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Poly(glycerol–sebacate) Bioelastomers—Kinetics of Step-Growth Reactions Using Fourier Transform (FT)-Raman Spectroscopy

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ABSTRACT: Kinetic studies of the esterification of glycerol (G) and sebacic acid (SA) at three molar ratios (0.6, 0.8, 1.0) and at three temperatures (120, 130, 140°C) to form poly(glycerol–sebacate) were performed and assessed using FT-Raman spectroscopy. The quantitative changes in the concentrations of carboxylic acid and ester groups within the forming bioelastomer were measured and the chemical rate constants (k) determined from the kinetic scheme were first-order, with respect to sebacic acid concentration. Increasing the reaction temperature by 20°C is noted to increase the chemical rate constant (k) by a factor of up to 4.5 and the total extent of conversion at early times for the molar ratios investigated. The activation energy (E_a) and the pre-exponential factor (A_0) for these three stoichiometric ratios were calculated, which varied in accordance with the average functionality of the system. Under isothermal conditions, the chemical rate constant remained unchanged with an increase in the extent of the reaction (α) until a spontaneous transition resulted in the shift in the mechanism from kinetics to diffusion controlled. The Young's moduli of the PGS polymers were found to depend primarily on the average functionality of the system and the curing period. This investigation confirms the reaction mechanism for PGS polymer synthesis and shows the flexibility afforded to PGS properties and reaction times through varying the stoichiometric ratios of glycerol to sebacic acid. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: biomaterials; biopolymers renewable polymers; kinetics

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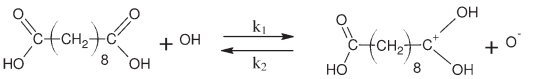
INTRODUCTION

Poly(glycerol–sebacate) (PGS) is a bioelastomer with a covalently crosslinked, three-dimensional network of random coils with hydroxyl groups attached to its backbone. This biodegradable polymer is biocompatible (*in vitro* and *in vivo*), tough, elastic, inexpensive, and flexible.[1] These materials are finding usage in fields such as soft tissue engineering,[2,3] microfabrication,[4] nerve-guide application,[5] drug delivery, and *in vivo* sensing.[1] The molecular weight distribution of a polyester synthesized by polycondensation is completely defined by the mole ratio of the reactants and the extent of the reaction.[6] Reaction rates of these step-growth reactions depend exclusively on concentrations and temperature, and not on the cure history or the rate at which the temperature may be varying. A unique reaction rate may thus be defined for a given concentration and temperature.[7] Further, many reactive polymer systems employ an overall formulation such that the average functionality is 2 or slightly greater than 2. In other words, by varying the density of crosslinking in the network structure through average functionality (f_{av}) and curing period, a flexible to tough elastomer can be obtained and tailored to fit with various tissue-engineering applications.[8,9]

PGS prepolymer is synthesized following a step-growth reaction scheme. In the presence of a solvent like toluene, this is generally a very slow reaction requiring 2–3 days to reach gelation. A continuous process, if developed, could address the inherent deficiencies (e.g., long residence time, venting) associated with the large-scale synthesis of such bioelastomers. However, in order to assess whether this particular system may be adapted to continuous processes, such as reactive extrusion, kinetic studies of such controlled condensation reactions are important.

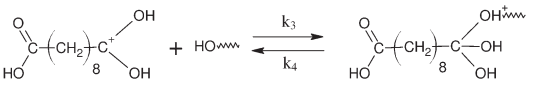
FT-Raman spectroscopy is an important spectroscopic method used to determine the presence of functional and end-groups, monomer and polymer structure and conformation, orientation of chains, and further, it can also be used to follow changes in

The hydroxyl groups of the triol act as an initiator for the reaction. A primary hydroxyl group of glycerol attacks a carboxyl group of the diacid to form a monoester with a free carboxyl group.



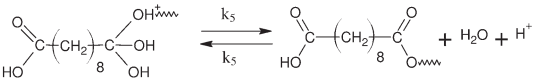
I

The protonated species I react with another primary hydroxyl group to yield another protonated species II.



II

The protonated species II dissociate to form monoester III



III

Scheme 1. The proposed reaction scheme for the formation of poly (glycerol-sebacate).

structural parameters as the polymers are exposed to environmental or mechanical stresses.[10] The peaks in a Raman spectrogram correspond to fundamental transitions and hence provide precise chemical information. FT-Raman spectroscopy has been used in numerous esterification studies to, for example, investigate polyester structure,[11] monitor transesterification,[12] determine chain conformation distributions,[13] study cyclic anhydride intermediates,[14] investigate kinetics of (polyurethane) polymerization,[15] determine the extent of O-esterification,[16] quantify the presence of ethyl esters during transesterification,[17] study intermolecular interactions in oligomers,[18] and elucidate mechanisms of polyesterification.[19]

Because of the dependence of the reaction rate on concentration and temperature three molar ratios (0.6, 0.8, 1.0) of glycerol (G) to sebacic acid (SA) and three temperatures (120, 130, 140°C) were selected for this investigation of the PGS reaction kinetics using FT-Raman spectroscopy. This investigation focuses on the effects of variations in molar ratio on the density of crosslinking and resultant mechanical properties of the PGS bioelastomers.

EXPERIMENTAL SECTION

Materials

Glycerol (Reagent Plus >99% pure) and sebacic acid (99% pure) were obtained from Sigma-Aldrich, Sydney. They were used without any further purification.

Reaction Method

Stoichiometric quantities (G: SA = 0.6, 0.8, 1.0-molar ratio) of the monomers were mixed with toluene (40% of combined monomer weight) in a round-bottomed flask, which was fitted with a Dean-Stark trap (for water-removal) and a reflux condenser. Esterification was carried out at three different temperatures (120, 130, and 140°C). Samples were collected in tightly sealed glass vials after every 2 h until gelation and stored in an ice-bath to avoid further reaction. The bioelastomers will be designated as PGS 0.6, PGS 0.8, and PGS 1.0, respectively throughout the remainder of the discussion.

FT-Raman Spectroscopy

All spectroscopic experiments were carried out on a Perkin-Elmer System 2000 NIR FT-Raman spectrometer, equipped with a diode pumped Nd-YAG laser (λ = 1064 nm) as an excitation source and a room temperature InGaAs photoelectric detector. Typical spectra were recorded in a range of 200–3800 cm^{-1} at a laser power of 320 mW and at a spectral resolution of 8 cm^{-1}.

Compression Tests

Specimens (15 mm Φ, 4 mm thickness) were prepared by curing the prepolymers in a mold in a vacuum oven at 130°C and 50 mbar for 24 h. Uniaxial compression tests were thereafter conducted on PGS specimens using an Instron ElectroPuls® test machine (type E1000) fitted with a 50*N* load cell. The samples were compressed at a crosshead speed of 0.1 mm/s to 0.15 mm.

RESULTS AND DISCUSSION

Reaction Scheme and Analysis of Spectra

The reaction between glycerol and sebacic acid to yield poly (glycerol–sebacate) is a step-growth reaction. The possible reaction scheme is shown in Scheme I. The symbol ~~~~ indicates all acid or alcohol species in the reaction mixture (monomer, dimer, trimer, etc).

The monoester III then reacts with another primary hydroxyl group from another glycerol molecule to yield a diester and a new secondary hydroxyl group. When the secondary hydroxyl groups on the successive esters formed react with new carboxyl groups, it leads to crosslinking and eventually gelation.

A sample FT-Raman spectrum of PGS 0.6 is shown in Figure 1. In the spectra no side reactions were observed. The sum of intensity of peaks at 1642 and 1738 cm^{-1} was used for all spectra as an internal normalization standard. The relative decrease in carboxyl groups until gelation was observed at 1642 cm^{-1} whereas, a corresponding increase in the ester groups was observed at 1738 cm^{-1}. The peak assignments were made using standard references.[20–22]

FT-Raman spectra showing acid (1642 cm^{-1}) and ester (1738 cm^{-1}) peaks of PGS 0.6, PGS 0.8, and PGS 1.0 at 120°C at time zero and gelation are shown in Figure 2. Similar spectra were observed for experiments at 130 and 140°C (data not shown).

The carboxyl functional group peak intensities are expected to decrease progressively throughout the reaction. To follow the total conversion of acid groups on sebacic acid throughout each

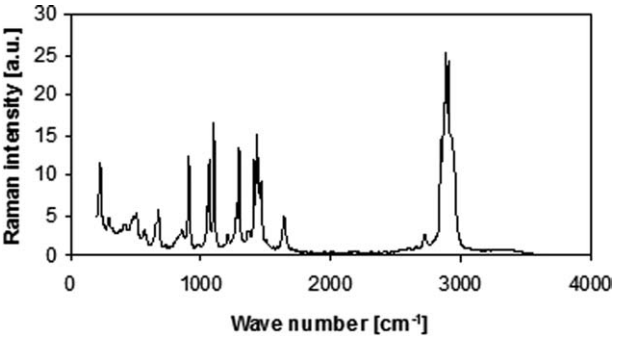


Figure 1. FT-Raman spectrum of PGS 0.6 at 120°C at t = 0.

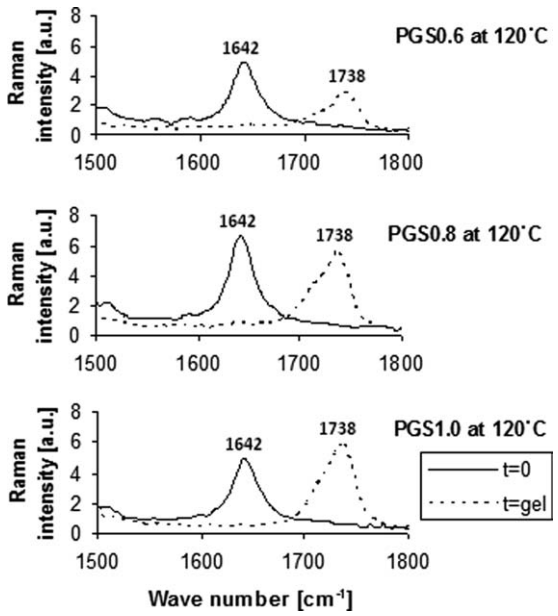


Figure 2. Raman spectra of acid (1642 cm^{-1}) and ester (1738 cm^{-1}) peaks at 120°C.

reaction as a function of G:SA ratio and temperature, the peak areas at 1642 cm^{-1} were calculated (see Figure 3). To convert these peak areas to a calculated sebacic acid concentration, the initial sebacic acid concentrations of 3.888 mol/kg (for PGS 0.6), 3.638 mol/kg (for PGS 0.8), and 3.401 mol/kg (for PGS 1.0) were taken into consideration.

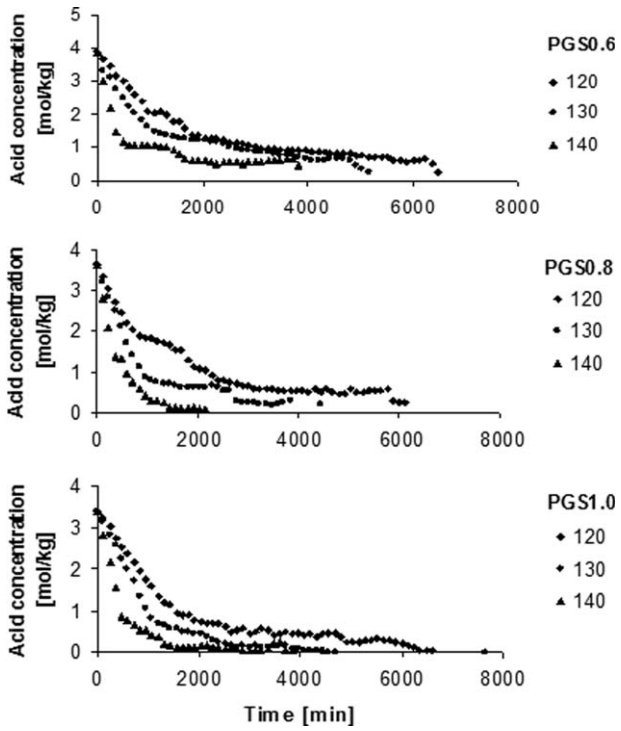


Figure 3. Calculated carboxylic acid group (1642 cm^{-1}) concentration as a function of PGS ratio and temperature.

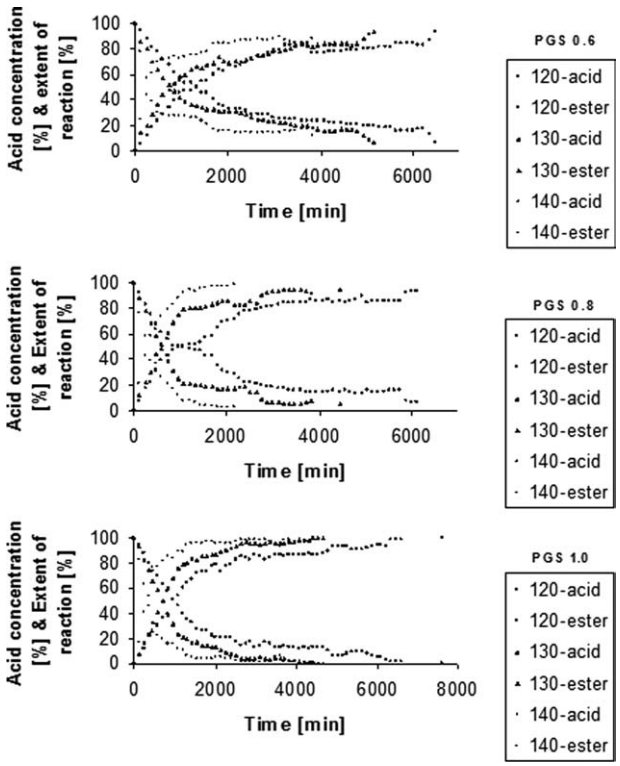


Figure 4. Acid concentration (%) and extent of reaction (based on ester peak (1738 cm^{-1}) variation) as a function of PGS ratio and temperature.

Similarly, the relative increase in bands correlating to ester group formation can be observed from the spectra at 1738 cm^{-1}. The acid concentration (calculated using acid peaks) and the extent of the reaction determined from the appearance of aliphatic ester peaks (1738 cm^{-1}) of PGS 0.6, PGS 0.8, and PGS 1.0 at three different temperatures are shown in Figure 4. The extent of esterification was calculated according to eq. (1).

$$\beta = \frac{I^{1738}_{(t)N} - I^{1738}_{(0)N}}{I^{1738}_{(\infty)N} - I^{1738}_{(0)N}} \quad (1)$$

where, β is the extent of the esterification reaction, $I_{(t)N}$ is the normalized Raman intensity at time, t, $I_{(0)N}$ is the normalized intensity at $t = 0$, and $I_{(\infty)N}$ is the normalized Raman intensity at gelation.

The average functionalities (f_{av}) of stoichiometric mixtures PGS 0.6, PGS 0.8, and PGS 1.0, calculated using Pinner's equation,[23] are 2.25, 2.22, and 2.0, respectively. The higher the value of f_{av}, the higher the degree of polymerization that will occur in the system.[8] All step-growth reactions are characterized by the growth of branching chains resulting in an increase in the viscosity and molecular weight of the system. During this process, an irreversible transformation from a viscous liquid to a rubbery state without any chemical change leads to gelation. Here, the molecular weight of the system diverges to infinity.[24] The reaction is said to be in the kinetic regime until the solution turns viscous. Thereafter, there is a considerable increase in the molecular weight of the polymer from the onset of microgel

Table I. Gel Points, Degree of Polymerization, and Molecular Weights of PGS Systems

PGS	p_{gel} Carother's eq	p_{gel} experimental	f_{av}	p	DP	M_w (DP*441)
PGS 0.6	0.889	0.935 (120°C)		0.85	22.85	10,080
		0.931 (130°C)	2.25	0.88	100	44,100
		0.884 (140 °C)		0.885	228.57	100,799
				0.888	1000	441,000
PGS 0.8	0.901	0.935 (120°C)		0.89	82.64	36,446
		0.945 (130°C)	2.22	0.895	152.67	67,328
		0.974 (140°C)		0.899	473.93	209,004
				0.9	1000	441,000
PGS 1.0	1.0	0.994 (120°C)		0.95	20	8,820
		0.997 (130°C)	2.00	0.98	50	22,050
		0.999 (140°C)		0.995	200	88,200
				0.999	1000	441,000

formation until the completion of gelation. Here, a sufficient molar concentration of tetramer or higher polymers is formed to bring about a state of arrested motion.[25] The polymerization now becomes diffusion-controlled, as the mobility becomes too low to allow the maintenance of the equilibrium concentrations of reactive pairs (G and SA) and their collision frequencies.[8] As a result, we find a sharp increase in the molecular weight (and hence extent of reaction) from the onset of gelation to completion (see Figure 4). Beyond gelation, a transition from rubber to glass state leads to vitrification, which is marked by changes in the physical and thermodynamic properties of the system.[26]

From Figure 4, it can be noted that as the stoichiometric ratio approaches 1.0, an increase in the time to reach gelation is observed, which suggests that as the chain length is increased, it becomes more difficult for the reactive groups on the molecules to come in contact. This will likely result in the synthesis of softer resins, but we shall come back to this later. The experimental gel points, degree of polymerization (DP) and weight average molecular weights (M_w; derived from the Carothers equation) for different extents of reaction (p) for the three systems approaching gelation (at temperatures varying from 120 to 140°C) are shown in Table I.

Rate Curves and Kinetic Analysis

The measured data for the consumption of carboxylic groups of PGS 0.6, PGS 0.8, and PGS 1.0 (shown graphically in Figure 3) can now be plotted in a linearized first-order kinetic plot (Figure 5) using the following equation.

$$-\ln[C_B/C_{B0}] = \mathrm{kt} \tag{2}$$

where, C_{B0} is the initial concentration of sebacic acid, C_B is the concentration at any time, t, and k is the kinetic rate constant. (note: other possible reaction orders (second, third, other) were tested. The best fit was first order reaction).

For step-growth reaction schemes, for a given concentration and temperature, a unique value of the reaction rate may be defined.[7] Regardless of temperature and PGS ratio, we observe that the reactions follow first order kinetics in the kinetics regime, and with increasing temperatures (120–140°C) and molar ratio (G:SA), the dependency on first order kinetics increases in the kinetics regime. A 20°C increase in the reaction temperature is noted to increase the chemical rate constant (k) by a factor of 4.5 in the case of PGS 0.6 and by a factor of 3 in each of PGS 0.8 and PGS 1.0. Assuming Arrhenius dependency of the rate constants on temperature (shown in Figure 6) the activation energy (E_a) and pre-exponential factors (A_0) were calculated for the three systems using the following equation:

$$k = A_0 \ \mathrm{Exp}\ [-E_a/\mathrm{RT}] \tag{3}$$

where, R is the universal gas constant (kJ/mol/K) and T is the temperature.

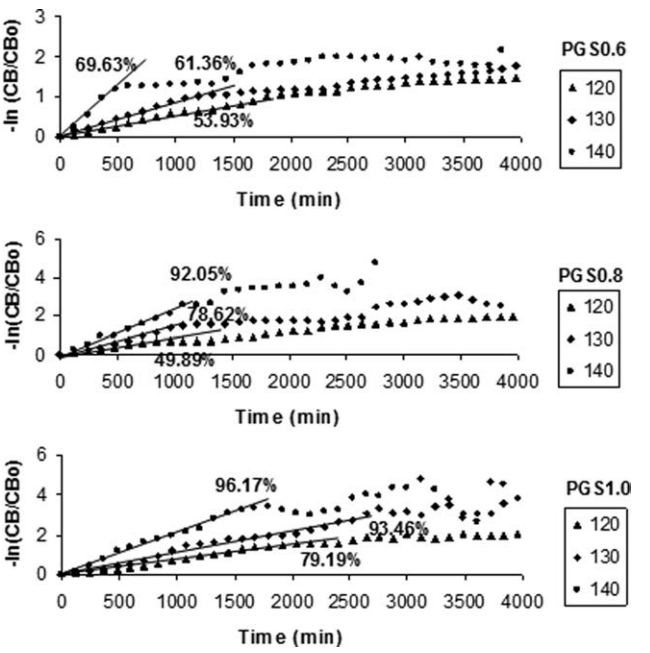


Figure 5. Linearized first-order kinetic plot (C_B = concentration of sebacic acid in mol/kg) for varying PGS ratios at 120, 130, 140°C.

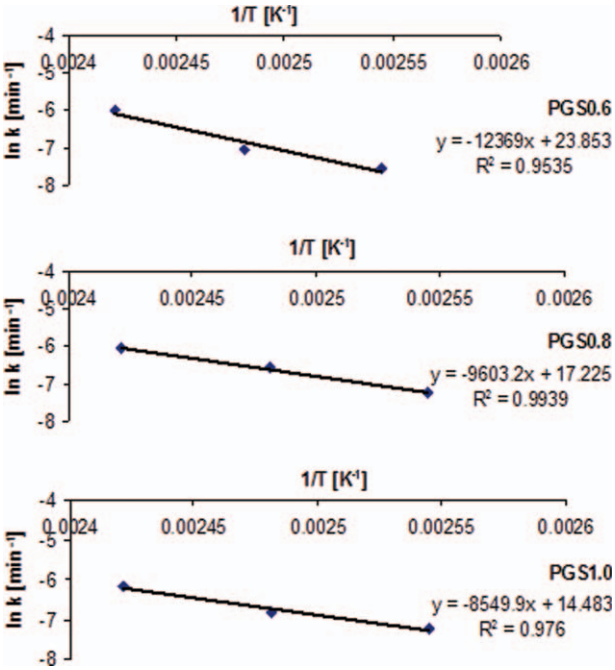


Figure 6. Arrhenius plot of ln k vs. $1/T$ for varying PGS ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The extracted chemical rate constants are shown in Table II. In the case of PGS 1.0, at 140°C the reaction follows first-order kinetics up to 96% conversion. As the temperature of the reaction increases, the rate becomes predominantly kinetic-controlled, wherein the reaction rate does not depend upon the sizes of reactant molecules. Under the kinetic regime, the rate-determining step will be the decomposition of the activated complex into reaction products.[7] As polymerization progresses, the viscosity of the system gradually increases. Under isothermal conditions, the chemical rate constant remains unchanged with increase in the extent of the reaction (α) until a spontaneous transition results in the change in the reaction mechanism from kinetics to diffusion-control.[27] This transition is shown by a sharp decrease or flattening of the value of $-\ln(C_B/C_{B0})$ (see Figure 5), where $C_B/C_{B0} = 1\text{-}\alpha$. As discussed before, once the reaction proceeds to gelation under the diffusion-regime, there is a substantial increase in the molecular weight of the polymer.

Table II. Values of Rate Constant (k), Energy of Activation (E_a), and Pre-Exponential Factor (ln A_0) for All PGS Ratios Investigated as a Function of Temperature

Temperature	k (min^{-1}) $\times 10^{-4}$	E_a (kJ/mol)	ln A_0 (min^{-1})
PGS 0.6-120°C	5.382		
PGS 0.6-130°C	8.805	102.8	22.794
PGS 0.6-140°C	24.831		
PGS 0.8-120°C	7.194		
PGS 0.8-130°C	14.826	79.8	17.225
PGS 0.8-140°C	23.445		
PGS 1.0-120°C	7.268		
PGS 1.0-130°C	10.823	71.1	14.483
PGS 1.0-140°C	20.916		

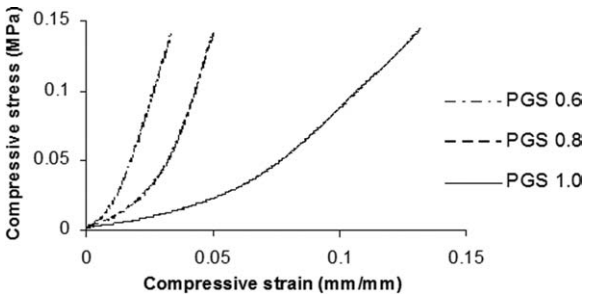


Figure 7. Compression test data of PGS polymers.

The calculated values of the rate constants, activation energy (E_a), and pre-exponential factors (ln A_0) are shown in Table II.

The activation energy (E_a) is the energy level to be exceeded for the reaction to take place.[28] The high activation energy values for PGS systems (refer Table II) indicate that these reactions are largely in the kinetically controlled regimes, as expected.[29] The energy of activation and the pre-exponential factor [ln A_0] for the synthesis of poly(hexamethylene adipate) glycol are reported[30] to be 84.1 kJ/mol and 28 kg^2/eq^2 h, respectively. The reported values of E_a for the esterification of behenic acid and various alcohols namely, decanol, lauryl alcohol, myristyl alcohol, and cetyl alcohol are 86.2, 79.6, 78.6, and 87.1 kJ/mol, respectively.[31] According to Simitzis et al.,[28] a variation in the molar ratio of a mixture of diacids in the polyesterification of diacids with ethylene glycol has a direct impact on the energy of activation and the pre-exponential factor of those systems. Here, when the maleic acid to adipic acid ratio was changed from 33 : 67 to 50 : 50 during their esterification with ethylene glycol, the values of the energy of activation and the pre-exponential factors (ln A_0) were found to decrease from 65.4 kJ/mol and 17.87 min^{-1} to 57.73 kJ/mol and 15.14 min^{-1}, respectively. For the PGS system, an increase in the molar ratio (G : SA) decreases the average functionality (f_{av}) and hence the density of crosslinking of the system. As a result, the threshold energy required by the functional groups to react at the available crosslinkable sites to form activated complexes decreases. This should also decrease the pre-exponential factor due to a decrease in the available reactive functional groups on the polymer chains. As we move from PGS 0.6 to PGS 1.0, a decrease in the activation energy and pre-exponential factor is observed (see Table II). This is in agreement with this hypothesis and previous

Table III. Young's Moduli (Compression) of PGS Bioelastomers (σ = 1st std. dev.)

Polymer	Young's modulus (compression) E (kPa)
PGS 0.6	718.55 (σ = 8.84)
PGS 0.8	570.29 (σ = 5.94)
PGS 1.0	253.41 (σ = 7.47)

outcomes with similar systems. In other words, decreasing the average functionality of the system will yield softer resins.

The results of uniaxial compression tests conducted on Instron ElectroPuls® test machine (Type E 1000) are shown in Figure 7. It has been reported that in epoxy networks the crosslink density directly affects the relaxation modulus (E_0) of the system.[32]

The Young's moduli (generally for rubber materials, $\nu = 0.5$; so $K = E$) of these systems were found to decrease in the following order: PGS 0.6 > PGS 0.8 > PGS 1.0 (see Table III). The differences in f_{av} seem to be in agreement with the trend. Here, it is important to note that the duration of curing also affects the crosslinking density of the system.

The crosslinking densities (n) for the three systems calculated using[33] eq. (4) (given below), where E_0 is Young's modulus, R is the universal gas constant, and T is the temperature, are 71.48 ± 8.84 mol/m^3, 56.73 ± 5.94 mol/m^3, and 25.21 ± 8.84 mol/m^3, respectively.

$$n = E_0/3\mathrm{RT} \quad (4)$$

Overall, for tissue-engineering applications, the above systems can thus be treated as kinetically tailored bioelastomers. Based on the requirements of a particular tissue engineering application, the mechanical properties of a bioelastomer can be suitably tailored by using appropriate average functionality, crosslinking density, and curing period. Further, the dicarboxylate end groups of PGS may be modified to control the rate of degradation, exemplifying the utility of PGS as an ideal candidate for a multitude of biomaterial scaffold applications.

CONCLUSIONS

FT-Raman spectroscopy has been used to study the kinetics of the step-growth reaction between glycerol and sebacic acid at three molar ratios (G:SA = 0.6,0.8,1.0) and three temperatures (120, 130, 140°C). From the spectra, the quantitative concentrations of the carboxylic acid and the ester groups as a function of time were calculated. No side reactions were observed in the spectra. The rate curves followed first-order kinetics in the kinetics regime. Thereafter, the reaction became diffusion-controlled because of a substantial increase in the molecular weight of the polymer resulting in the mobility of reactants becoming too low to allow the maintenance of the equilibrium concentrations of reactive pairs. At higher temperatures the reaction mechanism continues to follow first-order kinetics, with an increase in conversion in the kinetic-controlled regime. An increase in the molar ratio (G:SA) of the reactants decreases the average functionality of the system and the crosslinking density, resulting in the lowering of the activation energy and the pre-exponential factor. The average functionality of the system thus has a profound effect on the crosslinking density, mechanical properties, and the reaction kinetics of the system. Based on the requirements of the tissue to be replaced, PGS bioelastomers can be kinetically tailored to address the chosen application. The elucidated reaction mechanism and quantified rate constants and Arrhenius parameters provide useful insight for developing a continuous process for the synthesis of bioelastomers with desired mechanical properties for a multitude of tissue engineering applications.

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