

Structure and Properties of Thermoplastic Poly(glycerol sebacate) Elastomers Originating from Prepolymers with Different Molecular Weights

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Received 29 June 2006; accepted 5 October 2006

DOI 10.1002/app.25606

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Thermoplastic poly(glycerol sebacate) (TMPGS) elastomers originating from three prepolymers with different molecular weights were prepared first, and then the structure and properties were studied. Specifically, by swelling tests, gel permeation chromatography, X-ray diffraction, and differential scanning calorimetry, the crosslinking densities, sol contents and compositions, crystallization, and thermal performances of three TMPGSs were examined. Finally, the degradability in a 37°C phosphate-buffered saline solution (pH = 7.4) was also illuminated. The

three TMPGSs had similar chemical structures, but the different molecular weights of the prepolymers influenced their final compositions and properties to a great extent. Furthermore, both hydrogen bonding and plasticization action in the elastomers played important roles in balancing the overall properties of the TMPGS elastomers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1131–1137, 2007

Key words: elastomers; structure-property relations; thermal properties; thermoplastics

INTRODUCTION

Elastomers are generally divided into two types: thermoplastic elastomers and thermoset elastomers. Thermoplastic elastomers are usually phase-separated block copolymers,^{1–3} whereas thermoset elastomers are formed sometimes by the crosslinking of star-shaped prepolymers.^{4–8} Thermoplastic and thermoset elastomers can be prepared by special methods.^{9–12}

Thermoset poly(glycerol sebacate) (PGS) elastomers have shown good flexibility, biocompatibility, and biodegradation.^{10,13} The preparation method is as follows. First, the prepolymers are synthesized, and then the prepolymer solution is poured with anhydrous 1,3-dioxolane as a solvent into a mold for further curing and shaping under a high vacuum. The

final thermoset products cannot be processed to a new expected shape again.

To achieve PGS elastomers with thermoplasticity, we first prepared PGS elastomers composed of a sol and a gel by a one-step method without the assistance of a solvent¹⁵ and then put forward a two-step method.¹⁶ Using the two methods, we can obtain thermoplastic poly(glycerol sebacate) (TMPGS) elastomers, and we have found that the two-step method is easy to control and can optimize the properties of materials. With the goal of deeply illuminating the two-step method, in this article, we describe three elastomers that came from prepolymers with different molecular weights. As a result, the TMPGSs had similar chemical structures, but many factors, such as the sol contents and compositions, hydrogen bonding, and plasticization action, influenced their final properties. In other words, the sols in the TMPGSs corresponded to the soluble parts with tetrahydrofuran as a solvent, whereas the gels were insoluble.

EXPERIMENTAL

Materials

Glycerol (analytical-grade, weight content > 99.0%) was obtained from the Beijing Chemical Plant (Beijing, China). Sebacic acid (analytical-grade, weight content > 99.0%) was obtained from the Guangfu Fine Chemi-

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Contract grant sponsor: Key Project of Beijing National Science Foundation; contract grant number: 2061002.

Contract grant sponsor: Key Laboratory of Beijing City on the Preparation and Processing of Novel Polymer Materials at Beijing University of Chemical Technology.

Contract grant sponsor: Laboratory of Bone Tissue Engineering, Beijing Research Institute of Traumatology and Orthopaedics, Department of Spine Surgery, Beijing Jishuitan Hospital.

Journal of Applied Polymer Science, Vol. 104, 1131–1137 (2007)
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cal Institute of Tianjin (Tianjin, China). Tetrahydrofuran (analytical-grade) was obtained from the Beijing Century Red-Star Chemical Ltd. Corp. (Beijing, China). All reagents were used directly.

Preparation of the TMPGS elastomers

After glycerol and sebacic acid were blended in a flask in a molar ratio of 1/1, they were heated until they completely melted in 1 h. Under controlled conditions of 130°C and 1 kPa, the reaction being continued for some time, three prepolymers with different molecular weights were attained. Adding sebacic acid to the flask and allowing the total molar ratio to reach 2/2.5 (glycerol/sebacic acid), with the reaction continuing at 130°C and 1 kPa for some time, led to the wanted products. Nitrogen was always running into the flask slowly during the whole process.

These products were taken out of the flask and hot-pressed at 130°C and 15 MPa in a window mold and then were transferred to another cold-press machine and molded at room temperature. According to the increases in the molecular weight, the prepolymers were named p_1 , p_2 , and p_3 , and the corresponding elastomers were named e_1 , e_2 , and e_3 .

Characterization of the prepolymers

To investigate the structures of the prepolymers, a Bruker (Zurich, Switzerland) AV600 NMR spectrometer was employed to determine the $^1\text{H-NMR}$ spectra; it worked at 600.13 MHz for protons in chloroform- d_6 with tetramethylsilane as the standard. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polymer distribution index (PDI) of the prepolymers were reported by gel permeation chromatography (GPC) measurements on a Waters instrument equipped with three columns (Styragel HT3, HT5, and HT6E), with tetrahydrofuran as the eluent at a flow rate of 1 mL/min, and a Waters 2410 refractive-index detector, and a polystyrene standard was used for calibration.

Characterization of the TMPGS elastomers

Infrared spectra of the elastomers were recorded on a Nicolet (Madison, WI) 210 spectrophotometer with salt (KBr) flakes pressed together with the fragments of the elastomer films.

The sol contents of the elastomers and swelling degrees of the corresponding gels were measured with the following swelling tests.¹¹ A small disc sample (1 mm thick, 10 mm in diameter, ~ 0.09 g) of weight W_1 was dipped into tetrahydrofuran (20 mL) for 24 h and then was taken out. The disk was recorded with weight W_2 after the solvent on its surface was

absorbed by filter papers; the disk was then dried to constant weight W_3 in a vacuum oven. The sol content was $Q = (W_1 - W_3)/W_1 \times 100\%$, and the swelling degree of the corresponding gel was reported as follows: $R = (W_2 - W_3)/W_3 \times 100\%$. Two samples were applied in each experiment, and the average value was adopted. To get the composition information for the sols, especially the sebacic contents in the elastomers and the molecular weights of the sols, the sol solution in tetrahydrofuran that remained after the swelled gel was taken out was analyzed on the GPC instrument. Here, the sebacic acid content estimate was considered as a first approximation.

The specimens for mechanical testing were cut from 1-mm-thick samples according to ISO/DIS 37-1990 type 3 specifications (2-mm-wide dumbbell-shaped specimens). Tensile tests were performed with a universal tensile testing machine equipped with a 50N load cell and operated at a crosshead speed of 50 mm/min. The elongation of the specimens was derived from the extensometer separation of 15 mm. Young's modulus was determined from the initial slope of the stress-strain curve (1–5% strain range of the stress-strain curve). Three samples were tested at 23°C.

The wide-angle X-ray diffraction patterns of the elastomers were recorded on a Rigaku (Tokyo, Japan) model D/Max2500VB2+/PC X-ray diffractometer with nickel-filtered Cu $K\alpha$ radiation and with a 1-mm-thick sheet with a smooth surface.

The thermal properties of the elastomers (composed of gel and sol) and the corresponding gel parts (obtained by the dipping of the elastomers into tetrahydrofuran for 24 h and then drying to a constant weight) were evaluated with a differential scanning calorimeter (Perkin-Elmer, Norwalk, CT) test at a heating and cooling rate of 10°C/min. The sample (17–20 mg), placed in an aluminum pan, was first heated from 40 to 150°C and held there for 5 min; the cooling scan was then recorded from 150°C to -100°C , and subsequently, a second heating scan was conducted from -100 to 150°C.

The equilibrium water uptake in deionized water was defined as the fraction of gained weight of a small disc sample: $U_1 = (M_2 - M_1)/M_1 \times 100\%$ and $U_2 = (M_2 - M_3)/M_2 \times 100\%$, where M_1 is the initial weight of the specimen, M_2 is the weight after the specimen is dipped in deionized water for 24 h, and M_3 is the weight of the specimen first dipped in deionized water for 24 h and then dried to a constant weight in a vacuum oven. Three samples were tested, and the average value was obtained.

The hydrophilicity of the elastomers was characterized by the measurement of the water-in-air contact angle (WCA) of smooth surfaces of 1-mm-thick samples with a Germany Dataphysics OCA20 water-contact-angle-measurement instrument (Filderstadt, Germany). The sessile drop method was adopted, and the result was the average of five values.

TABLE I
Molecular Weights and ^1H NMR Results for the Prepolymers

Prepolymer	M_n	M_w	PDI	F	E_1 (%)	E_2 (%)	I (%)
p ₁	1,681	2,696	1.60	0.97/1	53.48	11.33	35.19
p ₂	2,426	5,725	2.36	0.98/1	55.02	12.45	32.53
p ₃	4,429	31,798	7.18	0.94/1	56.13	11.53	32.34

The small disc samples (10 mm in diameter, 1 mm thick, ~ 0.09 g) were used for the degradation study. We mainly considered hydrolysis degradation. A sample of weight G_1 was put into a taper bottle and immersed in phosphate-buffered saline (PBS; pH = 7.4) at 37°C in an oven. The PBS was replaced every 2 days to ensure a constant pH of 7.4. The samples were removed after a certain time, washed three times with deionized water, and then dried to constant weight G_2 in a vacuum oven. The mass loss was calculated as follows: mass loss = $(G_1 - G_2)/G_1 \times 100\%$. Three specimens were tested to achieve the average value.

RESULTS AND DISCUSSION

^1H -NMR and GPC analysis of the prepolymers

The actual molar ratio of the reactants (F), the esterification degrees of $-\text{CH}_2-\text{OH}$ (E_1) and $-\text{CH}-\text{OH}$ (E_2) in 1 mol of glycerol, and the percentage of residue hydroxyl groups (I) in the prepolymers were calculated from the data of the ^1H -NMR measurement as reported.^{5,16–18} All the results for the prepolymers are listed in Table I.

According to Table I, the actual molar ratios of p₁, p₂, and p₃ were similar and close to 1 : 1, and the molecular weight and PDI increased with the reaction time as expected, whereas the residue hydroxyl groups of

p₁, p₂, and p₃ decreased in turn. It can be concluded that increasing the molecular weight will lead to a decreasing number of hydroxyl groups in the prepolymers because of the simultaneous proceeding of chain propagation and esterification of hydroxyl. Furthermore, from the esterification degrees of different hydroxyls, it has been found that the most of the residual hydroxyl groups are $-\text{CH}-\text{OH}$. The presence of hydroxyl groups will provide reactive points for the second step of the reaction. $-\text{CH}_2-\text{OH}$ will mainly serve the chain propagation, whereas $-\text{CH}-\text{OH}$ mainly contributes to the branching and crosslinking reaction.

Fourier transform infrared (FTIR) spectra of the TMPGS elastomers

Figure 1 shows the FTIR spectra of the TMPGS elastomers. The spectra of e₁, e₂, and e₃ were almost accordant: the absorption at 2686 cm^{-1} belonged to the hydroxyl groups in carboxyl; the absorption at 1747 cm^{-1} corresponded to the ester carbonyl; and the absorption at 3461 cm^{-1} correlated to the hydroxyl groups, which was at lower wave numbers compared with that of free hydroxyl groups, and illustrated the strong action of hydrogen bonding in the elastomers. All these demonstrated that the three elastomers had similar chemical structures.

Swelling degrees and composition analysis of the TMPGS elastomers

As shown in Table II, with an increase in the molecular weight of the prepolymers, the sol content, swelling degree, sebacic content of the sol, and molecular weight of the sol first increased and then decreased. As shown in Figure 2, first, all the GPC curves of sols displayed two distinct peaks, which indicated that the sols were composed mainly of two components

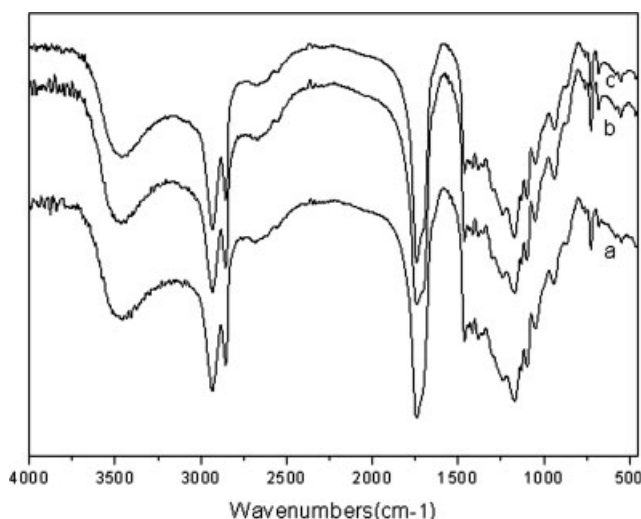


Figure 1 FTIR spectra of the TMPGS elastomers (KBr salt flakes pressed with the fragments of the elastomer films): (a) e₁, (b) e₂, and (c) e₃.

TABLE II
Sol Content (Q), Swelling Degree (R), Sebacic Content (Y), and Molecular Weights of the Sols of the TMPGS Elastomers

Elastomer	Q (%)	R (%)	Y (%)	M_n (P ₁ peak)	M_w (P ₁ peak)
e ₁	61.87	2,112	13.56	3,335	15,715
e ₂	66.88	2,518	17.73	3,759	22,268
e ₃	62.75	2,074	16.74	3,636	19,478

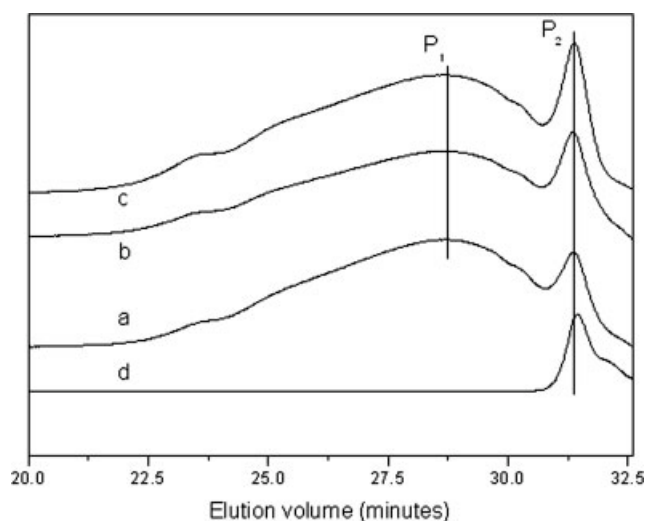


Figure 2 Sol GPC curves for the TMPGS elastomers (the sol solution originated from the solution remaining after the swelling experiment with the sample in 20 mL of tetrahydrofuran, and the weight of the initial disc sample was ca. 0.09 g; the flow rate for the eluent was 1 mL/min): (a) e_1 , (b) e_2 , (c) e_3 , and (d) sebacic acid.

with different molecular weights; second, all the GPC curves of the sols displayed a slight sidestep on the leftmost position of the P_1 peak, which might have been caused by the large transformation of the molecular weight and the branch degree of the sols. Comparing the GPC curves of the sol with one of sebacic acid, we find that the P_2 peaks might correspond to sebacic acid, and P_1 might be related to the sol. M_n and M_w of the sols were reported as 3500 and 20,000 or so, respectively. Subsequently, the sebacic content of the sols could be determined by the division and integral treatment of the peaks in the GPC curves. Some sebacic acid existing in the elastomer acted as a plasticizer to contribute to the thermoplasticity of the material.

p_1 , p_2 , and p_3 with adjacent actual molar ratios had increased molecular weights in turn, and it is known that different molecular weights of the prepolymers will make the reacting mixtures display different viscosities and reactive activities at the next step, which must cause distinguished branching degree and cross-

linking density of the final products. A higher molecular weight prepolymer results in a higher viscosity, which will hinder the chain propagation while enhancing the branching and crosslinking of the prepolymer after the addition of sebacic acid again in the second step of the reaction. Therefore, e_3 had a higher crosslinking density and lower sol content, and the sebacic acid kept a higher residue because of the higher viscosity of the system and weaker activity of $-\text{CH}-\text{OH}$. A lower molecular weight prepolymer induces a low viscosity, which will benefit the chain propagation, branching, and crosslinking. Consequently, the final products kept a higher crosslinking density, lower sol content, and lowest residue of sebacic acid (e.g., e_1).

In our previous work,¹⁵ the sol content in the elastomer with the same molar ratio of sebacic acid to glycerol prepared by the one-step method was around 70%, prominently higher than that of e_1 and e_3 , and the swelling degree was about 3700%, also much higher than that of e_1 and e_3 . These illustrated that using the two-step method could make the gel content and crosslinking density of the elastomers bigger than using the one-step method.

Mechanical performance, ordered structure, and thermal properties of the TMPGS elastomers

The mechanical properties (tensile stress, tensile strain, elastic modulus, and tensile permanent set) of the TMPGS elastomers are listed in Table III. Elastomer e_2 had the lowest tensile strength and elongation at break, which apparently correlated with its highest sol content and lowest gel crosslinking density. Elastomer e_1 had a moderate tensile strength and the longest elongation at break, probably because it possessed the lowest sol content and higher gel crosslinking density. From the elasticity theory of rubber, with the right crosslinking density (5×10^{-5} mol/cm³ or so), a certain molecular weight will guarantee certain tensile properties. The noncrosslinked components, such as low-molecular-weight sols and sebacic acid, will degrade the mechanical properties of an elastomer, which acts similarly to a plasticizer. However, a low crosslinking degree and high sol content are quite necessary for the thermal moldability of a crosslinked network. There-

TABLE III
Mechanical Properties of the TMPGS Elastomers

Elastomer	Tensile stress (MPa)	Elastic modulus (MPa)	Tensile strain (%)	Permanent set (%)
e_1	0.61 ± 0.06	0.55 ± 0.23	236 ± 31	0
e_2	0.41 ± 0.07	0.49 ± 0.03	109 ± 2	0
e_3	0.64 ± 0.07	0.45 ± 0.08	179 ± 13	0

The specimens were dumbbell-shaped with a thickness of 1 mm and a width of 2 mm; a 50N load cell and a crosshead speed of 50 mm/min were used.

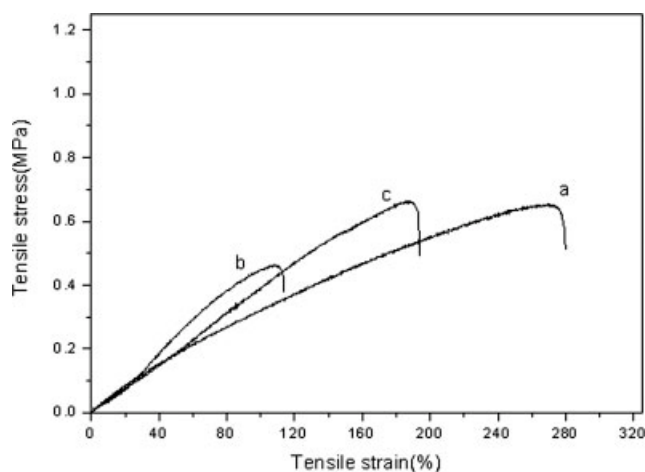


Figure 3 Stress-strain curves for the TMPGS elastomers (1-mm-thick and 2-mm-wide dumbbell-shaped specimens, a 50N load cell, and a crosshead speed of 50 mm/min): (a) e_1 , (b) e_2 , and (c) e_3 .

fore, a balance of the sol content and crosslinking density is needed and can help to adjust the mechanical and thermal-processing performance of an elastomer. The permanent set of the materials is zero, which should be concerned with a thermoplastic elastomer. Figure 3 shows representative stress-strain curves.

Figure 4 displays the X-ray diffraction (XRD) patterns of the elastomers. The patterns of e_1 and e_2 present similar peaks, which are slightly different from that of e_3 . No matter how, these XRD peaks indicate that all the elastomers possessed similar crystal components or ordered structures at room temperature, which affected the mechanical properties, degradation performance, and so on of the elastomers.

Figures 5 and 6 show the crystallization and melting curves of the elastomers by the differential scan-

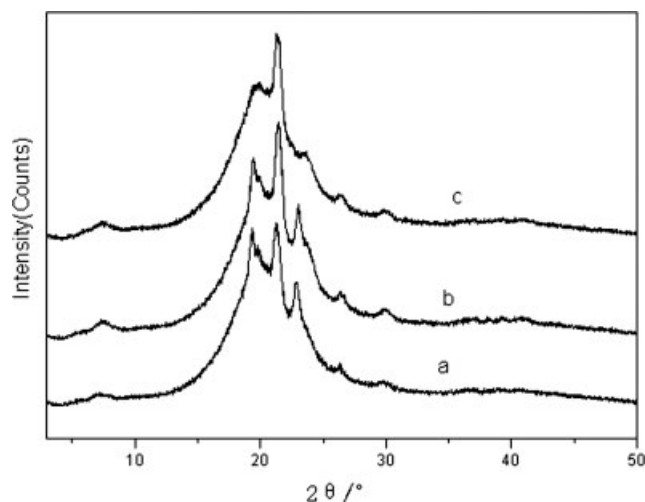


Figure 4 XRD patterns of the TMPGS elastomers: (a) e_1 , (b) e_2 , and (c) e_3 .

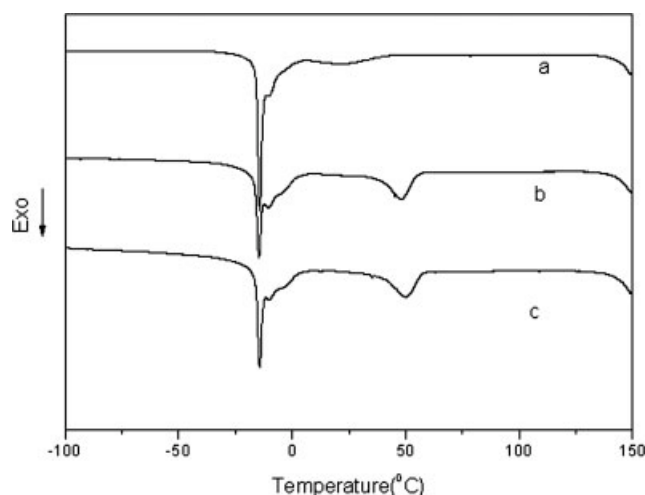


Figure 5 DSC crystallization curves for the TMPGS elastomers: (a) e_1 , (b) e_2 , and (c) e_3 .

ning calorimetry (DSC) method; Tables IV and V list the glass-transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), and absolute crystallization enthalpy ($-\Delta H$) of the elastomers and gel parts. First, all the elastomers have two crystal regions. The region at the lower T_c , correlated to the gel parts, is vicinal because the gels have similar crosslinking structures, whereas the one at the higher T_c , corresponding to the sol and sebacic parts, is a bit different because the elastomers contain different contents of the sol and sebacic acid. The region at the higher T_c will be influenced by hydrogen bonding or other interactions among the sol, gel, and sebacic acid because sebacic acid possesses the highest T_c and the sol possesses a medium T_c . The existence of the sol and sebacic acid in TMPGS will endow the materials with crystallization at room temperature, as demon-

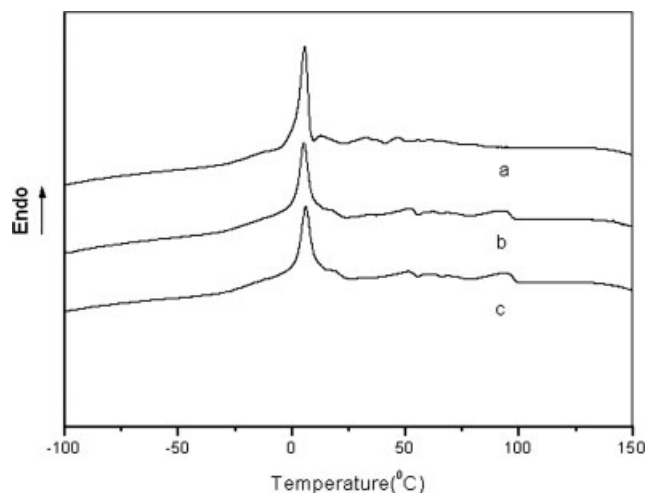


Figure 6 DSC melting curves for the TMPGS elastomers: (a) e_1 , (b) e_2 , and (c) e_3 .

TABLE IV
DSC Results for the Elastomers (Sol and Gel)

Elastomer	T_g (°C)	T_m (°C)	T_c (°C)	$-\Delta H$ (J/g)
e ₁	-22.5	5.6	-14.3	23.8
e ₂	-26.1	5.2	-14.7	47.9
e ₃	-26.2	6.0	-14.3	50.0

strated by the XRD results. According to the DSC curves, the crystallization degrees of the sol and sebacic acid above room temperature are not high; however, they should be partially responsible for the modulus regulation presented by the stress-strain curves. In addition, accurately speaking, we find that the crystallization of gels under room temperature and the noncrystallization parts in sols favor the thermal moldability of the networks, and the crystallization of the sol and sebacic acid above room temperature favor the solidification of networks of TMPGS after thermal deformation and cooling.

Second, it can be observed that all the elastomers have a vicinal T_g that comes mainly from the gels. Because the sols and gels possess similar chemical structures, it is reasonable to conclude that the sol molecules and gel networks interpenetrate each other to form semi-interpenetrated polymer networks.

Third, as shown in Table IV, T_g was the highest for e₁ (exceeding others by more than 3°C); for the gel parts of e₁, as shown in Table V, T_g was close to those of e₂ and e₃. On the one hand, this phenomenon deeply illuminated that the strong hydrogen bonding between the gels and sols would greatly limit the movement of the molecular chains of the gels; on the other hand, it revealed that the hydrogen-bond crosslinking action of the sols was bigger than the plasticization action of some other sols and sebacic acid in e₁, whereas both actions reached a certain balance in e₂ and e₃. Besides, T_c and $-\Delta H$ originating from sols in e₁ were lower than those of e₂ and e₃, and this was related to its lowest contents of the sol and sebacic acid. Considering T_c and $-\Delta H$ originating from the gels, as shown in Tables IV and V, we find that after the sols were extracted, both T_c and $-\Delta H$ were reduced, and this proved that the hydrogen-bonding action between the sols and gels tended to promote the crystallization of the gels.

TABLE V
DSC Results for the Gel Parts

Gel of the elastomer	T_g (°C)	T_m (°C)	T_c (°C)	$-\Delta H$ (J/g)
e ₁	-26.4	2.0	-18.5	28.36
e ₂	-26.5	1.8	-18.9	26.52
e ₃	-26.2	3.5	-18.4	28.07

TABLE VI
Water Uptake and WCAs of the TMPGS Elastomers

Elastomer	U_1 (%)	U_2 (%)	WCA (°)
e ₁	8.24	11.67	37.8
e ₂	3.775	8.38	43.4
e ₃	1.54	6.12	42.5

Water uptake, hydrophilicity, and degradability of the TMPGS elastomers

The water uptake and WCAs of the elastomers are listed in Table VI. The difference between U_1 and U_2 showed that the elastomers had been degraded partly during the course of the water-uptake tests. Generally, the crosslinking of an elastomer will evidently restrict the swelling of itself in a solvent, and crystal regions will also prevent an elastomer from swelling except so that the crystallization can be dissolved. For e₃, the highest crosslinking density and lots of crystal regions together contribute to the lowest water uptake. For e₁, the apparent absence of crystallization leads to the highest water uptake, although its crosslinking density is also higher.

From the WCAs, it is known that the three elastomers were all hydrophilic because they contained many polar groups in molecular chains, such as the hydroxyls displayed in the aforementioned FTIR spectra. Compared with the amorphous state, the crystallization state tends to express a higher surface energy because of the compact stacking, so e₁ had the smallest contact angle of the three elastomers; this illustrates that it had the best hydrophilicity because of its lower crystallization.

Figure 7 shows the mass-loss/time curves of the elastomers in 37°C PBS solutions (pH = 7.4) at differ-

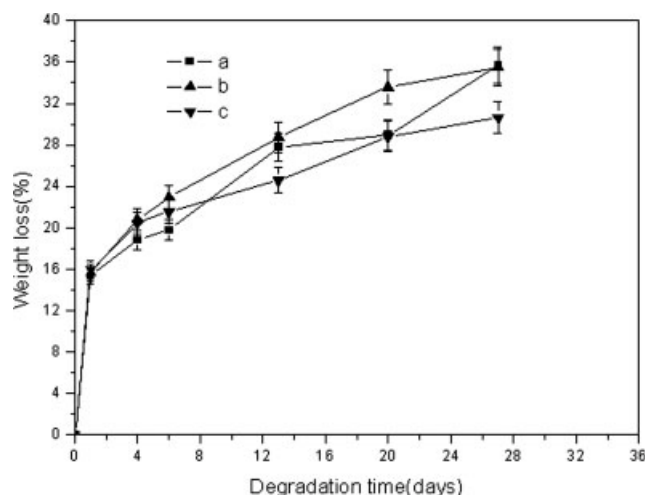


Figure 7 Mass-loss/time curves for the TMPGS elastomers [10-mm-diameter and 1-mm-thick disc samples and a PBS solution (pH = 7.4), with the solution replaced every 2 days]: (a) e₁, (b) e₂, and (c) e₃.

ent degradation periods (1, 4, 6, 13, 20, and 27 days), which characterized the *in vitro* degradation. The elastomers displayed similar degradation phenomena. The mass loss of all the elastomers was about 15% after 1 day of degradation, and the mass-loss rate decreased in the latter periods. Among e_1 , e_2 , and e_3 , e_2 degraded the most in the corresponding periods because it had the most sol and sebacic acid and the lowest crosslinking density of the gels. Here, it can be speculated that sols in elastomers will degrade in preference to gels because of the crosslinked network structure of the gels.

CONCLUSIONS

Three TMPGS elastomers originating from three prepolymers with different molecular weights were prepared by a two-step method, and the relation between their structure and properties was researched. Although all the elastomers had similar chemical structures, the molecular weights of the prepolymers influenced the composition of the TMPGS elastomers and then affected their performance. The right high sol content, low crosslinking density of semi-interpenetrated polymer networks, and crystallization structure endowed the elastomers with necessary thermal moldability. Hydrogen-bonding action between the gels and sols favored the crystallization and crosslinking of the elastomers; however, the existence of some sols and sebacic acid tended to plasticize the elastomers, so both sides played important roles in balancing the overall properties of the elastomers. The three elastomers exhibited similar degradation characteristic in 37°C PBS (pH = 7.4), but

more sols and sebacic acid in the elastomers and a lower crosslinking density sped the degradation of the elastomers.

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