Biosourced Amphiphilic Degradable Elastomers of Poly(glycerol sebacate): Synthesis and Network and Oligomer Characterization

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Supporting Information

ABSTRACT: Glycerol (G, a triol) and sebacic acid (S, an α,ω-dicarboxylic acid) were condensed in the bulk to obtain poly(glycerol sebacate) (PGS) cross-linked elastomers which were characterized in terms of their swelling, thermal, and mechanical properties. The soluble precursors to the elastomers were characterized in terms of their size, size distribution, and composition. In particular, G−S mixtures of five different compositions (molar G:S ratio = 2:1, 2:2, 2:3, 2:4, and 2:5) were copolymerized in the bulk at 120 °C in a three-step strategy (first step under inert gas atmosphere, followed by two steps in vacuo). When the G:S molar ratio was equal to (2:3) or close to (2:4), the stoichiometrically matched, network formation took place from the second condensation step, whereas three reaction steps were necessary for network formation far from stoichiometry, at G:S molar ratios equal to 2:2 and 2:5; at a G:S molar ratio of 2:1, no network formation was observed at all. Network composition also proved to be an important structural property, directly influencing the swelling and thermomechanical behavior of the elastomers. In particular, at the stoichiometrically matched G:S ratio of 2:3, corresponding to the cross-linking density maximum, the sol fraction extracted from the elastomers and the elastomer degree of swelling in aqueous media and in organic solvents presented a minimum, whereas the storage moduli of PGS elastomeric membranes in the dry state, measured within the temperature range between 35 and 140 °C, exhibited a maximum. The molecular weights of all soluble network precursors were found to be below 5000 g mol⁻¹ (gel permeation chromatography), containing but traces of oligomers (electron-spray ionization mass spectrometry). ¹H NMR spectroscopy indicated that the precursor composition was close to that expected on the basis of the G:S feed ratio and that monomer-to-polymer conversion increased from the first to the second condensation step.

INTRODUCTION

Amphiphilic conetworks (APCNs) represent a new class of cross-linked polymeric materials comprising hydrophilic and hydrophobic segments and sharing several of the attributes of hydrogels and surfactants.¹⁻⁴ Similar to surfactants,⁵,⁶ APCNs phase separate in selective solvents, aqueous or nonpolar, on the nanoscale to form polar and nonpolar domains delineated by a large interfacial area.⁷ Furthermore, similar to hydrogels,⁸,⁹ APCNs swell in water but also in nonpolar organic solvents, absorbing the appropriate solvent in the nanophase with which it is compatible; adsorption of solutes, polar and nonpolar, also takes place in a similar fashion within the respective domain.

The interconnection of the (linear) polymeric components to the final APCNs can be performed in different ways, securing various degrees of APCN structural perfection.¹⁰⁻¹³ These components have, most of the times, been addition polymers,¹⁻⁴ usually prepared by conventional free radical polymerization, but, more recently, also by controlled polymerization,¹⁴,¹³ leading to polymer segments of well-defined length. Given this progress in the homogeneity of network components, it may appear counterintuitive to pursue the synthesis of APCNs based on components prepared by condensation polymerization, whose products are less homogeneous in size, characterized by the “most probable” or Schulz−Flory molecular weight distribution. However, condensation polymers also come with other important attributes, most notably monomer sustainability¹⁶⁻¹⁸ and polymer biocompatibility, resulting in a broad spectrum of applications in the biomedical field.

An example of a condensation polymer that may represent an interesting APCPN system is poly(glycerol sebacate) (PGS),¹⁹,²⁰ prepared from the reaction of the hydrophilic triol glycerol with the hydrophobic dicarboxylic acid sebacic acid (1,10-decanedioic acid). Sebacic acid is produced from the alkaline thermolysis of ricinoleic acid (12-hydroxy-9-cis-octadecenoic acid), the main product of the saponification of castor oil, extracted from the seed of the tropical plant Ricinus communis.²¹ On the other hand, glycerol is obtained from the saponification of the...
of fats and oils (including that of castor oil). During the past 10 years, PGS networks received great attention by the scientific and medical community, as a result of their toughness, good flexibility, 2−26 biocompatibility, 27−30 biodegradability, 31−35 and cost-effective production. 20 Explored biomedical applications range from hard (bone) to soft (cardiac muscle, nerve, cartilage, and retina) tissue engineering, controlled drug delivery, and tissue adhesives. 20

Because of the great attention paid to their biological properties and applications, the physicochemical properties of the PGS elastomers have not yet been thoroughly explored. In this investigation, we aim to study the PGS physicochemical properties from the APCN point of view and also to analyze the size characteristics of the soluble PGS precursors. In particular, we prepared PGSs of five different compositions and characterized them as APCNs by exploring their swelling behavior in various organic solvents and in water at different pH values. The measurements in water indicated that the PGS elastomers were stable for (at least) 21 days under most conditions employed but also revealed extensive swelling and eventual hydrolysis and dissolution at pH > 8.5. Furthermore, a mass spectrometry study was performed on the PGS prepolymers which unveiled the size and relative abundance of the oligomers produced during the course of the condensation polymerization.

### EXPERIMENTAL SECTION

#### Materials

The main reagents used for the polymerizations were purchased from Aldrich, Germany. These were sebacic acid (S, 99%), glycerol (G, 99%), 1-octanol (99%), n-hexane (96%), a NaOH standard solution (0.5 M), and a HCl standard solution (0.5 M). Tetrahydrofuran (THF, 99.8%) was purchased from Scharlau, Spain, and was used as the mobile phase in chromatography (HPLC grade) and as a solvent (reagent grade) for the extraction of the sol fraction and the swelling measurements.

#### Polymer Synthesis

The synthesis of the PGS elastomers was performed using a three-step polycondensation reaction between S and G. 36 Five G:S molar ratios (2:1, 2:2, 2:3, 2:4, and 2:5) were used to prepare PGS elastomers of different cross-linking densities and compositions. The polymerization procedure for the synthesis of one polymerization step, a G:S molar ratio of 2:2, is detailed below. In the second reaction step, the cross-linked elastomer, with a G:S molar ratio of 2:2, is detailed below. In the last two (seventh and eighth) samples, 5 mL of deionized water was added (pH < 7) by the addition of small volumes of a 0.5 M NaOH standard solution (3, 6, and 9 drops). The pH values of these three samples ranged between 8 and 11. Two samples were acidic (pH < 7) by the addition of small volumes of a 0.5 M HCl standard solution (2 and 4 drops), and the last sample remained neutral (no acid or base was added to it), just the 5 mL of deionized water. The PGS elastomers were stable for (at least) 21 days under most conditions employed but also revealed extensive swelling and eventual hydrolysis and dissolution at pH > 8.5. Furthermore, a mass spectrometry study was performed on the PGS prepolymers which unveiled the size and relative abundance of the oligomers produced during the course of the condensation polymerization.

#### Elastomer Characterization. Determination of the Sol Fraction

To determine the mass of the dried extracted polymer to the measured dry mass of the elastomer. The dried extracts were finally characterized in terms of their MW, composition, and monomer conversion using GPC and 1H NMR spectroscopy, described previously.

The degree of swelling (DS) of the elastomers was calculated gravimetrically. First, the swollen samples of eight cubic samples (edge size 5−10 mm; each sample was in a separate glass vial) from each elastomer were measured after equilibration for 2 weeks in THF. Next, the dry mass of each sample was determined after removing the THF by placing all samples for 96 h in a vacuum oven at room temperature. Then, 5 mL of Milli-Q (deionized) water was added in the six vials. For each elastomer, three of its samples became alkaline by the addition of a 0.5 M NaOH standard solution (3, 6, and 9 drops). The pH values of these three samples ranged between 8 and 11. Two samples were acidic (pH < 7) by the addition of small volumes of a 0.5 M HCl standard solution (2 and 4 drops), and the last sample remained neutral (no acid or base was added to it), just the 5 mL of deionized water. The PGS elastomers were stable for (at least) 21 days under most conditions employed but also revealed extensive swelling and eventual hydrolysis and dissolution at pH > 8.5. Furthermore, a mass spectrometry study was performed on the PGS prepolymers which unveiled the size and relative abundance of the oligomers produced during the course of the condensation polymerization.

#### Dynamic Mechanical Thermal Analysis (DMTA)

For the dynamic mechanical thermal analysis (DMTA) measurements, a Tritec 2000 index (RI) signal was measured using an ERC-7515A RI detector supplied by Polymer Laboratories. The calibration curve was based on eight narrow MW (630, 2680, 4250, 13 000, 28 900, 50 000, 128 000, and 260 000 g mol−1) linear polyMMA standards also supplied by Polymer Laboratories. For each sample, the following quantities were calculated from GPC: the number-average MW, Mn, the polydispersity index (PDI = Mw/Mn, where Mw is the weight-average MW), and the peak MW, Mw, which is the MW at the peak maximum.

1H NMR Spectroscopy. The composition of the PGS prepolymers and the conversion of the minority groups were determined using proton nuclear magnetic resonance (1H NMR) spectroscopy. The spectra of the prepolymers in deuterated chloroform (CDCl3) were recorded using a 300 MHz Avance Bruker spectrometer equipped with an Ultrashield magnet, and the calibration was based on the signal from the residual protonated solvent (CHCl3) at 7.27 ppm. The resonances of the four methylene protons of S at 1.6 ppm and those of G in the range 3.6−4.4 ppm (3.6−3.9 ppm for the protons in non-esterified G and 4.1−4.4 ppm for methylene protons in esterified G) were used for the calculations.

ESI-Q iontrap-MS. The MWs of the PGS prepolymers were determined using a Bruker Daltonics HCT Ultra instrument equipped with an electrospray ionization (ESI) source, a quadrupole ion-trap (Q iontrap) mass analyzer, and mass spectrometer as mass detector. The PGS prepolymers were dissolved in THF at a concentration of 0.03 mg mL−1. A small amount of MeOH was added to the PGS solution for better ionization before introducing the samples into the instrument using an automatic syringe pump at a rate of 200 μL h−1. The spectra were obtained in positive mode.

#### Elastomer Characterization. Determination of the Sol Fraction (Extractables) of the Elastomers

The PGS elastomers with G:S molar ratios of 2:3 and 2:4 (henceforth referred to as PGS 2:3 and PGS 2:4, respectively) were removed from the polymerization flasks after breaking the flasks, and they were transferred to glass bottles and were washed in 300 mL of THF for 1 week (swelling equilibrium is attained within 2−3 days, as confirmed by gravimetric measurements) to extract the sol fraction. The THF solution of the sol fraction was then separated from any elastomer pieces by filtration and was collected, and the solvent was removed using a rotary evaporator. The recovered polymer was placed in a vacuum oven at room temperature for 72 h to completely dry it. The sol fraction was calculated as the ratio of the mass of the dried extracted polymer to the measured dry mass of the elastomer. The dried extracts were finally characterized in terms of their MW, composition, and monomer conversion using GPC and 1H NMR spectroscopy, as described previously.

Elastomer Characterization. Determination of the Degree of Swelling (DS) of the Elastomers

The DSs of all the elastomers were measured in pure water, in aqueous solutions of various pHs covering the range between 2 and 11, and also in THF, n-hexane, and 1-octanol. The DSs were calculated as the ratio of the swollen divided by the dry elastomer mass. All masses were determined gravimetrically. First, the swollen masses of eight cubic samples (edge size 5−10 mm; each sample was in a separate glass vial) from each elastomer were measured after equilibration for 2 weeks in THF. Next, the dry mass of each sample was determined after removing the THF by placing all samples for 96 h in a vacuum oven at room temperature. Then, 5 mL of Milli-Q (deionized) water was added in the six vials. For each elastomer, three of its samples became alkaline by the addition of a 0.5 M NaOH standard solution (3, 6, and 9 drops). The pH values of these three samples ranged between 8 and 11. Two samples were acidic (pH < 7) by the addition of small volumes of a 0.5 M HCl standard solution (2 and 4 drops), and the last sample remained neutral (no acid or base was added to it), just the 5 mL of deionized water. The PGS elastomers were stable for (at least) 21 days under most conditions employed but also revealed extensive swelling and eventual hydrolysis and dissolution at pH > 8.5. Furthermore, a mass spectrometry study was performed on the PGS prepolymers which unveiled the size and relative abundance of the oligomers produced during the course of the condensation polymerization.

#### Dynamic Mechanical Thermal Analysis (DMTA)

For the dynamic mechanical thermal analysis (DMTA) measurements, a Tritec 2000
DMA instrument (Triton Technologies Ltd.) was used. Specimen dimensions were about 3.5 mm in thickness, 10 mm in width, and 10 mm in effective length. The dynamic load was sinusoidal with amplitude of 0.25 mm and at a frequency of 10 Hz to match the beating frequency of the mouse heart. The temperature was varied between 35 and 140 °C for all tests.

■ RESULTS AND DISCUSSION

Polymer Synthesis. The synthesis of the PGS elastomers was performed by the polycondensation reaction of sebacic acid (S) and glycerol (G) in three steps.20,36 The chemical structures of the two monomers are shown in Figure 1.

A schematic representation of the synthetic procedure followed for the preparation of the PGS elastomers is illustrated in Figure 2. The first two reaction steps resulted in a PGS branched prepolymer, which was further condensed to a cross-linked elastomer in the third and final step.

PGS elastomers of five different compositions in the two comonomers were synthesized. In particular, the G:S molar ratio was varied from 2:1 to 2:5. For G:S molar ratios of 2:2 and 2:5, the products of the first and second reaction steps were soluble oligomers, which were converted to cross-linked elastomers in the third and final reaction step. In contrast, the preparation with the 2:1 molar ratio gave soluble products after all three reaction steps. On the other hand, for G:S molar ratios of 2:3 and 2:4, the soluble oligomer products of the first reaction step were transformed to cross-linked PGS elastomers from the second reaction step.

Molecular Weights. Figure 3 shows the GPC traces of the five PGS prepolymers with the different monomer molar ratios at the various reaction steps, whereas the results of the calculations of the MWs from these traces are listed in Table 1. The MWDs of the prepolymers synthesized in the first step were multimodal, containing rather low-MW peaks. The $M_n$ of the prepolymers with G:S compositions 2:1 were similar in reaction steps two and three. In contrast, the MWD of the PGS prepolymer with G:S composition 2:2, produced after the second synthetic step, was unimodal but with a very high PDI and an $M_p$ 6.5 times higher than that of the prepolymer produced after the first step. The MWDs of the PGS prepolymers with G:S compositions 2:3, 2:4, and 2:5 were multimodal. The $M_n$ of the prepolymers with G:S compositions 2:3 and 2:4 produced after the first reaction step were very low and similar to each other, while the $M_n$ of the prepolymers with G:S compositions 2:1, 2:2, and 2:5 prepared after the first step were relatively higher.

ESI-MS was also used to determine the exact MWs of the oligomers produced in the various reaction steps. While there are several studies for the MS characterization of polyesters produced by condensation polymerization,37−40 to our knowledge this is the first MS study on PGS precursors. Table 2 shows the theoretically possible and the experimentally determined MWs of the PGS oligomers, while Scheme 1 illustrates schematically the structures of these oligomers up to the nonamer. The mass spectrum of the reaction product from the first synthetic step of the PGS 2:2 prepolymer along with

Table 1. Molecular Weight Characteristics of the PGS Prepolymers As Measured Using Gel Permeation Chromatography (GPC)

| sample | GPC on linear precursors |  |  |
|--------|-------------------------|  |  |
| G:S step | $M_n$ (g mol$^{-1}$) | $M_w$ (g mol$^{-1}$) | $M_w/M_n$ |
| 2:1 | 677, 412, 71 | 187 | 2.52 |
| 2:1 | 1250, 783, 400, 65 | 211 | 3.13 |
| 2:1 | 1250, 855, 536, 258 | 343 | 3.45 |
| 2:2 | 639, 299, 60 | 250 | 2.17 |
| 2:2 | 4142, 75 | 792 | 7.91 |
| 2:3 | 980, 602, 377, 210, 65 | 273 | 2.86 |
| 2:4 | 1049, 657, 356, 128, 65 | 229 | 2.70 |
| 2:5 | 1326, 697, 377, 152, 65 | 220 | 2.67 |
| 2:5 | 1179, 400, 144, 67 | 242 | 3.11 |

Figure 3. GPC traces of the five PGS prepolymers to the elastomers of different compositions produced at the various reaction steps.
Table 2. Molecular Weight Characteristics of the PGS Prepolymers As Measured Using Mass Spectrometry

<table>
<thead>
<tr>
<th>Oligomer Structure</th>
<th>Theoretical MW (g mol$^{-1}$)</th>
<th>Presence of Species in Mass Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S % mol</td>
<td>PGS (2:1) 1$^{a}$ step</td>
</tr>
<tr>
<td>S</td>
<td>92</td>
<td>O</td>
</tr>
<tr>
<td>GS cyclized dimer</td>
<td>202</td>
<td>S</td>
</tr>
<tr>
<td>GS dimer</td>
<td>258</td>
<td>M</td>
</tr>
<tr>
<td>GSG trimer</td>
<td>276</td>
<td>L</td>
</tr>
<tr>
<td>GSGS cyclized trimer</td>
<td>359</td>
<td>S</td>
</tr>
<tr>
<td>SGS trimer</td>
<td>460</td>
<td>L</td>
</tr>
<tr>
<td>GSGS cyclized tetramer</td>
<td>516</td>
<td>O</td>
</tr>
<tr>
<td>GSGS trimer</td>
<td>534</td>
<td>M</td>
</tr>
<tr>
<td>GSGS(GS) trimer</td>
<td>608</td>
<td>L</td>
</tr>
<tr>
<td>GS star</td>
<td>644</td>
<td>L</td>
</tr>
<tr>
<td>SGS/SGS cyclized linear pentamer or SGS/SGS cyclized star pentamer</td>
<td>700</td>
<td>O</td>
</tr>
<tr>
<td>SGS(GS)S linear pentamer or SGS(GS)S cyclized pentamer</td>
<td>718</td>
<td>O</td>
</tr>
<tr>
<td>SGS(GS)S cyclized linear hexamer or SGS(GS)S cyclized star hexamer</td>
<td>734</td>
<td>O</td>
</tr>
<tr>
<td>SGS(GS)S linear hexamer or SGS(GS)S star hexamer</td>
<td>792</td>
<td>O</td>
</tr>
<tr>
<td>SGS(GS)S cyclized hexamer or SGS(GS)S cyclized star heptamer</td>
<td>866</td>
<td>O</td>
</tr>
<tr>
<td>SGS(GS)S cyclized star hexamer</td>
<td>884</td>
<td>O</td>
</tr>
<tr>
<td>SGS(GS)S star heptamer</td>
<td>958</td>
<td>O</td>
</tr>
<tr>
<td>GSGS(GS)S cyclized linear octamer or SGS(GS)S cyclized star octamer</td>
<td>1032</td>
<td>O</td>
</tr>
<tr>
<td>GSGS(GS)S cyclized linear heptamer or SGS(GS)S cyclized star heptamer</td>
<td>1050</td>
<td>O</td>
</tr>
<tr>
<td>GSGS(GS)S hyperbranched heptamer</td>
<td>1124</td>
<td>O</td>
</tr>
</tbody>
</table>

**Key:** O = no peak; LL = largest peak; L = large peak; M = medium-size peak; S = small peak. Yellow-highlighted row: species not encountered in any precursor sample. Gray-highlighted row: even-numbered rows alternatingly highlighted (only when not already yellow-highlighted) for guiding the eye.

Scheme 1. Schematic Representations of the Possible Oligomers (Dimer through Nonamer) Produced upon the Polycondensation of Glycerol (G) and Sebacic Acid (S)

oligomer peak identification is shown in Figure 4, whereas the spectra of the other samples are given in Figures S1 and S2 of the Supporting Information. Since sodium was used as the counterion in the MS experiments, 23 g mol$^{-1}$ must be
subtracted from the MWs indicated in the spectrum to calculate the correct oligomer MWs. Three families of peaks are indicated in Figure 4: one in black, the second in red, and the third in blue. Within each family, the species differ from the adjacent homologue by the constant value of 258.2 g mol$^{-1}$, corresponding to the mass of the G$\_S$ dimer. The family in black is the one of the oligomers with an even number of monomer repeating units, 2, 4, 6, and 8, whereas the other two families are those of oligomers with a degree of polymerization which is an odd number; the family in red concerns oligomers with both G end units, whereas the one in blue corresponds to oligomers with both S end units. In the spectrum, a small peak at 667 g mol$^{-1}$ (sodiated species, MW of pure species of 644 g mol$^{-1}$) is visible, corresponding to the GS$_3$ “star” tetramer. No peaks corresponding to ring structures were observed in this spectrum, probably a result of the high concentrations (bulk) employed for the syntheses, favoring intermolecular over intramolecular reactions. This was also the reason why ring structures were not detected in the other samples (Figures S1 and S2), with the exception of a small peak in the spectrum of the first reaction step from PGS 2:5, corresponding to the cyclized pentamer with a (true) MW of 700 g mol$^{-1}$.

In addition to the peaks expected on the basis of S$\_G$ condensations, some other peaks were also identified, especially in the S-rich compositions (Figures S1 and S2). Those samples exhibited peaks with MWs of 381, 437, and 647 g mol$^{-1}$ (sodiated species), which can be explained through the 1,5-hydrogen rearrangement of S, resulting in oct-7-enoic acid, which may further react to yield the observed species (Figure S3).

The composition of the prepolymers and the reaction conversion were determined using $^1$H NMR spectroscopy and are listed in Table 3, along with the theoretical prepolymer composition based on the comonomer feed ratio. The compositions were in reasonably good agreement with the theoretical ones. In all cases, the reaction conversion increased from the first to the second or third reaction steps. The PGS 2:3 and PGS 2:4 prepolymers presented relatively high conversions from the first reaction step, which explains why elastomer formation took place from the second reaction step.

**Elastomer Characterization. Sol Fraction.** Table 4 presents the percentage of polymeric material extracted (sol fraction) from each PGS elastomer. In all cases, the sol fraction was relatively high, ranging between 20 and 41% w/w. The sol fraction depended on elastomer composition. The lowest sol fraction was observed for the elastomer whose G:S molar ratio matched the stoichiometric (2:3), and it therefore had the highest cross-linking density, while the highest sol fraction was extracted from the elastomer with a G:S molar ratio of 2:5, which was the one furthest away from stoichiometry and exhibiting the lowest cross-linking density. The extractables were characterized using GPC and the calculated MWs are also listed in Table 4. In all cases, the MWD of the extractables was bimodal or trimodal, containing low MW peaks, where the MWs were slightly higher than but close to those of the PGS prepolymers, suggesting that the extractables mainly originated from unattached oligomers.

*Degrees of Swelling.* Knowledge of the swelling behavior of the PGS elastomers is necessary for their applications. The aqueous swelling properties, including degradability, are highly relevant to in vivo uses. However, swelling properties in organic solvents are also important for the processing and formulation of these materials in such solvents. To this end, the DSs of all PGS elastomers in various solvents were measured at different times over a 21 day period. This period was judged long enough to achieve swelling equilibrium and also sufficient to reveal elastomer degradation (manifested as a reduction in elastomer swollen mass). The swelling solvents chosen were water (in a very broad pH range), THF, 1-octanol, and n-hexane, covering a wide polarity range.

Figure 5 shows the temporal evolution for 21 days of the DSs of the four PGS elastomers in n-hexane and in 1-octanol. In all cases, the DSs of the elastomers remained stable over time, suggesting rapid swelling equilibration and also chemical stability (lack of hydrolysis). All elastomers were practically collapsed in n-hexane, exhibiting DSs between 1.2 and 1.7, manifesting the incompatibility of both monomer units, the hydroxyl and carboxylic acid end groups, and the formed ester groups with n-hexane. The lowest DS in n-hexane was displayed by the PGS 2:3 elastomer, i.e., the one with the stoichiometrically matched composition and, consequently, the one with the highest cross-linking density. The elastomer DSs in 1-octanol were visibly higher than those in n-hexane, a result of the greater polarity of 1-octanol than n-hexane and the better compatibility of the polar end groups and formed ester groups with this solvent.

Figure 6 shows the temporal evolution of the DSs of the four PGS elastomers in aqueous solutions at various pH values. Again, the DSs were practically time-invariant from the beginning, manifesting fast equilibration and hydrolytic stability. Furthermore, for each elastomer, the DSs appeared

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**Table 3. Composition of the PGS Prepolymers and Reaction Conversion As Calculated Using $^1$H NMR Spectroscopy**

<table>
<thead>
<tr>
<th>sample</th>
<th>% mol sebacic acid</th>
<th>% reaction conversion</th>
<th>by $^1$H NMR theoretical</th>
<th>by $^1$H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGS 2:1</td>
<td>36.3</td>
<td>33.3</td>
<td>33.5</td>
<td></td>
</tr>
<tr>
<td>PGS 2:2</td>
<td>36.3</td>
<td>33.3</td>
<td>44.4</td>
<td></td>
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<tr>
<td>PGS 2:3</td>
<td>40.2</td>
<td>33.3</td>
<td>71.4</td>
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</tr>
<tr>
<td>PGS 2:4</td>
<td>55.9</td>
<td>50.0</td>
<td>59.0</td>
<td></td>
</tr>
<tr>
<td>PGS 2:5</td>
<td>50.0</td>
<td>50.0</td>
<td>85.5</td>
<td></td>
</tr>
</tbody>
</table>

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Figure 4. ESI mass spectrum of the prepolymer PGS 2:2 prepared from the first reaction step. The molecular weights indicated in the spectrum are increased by 23 g mol$^{-1}$, the atomic mass of the Na$^+$ counterion.
to increase with the pH, a result of both the ionization of the carboxylic acid end-groups and elastomer hydrolysis through cleavage of the ester linkages. The smallest increase of the aqueous DSs with pH was observed with the stoichiometrically matched elastomer PGS 2:3, presenting the highest cross-linking density.

Figure 7 summarizes the results of Figure 6 by plotting the equilibrium (on day 21) aqueous DSs of all the elastomers against the pH of the supernatant solution. From these plots, it is clear that the elastomers remained collapsed (DSs around 2) until a pH value of around 8.5, above which they remarkably swelled. As already mentioned in the previous paragraph, this increase was due to the ionization of the terminal carboxylic acid groups, which resulted in an increase in the osmotic pressure within the elastomer from the cloud of the sodium countercations to the carboxylates and in electrostatic repulsions between the charged polymer termini. In the case of the elastomer with a G:S molar ratio of 2:5, this elastomer was completely dissolved within 3 days at pH values higher than 9, suggestive of the hydrolysis of the ester groups in the presence of relatively high concentrations of NaOH.

Table 5 and Figure 8 summarize the equilibrium (21st day) DSs of all elastomers in all solvents: THF, n-hexane, 1-octanol, and high-, neutral-, and low-pH water. The DSs were highest in THF followed by those in high-pH water, 1-octanol, low-pH water, neutral-pH water, and n-hexane. THF is a polar organic solvent with which the S and the G units, the formed ester groups, and the hydroxyl and carboxylic acid end groups appear to be very compatible, leading to the highest DSs. Alkaline water (pH ~ 9) appears to be the next best solvent, as a result of the ionization of the carboxylic acid groups of the elastomers. When not ionized (neutral and acidic pH), the elastomers swelled in water much less. The lowest DSs were measured in the nonpolar n-hexane, as the very polar end groups and the polar ester groups of the elastomer are particularly incompatible with this solvent. Slightly higher DSs were measured in the slightly more polar 1-octanol which offered a better environment for the solubilization of the polar elastomer groups.

In each solvent, the DSs of the PGS elastomers greatly depended on their composition. In particular, the DSs exhibited a minimum at the stoichiometrically matched (G:S molar ratio of 2:3) composition, corresponding to the highest cross-linking density. Elastomers with compositions away from the stoichiometrically matched displayed progressively higher DSs. This trend is also consistent with the differences in the sol fraction of the elastomers. Thus, the DSs presented a dependence on elastomer composition, qualitatively similar to that of the sol fraction, as expected. The elastomers with G:S molar ratios 2:2 and 2:4, having approximately the same cross-linking density, presented similar DSs: 1.4 in n-hexane, 2.6 in 1-octanol, and about 1.8 in neutral- and low-pH water.
**DMTA Results.** Table 6 shows the values of the storage moduli for all the PGS elastomers of this study, as measured using DMTA in the range of temperatures between 35 and 140 °C, whereas Figure S4 in the Supporting Information displays a typical DMTA curve. With the exception of PGS 2:2, the storage modulus of the remaining elastomers decreased with an increase in temperature. In the case of samples PGS 2:3 and 2:5, these elastomers became extremely soft at temperatures higher than 80–85 °C and were, therefore, unsuitable for measurement (storage modulus below instrument limit). At low temperatures (≈35 °C), the highest storage modulus measured was that for the stoichiometrically matched PGS 2:3 elastomer and the lowest that for the PGS 2:2 elastomer. These results are consistent with those for the sol fraction and the DSs of the elastomers. The elastomers with compositions far from stoichiometry were softer due to the lower cross-linking...
units. The sol fraction, the swelling, and the mechanical properties of the elastomers highly depended on elastomer composition. The sol fraction extracted from the PGS elastomers and their DSs in all solvents presented a minimum with respect to the sebacic acid content. It was found that the PGS 2:3 elastomer was the stiffest, with the lowest DSs and sol fraction, while the PGS 2:5 elastomer was one of the softest, also exhibiting the highest DS and sol fraction.

As future work, the present biosourced branched oligomers and elastomers can be grafted with conventional olefinic monomers using addition polymerization. This can be most interestingly performed via controlled radical polymerization, and, in particular, atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization. To this end, the appropriate ATRP initiator or RAFT polymerization chain transfer agent would be attached to the hydroxyl or carboxylic acid end functionalities of the PGS polymers, followed by the controlled (co)polymerization of monomers to obtain hybrid materials of increased added value.

### ASSOCIATED CONTENT

#### Supporting Information

All mass spectra and possible structures of the extra species observed, a typical curve for the temperature dependence of the modulus, powder X-ray diffractograms on the prepolymers, and differential scanning calorimetry thermograms on the elastomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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### REFERENCES


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Table 5. Degrees of Swelling of the PGS Elastomers in THF, n-Hexane, 1-Octanol, and Acidic, Neutral, and Basic Water

<table>
<thead>
<tr>
<th>sample</th>
<th>degrees of swelling</th>
</tr>
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<tbody>
<tr>
<td>G:S step</td>
<td>THF</td>
</tr>
<tr>
<td>2:2</td>
<td>3</td>
</tr>
<tr>
<td>2:3</td>
<td>2</td>
</tr>
<tr>
<td>2:4</td>
<td>2</td>
</tr>
<tr>
<td>2:5</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 8. Composition dependence of the equilibrium degrees of swelling of the PGS elastomers in various solvents.

Table 6. Storage Moduli of the PGS Elastomers at Various Temperatures Measured Using DMTA

<table>
<thead>
<tr>
<th>sample</th>
<th>storage modulus at 35 °C (MPa)</th>
<th>storage modulus at 75 °C (MPa)</th>
<th>storage modulus at 135 °C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G:S step</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:2</td>
<td>3</td>
<td>0.75</td>
<td>0.80</td>
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<tr>
<td>2:3</td>
<td>2</td>
<td>4.70</td>
<td>3.11</td>
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<td>2:4</td>
<td>2</td>
<td>3.58</td>
<td>1.19</td>
</tr>
<tr>
<td>2:5</td>
<td>3</td>
<td>1.35</td>
<td>0.27</td>
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</table>