second heating period.

In the mass loss and water absorption studies, for each time point, three parallel test specimens were immersed in 10 ml of phosphate buffer solution (PBS, pH 7.4, FF-Chemicals Ltd.) in test tubes at a temperature of 37 °C. The air-bath (Infors Ag) was set to shake the test tubes at a rate of 100 rpm. Oligomers were immersed for up to 28 days.

The pH was monitored daily and no change in pH was observed. The form of the analysis depended on the physical state of the oligomers. Test specimens of the solid and waxy oligomers, which retained their shape at room temperature, were prepared by melt pressing to discoids (6 mm in diameter and 2 mm in height) at 60 °C. The discoids were recovered from the test tubes at different intervals and weighed, and then vacuum-dried for one week. The viscous liquid oligomers were weighed, with corresponding weights to the discoids, into vacuum-dried test tubes and buffer solution was added. After the immersion period, the buffer solution was gently poured from the test tube, while the sample was kept in the test tube. The test tubes, with the specimens, were then vacuum-dried for one week. Because these specimens were viscous liquids, their water absorptions could not be monitored.

The water contact angles of the oligomers were determined from thin films spin-coated from chloroform on silica surface. A CAM 200 contact angle goniometer (KSV Instruments Ltd.) was used for determination of static contact angles of sessile drops at room temperature. The water was purified ultra high quality (UHQ) water in equilibrium with air (prepared with ELGA PURELAB UHQ), and the size of the water drop was 7 μ l in air. Contact angles were calculated by asymmetric drop shape analysis (ADSA) using software delivered with the instrument. This analysis is based on fitting the full equations for drop profiles for sessile drops derived from the Young–Laplace equation. The



Scheme 1. Preparation of acid-functionalized star-shaped PCL oligomers.

equilibrium contact angles reported were measured within 16 s of releasing the drop and are averages of measurements on three different films. The standard deviations for all the contact angle measurements were under 2°. The silica (SiO₂) surfaces were those of smooth silicon wafers (Okmetic Ltd.). The silica surfaces were purified with UV-ozone treatment, after which the static contact angle of the water drop on the SiO₂ surface was 0°.

3. Results and discussion

The reaction scheme of the polymerizations is presented in Scheme 1. The synthesis of acid-terminated oligomers consisted of two steps. First, ϵ -caprolactone monomers were polymerized to hydroxyl telechelic oligomers by ring-opening polymerization. In the next step, the hydroxyl termination was changed to acid termination through reaction with succinic anhydride (SAH) or an alkenylsuccinic anhydride (ASA) containing either 8 or 18 carbons in the alkenyl chain.

3.1. Synthesis and characterization of oligomers

The polymerizations of the hydroxyl-terminated oligomers are presented in Table 1. The molecular weights calculated from the NMR spectra coincided well with theoretical molecular weights calculated from the feed ratios. The initiation activity of the hydroxyl groups was determined from the ¹H NMR spectra from the ratio of reacted and unreacted hydroxyl groups of co-initiator. Contrary to the linear oligomers, the unreacted hydroxyl groups were observed in all the star-shaped oligomers, although the peak intensity decreased consistently with increase in the feed molar ratio. Resonances at 3.48 ppm in the ¹H NMR spectra showed the residual hydroxyls of pentaerythritol to vary between 15% for STAR-4000-OH and 21% for STAR-1000-OH. Similar results for the residual hydroxyls of pentaerythritol have been reported by Lang and Chu [29]. They concluded that, even at a feed molar ratio of ϵ -caprolactone monomer to pentaerythritol as high as 40:1, it is difficult to convert all four hydroxyls of pentaerythritol to PCL arms, and the final product is a mixture of three- and four-arm oligomers.

Carboxylic acid-terminated oligomers were obtained by conversion of the terminal hydroxyl end groups of the PCL

Table 1
Molecular weights and thermal properties of the hydroxyl-terminated oligomers.

Oligomer	Oligomer			NMR			SEC		DSC			State at room temperature	
	Co-initiator	Co-initiator (mol%)	Segment (theor.) (CL units)	M _n (theor.) (g/mol)	M _n (g/mol)	X ^a (%)	M _n (g/mol)	M _w (g/mol)	MWD	T _g (°C)	T _m (°C)		ΔH (J/g)
LIN-1000-OH ^b	BD	10	4.5	1120	1060	>99	2400	2800	1.2	-66	36	84	Waxy
LIN-2000-OH ^b	BD	5	9	2150	2130	>99	4600	5500	1.2	-62	48	85	Solid
STAR-1000-OH	PERYT	10	2.25	1160	1130	>99	1800	2600	1.4	-64	-1 & 16	38	Viscous liquid
STAR-1500-OH	PERYT	7.5	3	1510	1510	>99	2600	3600	1.4	-61	18 & 30	51	Waxy
STAR-2000-OH	PERYT	5	4.5	2190	2170	>99	3900	5500	1.4	-61	32 & 41	60	Solid
STAR-4000-OH	PERYT	2.5	9	4250	4270	>99	7100	11800	1.6	-61	46 & 51	70	Solid

^a Monomer conversion.

^b Abated from Ref. [25].

to carboxylic acid groups with succinic anhydride (SAH) or an alkenylsuccinic anhydride (ASA) containing 8 or 18 carbons in the alkenyl chain (Scheme 1, step two). An overview of the acid functionalizations is presented in Table 2. The chemical structures of the resulting carboxylic acid-terminated oligomers were confirmed from FTIR and NMR spectra. In the FTIR spectra, the original broad band for the hydroxyl absorption disappeared upon incorporation of the succinate, and the new broad peak at 3000–3500 cm^{-1} for carboxylic acid appeared. The degree of substitution (DS) was calculated from ^1H NMR spectra. Since the terminal hydroxyl group in the PCL chain is a primary hydroxyl, its reactivity with cyclic anhydrides is good [29]. Thus, the degree of substitution for all the acid-functionalized oligomers was over 96%.

The alkenyl chain of ASA can locate in two positions: next to the terminal carboxylic acid (c in Fig. 1) or next to the succinate ester group (b' in Fig. 1). Comparison of the values of the NMR spectra with calculated values (ACD labs) suggests that both alkenyl chain locations are present in the final oligomer (Fig. 1 a and b). Resonances for the two locations of the alkenyl chain were found more clearly in the ^{13}C NMR spectra. When the alkenyl chain is located at C next to the terminal carboxylic acid, the succinate carbons resonate at 41.24 ppm and at 34.90 ppm. In contrast, when the alkenyl chain is instead located at b', the succinate carbons resonate at 42.06 ppm and at 34.70 ppm. In addition, because the alkenyl chain is present in two different positions, the carbonyl in the terminal carboxylic acid gives two peaks, at 179.38 (d) and 177.15 ppm (d'), and the carbonyl of the succinate ester resonates at 174.20 (a') and 171.93 (a) ppm.

3.2. Thermal properties of oligomers

Depending on the molecular weight, the physical state of the hydroxyl-terminated oligomers varied from solid to viscous liquid. While the SAH functionalization did not markedly affect thermal properties of the linear oligomers, it lowered the crystallinities and melting temperatures of the star-shaped oligomers. Independently of the molecular architecture, the ASA functionalization decreased thermal transitions of the oligomers (Table 2). For example, the STAR-2000-0 had a melting temperature of 34 °C, whereas melting temperatures of 26 and 16 °C were measured for the STAR-2000-8 and STAR-2000-18 oligomers. Although the alkenyl chains of the ASAs lowered the crystallinities of the oligomers in general, the 18-ASA-substituted star-shaped oligomers showed increased crystallinity in the case of lower molecular weight oligomers. The crystallinity may be due to the 18 carbon alkenyl side chain being long enough to form crystalline structures.

The effect of the molecular architecture on the melting temperatures is presented in Fig. 2. With the same molecular weight, the average chain lengths of PCL segments are theoretically half as long in the star-shaped oligomers as in the linear oligomers. Due to the shorter segments, the melting temperatures of the star-shaped oligomers were 15–30 °C lower than linear oligomers of corresponding molecular weights. When the average chain lengths of

Table 2
Molecular weights and thermal properties of the acid-terminated oligomers.

Oligomer	Oligomer			NMR	SEC		MWD		DSC	T_m (°C)	ΔH (J/g)	State at room temperature
	Co-initiator	Co-initiator (mol%)	Segment (theor.) (CL units)		Alkenyl chain (carbons)	DS (%)	M_n (g/mol)	M_w (g/mol)				
LIN-1000-0 ^b	BD	10	4.5	0	>99	2900	3600	1.3	-56	38	58	Waxy
LIN-1000-8 ^b	BD	10	4.5	8	>99	2700	3400	1.3	-58	15	47	Viscous liquid
LIN-1000-18 ^b	BD	10	4.5	18	96	3200	4200	1.3	-57	10	43	Viscous liquid
LIN-2000-0 ^b	BD	5	9	0	>99	5000	6700	1.3	-57	50	83	Solid
LIN-2000-8 ^b	BD	5	9	8	>99	5100	6400	1.3	-57	33 & 42	65	Waxy
LIN-2000-18 ^b	BD	5	9	18	97	5600	7000	1.2	-57	30 & 40	65	Waxy
STAR-1000-0	PERY	10	2.25	0	>99	3100	4500	1.4	-51	-	-	Viscous liquid
STAR-1000-8	PERY	10	2.25	8	>99	3400	4700	1.4	-50	-	-	Viscous liquid
STAR-1000-18	PERY	10	2.25	18	>99	4800	7000	1.4	-50	19	42	Viscous liquid
STAR-1500-0	PERY	7.5	3	0	>99	3700	5600	1.5	-50	-	-	Viscous liquid
STAR-1500-8	PERY	7.5	3	8	>99	4100	5500	1.3	-51	-	-	Viscous liquid
STAR-1500-18	PERY	7.5	3	18	99	5200	8100	1.5	-53	17	39	Viscous liquid
STAR-2000-0	PERY	5	4.5	0	>99	5300	7800	1.4	-53	34	50	Waxy
STAR-2000-8	PERY	5	4.5	8	99	5700	7600	1.3	-54	26	14	Waxy
STAR-2000-18	PERY	5	4.5	18	98	6900	10200	1.5	-53	16	34	Viscous liquid
STAR-4000-0	PERY	2.5	9	0	>99	9000	16100	1.7	-53	43 & 49	60	Solid
STAR-4000-8	PERY	2.5	9	8	98	10000	14500	1.5	-54	46	54	Solid
STAR-4000-18	PERY	2.5	9	18	96	11300	18300	1.6	-56	45	49	Solid

^a Not detected.

^b Adapted from Ref. [25].

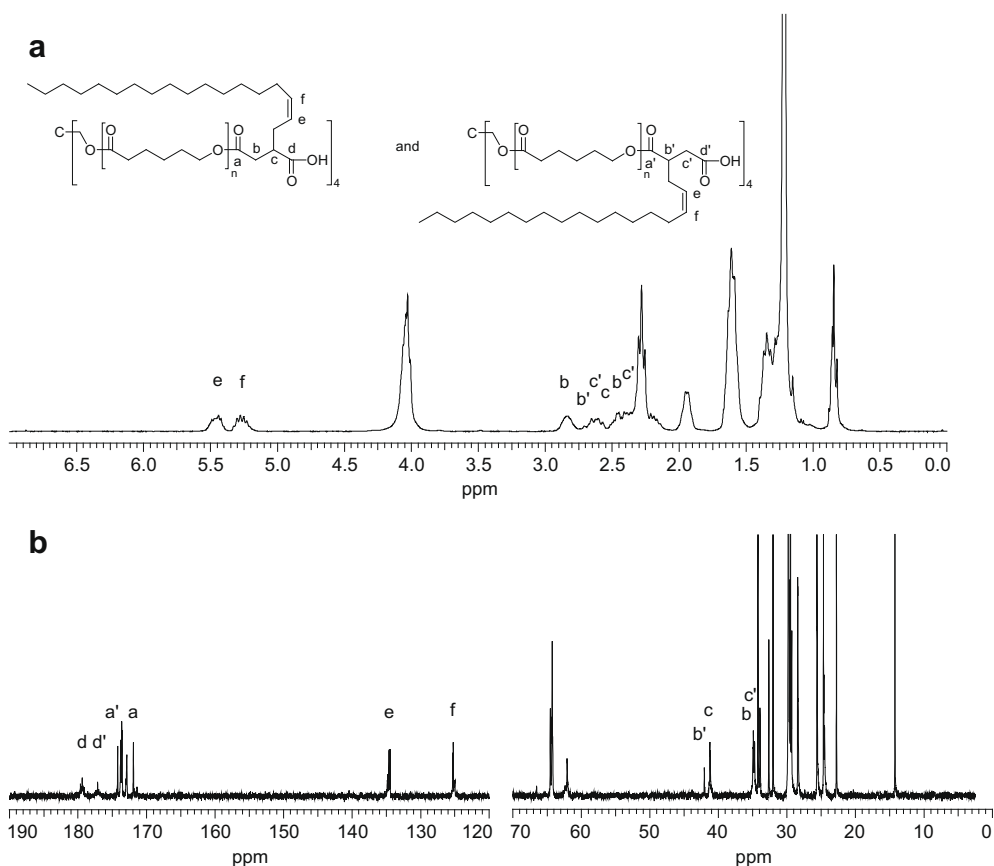


Fig. 1. ¹H NMR (a) and ¹³C NMR (b) spectra of 18-ASA-functionalized STAR-1000 oligomers.

the PCL segments in the star-shaped and linear oligomers were the same (STAR-4000 and LIN-2000), the melting temperatures of the oligomers were nearly the same.

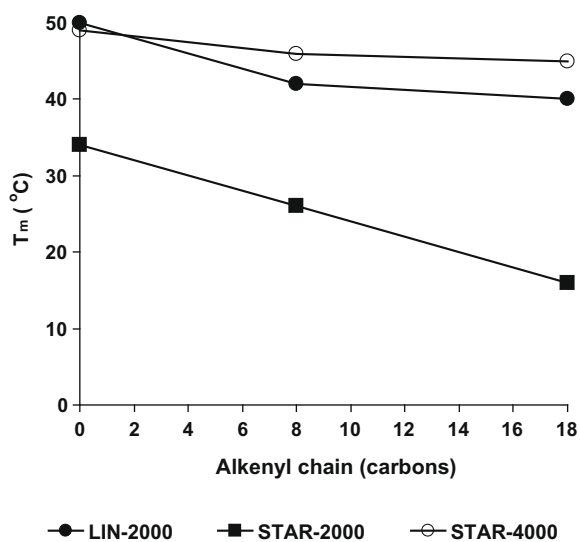


Fig. 2. Melting temperatures as a function of alkenyl chain length of SAH-, 8-ASA- and 18-ASA-functionalized oligomers with different molecular weight and architecture.

3.3. Hydrophobicity of oligomers; immersion study

Mass loss and water absorption are useful measures of the hydrophobicity of biodegradable polymers. The highest molecular weight SAH- and ASA-functionalized oligomers showed virtually no mass loss in 28 days. These oligomers had melting temperatures above the measuring temperature of 37 °C. Furthermore, water absorptions were at the same level (less than 9%) for the oligomers during the 28 day test period. The differences on the hydrophobicity of the acid-functionalized high molecular weight (STAR-4000 and LIN-2000) oligomers could not be detected therefore.

Differences between the SAH-functionalized and ASA-functionalized oligomers were observed when the molecular weight of the oligomer was halved. Mass losses of the acid-functionalized STAR-2000 oligomers are shown in Fig. 3a. The SAH-functionalized STAR-2000-0 oligomer exhibited 65% mass loss in 7 days. However, no mass loss was observed for the 8-ASA-functionalized oligomer in 7 days, nor for the 18-ASA-functionalized oligomer in 28 days, even though these viscous liquid samples had melting temperatures below 37 °C. Similarly to the STAR-2000-0 oligomer, the LIN-1000-0 oligomer with corresponding PCL segment length dissolved almost completely within 3 days, while the oligomers containing alkenyl chain did not exhibit any mass loss in 7 days.

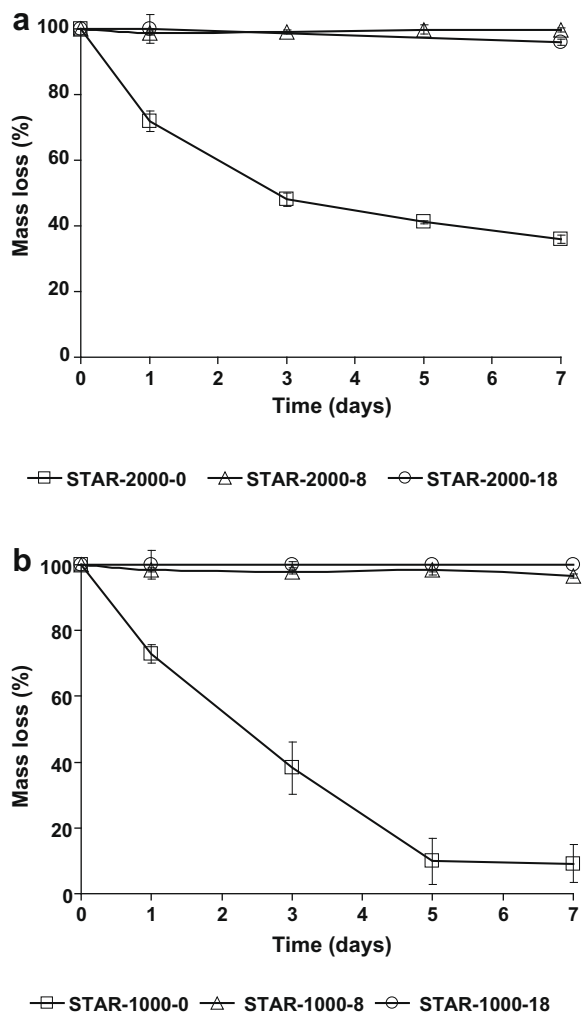


Fig. 3. Mass loss of SAH-, 8-ASA- and 18-ASA-functionalized STAR-2000 (a) and STAR-1000 (b) oligomers.

The same trend was observed for the lowest molecular weight oligomers as seen in Fig. 3b for STAR-1000 oligomers. Preservation of the mass of the 8-ASA-functionalized and the 18-ASA-functionalized samples indicated increase of the hydrophobicity, evidently due to the presence of the hydrophobic alkenyl chains. However, owing to the viscous liquid state of the oligomers, the samples could not be removed from the test tubes, and the water absorptions of the oligomers could not be quantitatively measured.

3.4. Hydrophobicity of oligomers; contact angle measurements

As noted above, immersion studies are the usual approach for the estimation of hydrophobicities of biodegradable polymers. In this study, however, most of the oligomers had melting temperatures below 37 °C, and after their immersion, the determination of water absorption was not possible. Since the immersion results did not

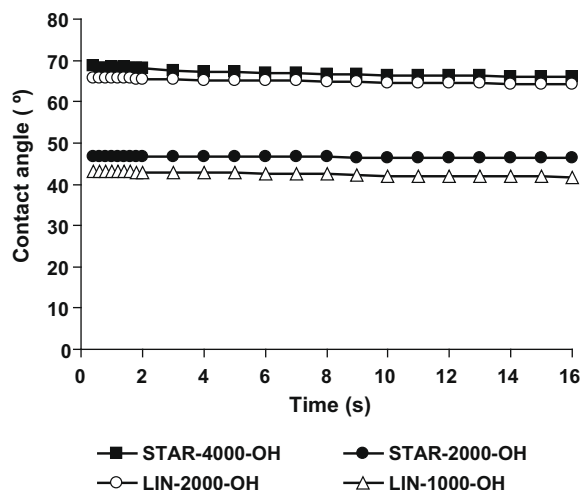


Fig. 4. Contact angles of linear and star-shaped hydroxyl-terminated PCL oligomers with different molecular weights.

reveal differences between 8- and 18-ASAs, the effect of alkenyl chain length on the hydrophobicity of the oligomers was instead studied by contact angle measurements. Water contact angles were measured for star-shaped oligomers with different molecular weights. In addition, linear oligomers of corresponding molecular weights were studied to determine whether there is a significant difference in the hydrophobicities between different molecular architectures.

Fig. 4 shows the contact angles as a function of time for hydroxyl-terminated oligomers with different molecular weights. As expected, the contact angles increase when the molecular weight increases. For example, the equilibrium contact angle for the LIN-1000-OH oligomer was 42°, and the angle increased to 64° when the molecular weight was doubled in the LIN-2000-OH oligomer. Toselli et al. [30] obtained similar results. They state that the contact angles of PCL oligomers increase with the molecular weight. They also report an advancing contact angle of 40° for a PCL oligomer of similar molecular weight to our LIN-1000-OH oligomer which had contact angle of 42°. Fig. 4 shows also the effect of the molecular architecture to contact angles. The contact angle of LIN-2000-OH was 64°, whereas that of STAR-2000-OH with the same molecular weight but double the amount of polar hydroxyl end groups was 46°. Comparison of oligomers with same PCL segment length (LIN-2000-OH and STAR-4000-OH) shows the contact angles to be at the same level despite the half lower molecular weight of the star-shaped oligomer. Numata et al. [31] report similar results for poly(lactides): the contact angle values of linear and branched PLLA oligomers increase with the molecular weight, and the contact angles of linear and branched PLLAs with same segment length are almost identical.

The relation between the physical state of the oligomers and the contact angle values is seen in Fig. 5, where contact angle curves are presented as a function of time for LIN-1000 oligomers. Fig. 5 shows that there is only a slight difference between the instantaneous and equilibrium

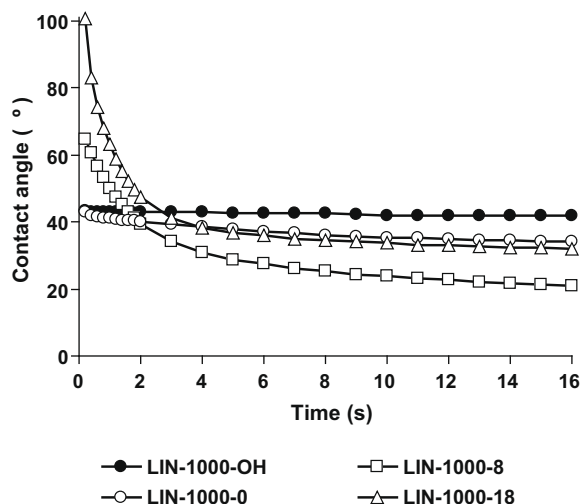


Fig. 5. Contact angles of hydroxyl-terminated, and SAH-, 8-ASA- and 18-ASA-functionalized LIN-1000 oligomers.

contact angles of the waxy LIN-1000-OH and LIN-1000-0 oligomers, and the contact angle versus time curve is linear. In contrast, the alkenyl chain containing oligomers appeared as viscous liquids, and the instantaneous contact angles of the ASA-functionalized oligomers are noticeably higher than those of the hydroxyl-terminated and SAH-functionalized oligomers. However, the contact angle curves fall off sharply at the beginning of the measurement until the equilibrium contact angle is reached. Apparently, when the viscous film of ASA-functionalized oligomers gets in contact with water the initial hydrophobicity decreases owing to the rearrangement of the oligomers into more energetically favorable conformation in the viscous film [32]. This strongly suggests that the equilibrium contact angles are comparable to each other only when the oligomers appear in the same physical state.

The effect of alkenyl chain length on hydrophobicity can be seen clearly in Fig. 6, which presents contact angle

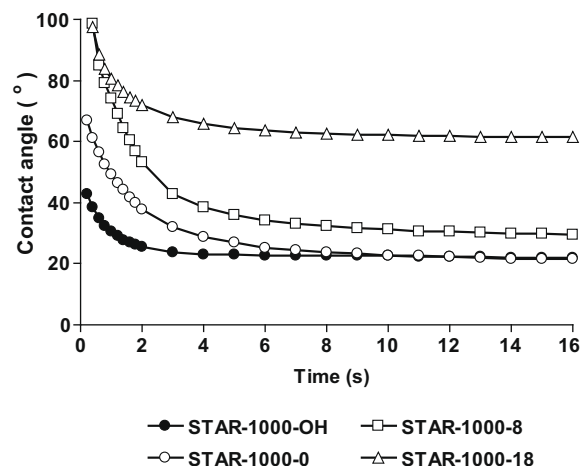


Fig. 6. Contact angles of hydroxyl-terminated, and SAH-, 8-ASA- and 18-ASA-functionalized STAR-1000 oligomers.

curves for STAR-1000 oligomers. In this case, all the oligomers were at the same physical state, and thus the results are comparable. The hydroxyl-terminated and SAH-functionalized oligomers (i.e., oligomers without alkenyl chain) had an equilibrium contact angle of 20° showing that the acid functionalization without alkenyl chain did not considerably affect equilibrium contact angles. However, adding 8 or 18 carbon alkenyl chain to the oligomers clearly increased the contact angles. When 8 carbon alkenyl chain was introduced, the equilibrium contact angle increased to 30°, and when more hydrophobic 18 carbon alkenyl chain was present, the angle increased further to 60°. Park et al. [33] have similarly reported increased contact angles of cured epoxy resins with increase of the alkenyl chain length of ASAs, and Chi et al. [24] have reported an increase in the contact angle of starch from 43° even to 123° when starch is functionalized with dodecyl succinic anhydride (i.e., with ASA containing a 12 carbon alkenyl chain).

In addition to the alkenyl chain length, the molecular weight and the molecular architecture of the oligomers had a clear effect on the contact angles. Fig. 7 shows the contact angles of the ASA-functionalized oligomers with different molecular architectures. Due to the higher concentration of hydrophobic alkenyl chains, the star-shaped oligomers had considerably higher contact angles than their linear counterparts with the same molecular weight: the contact angle of the STAR-1000-18 with double the amount of hydrophobic 18 carbon alkenyl chains was 62°, whereas that of the LIN-1000-18 was 32°. In comparison of the oligomers with the same PCL segment length, the STAR-2000-18 with double the molecular weight had higher equilibrium contact angle of 42° than the LIN-1000-18 that exhibited contact angle of 32°.

An overview of the instantaneous and equilibrium contact angles of all the oligomers are shown in Fig. 8a and b. The physical state of the oligomers affected the difference between instantaneous and equilibrium contact angles, i.e., contact angles of the viscous liquids decreased during the measurement time of 16 s. This caused that, unlike instantaneous contact angles, the equilibrium contact an-

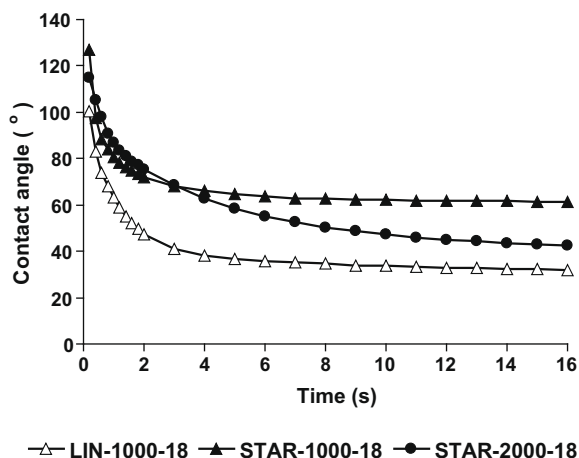


Fig. 7. Contact angles of 18-ASA-functionalized STAR-1000, STAR-2000 and LIN-1000 oligomers.

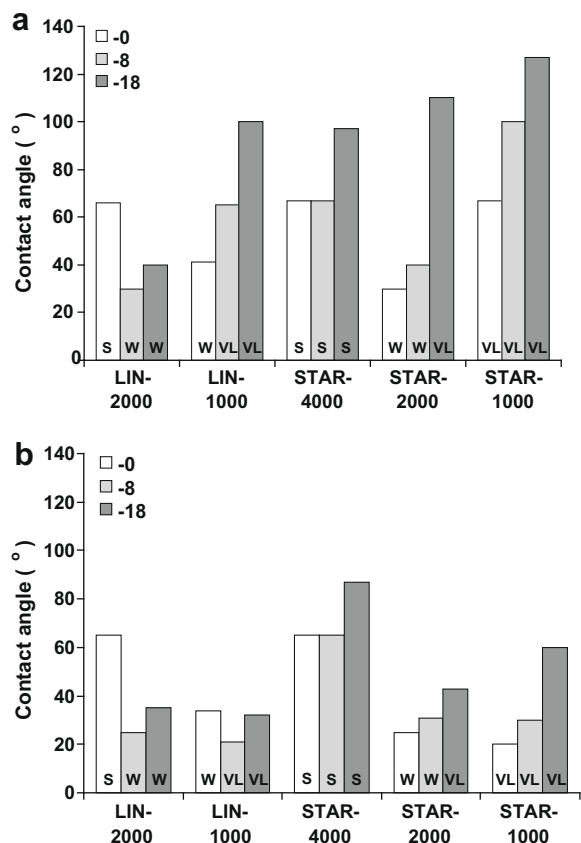


Fig. 8. Instantaneous (a) and equilibrium (b) contact angles of SAH-, 8-ASA- and 18-ASA-functionalized linear and star-shaped PCL oligomers. Physical states of the oligomers are denoted as S for solid, W for waxy and VL for viscous liquid.

gles were higher for the solid STAR-4000 oligomers than for the lower molecular weight STAR-1000 oligomers, which had high concentration of hydrophobic alkenyl chains but appeared in the form of viscous liquids. In general, however, ASA functionalization increased instantaneous and equilibrium contact angles. The increase in contact angle with length of the alkenyl chain is seen in every case, independently of the molecular weight: the 18-ASA-functionalized oligomers show considerably higher contact angles than the corresponding 8-ASA-substituted oligomers. Similarly, in the case of the lower molecular weight oligomers with high alkenyl chain concentration, the 8-ASA-functionalized oligomers exhibit higher contact angles than the SAH-functionalized oligomers.

4. Conclusions

Hydrophobicities of poly(ϵ -caprolactone) oligomers were modified by functionalization with succinic anhydride or with alkenylsuccinic anhydrides containing alkenyl chains of 8 or 18 carbons. The effect of the alkenyl chain length on the hydrophobicity of the star-shaped oligomers and their linear counterparts was investigated by

immersion studies and measurements of water contact angles. In comparison with the succinic anhydride functionalized oligomers, higher hydrophobicities were measured for the alkenyl chain containing oligomers. In particular, the contact angles increased considerably with lengthening of the alkenyl chain from 8 to 18 carbons. These hydrophobically modified oligomers can be used as additives or precursors for biodegradable polymers, where tailoring the hydrophobicity of the oligomers will provide a way to modify and tailor degradation rates.

Acknowledgment

This work has been carried out within the Bio- and Nanopolymers Research Group, which is funded by the Academy of Finland (CoE program code number 211493).

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