

Hydrolysis behaviour of crosslinked poly(ester anhydride) networks prepared from functionalised poly(ϵ -caprolactone) precursors

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ABSTRACT

Biodegradable poly(ester anhydride) networks based on functionalised poly(ϵ -caprolactone) precursors with different hydrophobicities, molecular weights and architectures were synthesised. Networks that were prepared from the star-shaped precursors clearly showed higher gel contents and crosslinking densities than the networks that were prepared from the linear precursors. Functionalising with different alkenylsuccinic anhydrides and/or varying the molecular weight of the precursor, the thermal properties, surface hydrophobicity and erosion of the crosslinked networks were widely tailored. The dissolution behaviour of the networks changed dramatically as the molecular weight of the precursor increased from 2000 to 4000 g/mol or the alkenyl chain of the alkenylsuccinic anhydride increased from 8 to 18 carbons. The networks that were prepared from the lower molecular weight precursors, without an alkenyl chain or with an 8 carbon alkenyl chain, lost their mass in a few days, whereas the networks that were prepared from higher molecular weight precursors or contained a hydrophobic 18 carbon alkenyl chain did not show any mass loss over a period of 8 weeks.

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1. Introduction

Crosslinking is an attractive route for synthesising biodegradable polymers and provides an effective tool for tailoring the thermal, mechanical, and degradation properties [1–3]. The properties of the final network can be easily altered by varying the chemical composition and structure of the network precursors [3–6]. For example, the thermal properties of the crosslinked poly(ϵ -caprolactones) can be controlled by the chain length of the precursor and/or copolymerisation with other monomers, such as lactides [7,8]. The properties of the networks can also be modified by varying the molecular architecture; for example, precursors that have more and shorter arms exhibit a greater crosslinking density and, usually, higher mechanical strength [9]. Furthermore, Uto et al. [10] have modified the properties of ϵ -caprolactone-based crosslinked networks using a combination of two different molecular architectures, i.e., linear and star-shaped precursors. As a result, the mixing ratios could modulate the transition temperature of the crosslinked materials.

Various strategies have been examined for preparing highly crosslinked biodegradable networks [6]. The most popular studied methods have been via free-radical curing with heat and/or radiation of hydrolytically degradable precursors containing acrylic [11], methacrylic [12], fumaric [13], maleic [14], or itaconic [15]

double bonds. Among the curing methods, photo-initiated crosslinking has many advantages, such as fast crosslinking rates, mild reaction conditions and easy control of the reaction by controlling the light source [16]. However, for photo crosslinking, the viscosity of the crosslinkable material should be low. Thermal crosslinking is easily applied to materials that sustain heat and are highly viscous or even solid at room temperature. In addition, thermal crosslinking is suitable for very thick specimens or complex structures, where the absorption and scattering of the polymerising light is restricted [17].

Tailoring the degradation of biodegradable polymers is a key factor for several applications [16]. The degradation mechanism of biopolymers is commonly divided into bulk and surface erosion [18]. In bulk erosion, the degradation process proceeds homogeneously throughout the entire polymer sample, whereas in surface erosion, the degradation process occurs at the surface, and the sample decreases as the degradation proceeds [19]. In general, polyester networks show bulk erosion, whereas polyanhydride networks are commonly known to erode from the surface. The degradation mechanism and the rate of degradation can be controlled by the number and/or type (e.g., ester, amide, and anhydride) of degradable chemical bonds in each precursor, the molecular weight of the precursor, and the hydrophilic/hydrophobic nature of the precursors [16]. For example, Anseth et al. [17,20] prepared crosslinked polyanhydrides and observed that the degradation time of these networks can be adjusted to between 2 days and 1 year by varying the network composition. The mass loss of these

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crosslinked polyanhydrides increased linearly with time, which supports a surface-erosion-type mechanism [21].

Previously, we have altered the degradation mechanism of crosslinked poly(ϵ -caprolactone) networks from bulk to surface erosion by adding anhydride bonds to the network precursors [22]. Because these poly(ester anhydride) networks rapidly eroded, for the next study, we slowed the erosion of the networks slightly by functionalising precursors with hydrophobic alkenylsuccinic anhydrides (ASAs) [23,24]. In this work, our aim is to further slow the erosion of these functionalised poly(ester anhydride) networks by increasing the molecular weights of the precursors. Increasing the molecular weight of the precursor affects network properties, such as thermal transitions, hydrophobicity and crosslinking density, which all affect the erosion of the networks. The main objective of the present study was to slow the hydrolytic degradation while maintaining the surface erosion mechanism of the crosslinked poly(ester anhydrides). These types of surface eroding polymers are suitable for several medical applications, such as controlled drug delivery and tissue engineering.

2. Experimental section

2.1. Materials

The ϵ -caprolactone (CL) was purchased from Solvay Interlox, Ltd. (Warrington, England) and was redistilled and dried over molecular sieves. Stannous octoate (SnOct_2 , 95%), (+/-)-2-octen-1-ylsuccinic anhydride (8-ASA, 97%), methacrylic anhydride (MAAH, 94%), and dibenzoyl peroxide (DBPO, 50%) were purchased from Sigma-Aldrich (Steinheim, Germany). Pentaerythritol (PERYT, 98%), 1,4-butanediol (BD, 99+%), and succinic anhydride (SAH, 99+%) were purchased from Acros Organics (Geel, Belgium). *n*-Octadecylsuccinic anhydride (18-ASA, mixture of isomer) was purchased from Tokyo Kasei Organic Chemicals (Zwijndrecht, Belgium). All chemicals, except ϵ -caprolactone, were used as received.

2.2. Synthesis of poly(ester anhydride) precursors

The acid-functionalised linear and star-shaped ϵ -caprolactone-based oligomers were prepared using methods reported in our previous work [23,24] and are denoted as LIN-2000-8 or STAR-2000-8, where LIN and STAR indicate a linear and star-shaped molecular architecture, 2000 indicates the molecular weight of the hydroxyl-terminated oligomer (molecular weight before acid-functionalisation), and 8 indicates the alkenyl chain lengths of 8 carbons. Crosslinkable poly(ester anhydride) precursors that have labile anhydride bonds were obtained by allowing the acid-terminated oligomers to react with methacrylic anhydride (MAAH). The methacrylated precursors are indicated by an m at the end of precursor denotation (LIN-2000-8m or STAR-2000-8m).

2.3. Crosslinking of poly(ester anhydride) precursors

The crosslinking of the methacrylated ϵ -caprolactone-based precursors was performed by thermal initiation. The methacrylated precursors were heated to 60 °C, and 2 wt.% of DBPO was added. At 60 °C, all of the functionalised network precursors were in the liquid state and the DBPO could be added to the reaction mixture. The mixture was stirred until homogeneity was achieved and was then applied to a mould to obtain discoids (2 mm in thickness, 6 mm in diameter and ~50 mg in weight). The precursors were cured in the mould for 1 h at 120 °C to produce crosslinked networks. The networks are indicated by an nw at the end of the network denotation (LIN-2000-8nw or STAR-2000-8nw).

2.4. Characterisation

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (MWD) of the methacrylated precursors were determined with respect to polystyrene standards using size exclusion chromatography (SEC). A Waters Associates system was equipped with a Waters 717plus Satellite autosampler, a Waters 510 HPLC solvent pump, four linear PL gel columns (10⁴, 10⁵, 10³, and 100 Å) connected in series, and a Waters 2414 differential refractometer. All samples were analysed at room temperature. Chloroform (Riedel-de Haën Ag, stabilised with 1% ethanol) was used as the eluent and was delivered at a flow rate of 1.0 ml min⁻¹. The samples were dissolved in chloroform to a concentration of 0.1% (w/v). The injection volume was 200 μ l. All samples were analysed at room temperature.

NMR spectra were recorded on a Varian Gemini 2000 300 MHz spectrometer. For the ¹H NMR measurements, the samples were dissolved in chloroform-d₁ (Fluka Chemica) with deuteration at no less than 99.8%, in 5-mm NMR tubes, at room temperature. The sample concentration was approximately 1.0% by weight. The ¹³C NMR measurement was performed with a 10% sample concentration in 10-mm tubes. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet Magna-FTIR spectrometer 750 with 2 cm⁻¹ resolution. The precursor samples were dissolved in chloroform at a concentration of 0.1% (w/v) and film-cast onto a NaCl slide, whilst the crosslinked samples were measured using KBr disks, and the amount of the sample in the disks was 1 wt.%.

Differential scanning calorimetric (DSC) measurements were performed using a Mettler Toledo Star^e DSC 821^e. For the methacrylated precursors, the first heating (to avoid premature crosslinking) was run from -100 to 60 °C, and the second heating was run from -100 to 200 °C. In both cases, the heating and cooling rates were 10 °C min⁻¹. Both of the ramps for the crosslinked samples were run from -100 to 200 °C, and the heating and cooling rates were also 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.

For the crosslinked samples, the isolated weight (m_{iso}) was determined before the extraction and swelling tests. The swelling and extraction experiments were performed in dichloromethane at room temperature using three parallel specimens. A sample discoid was swollen for 24 h, the surface was carefully dried, and then the discoid was weighed (m_{sw}). After drying at room temperature under reduced pressure for 1 week, the sample was weighed again (m_{dry}). The gel content (G) was calculated using the following equation:

$$G = \frac{m_{\text{dry}}}{m_{\text{iso}}} \quad (1)$$

The degree of swelling (Q) of the polymer networks in dichloromethane was calculated as follows [25]:

$$Q = 1 + \rho_p \cdot \left(\frac{m_{\text{sw}}}{m_{\text{dry}} \cdot \rho_s} - \frac{1}{\rho_s} \right) \quad (2)$$

where ρ_s and ρ_p are the specific densities of the solvent (1.326 g cm⁻³ for dichloromethane) and the polymer, respectively. The density of amorphous poly(ϵ -caprolactone) (1.094 g cm⁻³) was used as ρ_p for the crosslinked polymer samples [25].

The water contact angles of the different networks were determined from the surface of the crosslinked discoids. A CAM 200 contact angle goniometer (KSV Instruments, Ltd.) was used for determining the static contact angles of sessile drops at room temperature. Ultra-high quality (UHQ) water in equilibrium with air (prepared using ELGA PURELAB UHQ) was used. The size of the water drop was 7 μ l in air. The contact angles were calculated by

Table 1
Properties of the methacrylated poly(ester anhydride) precursors.

	Precursor				¹³ C NMR DS (%)	Theoretical M_n (g/mol)	SEC ^a			State at room temperature
	Type of co-init. ^b	Amount of co-init. (mol-%) ^c	Theoret. segment length (units) ^d	Alkenyl chain length (carbons) ^e			M_n (g/mol)	M_w (g/mol)	MWD	
LIN-2000-0m	BD	5	9	0	97	2480	5600	7200	1.3	Solid
LIN-2000-8m	BD	5	9	8	98	2700	6300	7800	1.2	Waxy
LIN-2000-18m	BD	5	9	18	98	2980	7600	10,800	1.4	Waxy
STAR-1500-0m	PERYT	7.5	3	0	94	2180	6300	9900	1.6	Visc. liquid
STAR-1500-8m	PERYT	7.5	3	8	99	2620	5500	7200	1.3	Visc. liquid
STAR-1500-18m	PERYT	7.5	3	18	98	3180	8400	13,800	1.6	Visc. liquid
STAR-2000-0m	PERYT	5	4.5	0	95	2860	7100	11,100	1.6	Waxy
STAR-2000-8m	PERYT	5	4.5	8	98	3300	7000	9500	1.4	Visc. liquid
STAR-2000-18m	PERYT	5	4.5	18	98	3860	9300	15,100	1.6	Visc. liquid
STAR-4000-0m	PERYT	2.5	9	0	97	4920	12,900	20,100	1.6	Solid
STAR-4000-8m	PERYT	2.5	9	8	99	5360	11,500	16,600	1.4	Waxy
STAR-4000-18m	PERYT	2.5	9	18	98	5920	14,300	22,500	1.6	Waxy

^a M_n and M_w are the number-average and weight-average molecular weights, respectively, and were determined with respect to polystyrene standards by SEC.

^b Type of co-initiator, BD = 1,4-butanediol, PERYT = pentaerythritol.

^c Amount of the co-initiator (mol-%).

^d Theoretical ϵ -caprolactone segment length of the precursor (ϵ -caprolactone units).

^e Amount of the carbons in the alkenyl chain.

Table 2
Properties of the crosslinked poly(ester anhydride) networks.

Oligomer	Methacrylated precursor (m)			Crosslinked network (nw)				
	T_g (°C)	T_m (°C)	ΔH (J/g)	T_g (°C)	T_m (°C)	ΔH (J/g)	Gel content (%)	Swelling degree (%)
LIN-2000-0	-59	41	76	-55	43	72	8.9 ± 0.2	800 ± 150
LIN-2000-8	-60	36	45	-52	42	55	13.5 ± 0.1	2000 ± 160
LIN-2000-18	-63	35	56	-53	40	51	48.7 ± 2.8	2200 ± 140
STAR-1500-0	-61	-	-	-46	-	-	94.4 ± 0.9	450 ± 20
STAR-1500-8	-62	-	-	-46	-	-	96.3 ± 0.7	360 ± 10
STAR-1500-18	^a	-4	35	^a	6	20	95.4 ± 0.8	360 ± 10
STAR-2000-0	-62	22	32	-51	-	-	96.1 ± 0.9	460 ± 20
STAR-2000-8	-63	19	5	-52	-	-	98.0 ± 0.5	360 ± 10
STAR-2000-18	-63	-14	22	-53	5	17	95.1 ± 0.8	360 ± 10
STAR-4000-0	-64	41	46	-52	41	40	95.5 ± 0.6	640 ± 30
STAR-4000-8	-62	41	41	-52	38	35	97.8 ± 0.1	470 ± 10
STAR-4000-18	-63	38	40	-53	36	33	96.6 ± 0.7	470 ± 10

^a Not detected.

the crosslink density. Changing the molecular architecture of the precursor from being linear to star-shaped had a clear increasing effect on the gel content of the crosslinked networks. The gel contents of the networks that were prepared from star-shaped precursors were all greater than 94%, whereas the networks that were prepared from linear precursors were all under 50% (Table 2). The amount of methacrylate end groups was higher for the star-shaped precursors, and this may be the reason for the more effective crosslinking. Increasing the molecular weight of the precursor or adding the alkenyl chain did not have an effect on the degree of crosslinking.

Due to the variation in gel contents, the swelling degrees of the networks that were prepared from the linear precursors (LIN-2000) varied from 800% to 2200% and were thus unreliable and incomparable to each other. The networks that were prepared from the star-shaped precursors had high gel contents and a low degree of swelling (360–640%). Similarly, Lendlein et al. [25] report, for networks that were crosslinked from poly(ϵ -caprolactone)-based dimethacrylates, that when the gel contents are high (94%), the degree of swelling values are low (between 410% and 490%). This result indicates high crosslinking densities. As expected, when the molecular weight of the precursor is decreased from 4000 to 2000 or 1500 g/mol, the swelling degree of the networks also

decreases. This decrease was clearly due to the shorter poly(ϵ -caprolactone) arms, which makes the network denser.

3.3. Thermal properties of poly(ester anhydride) precursors and networks

The thermal properties of the methacrylated precursors and the crosslinked networks were investigated using DSC. The results are reported in Table 2. In all of the DSC measurements, the first heating period was used to erase the effects of any previous thermal history, and the second heating period was used for evaluating the thermal properties. The methacrylation of the acid-terminated linear oligomers (LIN-2000) lowered both the glass transition temperatures (T_g 's) and melting transitions and changed the physical state of the oligomers at room temperature to be less viscous. Although the gel contents of the crosslinked networks that were prepared from the linear precursors were low, the crosslinking increased the T_g by 4–10 °C and the T_m by 2–6 °C and changed the state from a waxy precursor to a solid network. In addition, there was no residual reactivity detected for the networks in the first heating to 200 °C, further indicating that all of the double bonds have reacted, and 1 h at 120 °C was sufficient for thermal crosslinking.

When the structure of the precursor was changed from linear to star-shaped, the crosslinking likewise increased the T_g by approximately 10 °C. The network that was formed from the lowest molecular weight star-shaped precursors (STAR-1500) had higher T_g 's than the networks that were formed from the largest precursors (STAR-4000). The increase in the T_g from –53 to –46 °C, as the molecular weight of the precursor decreased from 4000 to 1500 g/mol, is clearly related to the higher crosslinking density at a low molecular weight because the distance between the crosslinks decreases and the poly(ϵ -caprolactone) chains become more tightly connected to each other. The presence of the alkenyl chains, regardless of the molecular weight of the precursor, did not have a marked effect on the T_g 's of the crosslinked networks.

In general, an increase in the molecular weight of the precursors changed the networks from being amorphous to semi-crystalline. In addition to the molecular weight of the precursor, the addition of the alkenyl chain had clear effects on the melting transitions of the networks. Melting transitions were only observed for networks that were prepared from the highest molecular weight precursors (STAR-4000) and for networks containing an 18 carbon alkenyl chain, i.e., STAR-2000-18nw and STAR-1500-18nw (Table 2). The networks that had been prepared from the lower molecular weight precursors likely had poly(ϵ -caprolactone) chains that were too short to crystallise and were amorphous, whereas the 18 carbon alkenyl chain was apparently long enough to crystallise. A similar crystallisation of the alkenyl chain has been reported for stearyl side chains [27,28]. As shown in Fig. 1, for the networks that were crosslinked from the higher molecular weight precursors, the alkenyl chain decreased the melting temperatures and enthalpies. For example, STAR-4000-0nw exhibited a T_m of 41 °C, and adding 8 and 18 carbon alkenyl chains further decreased the T_m to 38 and 36 °C, respectively. The melting enthalpies similarly decreased from 40 J/g to 35 and 33 J/g. Lower T_m and ΔH values have also been observed for thermoplastic poly(ϵ -caprolactone)-based poly(ester anhydride) polymers containing alkenyl chains [29].

3.4. Surface hydrophobicity of crosslinked poly(ester anhydride) networks

The surface hydrophobicities of all of the crosslinked poly(ester anhydride) networks, which were measured using the sessile drop contact angle method, are presented in Fig. 2. In addition to crosslinking, the alkenyl chain and the molecular weight of the star-shaped precursor had clear effects on the contact angles of the crosslinked networks. In the networks that were crosslinked from the highest molecular weight precursors (STAR-4000), the 8 carbon alkenyl chain had no effect on the contact angle value, whereas the more hydrophobic 18 carbon alkenyl chain increased the contact

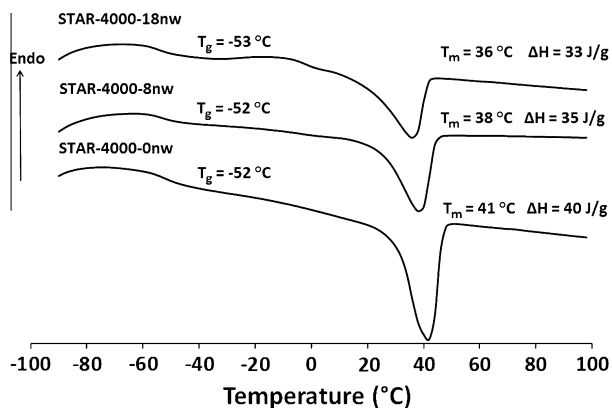


Fig. 1. The DSC curves of the STAR-4000 networks prepared from SAH-, 8-ASA-, and 18-ASA-functionalised star-shaped poly(ester anhydride) precursors.

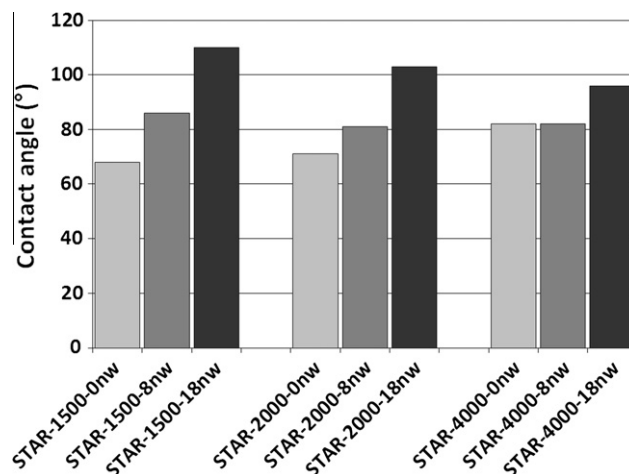


Fig. 2. The contact angles of the networks prepared from SAH- (light shaded), 8-ASA- (dark shaded), and 18-ASA-functionalised (black) star-shaped poly(ester anhydride) precursors.

angle from 82° to 96°. When the molecular weight of the precursor was halved (STAR-2000), the 8 carbon alkenyl chain was hydrophobic enough to increase the contact angle from 71° to 81°, whilst the more hydrophobic 18 carbon alkenyl chain further increased the contact angle to 103°.

Furthermore, in the networks crosslinked from the lowest molecular weight precursors (STAR-1500), the short 8 carbon alkenyl chain was hydrophobic enough to increase the contact angle even more, from 68° to 86°. This effect might be due to the high proportion of 8 carbon alkenyl chains relative to the short ϵ -caprolactone chains. An increase in the alkenyl chain length to 18 carbons increased the contact angles to 110°. The contact angle of 110°, which was observed for the STAR-1500-18nw network, is clearly higher than the contact angle of the crosslinked poly(ϵ -caprolactone) di- and triacrylates, which has been reported to be between 52° and 77° [11], or thermoplastic high molecular weight poly(ϵ -caprolactone) thin polymer films, which has been reported to be 78° [30]. Finally, the surface hydrophobicity of the crosslinked poly(ester anhydride) networks can be easily controlled by the molecular weight of the precursor and with different alkenylsuccinic anhydrides.

3.5. Dissolution studies of crosslinked poly(ester anhydride) networks

Based on the obviously lower degree of crosslinking, the networks that were prepared from the linear precursors (LIN-2000) were not studied in the dissolution test. During the dissolution studies, no change in pH was observed. The mass losses of the crosslinked networks that were prepared from the lowest molecular weight (STAR-1500) precursors are shown in Fig. 3. The networks without an alkenyl chain lost all of their mass in 2 days. The addition of the 8 carbon alkenyl chain increased the hydrophobicity of the networks and prolonged the mass loss for 1 day. The water absorptions were between 5% and 15%. The samples exhibited clear signs of surface erosion: a linear mass loss but an almost intact core. However, during the erosion of the STAR-1500-8nw samples, the degradation products were not completely soluble in the buffer but formed a very fine powder that turned the buffer solution cloudy.

The erosion of the most hydrophobic networks, i.e., the networks prepared from the lower molecular weight precursors containing an 18 carbon alkenyl chain (STAR-1500-18nw), was clearly different from that of the networks that were prepared from the corresponding SAH and 8-ASA-functionalised precursors. The STAR-1500-18nw networks did not show any mass loss in 8 weeks.

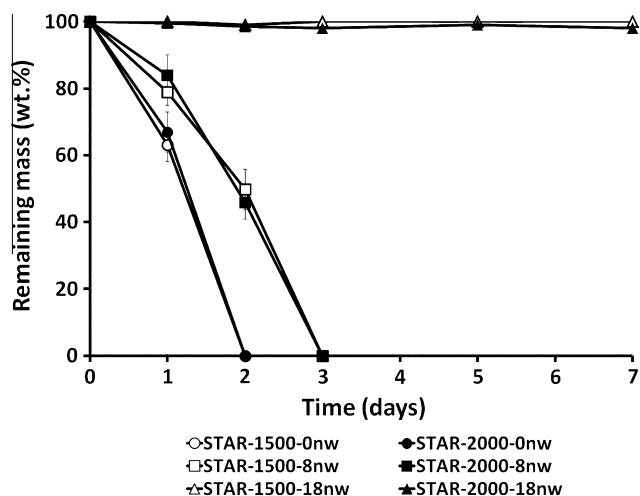


Fig. 3. The mass loss of the poly(ester anhydride) networks prepared from low molecular weight star-shaped precursors: STAR-1500-0nw (○), STAR-1500-8nw (□), STAR-1500-18nw (△), STAR-2000-0nw (●), STAR-2000-8nw (■), and STAR-2000-18nw (▲).

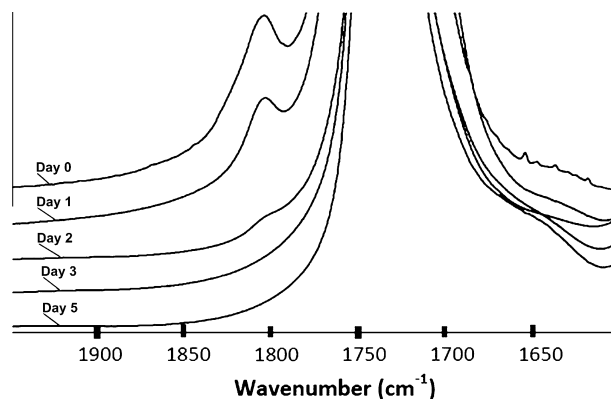


Fig. 4. The FTIR spectra of the anhydride bond at 1815 cm^{-1} of the STAR-1500-18nw network exposed to PBS for different times.

However, the discs lost their shape to an undefined structure, and the water absorptions could not be measured. Despite the increased hydrophobicity, according to the FTIR spectra, the anhydride bond at 1815 cm^{-1} disappeared in 3 days, as shown in Fig. 4 for the STAR-1500-18nw sample. We obtained similar results in our previous study of the thermoplastic poly(ester anhydrides) prepared from 18-ASA-functionalised linear oligomers [29]. Mass loss does not occur because the hydrophobic degradation products do not dissolve in the buffer solution. Göpferich et al. [31] have also reported, for poly(anhydride) copolymers consisting of a fatty acid dimer and sebacic acid, that poorly soluble degradation products can accumulate on the surface of the crosslinked discs. An increase in the molecular weight of the oligomer from 1500 to 2000 g/mol, i.e., a lengthening of the poly(ϵ -caprolactone) chain, did not have an effect on the erosion times, and the STAR-2000 networks eroded similarly (Fig. 3). This observation was clearly due to the similar hydrophobicity and thermal properties of the networks. Furthermore, both networks were prepared from oligomers and precursors that had melting temperatures under the dissolution temperature of $37\text{ }^\circ\text{C}$ [23].

However, a further increase of the molecular weight of the oligomer to 4000 g/mol had a clear effect on the melting transitions and thus on the mass loss and erosion behaviour of the crosslinked networks. The mass losses of the STAR-4000 networks are presented as

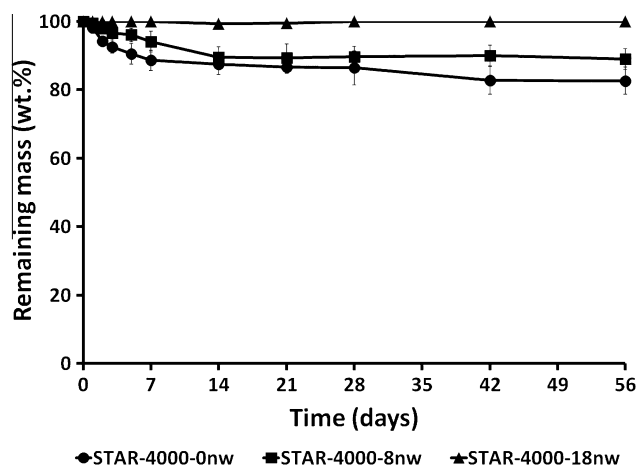


Fig. 5. The mass loss of the poly(ester anhydride) networks prepared from SAH- (●), 8-ASA- (■), and 18-ASA-functionalised (▲) STAR-4000 precursors.

a function of time in Fig. 5. While the STAR-2000-0nw and STAR-2000-8nw discs eroded from the surface in a couple of days, the doubling of the precursor molecular weight dramatically changed the dissolution behaviour; the STAR-4000-0nw and STAR-4000-8nw lost only 15–20% of their mass in 8 weeks. As expected, the STAR-4000-18nw network did not show any mass loss in 8 weeks. Although the mass loss was small, the samples lost their shape and the water absorptions could not be reliably measured.

These results indicate that the mass loss of the crosslinked poly(ester anhydride) networks depends on the hydrophobicity and thermal properties of the prepolymers. The low mass losses of the networks that were prepared from higher molecular weight precursors were likely due to the melting temperatures of the degradation products, i.e., acid-terminated oligomers that form after the hydrolysis of the anhydride bonds. The melting temperatures of the oligomers were greater than $43\text{ }^\circ\text{C}$, which is above the dissolution study temperature of $37\text{ }^\circ\text{C}$ [23]. When the melting temperature of the degradation products is greater than the dissolution temperature, the mass loss of the sample requires hydrolysis of the ester bonds; therefore, the polyester blocks are short enough to dissolve into the buffer solution.

4. Conclusions

A change in the molecular structure of alkenylsuccinic anhydride (ASA) functionalised poly(ester anhydride) precursors, from linear to star-shaped, significantly increased the degree of cross-linking of the crosslinked networks. The surface hydrophobicity and thermal properties of the crosslinked networks can be widely tailored by changing the molecular weight of the precursor and by varying the alkenyl chain length of the ASA. The dissolution behaviour of the crosslinked networks clearly changed from surface erosion towards bulk erosion because the molecular weight of the precursor increased from 2000 to 4000 g/mol or as the length of the alkenyl chain increased from 8 to 18 carbons. The networks prepared from the lower molecular weight precursors, without an alkenyl chain or with an 8 carbon alkenyl chain, lost their mass linearly in a few days, whereas the networks that were prepared from higher molecular weight precursors or that contained a hydrophobic 18 carbon alkenyl chain did not show any mass loss in 8 weeks.

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