# Synthesis and Degradation of Sorbitol-Based Polymers

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**ABSTRACT:** A new class of biodegradable copolyesters was synthesized by the catalyst-free melt condensation of sorbitol with citric acid, tartaric acid, and sebacic acid. The resulting polymers were designated as poly(sorbitol citric sebacate) [p(SCS)] and poly(sorbitol tartaric sebacate) [p(STS)]. The synthesized polymers were characterized by Fourier transform infrared spectroscopy, $^1$H-NMR spectroscopy, and differential scanning calorimetry analysis. Porous spongelike scaffolds were prepared with a salt-leaching technique and characterized with scanning electron microscopy. Tensile testing of the p(SCS) and p(STS) polymers showed that they exhibited a wide range of mechanical properties. The Young's modulus and tensile strengths of the polymers ranged from 1.06 ± 0.12 to 462.65 ± 34.21 MPa and from 0.45 ± 0.04 to 20.32 ± 2.54 MPa, respectively. *In vitro* degradation studies were performed on disc-shaped polymer samples. The half-life of the polymers ranged from 0.54 to 38.52 days. The percentage hydration of the polymers was in the range 9.36 ± 1.26 to 78.25 ± 1.91, with sol contents of 2–14%. At any given polymer composition, the Young's modulus and tensile strength of p(SCS) was higher than that of p(STS), whereas the degradation rates of p(SCS) was lower than that of p(STS). This was attributed to the structural difference between the citric and tartaric monomers and to the degree of crosslinking. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2861–2869, 2011

**Key words:** biocompatibility; biomaterials; strength

## INTRODUCTION

Synthetic biodegradable polymers offer advantages over other biomaterials made from ceramic and metallic materials because they can be tailored to give a wide range of mechanical, degradation, and physiochemical properties.[1–3] The development of new biodegradable polymers is of interest because of the increased demand, especially in many biomedical applications, such as scaffolds for tissue engineering,[4–6] controlled release of drugs,[7,8] orthopedic implants/fixation devices,[9–11] sutures,[12,13] and adhesives.[14,15] In most of these applications, the general criteria for the selection of a biodegradable polymer are to match the mechanical properties and the time of degradation to the needs of the application. Several biodegradable polymers, such as poly(glycerol sebacate),[16,17] poly(1,8-octane diol citrate),[18] poly(ethylene glycol-*co*-citric acid),[19] poly(polyol sebacate) (PPS),[20] and poly(glycerol citrate),[21] have been synthesized by the condensation of multifunctional alcohol and acid monomers, and they are considered to be the new generation materials for potential biomedical applications. However, the synthesis of most of these polymers requires high temperature, vacuum, and long postpolymerization time. Furthermore, these polymers cover only a modest range of mechanical and physiochemical properties.

The general criteria for the choice of these monomers are that (1) they should be inexpensive and readily available from renewable sources, (2) they should use multifunctional monomers that allow the formation of three-dimensional networks with a wide range of crosslinking densities, (3) precise control over the final properties should be achievable by the tuning of the monomer content in the polymer, and most importantly, (4) the monomers should be capable of being metabolized in the human body. Sorbitol (S) is completely metabolized to carbon dioxide,[22,23] sebacic acid (SA) is an intermediate in fatty acid oxidation,[24,25] citric acid (CA) is an intermediate in the Krebs cycle,[26] and tartaric acid (TA) is a natural product,[27,28] and thus, all of these monomers can be metabolized in the human body. Therefore, these monomers were chosen to synthesize various polymers in this study. Although it is possible to synthesize biodegradable polyesters[29,30] by regioselective, dehydration polycondensations of diols (glycerol or S) with dicarboxylic acids, such as TA and maleic acid without crosslinks and with the use of scandium trifluoromethanesulfonate as the catalyst, the main objective of the study was to allow the formation of randomly crosslinked

Additional Supporting Information may be found in the online version of this article.

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networks and create a wide range of crosslink densities, similar to that reported for the synthesis of biodegradable PPS.[20]

In this article, we report the synthesis and evaluation of a new class of biodegradable polymers created by the catalyst-free melt condensation of multifunctional monomers, including S, CA, TA, and SA, which are endogenous to human metabolism. The resulting polymers were designated as poly(sorbitol citric sebacate) [p(SCS)] and poly(sorbitol tartaric sebacate) [p(STS)]. These biodegradable polymers exhibited a wide range of physical, mechanical, and stability properties. We also investigated the effects of polymer composition on the final properties of the polymers.

## EXPERIMENTAL

### Materials

High-purity S, CA, TA, and SA were purchased from Sigma–Aldrich Corp. (St. Louis, MO) and were used as received. 1,4-Dioxane, ethanol, and phosphate buffer pellets were purchased from S.D. Fine Chemicals (Mumbai, India).

### Synthesis of the p(SCS) and p(STS) polymers

All of the p(SCS) and p(STS) polymers were synthesized by the catalyst-free melt condensation technique by the following procedure. Appropriate molar amounts of the monomers were placed into a 250-mL, three-necked round-bottom flask and melted at 150°C under the flow of nitrogen gas; this was followed by mixing for 2 h, which produced the p(SCS) and p(STS) prepolymers. The obtained prepolymers were then kept in an oven at 80°C for 5 days for further polyesterification. Twelve polymers of different compositions of p(SCS) and p(STS), as depicted in Table I, were synthesized in this study to investigate the effect of the monomer composition on the physical and mechanical properties of the p(SCS) and p(STS) polymers. The cured polymers were then stored in a desiccator for further use. The schematic of this synthesis is shown in Figure S1 (see Supporting Information). The resulting polymers were crosslinked at the reaction groups shown in Figure S1.[20] The —OR in Figure S1 indicates both crosslinked groups and/or —OH groups.

### Characterization of the synthesized p(SCS) and p(STS) polymers

#### Fourier transform infrared (FTIR) spectrometry analysis

The FTIR spectra of all of the synthesized polymers were obtained with FTIR spectroscopy (PerkinElmer) at room temperature. Prepolymer samples were dissolved in 1,4-dioxane (20% w/w), cast into Teflon Petri dishes to form thin sheets (~2 mm), and kept in an oven for 5 days at 80°C for solvent evaporation and further polycondensation. These thin sheets were then compressed to obtain submillimeter-thick films with a compression mold (S.C. Dey Co., Kolkata, India) maintained at 150°C and 10 MPa. These thin films were placed on the KBr crystal and scanned over the range 4500–500 $cm^{-1}$.

#### Nuclear magnetic resonance (NMR) spectroscopic analysis

Both p(SCS) and p(STS) prepolymers were purified before NMR analysis. Briefly, the prepolymers were precipitated in water with continuous agitation followed by filtration and freeze-drying. $^1$H-NMR spectra of the polymers were recorded on a Bruker NMR (Bruker AXS Inc., Madison, WI) spectroscope at 400 MHz with deuterated dimethylsulfoxide (DMSO) as a solvent and tetramethylsilane as the internal reference.

**TABLE I**
**Composition, Percentage Hydration, and Thermal Properties of p(SCS) and p(STS)**

| Polymer (S : CA or TA : SA) | Composition by $^1$H-NMR | Hydration (%) | $T_g$ (°C) | $T_m$ (°C) |
|---|---|---|---|---|
| p(SCS) (1 : 1 : 0.5) | 1.00 : 0.82 : 0.41 | 43.56 ± 1.49 | 19.4 | 73.4 |
| p(SCS) (1 : 1: 1) | 1.00 : 0.96 : 0.87 | 29.20 ± 1.86 | 17.8 | 112.6 |
| p(SCS) (1 : 1 : 2) | 1.00 : 0.87 : 1.52 | 9.36 ± 1.26 | 6.5 | 119.1 |
| p(SCS) (1 : 0.5 : 1) | 1.00 : 0.52 : 0.84 | 27.88 ± 1.39 | 4.5 | 91.3 |
| p(SCS) (1 : 2 : 1) | 1.00 : 1.75 : 0.94 | 46.45 ± 1.32 | 11.2 | 109.4 |
| p(SCS) (2 : 1 : 1) | 2.00 : 0.92 : 0.82 | 52.10 ± 3.57 | 9.6 | — |
| p(STS) (1 : 1 : 0.5) | 1.00 : 0.85 : 0.51 | 49.56 ± 2.97 | 26.3 | 80.3 |
| p(STS) (1 : 1 : 1) | 1.00 : 0.78 : 0.89 | 34.25 ± 1.81 | 23.2 | 119.3 |
| p(STS) (1 : 1 : 2) | 1.00 : 0.84 : 1.81 | 18.35 ± 1.11 | 12.8 | 114.3 |
| p(STS) (1 : 0.5 : 1) | 1.00 : 0.42 : 0.87 | 39.21 ± 1.96 | 3.5 | 84.2 |
| p(STS) (1 : 2 : 1) | 1.00 : 1.41 : 0.78 | 63.51 ± 3.17 | 15.4 | 107.6 |
| p(STS) (2 : 1 : 1) | 2.00 : 0.92 : 0.96 | 78.25 ± 1.91 | 10.3 | — |

The composition from NMR was determined by the prepolymers.

### Differential scanning calorimetry (DSC) analysis

The thermal properties, such as the glass-transition temperature ($T_g$), and melting temperature ($T_m$), of the p(SCS) and p(STS) polymers were evaluated with a DSC823[e] differential scanning calorimeter (Mettler–Toledo Inc., Columbus, OH) operating under a nitrogen atmosphere at a heating of 10°C/min in the temperature range −50 to 250°C.

### Contact angle measurement

The water-in-air contact angle of the polymers at room temperature was measured with the sessile drop method using a Rame Hart Model 100-00 (Netcong, NJ) contact angle goniometer and image analysis software provided by the same company. Measurements were taken at five different locations and averaged.

## Mechanical properties

The mechanical properties of the p(SCS) and p(STS) polymers of different compositions were measured at room temperature with a universal testing machine (S. C. Dey Co., India) equipped with 500-N load cell and data acquisition software. The dog-bone-shaped polymer strips were prepared according to ASTM D 638 (35 × 4 × 2 $mm^3$, Length × Width × Thickness = 1–2 mm) and pulled at a strain rate of 10 mm/min. The Young's modulus was calculated from the initial slope of the curve of the tensile stress versus strain. Each test was performed five times for each polymer sample. The crosslink density and the molecular weight between crosslinks were calculated with eq. (1) according to the theory of rubber elasticity:[20]

$$n = \frac{E_0}{3RT} = \frac{\rho}{M_c} \tag{1}$$

where $n$ is the number of active network chain segments per unit volume (mol/$m^3$), $M_c$ is the molecular weight between crosslinks (g/mol), $E_0$ is the Young's modulus (Pa), $R$ is the universal gas constant (8.314 J/mol. K), $T$ is the absolute temperature (298 K), and ρ is the density of the polymer (g/$m^3$). The densities of all of the polymer samples were measured on the basis of Archimedes' principle with absolute ethanol as the auxiliary liquid.

## *In vitro* degradation of the p(SCS) and p(STS) polymers

The *in vitro* degradation of the p(SCS) and p(STS) polymers via hydrolysis was conducted for disc-shaped (diameter = 10 mm, thickness = 1–1.5 mm) sol-free polymer samples in 20 mL of phosphate-buffered saline (PBS; pH = 7.4) or 0.1*M* NaOH solution at 37°C. Samples were removed at designated points of time, washed with distilled water, incubated in ethanol overnight, and dried to a constant weight. The percentage mass loss (%$M_{loss}$) of the polymer was calculated from the following equation:

$$\%M_{loss} = \frac{M_0 - M_t}{M_0} \tag{2}$$

where $M_0$ and $M_t$ are the masses of the polymer sample at the initial and given times.

## Hydration characteristics and sol contents of the polymers

We investigated the hydration characteristics of the polymers by incubating 10-mm polymer discs in Milli-Q water at 37°C. At different time intervals, we took out the discs and weighed them after wipe-cleaning their surfaces. The percentage hydration of the polymer discs were calculated with the following expression:

$$\text{Hydration}(\%) = \frac{m_w - m_0}{m_0} \times 100\% \tag{3}$$

where $m_0$ and $m_w$ are the masses of the polymer disc under the initial and wet conditions. After the polymers reached their equilibrium percentage hydration, the discs were dried to a constant weight, and the sol content was calculated with the following equation [eq. (4)], where $m_0$ and $m_d$ are the masses of the discs under the initial and dry conditions:

$$\text{Sol content}(\%) = \frac{m_0 - m_d}{m_0} \times 100\% \tag{4}$$

## Scaffold fabrication

Prepolymers of p(SCS) (1 : 1 : 1), p(SCS) (1 : 1 : 2), p(STS) (1 : 1 : 1), and p(STS) (1 : 1 : 2) were used to fabricate porous scaffold with the conventional salt-leaching technique, as described earlier.[18] Briefly, the prepolymer was dissolved in 1,4-dioxane to form a 25 wt % solution, and then, the sieved salt (225 ± 50 μm) was added. The resulting slurry was cast into polytetrafluoroethylene (PTFE) moulds and vacuum-dried for 24 h to remove the solvent; subsequently, the molds were transferred to an oven for postpolymerization at 80°C for 5 days. The resulting polymer–salt composites were leached with Milli-Q water by incubation for 96 h with water replacement every 12 h, and the obtained porous, spongelike scaffolds were freeze-dried and stored in a desiccator. Scanning electron microscopy (SEM) images of the scaffolds were taken with a field emission SEM (FSEM) (Sirion 200, FEI Company, Holland).

## RESULTS AND DISCUSSION

### Characterization of the synthesized p(SCS) and p(STS) polymers

#### FTIR analysis

Figure 1 depicts the FTIR spectra of the synthesized p(SCS) and p(STS) polymers. The absorption peak around 1740 $cm^{-1}$, corresponding to ester (C=O) groups, observed in all of the spectra of the polymers confirmed the formation of ester linkages.[18,20,31] The peaks around 1300 $cm^{-1}$ were characteristic of C—O absorption in the carboxyl (—COOH) groups from the CA, TA, and SA segments. The broad peaks centered at 3475 $cm^{-1}$ were attributed to the hydrogen-bonded hydroxyl groups.[32,33] The peaks centered at 2930 $cm^{-1}$ were assigned to methylene ($—CH_2$) groups[18] from SA and were observed in all of the spectra of all of the polymers.

#### NMR spectroscopic analysis

$^1$H-NMR spectra of all of the synthesized prepolymers were obtained. The chemical composition (reported in Table I) of the prepolymers was determined by comparison of the integral peak areas corresponding to the monomers. Figure 2(a,b) shows the $^1$H-NMR spectra of representative p(SCS) and p(STS) prepolymers, respectively.

The peaks at 3.5–5.5 ppm were assigned to protons in $—OCH_2[CH(OR)]_nCH_2O—$ from S.[20] The multiple peaks around 2.79 ppm were attributed to the protons in $—CH_2—$ from CA. These multiple peaks around 2.79 ppm have been observed in other studies,[18,34] and the multiple splits in the peak were due to the presence of unreacted terminal groups in CA.[35] The protons in —CH(OR)CO— from TA[27] showed peaks at 4.32 ppm. The peaks observed at 1.3, 1.6, and 2.3 ppm were assigned to the protons in $—COCH_2CH_2—$ from SA.[20] The peaks from 1.3 to 1.6 ppm were due to the protons from the central methylene units, whereas the peak at 2.3 ppm, was due to the terminal protons. This was consistent with the observation of similar peaks for SA in other studies.[20,35]

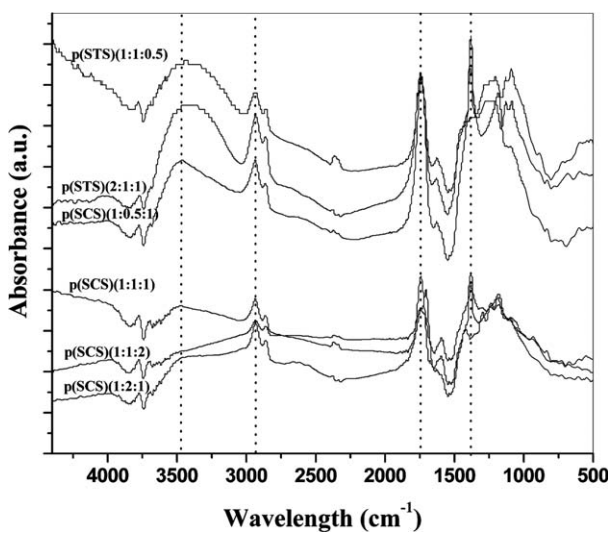


**Figure 1** FTIR spectra of the synthesized p(SCS) and p(STS) polymers.

#### DSC analysis

DSC thermograms were obtained for all of the synthesized polymers. The $T_g$ values are reported in Table I. The representative DSC curves of the p(SCS) and p(STS) polymers are shown in Figure 3. For the synthesized p(SCS) and p(STS) polymers, $T_g$ ranged from 3.5 to 26.3°C. $T_g$ decreased with increasing SA content in connection with the decrease of crystallinity of the polymers. A similar trend was observed in the case of poly(butylene succinate-co-butylene adipate) (PBSA) polymers.[36] An increase in the S content reduced the $T_g$ of the polymers because of the presence of unreacted pendant hydroxyl groups, which resulted in an increase in the free volume.[21]

### Mechanical properties

Tensile tests of the p(SCS) and p(STS) polymers showed that these polymers exhibited characteristics similar that of elastomers, thermoplastics, and stiff thermosets. The variation of the tensile stress with strain for the polymers is shown in Figure 4(a–c). The average Young's modulus, tensile strength, and percentage elongation at break of all of the synthesized polymers are reported in Table II. p(SCS) (1 : 1 : 2) was observed to be the stiffest material among the synthesized polymers with a Young's modulus of 442.65 ± 34.21 MPa, a tensile strength of 20.32 ± 2.54 MPa, and an elongation at break of 25.94 ± 4.02%, whereas p(STS) (2 : 1 : 1) was the softest material with a Young's modulus of 7.15 ± 0.38 MPa, a tensile strength of 0.45 ± 0.04 MPa, and an elongation at break of 578.36 ± 51.27%.

The Young's modulus and tensile strength increased with increasing SA content of the polymer, and this was attributed to the increased intermolecular bonding due to the close packing of molecules.[35] With increasing S content, the polymers became softer and more extensible. No clear trend was observed in the variation of the mechanical properties with increasing CA/TA content. At any given polymer composition, the tensile strength and Young's modulus of p(SCS) was higher than that of p(STS). This was ascribed to the structural

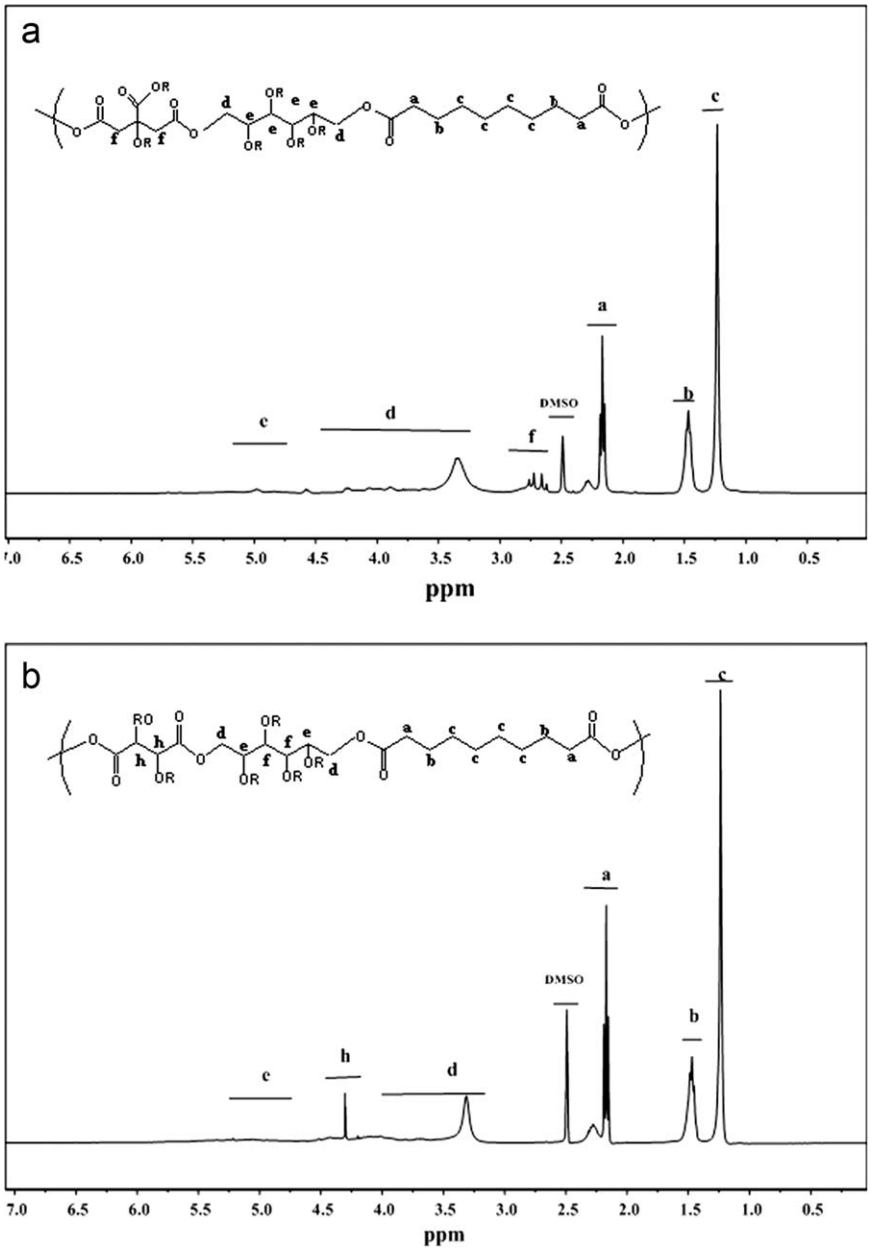


**Figure 2** $^{1}$H-NMR spectra of representative p(SCS) and p(STS) polymers: (a) p(SCS) (1 : 1 : 1) and (b) p(STS) (1 : 1 : 1).

differences between the CA (tricarboxylic) and TA (dicarboxylic) units in the polymer. The high degree of crosslinking in p(SCS) polymers compared to the p(STS) polymers was due to the rigid structure and one extra carboxylic group. From the results, it was clear that the mechanical properties of the p(SCS) and p(STS) polymers covered a wide range, which encompasses many biomedical applications. For example, the Young's modulus of the p(SCS) (1 : 1 : 2) polymer was comparable to that of the vertebral end plates (500 MPa),[37] and the tensile modulus of the other polymer networks, such as p(SCS) (1 : 1 : 1), p(SCS) (1 : 1 : 0.5), p(STS) (1 : 1 : 1), p(STS) (1 : 1 : 0.5), and p(STS) (1 : 1 : 2), were intermediate between that of cancellous bone (50–100 MPa) and cortical bone (17–20 GPa) and, therefore, could be useful for bone tissue engineering and osteosynthesis applications.[38] Similarly, elastic p(SCS) (1 : 0.5 : 1) and p(STS) (1 : 0.5 : 1) exhibited mechanical properties that were similar to elastin from bovine ligament (with Young's modulus and tensile strength values of 1.1 MPa and 2 MPa, respectively),[39] and the elongations at break were similar to that of blood vessels and veins ($\leq$260%).[39] Thus, these polymers are, therefore, expected to be useful for soft tissue engineering applications. The p(SCS) (2 : 1 : 1) and p(STS) (2 : 1 : 1) polymers also displayed mechanical properties markedly superior

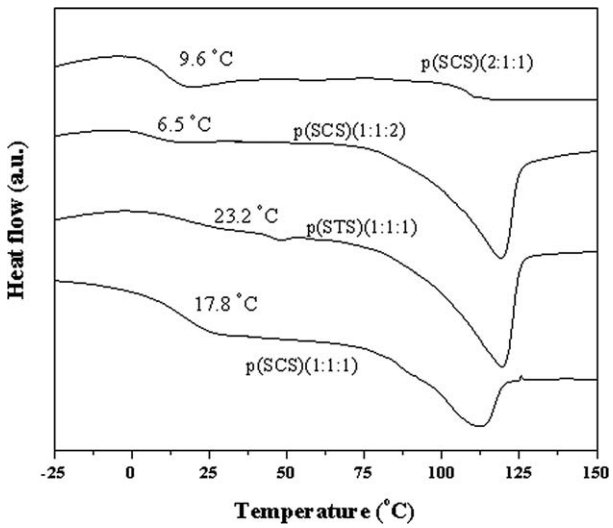


**Figure 3** DSC thermograms of representative p(SCS) and p(STS) polymers.

to that of fibrin (with tensile strength and Young's modulus values of 0.1 and 0.15 MPa, respectively), which is a tissue adhesive mainly used as a sealant and for adjoining delicate tissues as in nerve anastomoses.[1] Nevertheless, these polymers, after appropriate surface modifications, could be suitable for drug delivery, like poly(ethylene glycol-*co*-citric acid) polymers.[19]

### Hydration characteristics and sol content

The hydration characteristics of any polymeric biomaterial are often very important in understanding the interaction of biological systems with it.[35] Thus, the hydration characteristics of the synthesized p(SCS) and p(STS) polymers were investigated in water at 37°C. The hydration profiles of the polymers are shown in Figure 5. All of the polymers reached their equilibrium percentage hydration within 2–3 h with a maximum hydration of 78.25 ± 1.9% for p(STS) (2 : 1 : 1) and a minimum hydration of 9.36 ± 1.26% for the p(SCS) (1 : 1 : 2) polymer. The hydration characteristics of these polymers were attributed to the presence of hydrophilic hydroxyl and carboxyl groups and hydrophobic methylene segments. As discussed earlier, the presence of more hydrophobic long-chain segments such as SA retarded the water penetration and resulted in a low equilibrium hydration percentage. Thus, the p(SCS) (1 : 1 : 2) and p(STS) (1 : 1 : 2) polymers showed a low water uptake compared to the other polymer networks. The increased hydrophobicity of the polymers networks with SA content was also observed in the contact angle measurements; this showed an increase in the equilibrium contact angle (see Table III). The sol content of the polymers was calculated and found to be around 2–17% (see Table III). The higher values of sol content were ascribed to the presence of unreacted monomers or short-chain oligomers.

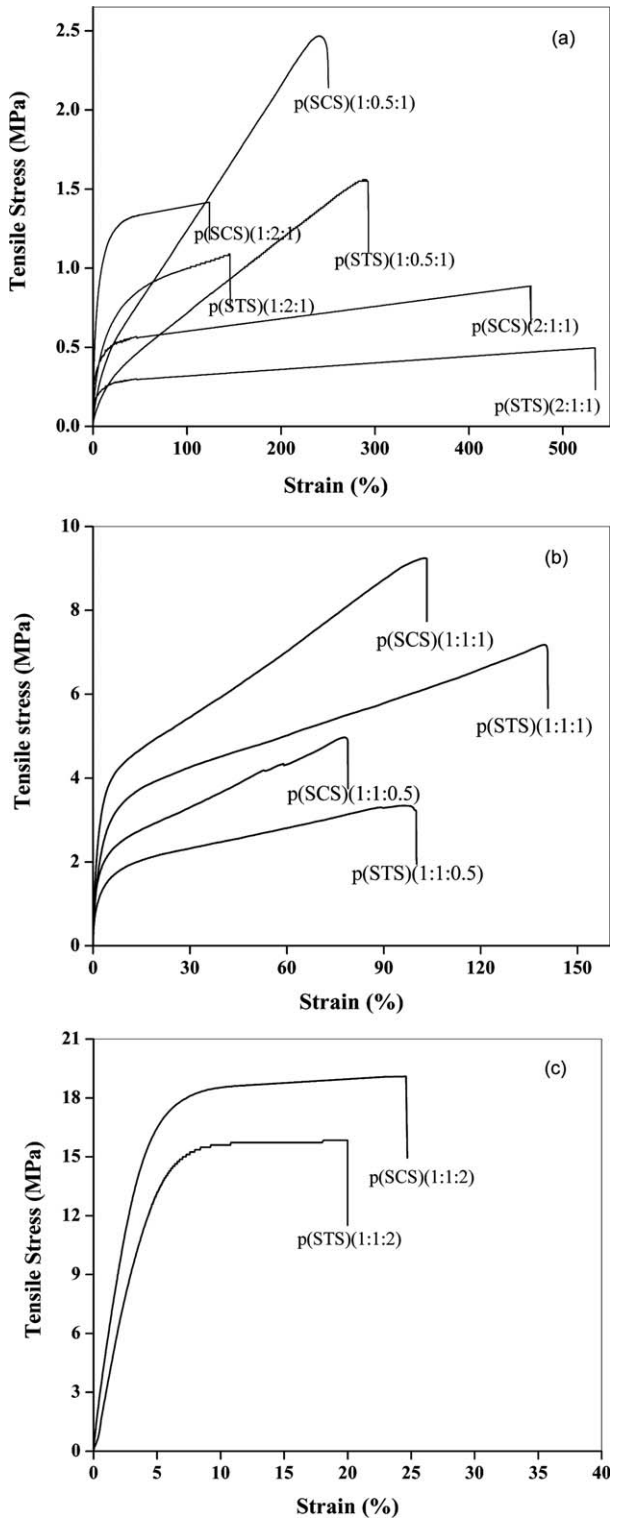


**Figure 4** Tensile stress versus strain curves of the (a) elastomeric, (b) thermoplastic, and (c) stiff thermoset p(SCS) and p(STS) polymers.

**TABLE II**
**Physical and Mechanical Properties of the p(SCS) and p(STS) Polymers**

| Polymer | Young's modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) | Density | $n$ (mol/m$^3$) | $M_c$ (g/mol) |
|---|---|---|---|---|---|---|
| p(SCS) (1 : 1 : 0.5) | 140.34 ± 26.31 | 5.26 ± 0.21 | 80.25 ± 9.58 | 1.434 ± 0.057 | n/a | n/a |
| p(SCS) (1 : 1 : 1) | 262.84 ± 23.18 | 11.36 ± 3.60 | 102.20 ± 12.52 | 1.381 ± 0.045 | n/a | n/a |
| p(SCS) (1 : 1 : 2) | 462.65 ± 34.21 | 20.32 ± 2.54 | 25.94 ± 5.02 | 1.357 ± 0.048 | n/a | n/a |
| p(SCS) (1 : 0.5 : 1) | 5.60 ± 0.17 | 2.68 ± 0.11 | 242.05 ± 17.91 | 1.349 ± 0.026 | 618 ± 22 | 2182 ± 88 |
| p(SCS) (1 : 2 : 1) | 36.30 ± 5.60 | 1.49 ± 0.19 | 136.21 ± 6.98 | 1.492 ± 0.086 | 4883 ± 753 | 305 ± 50 |
| p(SCS) (2 : 1 : 1) | 11.16 ± 0.87 | 0.84 ± 0.06 | 488.45 ± 34.17 | 1.494 ± 0.075 | 1501 ± 117 | 995 ± 92 |
| p(STS) (1 : 1 : 0.5) | 82.01 ± 18.81 | 3.25 ± 0.65 | 95.11 ± 6.37 | 1.398 ± 0.039 | n/a | n/a |
| p(STS) (1 : 1 : 1) | 205.65 ± 19.04 | 8.65 ± 1.95 | 140.20 ± 28.32 | 1.367 ± 0.014 | n/a | n/a |
| p(STS) (1 : 1 : 2) | 347.18 ± 41.12 | 18.05 ± 1.15 | 20.18 ± 3.44 | 1.308 ± 0.024 | n/a | n/a |
| p(STS) (1 : 0.5 : 1) | 1.06 ± 0.12 | 1.96 ± 0.20 | 300.10 ± 22.36 | 1.295 ± 0.003 | 142 ± 16 | 9119 ± 115 |
| p(STS) (1 : 2 : 1) | 8.39 ± 1.20 | 1.08 ± 0.09 | 155.87 ± 19.97 | 1.428 ± 0.016 | 1128 ± 161 | 1256 ± 19 |
| p(STS) (2 : 1 : 1) | 7.15 ± 0.38 | 0.45 ± 0.04 | 578.36 ± 51.27 | 1.416 ± 0.053 | 961 ± 51 | 1473 ± 97 |

n/a, not applicable.

### Scaffold fabrication

Porous spongelike scaffolds from representative p(SCS) (1 : 1 : 1) and p(STS) (1 : 1 : 1) polymers were fabricated with the salt-leaching technique (Fig. S2a, see Supporting Information) and characterized by SEM (Fig. S2b, see Supporting Information). Many micropores (30 ± 12 μm) were also distributed within the macropores; this was an essential characteristic and facilitated the transport of nutrients within the scaffold.[39] The other polymers could also be easily processed into various scaffold geometries by the adjustment of the curing conditions. The polymers were synthesized via the catalyst-free melt condensation technique, similar to that used for poly (glycerol sebacate), poly(1,8-octane diol citrate), and PPS polymers, and they also exhibited similar structural properties. Thus, these polymers were likely to exhibit *in vivo* degradability and compatibility.

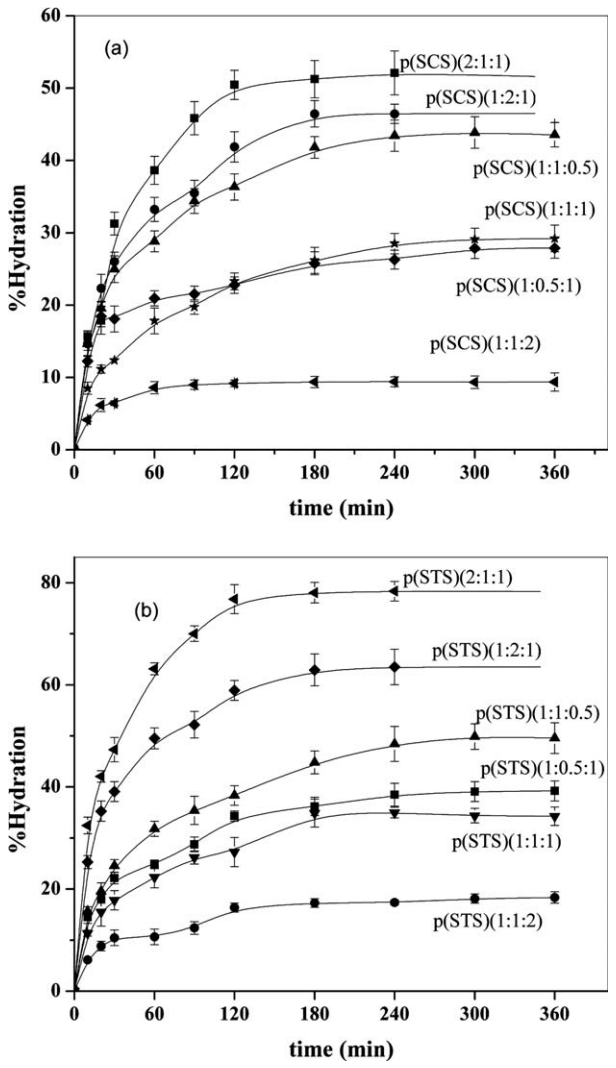


**Figure 5** Hydration characteristics of the (a) p(SCS) and (b) p(STS) polymers in water at 37°C.

### *In vitro* degradation of the p(SCS) and p(STS) polymers

The *in vitro* degradation of all of the synthesized p(SCS) and p(STS) polymers via hydrolysis was investigated in PBS (pH = 7.4 at 37°C). The results indicate that the degradation rates of the polymers varied considerably. The degradation profiles of p(SCS) and p(STS) in PBS are shown in Figures 6(a,b), respectively. From the degradation profiles, p(SCS) and p(STS) could be categorized into two classes, depending on their half-lives (calculated from the intersection of the degradation profile with the half-life line): (1) polymers having a half-life of less than 1 week and (b) polymers having a half-life of greater than 1 week. The *in vitro* degradation of p(SCS) and p(STS) polymers via hydrolysis was also investigated in a solution of 0.1*M* NaOH at a high pH of 13. All of the polymers except p(SCS) (1 : 1 : 2) and p(STS) (1 : 1 : 2) were degraded completely when incubated in the 0.1*M* NaOH at 37°C for 10 h, and the degradation profiles of the p(SCS) [Fig. 7(a)] and p(STS) [Fig. 7(b)] polymers were similar to those degraded in PBS at 37°C.

**TABLE III**
**Initial and Equilibrium Contact Angles and Sol Contents of p(SCS) and p(STS) Polymers**

| Polymer | Initial contact angle (°) | Equilibrium contact angle (°) | Sol content (%) |
|---|---|---|---|
| p(SCS) (1 : 1 : 0.5) | 57.03 ± 8.06 | 21.34 ± 2.18 | 2.12 ± 0.35 |
| p(SCS) (1 : 1 : 1) | 58.11 ± 4.72 | 38.24 ± 1.42 | 1.14 ± 0.21 |
| p(SCS) (1 : 1 : 2) | 87.06 ± 11.12 | 50.21 ± 4.65 | 1.85 ± 0.10 |
| p(SCS) (1 : 0.5 : 1) | 33.73 ± 2.16 | 18.12 ± 0.89 | 4.21 ± 1.04 |
| p(SCS) (1 : 2 : 1) | 36.57 ± 1.49 | 11.28 ± 3.25 | 8.24 ± 2.87 |
| p(SCS) (2 : 1 : 1) | 27.58 ± 1.12 | 14.94 ± 2.01 | 12.87 ± 1.58 |
| p(STS) (1 : 1 : 0.5) | 40.25 ± 6.42 | 22.34 ± 4.24 | 4.25 ± 0.56 |
| p(STS) (1 : 1 : 1) | 45.49 ± 2.44 | 26.21 ± 1.24 | 2.37 ± 0.18 |
| p(STS) (1 : 1 : 2) | 69.22 ± 5.55 | 41.28 ± 7.84 | 1.54 ± 0.56 |
| p(STS) (1 : 0.5 : 1) | 39.13 ± 2.55 | 12.28 ± 3.12 | 6.25 ± 0.17 |
| p(STS) (1 : 2 : 1) | 31.03 ± 1.89 | 13.89 ± 1.87 | 14.21 ± 1.24 |
| p(STS) (2 : 1 : 1) | 24.21 ± 3.21 | 9.84 ± 2.21 | 13.87 ± 3.21 |

The increase in the SA content in the polymer lowered the degradation as a result of increased resistance from longer hydrophobic chains of SA to the water penetration. The enhanced mass loss rate with increased CA/TA content in the polymers was due to the release of more carboxyl groups, which autocatalyzed the hydrolytic reaction.[40] The rapid degradation of p(SCS) (2 : 1 : 1) and p(STS) (2 : 1 : 1)

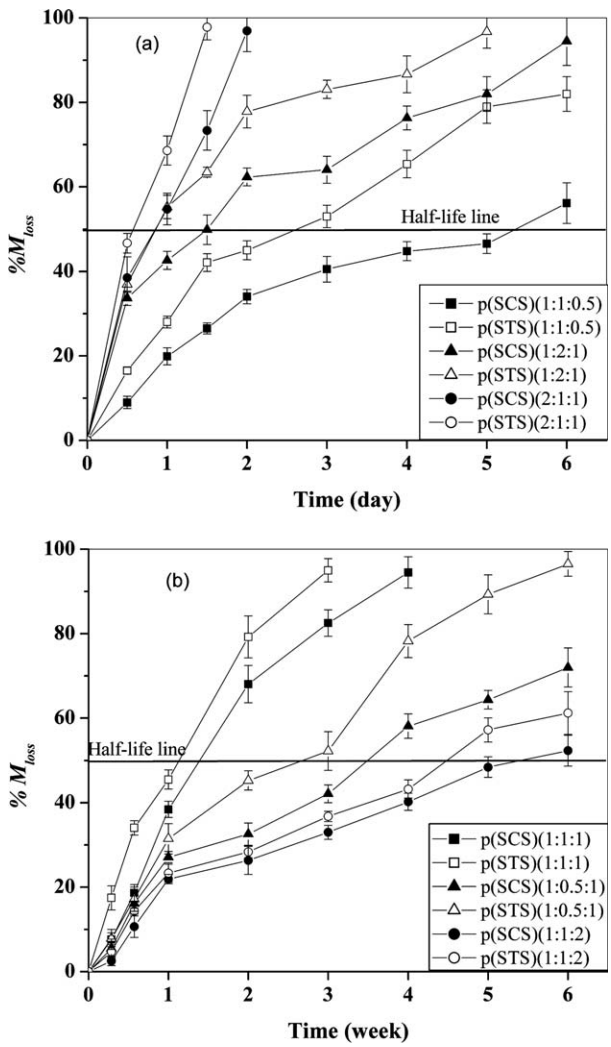


**Figure 6** *In vitro* degradation of the p(SCS) and p(STS) polymers having half-lives of (a) less than a week and (b) greater than 1 week in PBS at 37°C.

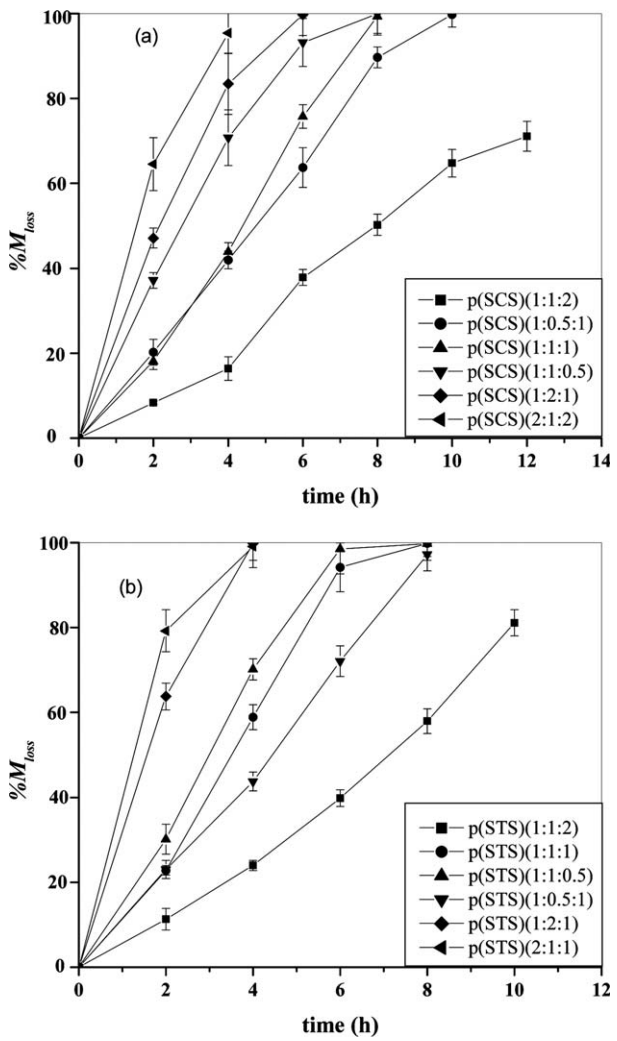


**Figure 7** Degradation of the (a) p(SCS) and (b) p(STS) polymers in 0.1*M* NaOH at 37°C.

could be attributed to the presence of more hydrophilic hydroxyl groups, which increased the water accessibility to the vicinities of the ester bonds. At any given monomer concentration, the degradation rates of p(STS) were higher than p(SCS) polymers. The reason was that the high degree of crosslinking in the p(SCS) over p(STS) polymers, which resulted in a high resistance to diffusional transport, decreased the rate of hydrolytic reaction.

Figure S3 (see Supporting Information) summarizes the results obtained for various systems. Figure S3a shows that the optical properties of the polymers could be also tuned. Figure S3b and S3c show that there was wide variation in the mechanical and degradation properties of p(SCS) and p(STS). Thus, these polymers exhibited a wide range of physical, mechanical, and degradation properties and, thus, could potentially be developed for a variety of biomedical applications.

## CONCLUSIONS

We synthesized two new families of biodegradable S-based polymers, namely, p(SCS) and p(STS), by reacting S with CA, TA, and SA. These monomers were chosen because of their potential to be endogenous to human metabolism, their low cost, and their ready obtainability from renewable sources. The synthesized polymers were characterized by a wide variety of spectroscopy and thermal techniques. Scaffolds were prepared with a salt-leaching technique and characterized with SEM. The physical, mechanical, and degradation properties of these materials were examined, and at any given polymer composition, the Young's modulus and tensile strength of the p(SCS) was higher than those of p(STS), whereas the *in vitro* degradation rates of p(STS) were higher than that of p(SCS).

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