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Synthesis and Characterization of Photocurable Elastomers from Poly(glycerol-*co*-sebacate)

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ABSTRACT

Elastomeric networks are increasingly being investigated for a variety of biomedical applications including drug delivery and tissue engineering. However, in some cases, their preparation requires the use of harsh processing conditions (e.g. high temperature) which limits their biomedical application. Herein, we demonstrate the ability to form elastomeric networks from poly(glycerol-*co*-sebacate)-acrylate (PGSA) under mild conditions while preserving a wide range of physical properties. These networks presented a Young's modulus between 0.05 to 1.38 MPa, ultimate strength from 0.05 to 0.50 MPa and elongation at break between 42 and 189% strain, by varying the degree of acrylation (DA) of PGSA. The *in vitro* enzymatic and hydrolytic degradation of the polymer networks were dependent on the DA. The copolymerization of poly(ethylene glycol) (PEG) diacrylate with PGSA allowed for an additional control of mechanical properties and swelling ratios in an aqueous environment, as well as enzymatic and hydrolytic degradation. Photocured PGSA networks demonstrated *in vitro* biocompatibility as judged by sufficient human primary cell adherence and subsequent proliferation into a confluent monolayer. These photocurable degradable elastomers could have potential application for the encapsulation of temperature sensitive factors and cells for tissue engineering.

KEYWORDS

Photocurable polymer, degradable elastomer, tissue engineering, scaffold, PGS.

1. Introduction

The development of biodegradable elastomers has increasingly become important in biomedical applications. Elastomers have gained popularity because they can provide stability and structural integrity within a mechanically dynamic environment without irritation to the hosting tissues [1,2] whilst elastomers exhibit mechanical properties similar to that of soft tissues [2-5]. Biodegradable elastomers can be important materials for a wide variety of medical applications including drug-delivery and tissue regeneration, where (cell seeded) constructs are designed to aid or replace damaged or diseased tissue [2-4]. Examples of applications for elastomeric biodegradable biomaterials are small diameter vascular grafts [6,7] and nerve conduits [8-10]. Current biodegradable elastomers include poly(glycerol-*co*-sebacate) [2], poly(citric-*co*-diol) [4], star-poly-ε-caprolactone-*co*-D,L-lactide) [5,11], poly(tri-methylene carbonate-co-ε-caprolactone) [12], and poly(tri-methylene carbonate-*co*-D,L-lactide) [13].

We recently created a tough biodegradable elastomer, poly(glycerol sebacate) (PGS) which features robust mechanical properties and *in vitro* and *in vivo* biocompatibility [2, 14]. However, harsh conditions (>80 °C, <5 Pa) and long reaction times (typically >24 h) are required for its curing and thus limit the ability to polymerize directly in a tissue or to incorporate cells or temperature sensitive molecules. As such, there is an unmet need to develop alternative processing strategies to overcome the limitations of thermally processing PGS. One convenient strategy is the implementation of photopolymerization. This technique has been utilized for several decades in biomedical research and has become an integral method for *in situ* delivery of resins in the practice of dentistry [15-17]. Recently there has been great interest in using photopolymerization techniques to prepare polymeric networks for tissue engineering applications as well as for minimally invasive medical procedures [18,19]. To this end, acrylate groups have been included in polymers for participation in chemical crosslinking between polymer chains by photo-induced free-radical polymerization [11,20-22].

In this report, we describe the synthesis and characterization of a photocurable polymer based on the chemical modification of PGS with acrylate moieties (designated poly(glycerol-sebacate)-acrylate, or PGSA). PGSA can be cured rapidly (within minutes) at ambient temperatures to form polymeric networks with a wide range of mechanical properties and *in vitro* enzymatic degradation and hydrolysis profiles. Incorporation of poly(ethylene glycol)-diacrylate (PEG-DA) allowed for additional control of mechanical properties and swelling ratios in an aqueous environment. Initial experiments with photocured PGSA networks demonstrated *in vitro* biocompatibility by sufficient cell adherence and subsequent proliferation into a confluent cell monolayer.

2. Experimental

2.1 Synthesis of PGS-acrylate (PGSA)

All chemicals were purchased from Sigma-Aldrich (Milwaukee, WI, USA), unless stated otherwise. PGS was synthesized according to previously published methods [2]. Briefly, the PGS pre-polymer was synthesized by polycondensation of equimolar glycerol and sebacic acid (Fluka, Buchs, Switzerland) at 120 ^{o}C under argon for 24 h before reducing the pressure from 1 Torr to 40 mTorr over 5 h. The polycondensation was continued for another 24 h. This material was used without any further purification. The PGS pre-polymer was acrylated in the following manner: a flame-dried round-bottom flask was charged with PGS pre-polymer (20 g, with 78 mmol hydroxyl groups), 200 mL anhydrous dichloromethane, and 4-(dimethylamino)-pyridine (DMAP) (20 mg, 0.18 mmol). The reaction flask was cooled to 0 °C under a positive pressure of N_2. Acryloyl chloride (0.25 - 0.80 mol per mol hydroxyl groups on PGS pre-polymer) was slowly added parallel to an equimolar amount of triethylamine. The reaction was allowed to reach room temperature and was stirred for an additional 24 h. The resulting mixture was dissolved in ethyl acetate, filtered and dried at 45 ^{o}C and 5 Pa.

2.2 Polymer Characterization

^{1}H Nuclear Magnetic Resonance (^{1}H-NMR) spectra of the PGS pre-polymer and PGSA were recorded (Varian Unity-300 NMR Spectrometer). Chemical shifts were referenced relative to $CDCl_3$ at 7.27 ppm. The chemical composition was determined by calculating the signal integrals of –COC$\underline{H_2}$C$\underline{H_2}$-C$\underline{H_2}$- at 1.2, 1.5, 2.2 ppm for the sebacic acid, -C$\underline{H_2}$-C$\underline{H}$- at 3.7, 4.2 and 5.2 ppm for glycerol and –C$\underline{H}$=C$\underline{H_2}$ at 5.9 ppm, 6.1 ppm and 6.5 ppm for the protons on the acrylate groups. The signal intensity of the methylene groups of the sebacic acid (1.2 ppm) and the acrylate groups (average signal intensity of 5.9, 6.1 and 6.5 ppm) were used to calculate the degree of acrylation (DA). The molecular weight of the PGS pre-polymer and PGSA were determined by gel permeation chromatography (GPC) using THF on Styragel colums (series of HR-4, HR-3, HR-2, and HR-1, Waters, Milford, MA, USA).

2.3 Preparation and characterization of photocured PGSA

PGSA networks were formed by mixing PGSA with 0.1% (w/w) photoinitiator (2,2-dimethoxy-2-phenyl-acetophenone) and the polymerization reaction was initiated by exposure to ultraviolet light (ca. 4 mW/cm^2, model 100AP, Blak-Ray) for 10 minutes. Attenuated total reflectance- Fourier transform infrared spectroscopy (ATR-FTIR) analysis was performed on a Nicolet Magna-IR 500 spectrophotometer to confirm the crosslink reaction. For that purpose, thermally cured PGS and photocured PGSA slabs, PGS pre-polymer, and PGSA dissolved in chloroform were placed on top of a ZnSe crystal. The thermal properties of discs from thermally cured PGS, photocured PGSA (DA of 0.31 and 0.54) and photocured PGSA (DA = 0.34) containing 5% PEG diacrylate were characterized using differential scanning calorimetry (DSC, DSC Q 1000), for 2 cycles, within the temperature range of -90 ^{o}C and 250 ^{o}C using a heating/cooling rate of 10 ^{o}C per minute. Tensile tests were conducted using an Instron 5542 (according to ASTM standard D412-98a) on dog-bone-shaped polymer strips (115 × 25 × 1.2 mm) cut from photocured PGSA sheets. The photocured networks were first soaked in 100% ethanol for 24 h, and subsequently soaked in PBS for 24 h prior to mechanical testing. The strain rate

was 50 mm/min and all samples were elongated to failure. Sol content was measured by mass differential after incubating PGSA samples in 100% ethanol for 24 h. Swelling by hydration was measured by mass differential after incubating PGSA samples in PBS for 24 h. The mass density was measured with a pycnometer (Humboldt, MFG. Co.). The density and Young's modulus of the samples were used to calculate the crosslinking density and relative molecular mass between crosslinks (M_c) as described previously [2].

2.4 Copolymerization of PEG diacrylate and PGSA

Networks of PGSA-PEG diacrylate were prepared by mixing 10, 50, 90% (w/w) PGSA (DA= 0.34) with PEG diacrylate (M_w= 700 Da) including 0.1% (w/w) photoinitiator, followed by photopolymerization under UV light for 10 minutes. Poly(ethylene glycol) polymers were prepared from PEG diacrylate (liquid) containing 0.1% (w/w) photoinitiator, followed by photopolymerization. The swelling ratio in PBS was determined by mass differential.

2.5 In vitro degradation

Degradation rates via hydrolysis was measured by incubating sol-free samples (n = 4) of PGS, photocured PGSA (DA of 0.31 and 0.54), photocured PGSA containing 5% PEG diacrylate, in 20 mL of 0.1 mM NaOH at 37 ^{o}C. Samples were removed, washed in ddH_20, dried at 90 ^{o}C for 7 days and weighed again to determine mass loss. In the enzyme degradation study, these samples (n = 4) were degraded *in vitro* in PBS in the presence of bovine pancreatic cholesterol esterase (40 units/mL) and incubated at 37 ^{o}C. Samples were removed, washed in ddH_20, dried at 90 ^{o}C for 7 days and weighed again to determine mass loss.

2.6 In vitro cell attachment and proliferation

Primary human foreskin fibroblasts (HFF, ATCC, Manassas, VA, USA) were cultured in high glucose Dulbecco's Minimal Essential Medium (DMEM) supplemented with 10% (v/v) fetal bovine serum (Invitrogen), 100 μg/mL streptomycin (Invitrogen), and 100 U/mL penicillin (Invitrogen) (further denoted as growth medium), at 37 ^{o}C and 5% CO_2. Cells between passage four and six were harvested by using Trypsin 0.025%/EDTA 0.01% and quenched with an equal volume of growth medium to re-suspend the cells. Photocured PGSA (DA= 0.34) covered glass slides (diameter 18 × 1 mm, n = 3) were prepared by spincoating 20% (w/v) PGSA in dimethylsulfoxide (DMSO) at 3,400 RPM for 5 min followed by a 10 min UV polymerization. The photocured spin coated PGSA discs were incubated with growth medium in a 12-well plate for 4 h in order to remove photoinitiator, residual DMSO, and any unreacted monomers prior to seeding. Each disc was seeded with 5,000 cells/cm^2 using 2 mL of growth medium. The cell attachment was evaluated after the cell seeded constructs were lightly washed with PBS after 4 hours and cell density was assessed and compared to cell attachment on tissue cultured polystyrene (TCPS). Subsequently, at predetermined times, these cell cultures were washed with PBS, fixed with 4% formaldehyde solution for 10 min, and cell density was determined by counting cells from randomly picked equally sized areas (0.005 cm^2, n = 9). Phase micrographs of cells were taken at 10x magnification and cell perimeter and cell area were calculated using Axiovision software (Zeiss, Germany). For the cell morphology measurements, each data set consists of measurements of at least 100 cells across several images from randomly picked areas. Scanning electron microscope (SEM) images were taken after culture substrates were washed three times in PBS and fixed with 4% (v/v) paraformaldehyde in PBS. After rinsing with PBS buffer 3 times, the dishes were dehydrated in graded alcohols (50%, 70%, 80% 90%, 95% and 100%) and then air dried in HMDS. The samples were then sputter-coated with platinum and examined on a JEOL JSM-5910 scanning electron microscope.

3. Results and discussion

3.1 Polymer characterization

PGSA was prepared by the acrylation of PGS pre-polymer (**Figs.1A and 1B**). The PGS pre-polymer had a weight average molecular weight (M_w) of 23 kDa, a number average molecular weight (M_n) of 6.5 kDa as determined by GPC and a polydispersity index (PDI) of 3.5. The molar composition of the PGS pre-polymer was approximately 1:1 glycerol : sebacic acid as confirmed by ^{1}H-NMR analyses (**Fig. 2A**). The incorporation of acrylate groups was confirmed by ^{1}H-NMR by the appearance of the peaks at δ 5.9, 6.1 and 6.4 ppm (**Fig. 2B**). This was also confirmed by ATR-FTIR by the appearance of an absorption band at 1375 cm^{-1}, corresponding to the –CH stretching of the secondary alkyl group related to the acrylate groups [23] and known not to be present in poly(acryloyl chloride) [24]. (**Fig. 2C**). Typically, 66% of the acryloyl chloride added in the experiment was incorporated in the pre-polymer as calculated from signal intensities of ^{1}H-NMR (**Fig.1C**). PGSA with a DA between 0.17 and 0.54 was obtained. The ^{1}H-NMR data show that acryloyl chloride reacts preferentially with the hydroxyl groups of glycerol compared to the carboxylate groups of sebacic acid. This was confirmed by the increase of the signal integral at δ 5.2 ppm, corresponding to the resonance of protons from the tri-substituted glycerol and the decrease of signal integral at ca. δ 3.7 ppm, corresponding to the resonance of protons from mono-substituted glycerol (**Fig. 2A and B**) with the increment of the DA. ^{1}H-^{1}H COSY NMR and quantitative ^{13}C NMR analysis showed minimal (<5%) substitution of terminal carboxylate groups (data not shown). As determined by GPC analysis, the M_w of the PGSA remained unchanged after acrylation (data not shown). The PGSA pre-polymer is not soluble in aqueous solutions but is soluble in most organic solvents like ethanol, dimethyl sulfoxide, benzene, tetrahydrofuran, acetyl acetate, dichloromethane and dimethylformamide.

3.2 Characterization of photocured PGSA

The polymerization of PGSA using UV light in the presence of the photoinitiator 2-dimethoxy-2-phenyl-acetophenone yields elastomeric networks. ATR-FTIR analysis of all photocured PGSA

elastomers (**Fig. 2C and D**) showed typical absorption bands of hydroxyl (3500-3200 cm^{-1}) and ester groups (1800-1600 cm^{-1}) in the polymer backbone, as was observed for thermally cured PGS. The broad peak at 3475 cm^{-1} is assigned to hydrogen bonded hydroxyl groups, likely from free hydroxyl groups which are not modified by acryloyl chloride. The formation of a polymer network after photocuring of PGSA was confirmed by the increase of the band at 2930 cm^{-1}, corresponding to the vibration of alkyl groups, and the elimination of the band at 1375 cm^{-1}, known to be associated with acrylate groups [23].

The T_g of thermally cured PGS, photocured PGSA (DA= 0.31, 0.54) and photocured PGSA (DA= 0.34) containing 5% PEG diacrylate were respectively -28.1, -32.2, -31.1 and -31.4 ^oC. These results indicate that all polymers and copolymers are in a rubbery state at 37 ^oC.

Currently, the mechanical properties of thermally cured PGS and other similar polymers can be controlled by altering processing conditions, or by changing the molecular weight of the di-functional precursors [2,4]. The introduction of acrylate groups into the pre-polymer facilitated an additional level of control. Specifically, the Young's modulus and ultimate tensile strength of the photocured PGSA were linearly proportional to the DA (**Fig. 3A and B**) and no permanent deformations were observed after mechanical testing. The mechanical properties of the photocured PGSA spanned from soft to relatively stiff as determined by the tensile Young's modulus of the polymer, which varied from 0.05 MPa (DA= 0.17) to 1.38 MPa (DA= 0.54). This demonstrates the potential to achieve the mechanical compliance of for instance the peripheral nerve, which has a Young's modulus of approximately 0.45 MPa [25]. The ultimate tensile strength ranged from 0.05 MPa to 0.50 MPa (**Fig. 3B**) whereas the strain to failure of photocured PGSA ranged from 170% to 47.4% with increasing DA (**Fig. 3A**).

The degree of swelling of the elastomeric networks in ethanol and water ranged from 50-70% and 8-12%, respectively, and did not change appreciably as a function of DA (**Fig 3C**). The high degree of swelling in ethanol facilitates removal of unreacted monomers (sol content) or potential incorporation of specific factors. The low degree of swelling in water may help to maintain the mechanical properties once implanted. The sol content of the polymer decreased from 40% to <10% by increasing the DA

from 0.20 to 0.54 (**Fig. 3C**). This is likely due to the increasing number of new crosslinks between the polymer chains. The high sol content, which was achieved with a lower DA, may be unfavorable for *in situ* polymerization where unreacted acrylated macromers would diffuse into the surrounding tissue. The mechanical properties however, are linearly proportional to the DA and are correlated to the formation of new crosslinks within the polymer network and not to the unreacted macromers in the network.

The density of the photocured elastomers decreased slightly with increasing DA (**Table 1**), which is similar to other thermally cured elastomers in which the density is inversely proportional to the curing time [26]. The crosslinking density and relative molecular mass between crosslinks (M_c) were calculated using the density and Young's modulus of the samples (**Table 1**) as previously described [2]. By increasing the DA in photocured PGSA from 0.17 to 0.54, the crosslinking density increased from 6.4 to 185 mol/m^3 and the relative molecular mass between crosslinks decreased from 18 to 0.6 kDa.

3.3 Copolymerization of PGSA with PEG diacrylate

Another advantage of photocurable PGSA is that it can be easily combined with other acrylated precursors to achieve a wider range of material properties. As an example, we chose to copolymerize PGSA with PEG diacrylate (0.7 kDa), a hydrophilic non-degradable polymer. The effect on physical properties (Young's modulus, ultimate strength, elongation and swelling ratio in water) were studied of elastomers formed by changing the weight percentage of PEG diacrylate with PGSA (DA = 0.34) (**Fig. 4**). Specifically, by increasing the concentration of PEG diacrylate, the elongation ranged from 60 to 4%, Young's modulus from 0.6 to 20 MPa and ultimate strength from 0.270 to 0.890 MPa. The elastomer formed by the copolymerization of PEG diacrylate with PGSA (DA = 0.34) mixed with equal masses, 50:50 PGSA-PEG, showed a ten fold higher Young's modulus and ultimate strength than the 95:05 PGSA-PEG elastomer, while maintaining its elongation. Furthermore, the swelling behavior of

these networks could be tuned from 45% to 10% by changing the concentration of PEG diacrylate from 90% to 0%.

3.4 In vitro degradation of photocured PGSA

Previous studies have shown that the degradation of PGS *in vitro* is difficult to correlate with the *in vivo* degradation [2,14]. PGS degrades 15% in 10 weeks in PBS, whereas full degradation is observed after 6 weeks *in vivo*. Similar to PGS, PGSA (DA = 0.31) degraded only 10% after 10 weeks in PBS (data not shown). Given this discrepancy between *in vitro* degradation and *in vivo* degradation results, we performed *in vitro* hydrolysis and enzymatic degradation studies to examine the relative differences in mass loss over time between the different polymer networks. The polymer networks that were examined in these degradation studies were thermally cured PGS, photocured PGSA with two degrees of acrylation (low degree of acrylation, PGSA-LA (DA = 0.31) and high degree of acrylation, PGSA-HA (DA = 0.54)), and PGSA-PEG (PGSA-LA copolymerized with 5% PEG diacrylate).

In the enzyme degradation study, these polymers were degraded *in vitro* in PBS in the presence of bovine pancreatic cholesterol esterase (40 units/mL). Pancreatic cholesterol esterase has been shown to be identical to the esterases associated with macrophages that are known to degrade polyesters [27-29]. PGS and PGSA-LA showed mass loss over time, whereas PGSA-HA and PGSA-PEG did not. PGS degraded by 60% over 48 h, while PGSA-LA, which has a lower crosslinking density, only degraded by 40% (**Fig. 5A**). These results suggest that the alkyl cross-links formed in PGSA networks by the acrylate groups, may be less susceptible to cholesterol esterase than the polymer networks with only ester cross-links, as formed in PGS networks.

The hydrolysis study was performed in a sodium hydroxide (0.1 mM) solution as described previously [4,26]. The mass loss profile via hydrolysis of photocured PGSA-LA and PGSA-HA was similar to PGS (**Fig. 5B**). However, the absolute mass loss of PGSA-LA was significantly ($P < 0.01$) higher

compared to PGS and PGSA-HA in all time points. Interestingly, the rate of mass loss of PGSA-PEG was significantly ($P < 0.01$) lower compared to PGS and PGSA-HA and the mass loss revealed a more linear profile. Hence, copolymerization of PGSA-LA with 5% PEG diacrylate resulted in elastomers with similar mechanical properties (**Fig. 4**) as PGSA-HA, but showed a much slower degradation rate via hydrolysis when compared to photocured PGSA and PGS (**Fig. 5B**). These results show that the *in vitro* hydrolytic degradation rate of photocured PGSA can be decreased, independent of the initial mechanical strength.

3.5 In vitro cell adhesion and proliferation on photocured PGSA

Our initial *in vitro* biocompatibility study showed that the photocured elastomers support cell adhesion and proliferation: 59 ± 12% of the primary human foreskin fibroblasts seeded on photocured PGSA attached after 4 h, as compared to the attachment on tissue cultured polystyrene (TCPS), which we set at a 100%. The cells were viable, assessed by trypan blue staining, as only 1.4% (± 0.5%) of the cells were positive. The attached cells showed a relatively normal morphology, as displayed in **Fig. 6A-C**. **Fig. 6B** shows a detailed SEM image of cell spreading (F = fibroblast). Morphometric data revealed a similar cell surface area (*A*) as compared to the fibroblasts seeded on TCPS (**Fig. 6E**, $p > 0.05$). However, the circularity index (*C*) was less for the fibroblasts cultured on the PGSA as compared to TCPS (**Fig. 6F**, $p < 0.05$). There was more variety in the morphometric data of the fibroblasts cultured on the PGSA, leading to larger standard deviations than for the fibroblasts cultured on TCPS. The difference of cell attachment on PGSA and TCPS might be related to several factors including surface topography and protein adsorption on the material's surface. The attached cells on the PGSA however proliferated in a linear fashion, forming a confluent cell monolayer at day 12 (**Fig. 6D**). This shows that the *in vitro* biocompatibility of photocured PGSA allows for cellular attachment and subsequent proliferation into a confluent cell monolayer of primary human fibroblasts.

4. Conclusions

We synthesized novel biocompatible, elastomeric biomaterials that are rapidly polymerized at room temperature using UV photopolymerization. These elastomers contain functional hydroxyl groups and exhibit tunable mechanical properties. The liquid acrylated polymer precursor can be combined with other acrylated molecules to further control physical properties. The development of these novel elastomers could therefore lead to new materials for a variety of potential biomedical applications.

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FIGURE CAPTIONS

Figure 1. (A) Polycondensation of glycerol and sebacic acid, yielding the PGS pre-polymer. R represents H or polymer chain. (B) Acrylation of the pre-polymer (not all binding possibilities are shown). To simplify the scheme, 100% conversion is shown. The hydroxyl groups in the PGS are the preferred site of acrylation. The acrylation of carboxylic acid groups occurs to a much lesser degree. (C) Increasing the molar equivalent of acryloyl chloride increases the degree of acrylation linearly.

Figure 2. ^{1}H-NMR spectrum of (A) PGS pre-polymer and (B) PGSA. The sebacic acid and glycerol in the polymer matrix were identified at 1.2, 1.5, 2.2 ppm and 3.7, 4.2 and 5.2 ppm by hydrogens located on the carbons labeled 'a'-'e'. Vinyl groups located on the PGSA were identified at 5.9 ppm, 6.1 ppm and 6.4 ppm labeled 'f'-'i'. (C) ATR-FTIR spectra of PGS pre-polymer (Ci), PGSA (DA of 0.20) (Cii), PGSA (DA= 0.54) (Ciii), thermally cured PGS (Di), photocured PGSA (DA = 0.20) (Dii) and photocured PGSA (DA= 0.54) (Diii). The absorption band at 1375 cm^{-1} associated with acrylate groups (spectra in Cii and Ciii) disappeared after the photopolymerization reaction (spectra in Dii and Diii).

Figure 3. (A) Stress-strain curves of photocured PGSA elastomer from a representative experiment (n = 4). (B) Through increasing the degree of acrylation, the ultimate tensile strength and Young's modulus increased linearly. (C) Degree of swelling in ethanol and water, and sol content as a function of the degree of acrylation.

Figure 4. Copolymerization of PGSA (DA = 0.34) and PEG diacrylate (Mw = 700 Da) where PEG chains become incorporated as crosslinks within the PGSA network. Increasing the concentration of

PGSA decreases the Young's modulus, ultimate strength and swelling in water whereas the elongation increases.

Figure 5. (A) *In vitro* enzymatic degradation of PGS, photocured PGSA (DA= 0.31, 0.54) and PGSA (DA = 0.34 + 5% PEG diacrylate) in bovine cholesterol esterase (pH 7.2, 37 ^{o}C) (n=3) for 4, 8, 24 and 48 hours. (B) *In vitro* hydrolytic degradation of PGS, photocured PGSA (DA= 0.31, 0.54) and PGSA (DA = 0.34 + 5% PEG diacrylate) in NaOH (0.1 mM) (n=3) for 0, 1.5, 3, 4.5, and 6 hours at 37 °C.

Figure 6. (A) Representative SEM image of the confluent cell monolayer after 12 days culture on photocured PGSA (DA= 0.34). (B) Representative SEM image of a single fibroblast spreading (arrow) after 24 hours of culture on PGSA (DA= 0.34). F = fibroblast. (C) Representative phase-contrast image of the confluent cell monolayer after 12 days culture on photocured PGSA (DA= 0.34) (Black bar represents 100 micron). (D) Cell attachment and subsequent proliferation of primary human fibroblasts *in vitro* on photocured PGSA (DA = 0.34). (F) The cell area, *A*, in square microns after 24 hours of culture on PGSA or TCPS. Error bars represent standard deviation of the mean. P value > 0.05. (F) The circularity of non-confluent cells was calculated with the equation: $C = 4(\pi)A/P^2$, where *P* is the perimeter of the cell in microns and A is the area of the cell in square microns. Error bars represent standard deviation of the mean. * P value < 0.05.

Table 1. Physical and Mechanical Properties of PGSA Networks. Values are reported as mean followed by standard deviation in parenthesis.

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Figure 1

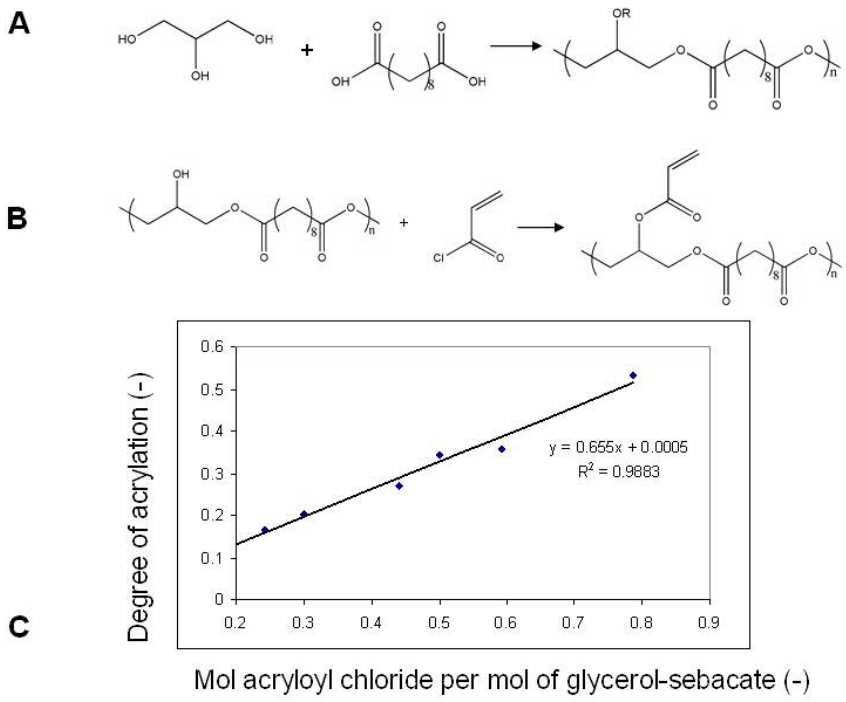
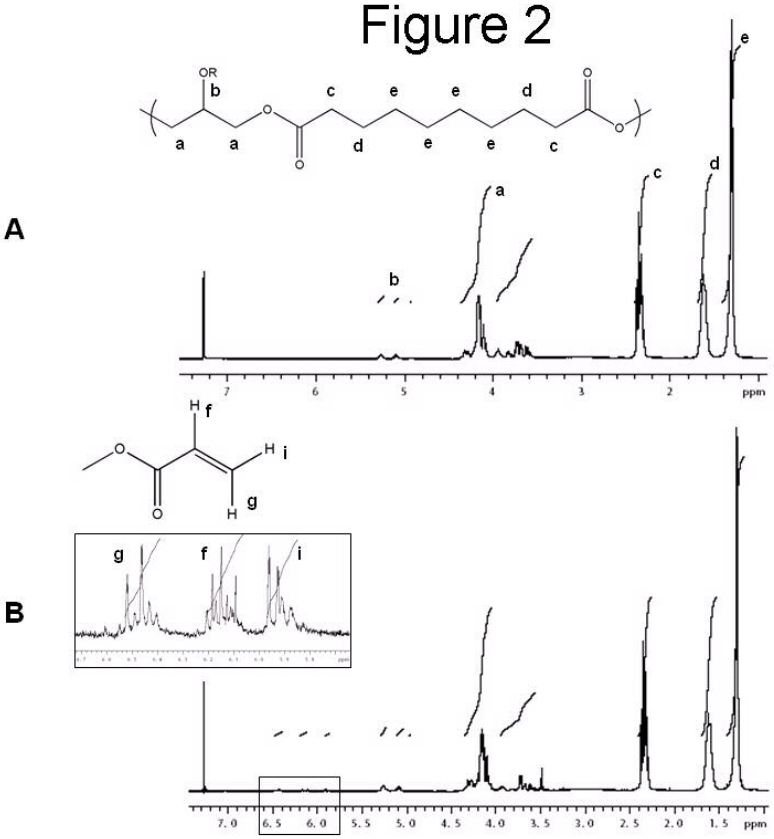


Figure 2



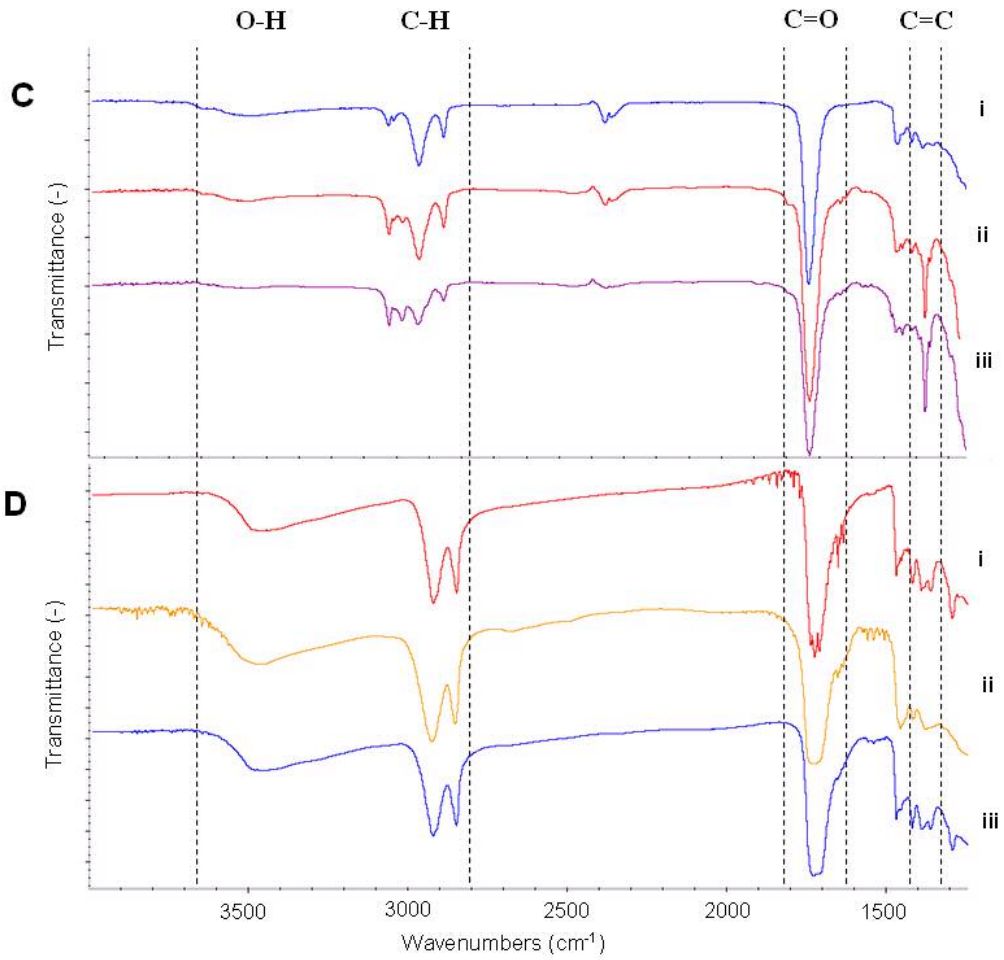


Figure 3

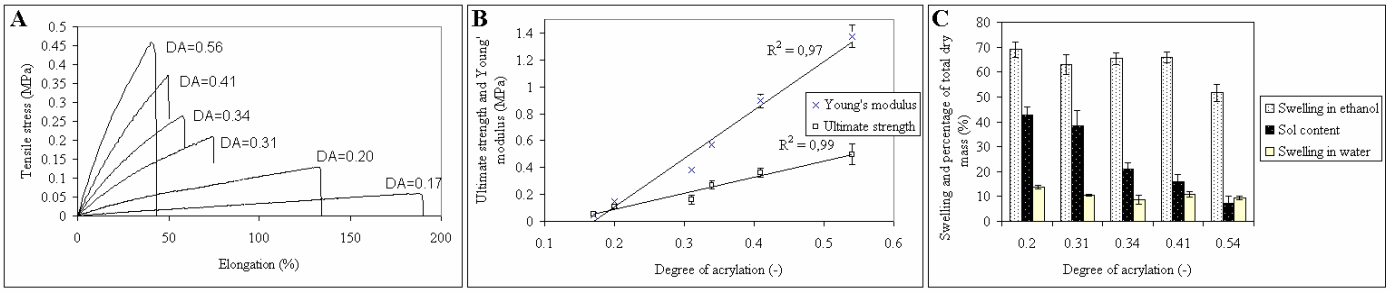


Figure 4

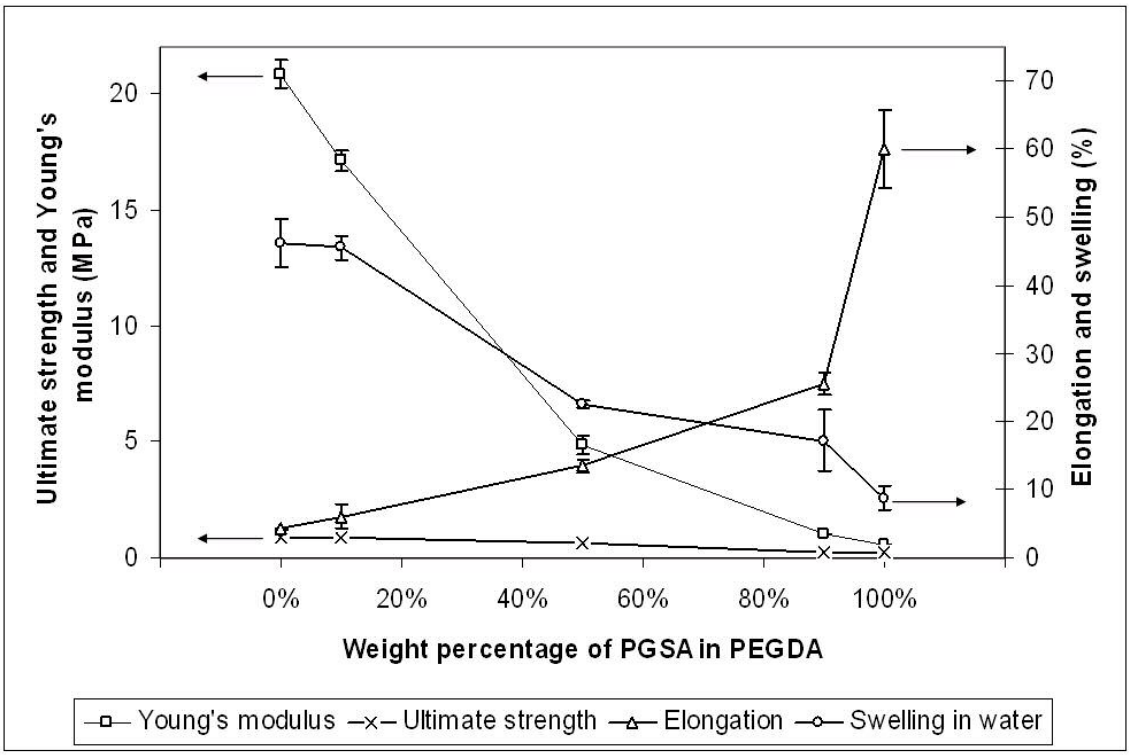


Figure 5

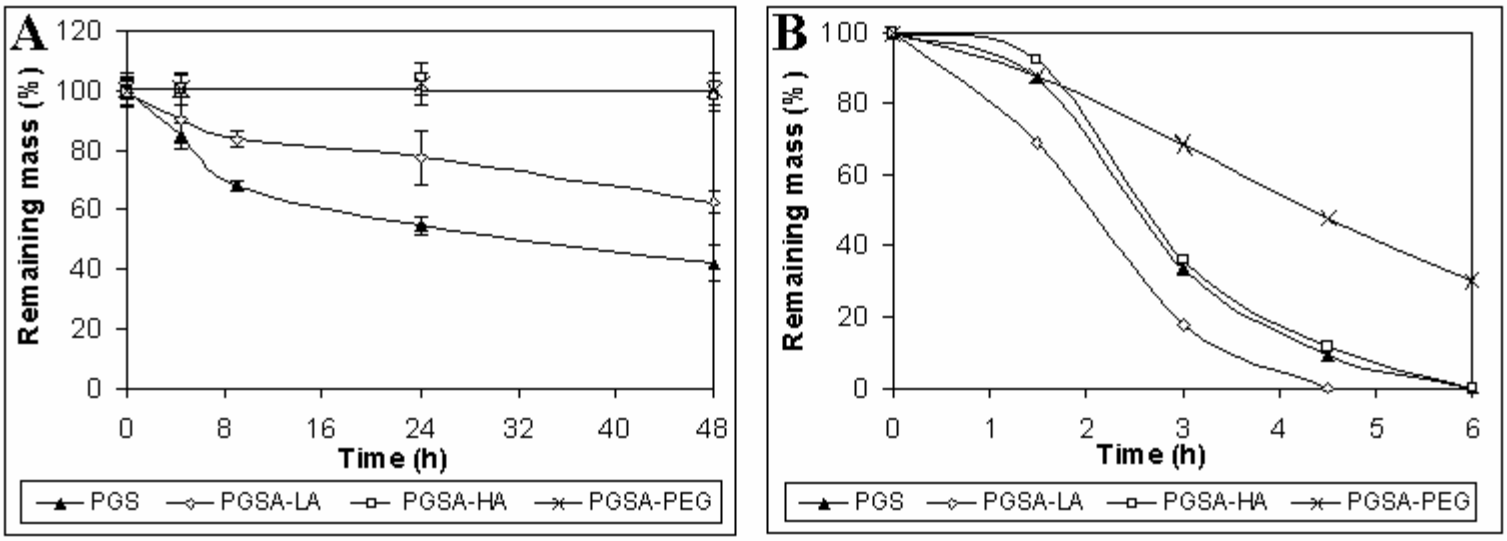
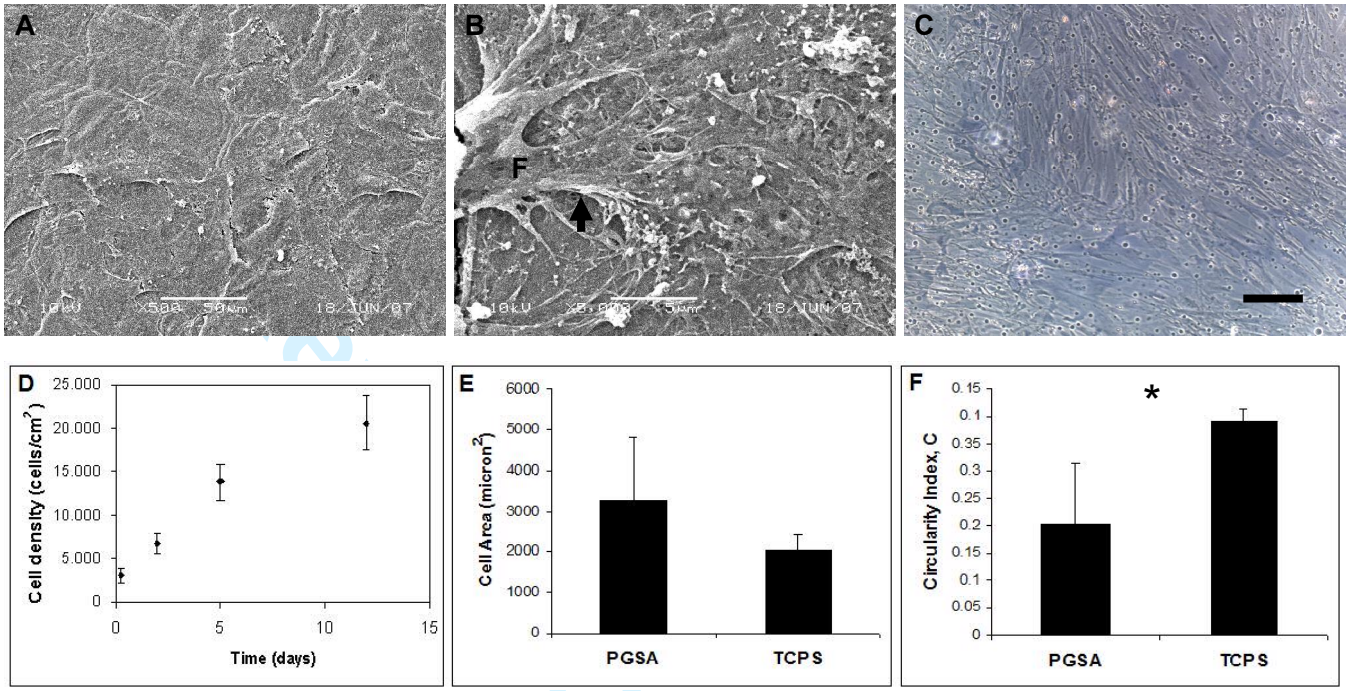


Figure 6



Degree of acrylation	Density (g/cm3)	Young's modulus (MPa)	Elongation (%)	Ultimate strength (MPa)	Crosslinking density (mol/m3)	Relative molecular mass between crosslinks (Mc) (g/mol)
0.17	1.21 {0.02}	0.048 {0.005}	170 {17.2}	0.054 {0.005}	6.4 {0.7}	18906 {232}
0.20	1.19 {0.02}	0.148 {0.004}	101 {26.5}	0.109 {0.011}	19.8 {0.6}	6013 {253}
0.31	1.16 {0.02}	0.383 {0.028}	54.7 {14.1}	0.163 {0.034}	51.5 {3.9}	2262 {185}
0.34	1.15 {0.01}	0.568 {0.222}	60.1 {5.73}	0.270 {0.032}	76.4 {3.0}	1514 {73.3}
0.41	1.15 {0.02}	0.895 {0.052}	51.1 {7.41}	0.364 {0.034}	120.4 {7.0}	953.9 {69.1}
0.54	1.15 {0.01}	1.375 {0.084}	47.4 {11.3}	0.498 {0.079}	185 {11.3}	620.1 {42.4}

Table 1

Table of Contents Graphic

Title: Synthesis and Characterization of Photocurable Elastomers from Poly(glycerol-co-sebacate)

Authors: Christiaan L.E. Nijst, Joost P. Bruggeman, Jeffrey M. Karp, Lino Ferreira, Andreas Zumbuehl, Christopher J. Bettinger, Robert Langer