Effects of Swelling on the Viscoelastic Properties of Polyester Films Made from Glycerol and Glutaric Acid

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ABSTRACT: Viscoelastic properties have been determined for poly(glycerol-*co*-glutaric acid) films synthesized from Lewis acid-catalyzed polyesterifications. The polymers were prepared by synthesizing polymer gels that were subsequently cured at 125°C to form polymer films. The polymers were evaluated for the extent of reaction before and after curing by Fourier transform infrared spectroscopy. They were subsequently immersed in dimethylsulfoxide, tetrahydrofuran, water, methanol, and hexane for 24 h. The amounts of solvent absorbed were monitored and recorded. Dependent up the solvent used, the polymers were able to absorb 9.5–261% of its weight. The effects of the solvent absorption on the viscoelastic properties of the polyester films were evaluated by determining their elastic modulus (G'), viscous modulus (G''), tan $\delta G''/G'$, and complex viscosity (η^*) by performing oscillatory frequency sweep experiments. The elastic modulus (G') and viscous modulus (G'') were both higher for the dry polymers than the solvent-absorbed polymers. However, the polymer films were all higher in elastic (G') character than viscous (G'') character. Therefore, tan $\delta G''/G' < 1$ before and after immersion in solvents. Values for η^* decreased with angular frequency for all of the polyesters tested in this study. © 2012 Wiley Periodicals, Inc.[†] J Appl Polym Sci 000: 000–000, 2012

Key words: viscoelastic properties; swelling; hyperbranched; gels

INTRODUCTION

In response to the need to find new uses for the additional amounts of glycerol generated from the production of biodiesel, our research team has focused on the synthesis and characterization of glycerol-based hyperbranched polymers.[1–4] These polymers have been synthesized under varying conditions using several diacids coreacted with glycerol. They were subsequently analyzed to determine the variables that significantly affect their physical and mechanical properties such as molecular weight, polydispersity, viscosity, thermal stability, and degree of branching. It is our goal to take what we have learned about these polymers and find suitable applications for them. When preparing these polymers for various analytical studies, it was often noted that the solid materials were not soluble. Instead, they soaked up the solvent and swelled. Such an observation was an indication that these polymers may be useful as polymeric gels. Polymer gels are fascinating materials that can exist as solids, viscous gels, or as powders derived from ground solids. They are composed of amorphous and crystalline regions that cannot dissolve but swell in the presence of solvents because of their network structure. They can be engineered to respond to changes in solvent composition,[5–7] pH,[8] temperature,[9] and salt concentrations[10] by changing their molecular composition or altering their polarity or ionic properties through functionalization.

Polymeric gels are three-dimensional networks that have the ability to absorb large amounts of water (hydrogels) or organic solvent (organogels). Hydrogel research has been extensive and has led to uses in food, agriculture, and medicine.[11–13] These applications include superabsorbent materials,[14] sensors,[15] transport,[16] drug delivery,[17] and water remediation.[18] Research interest in the area of organogels has been minimal by comparison. However, research efforts dedicated to organogels are increasing[19–21] primarily because they are chemically more versatile than hydrogels. They have the capability to respond to a variety of solvents and organic species. Similar to hydrogels, organogels are useful in the production of controlled released drugs.[21] They are also used as industrial absorbants,[22] enzyme immobilizers,[23] and analytical separation devices.[23] It is conceivable that hydrogel technology used to produce controlled-released fragrances[24] and hand

sanitizers[25] are transferable to organogels. Previous research has shown that organogels can absorb many organic solvents including carbon tetrachloride, dichloromethane, tetrahydrofuran (THF), chloroform, and toluene.[20] They can also absorb polar aprotic solvents and alcohols.[26]

Solid polymer gels have properties similar to those of ordinary solids. However, investigations have shown that when these polymers swell to dimensions much larger than their dry size, changes to their rheological and thermal properties can occur.[27] The introduction of solvent into the polymer matrix can cause changes to the proportions of the crystalline and amorphous regions. Therefore, the relationships among the polymer composition, solvent, and physical and mechanical properties need to be understood. Organogels are typically prepared by polymerizing various combinations of acrylates,[26,28,29] lactones,[17] carbonates,[30] sulfonates,[26] alcohols,[17,31] and amines.[5] When polyglycerols are used as polymeric gels, their applications are generally limited to hydrogel technologies owing to their excellent compatibility with water and biodegradability.[32]

Aside from the observation that highly crosslinked hyperbranched polymers made from glycerol and diacids swell in solvent, little is known about the nature of the absorption mechanism. Polymerizing diacids with glycerol gives a variety of products owing to the structural and chemical diversity of the diacid used. More importantly, the large number of free hydroxyl and carboxyl groups can be functionalized with counterions or pendant groups.[32] Functionalization can optimize solvent uptake and also aid in the development of gels with the desired mechanical strength at optimal levels of solvent absorbency. Functionalization is very important to the development of pH- and temperature-responsive polymer gels that swell when stimulated by their environment.

In this study, five common solvents that vary in polarity have been selected to initiate studies intended to elucidate the solvent response of the unfunctionalized form of these polymers. The solvents chosen for this study are water, THF, hexane, dimethylsulfoxide (DMSO), and methanol. The ability to swell our polymers in these common solvents is critical to identifying how they can be used. DMSO and water are currently absorbed into polymer gels used in biological systems and hygiene products. It is well known that water is important to many medical applications. DMSO is a nontoxic, highly polar organic fluid that is used in anti-inflammatory, anticancer, and antioxidant therapies.[5,6,28,29] Alcohols such as methanol and ethanol have been extensively studied for the production of polymer gels that require high alcohol contents,[26] whereas solvents of lower polarity such as hexane and THF show the potential for polymer gels to be used in applications that involve the recovery of organic solvent and oils.[20]

We intend to determine the potential for hyperbranched polymers made from glycerol and diacids to be used as polymer gels by examining the types of chemical environment that cause these polymers to swell, the extent of absorption, and the effects of absorption on viscoelastic properties. Rheological analysis gives valuable information regarding the mechanical properties of materials such as elasticity and hardness.[33] The ability to control the mechanical properties of thermosets without affecting other properties is important for the introduction of materials into industrial markets.

EXPERIMENTAL

Materials

Glutaric acid (99%), reagent-grade glycerol (99.9%), HPLC-grade toluene (99.8%), and anhydrous THF (99.9%) were purchased from Sigma Aldrich (St. Louis, MO). Dibutyltin oxide was from Fluka/Sigma Aldrich (Steinheim, Germany). Spectrophotometric grade DMSO was purchased from Aldrich (St. Louis, MO). HPLC-grade methanol was purchased from Honeywell (Muskegon, MI). Hexanes were purchased from Fischer Scientific (Fair Lawn, NJ). Deionized water was obtained from our in-house system purified by Barnstead NANOpure (Boston, MA). Jars (Qorpak, 2 oz, Straight Side Round Jars with Teflon-Lined Caps) were purchased from Thomas Scientific (Swedesboro, NJ).

Synthesis of polymer films

Polymer films were made by first synthesizing polymers from glycerol and glutaric acid at 155°C as described previously.[1] A 1 : 1 molar ratio of glutaric acid (0.285 mol) and glycerol (0.290 mol) or a 2 : 1 molar ratio of glutaric acid (0.38 mol) and glycerol (0.195 mol) was reacted in the presence of 0.15% (w/w) (catalyst/reactants) dibutyltin(IV)oxide in a single-neck 250-mL round bottom flask with 125 mL of toluene. Experiments were performed at oil bath temperatures of 155°C for 10 h. A reflux condenser was connected to the top of a Dean–Stark apparatus used to assist in the removal of water over the course of the esterifications. Following reaction, the solvent was removed from the crude reaction products by rotary evaporation. Characterization of these polymers by Fourier transform infrared spectroscopy (FTIR) before they are cured is described herein. NMR studies (^{1}H and ^{13}C), including degree of

branching, for the precured polymers, were determined as described previously.[4]

Seven grams of the reaction mixture were then transferred to individual 57-mm aluminum weighing dishes from Thomas Scientific, (Swedesboro, NJ) and cured in an oven at 125°C for 5 h.

Infrared spectroscopy (FTIR)

FTIR measurements were made at room temperature on a Nicolet Nexus670 FTIR spectrometer (Madison, WI) equipped with a Smart Orbit diamond attenuated total reflection (ATR) accessory, a DTGS KBr detector, and a KBr beam splitter. All spectra were taken via the ATR method with resolution of 4 cm^{-1} and 128 scans. Sample, either in highly viscous or in powder form, was directly applied onto the diamond, and close contact was made with the surface by a pressure tower. The spectra were collected over the range from 4000 to 500 cm^{-1}.

Swelling measurements

The samples were bored from the aluminum pans into circles that were 1 in. in diameter. Samples were saved as controls for rheological testing by dynamic mechanical analysis (DMA). The remaining samples were weighed and immersed into respective solvents at room temperature for 24 h in 2 oz jars, blotted with a Kimwipe (Kimberly-Clark, Marietta, GA), and then reweighed. Weight changes owing to solvent absorption were then determined by the following equation

$$\% \, \text{Weight change} = (W_s - W_d)/W_d$$

where W_s and W_d represent the weight of the swelled and dry gels, respectively.

To evaluate the reusability of these materials, the polymer films were allowed to desorb onto Kimwipes until the polymer gel no longer lost weight. This process took less than 2 h for all polymeric films studied. The polymer films were once again allowed to absorb solvent. This absorption–desorption cycle was repeated three times for each polymer film.

Dynamic mechanical analysis

Rheological data were collected using a Texas Instruments (Dallas, TX) AR 2000 Rheometer using Hydan Technology (Hillsborough, NJ) Rheology Advantage Software (version 4.1). The samples were tested between 25 mm aluminum plates with a 1550 μm gap (on average) at 22°C. A strain experiment was run from 0.1 to 10% strain at a fixed frequency of 10 rad/s. The results indicated linearity in G' (elastic modulus) at 0.2% strain for all materials. Therefore, 0.2% strain was used for the frequency experiments which were analyzed between the frequency range of 0.1–100 rad/s to determine the elastic modulus (G'), viscous modulus (G''), and complex viscosity (η^*).

RESULTS AND DISCUSSION

Synthesis

The protocol chosen for these studies is from a previously described method for 10-h esterifications between glycerol and glutaric acid at 155°C.[1] Materials synthesized under these conditions give a thick, yet pourable polymer gel. The polymers made from the 2 : 1 (glutaric acid: glycerol) formulation should be predominately terminated with carboxylic acid groups and had a degree of branching of 51.1%. Polymers made from the 1 : 1 formulation had a degree of branching of only 25% owing to a theoretically higher percentage of unreacted hydroxyl groups. Consistent with the solubility characteristics of similar polymers,[1,3] these polymers were soluble in polar organic solvents but would not dissolve in water or nonpolar solvents.

The polymer gels were cured at 125°C and checked hourly to monitor the loss of tackiness. After 2.5–3 h, the polymers were solid films with smooth surfaces that lack any qualitative degree of tackiness. However, further manipulation of these materials to remove them from the aluminum pans revealed that the bottom surface cured at a slower rate than the top surface, yielding a polymer with a smooth top and a tacky bottom. Therefore, curing was extended to a total of 5 h to ensure complete reaction throughout the polymer. After 5 h of heating, the polymer made with a 1 : 1 (glutaric acid: glycerol) molar ratio lost an average of 3.6% of its initial weight. The polymer made with a 2 : 1 (glutaric acid : glycerol) molar ratio lost an average of 4.5% of its initial weight. The final products were flexible solids that were easy to cut. They were clear with a yellow hue.

Infrared spectroscopy (FTIR)

The polymeric films were subjected to the analysis by FTIR to assist in the determination of extent of reaction (Fig. 1, Table I). There are important bands to observe in the starting materials. Glutaric acid [Fig. 1(A)] has a band at 1680 that is indicative of a C=O stretch of a carboxyl group and a band in the region of 3500–2500 resulting from the alcohol (O—H) stretch from the carboxylic acid group. Free glycerol [Fig. 1(B)] has a large band in the range of
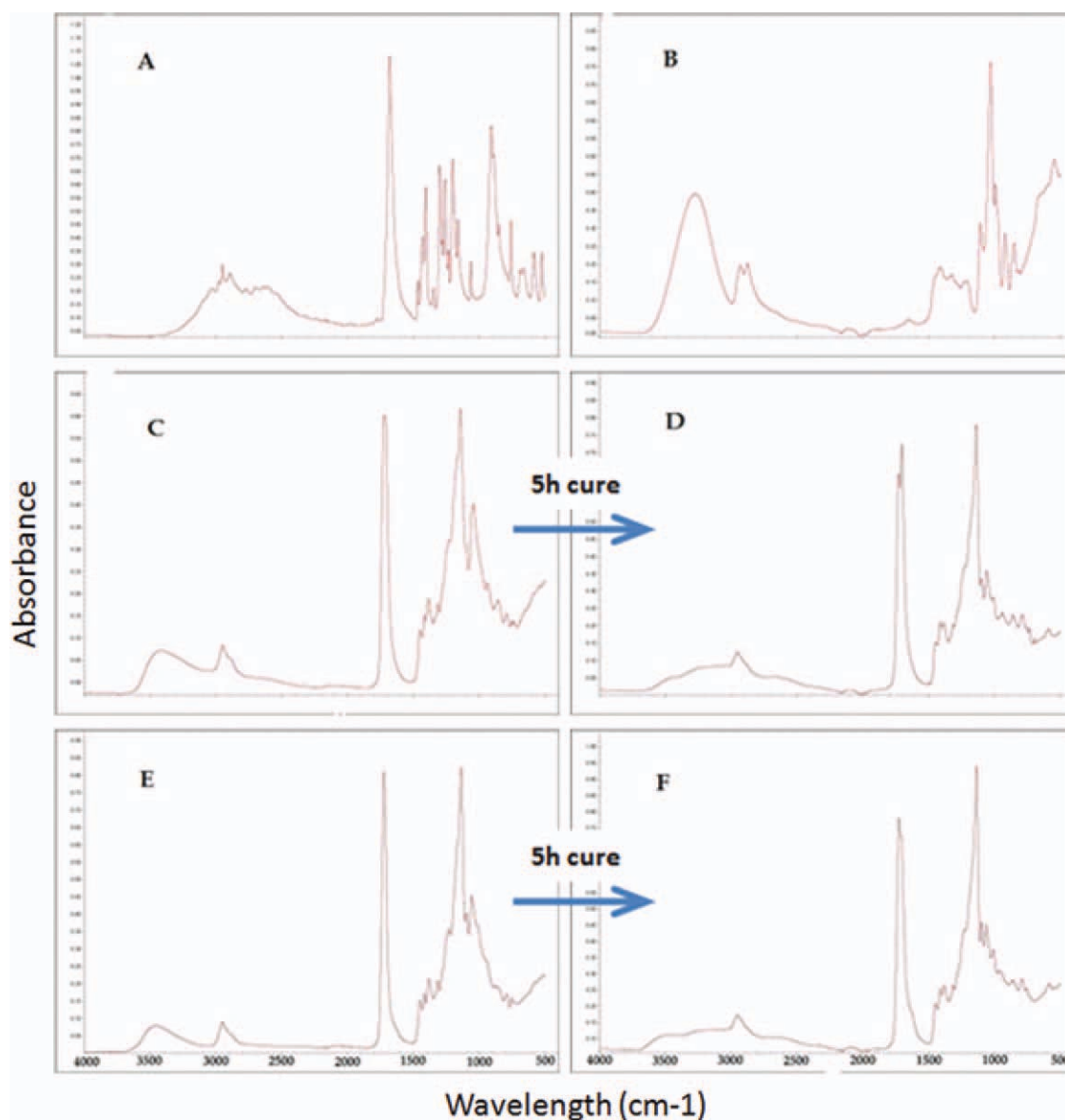
Figure 1 Infrared spectra of poly(glycerol-*co*-glutaric acid)s. A, glutaric acid; B, glycerol; C, 1 : 1 (glutaric acid : glycerol) product after 10 h polymerization; D, Polymer A cured at 125°C for 5 h; E, 2 : 1 (glutaric acid : glycerol) product after 10 h polymerization; and F, Polymer C cured at 125°C for 5 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3480–3100 where the stretching of free hydroxyls (O—H) occurs.

Figure 1(C,E) is of viscous, free-flowing materials made from 10 h esterifications of glycerol and glutaric acid at 1 : 1 and 2 : 1 (glutaric acid : glycerol) molar ratios. In those spectra, the C=O and O—H stretches of the carboxyl and hydroxyl groups of the glutaric acid have disappeared, whereas new bands have appeared in the region of 1705–1730 (spectra C through F). These new bands are the indications of esterification. An O—H stretch of reduced absorbance from the hydroxyl group of the free glycerol is still shown for spectra A and C. However, once the viscous liquids are cured, glycerol's free hydroxyl stretch disappears leaving only an aliphatic (C=H)

peak in the region of 2950–2880. Within the detection limits of FTIR, these data suggest that all of the starting materials have been consumed and a complete polymer network in the form of a film has been produced.

TABLE I
FTIR Analysis of Hyperbranched
Poly(Glycerol-*co*-Glutaric Acid)s

Wave number (cm^{-1})	Assignment
3480–3100	v(O—H) monomeric glycerol
3500–2500	v(O—H) alcohol, carboxylic acid
2950–2880	v(C=H) aliphatic
1705–1730	v(C=O) ester
1680	v(C=O) monomeric glutaric acid

TABLE II
Average (n = 2) Solvent Absorption over Time

Solvent (SPI, molar ratio (diacid : glycerol))	% wt Change				
	1 h	3 h	10 h	18 h	24 h
DMSO (6.5, 1 : 1)	35 + 2.0	82 + 6.1	170 + 9.4	170 + 16.7	261 + 21.4
DMSO (6.5, 2 : 1)	28 + 3.6	113 + 6.2	186 + 11.4	172 + 17.4	246 + 15.1
THF (4.2, 1 : 1)	17 + 0.2	39 + 3.6	86 + 5.0	115 + 3.6	120 + 1.5
THF (4.2, 2 : 1)	55 + 3.0	103 + 7.9	130 + 9.3	120 + 13.3	131 + 6.3
Methanol (6.6, 1 : 1)	9.3 + 0.2	12 + 0.7	27 + 3.5	29 + 0.9	33 + 4.2
Methanol (6.6, 2 : 1)	9.4 + 0.7	20 + 3.4	33 + 5.3	25 + 2.0	33 + 2.1
Water (9.0, 1 : 1)	3.1 + 0.1	3.1 + 1.2	4.7 + 1.2	7.5 + 0.5	11.1 + 0.3
Water (9.0, 2 : 1)	3.4 + 0.3	4.3 + 0.8	8.6 + 1.5	8.9 + 0.3	9.5 + 2.2
Hexane (0.0, 1 : 1)	0.0	0.0	0.0	0.0	0.0
Hexane (0.0, 2 : 1)	0.0	0.0	0.0	0.0	0.0

Swelling studies

Water, methanol, THF, and DMSO are four solvents chosen for this study because they are commonly used in hydrogel and organogel applications. Their Snyder Polarity Index (SPI)[34] ratings (water = 9; methanol = 6.6; DMSO = 6.5; THF = 4.2) cover the representative range of the most common solvents. The absorption rate of hexane (SPI = 0) was studied to extend the polarity range and solvent type. The swelling rate was monitored for each solvent over 24 h as the samples were removed from the solvent and weighed at intervals of 1, 3, 10, 18, and 24 h (Table II). The elasticity of the polymers was not high enough to hold all of the absorbed DMSO or THF. The materials became harder and eventually cracked upon expansion in DMSO and THF.

According to the data, there was no obvious trend that could be used to correlate the degree of swelling to polarity alone. After 24 h, only 11.1% (1 : 1 molar ratio of diacid : glycerol) and 9.5% (2 : 1 molar ratio of diacid : glycerol) of the gel weight could be attributed to water absorption. The polymers made by the methods described herein did not absorb hexane. However, the data suggest that aprotic polar solvents with average polarities, such as DMSO and THF, may be the most compatible solvents for these polymers. The polymer gels absorbed as much as 261% of their weight in DMSO and as much as 131% of their weight in THF (Table II). It was not immediately obvious why the average % weight change for polymer gels that absorbed polar aprotic solvents (DMSO and THF) were inconsistent after 10 h. As the optimization of this protocol is an on-going process, it can be postulated that external influences such at room temperature as well as experimental errors owing to leaks in the absorption chambers could influence the equilibrium within the system causing inconsistencies in absorption and desorption. These concerns should be evaluated in future studies. The polymer gels were less responsive to the polar protic solvent, methanol. The weight of the polymer gels increased by approximately 33% in the presence of methanol and the amount of absorption was independent of the molar ratio used.

Despite repeated trials, there was no indication that, within error, either formulation of the polymer matrix was significantly better at solvent absorption than the other. Studies to improve the mechanical strength or the intramolecular chemical stability of these polymers should be the focus of future investigations because the polymers were either not mechanically or not chemically strong enough to hold increased amounts of the aprotic polar solvents, DMSO and THF, without breaking.

The reusability of the polymer gels was investigated. Complete desorption of the solvents from the polymer gels was accomplished in approximately 2 h. The adsorption–desorption cycle was repeated three times with water, methanol, and THF. DMSO was not used as a solvent in these reusability studies because after the first desorption, the film crumbled into many pieces. Reliably reweighing the broken pieces was a difficult task. After three adsorption–desorption cycles, the ability of the polymer gels to reabsorb solvent showed only small changes (±2.6 % on average). However, the polymer gels swollen with THF became more brittle with each successive cycle and easily crumbled to pieces after the third cycle. The crumbled gels could also successfully absorb solvent. Therefore, dependent on the application, powered or shaven materials made from these polymer gels can also be used as absorbants.

Viscoelastic evaluation

For viscoelastic materials, the relationship between viscous and elastic behavior is frequency dependent. Tables III–VI and Figures 2 and 3 show the results of frequency experiments that were conducted to determine the elastic modulus (G'), viscous modulus

TABLE III
Frequency Sweep Step Data for the Elastic Modulus (G') of Hyperbranched Poly(Glycerol-*co*-Glutaric Acid) Films at 0.2% Strain

Angular frequency (rad/s)	G' (Elastic modulus, Pa)									
	Dry (1 : 1)	Dry (2 : 1)	DMSO (1 : 1)	DMSO (2 : 1)	THF (1 : 1)	THF (2 : 1)	MeOH (1 : 1)	MeOH (2 : 1)	Water (1 : 1)	Water (2 : 1)
1	1.35E + 05	1.25E + 05	6922	7129	11,060	21,760	89,910	29,490	21,860	67,170
1.259	1.40E + 05	1.25E + 05	6247	7172	10,580	21,100	1.06E + 05	29,590	21,920	67,180
1.586	1.41E + 05	1.26E + 05	6444	7226	10,300	20,700	1.07E + 05	29,550	21,940	67,330
1.995	1.41E + 05	1.26E + 05	6612	7279	10,200	20,450	1.08E + 05	29,590	21,980	67,410
2.512	1.42E + 05	1.26E + 05	6758	7525	10,240	20,220	1.10E + 05	29,610	22,020	67,490
3.163	1.42 + 05	1.27E + 05	6889	7227	9827	19,930	1.11E + 05	29,590	22,060	67,610
3.98	1.43E + 05	1.27E + 05	7028	7168	9664	19,650	1.12E + 05	29,570	22,110	67,700
5.011	1.43E + 05	1.27E + 05	7152	6699	9679	19,430	1.13E + 05	29,580	22,170	67,790
6.309	1.44E + 05	1.28E + 05	7307	5732	9598	19,200	1.13E + 05	29,660	22,230	67,900
7.943	1.44E + 05	1.28E + 05	7443	4569	9610	18,970	1.14E + 05	29,660	22,300	67,990
10.00	1.45E + 05	1.29E + 05	7567	3488	9537	18,670	1.14E + 05	29,640	22,370	68,110
12.59	1.46E + 05	1.30E + 05	7673	3103	9494	18,400	1.15E + 05	29,620	22,450	68,250
15.84	1.46E + 05	1.31E + 05	7776	3185	9452	18,130	1.15E + 05	29,570	22,530	68,400
19.95	1.48E + 05	1.32E + 05	7880	3525	9376	17,900	1.16E + 05	29,410	22,650	68,580
25.12	1.49E + 05	1.33E + 05	7988	3816	9328	17,680	1.16E + 05	29,210	22,760	68,770
31.63	1.51E + 05	1.35E + 05	8102	4035	9277	17,540	1.16E + 05	29,380	22,910	68,980
39.81	1.53E + 05	1.36E + 05	8210	4240	9197	17,360	1.16E + 05	29,890	23,080	69,280
50.11	1.54E + 05	1.39E + 05	8359	4532	9027	17,220	1.16E + 05	30,040	23,270	69,580
63.09	1.57E + 05	1.42E + 05	8516	4896	8908	17,160	1.17E + 05	30,050	23,530	69,910
79.43	1.59E + 05	1.45E + 05	8790	5285	9040	16,880	1.17E + 05	30,210	23,880	70,320
100.0	1.62E + 05	1.49E + 05	9146	5845	9176	16,840	1.17E + 05	30,300	24,340	70,840

(G''), complex viscosity (η^*), and tan δ. To obtain these data, strain sweeps were first performed from 0.1 to 1.0% strain at a fixed frequency of 10 rad/s to determine the region where the amount by which the material is deformed (the strain) is linearly related to the force causing the deformation (the stress). This behavior is described by Hooke's Law of elasticity.[35] Strain sweeps determined that for our polymers, the region that obeyed Hooke's law was at 0.2% strain. Outside of this range, the stress may

TABLE IV
Frequency Sweep Step Data for the Viscous Modulus (G'') of Hyperbranched Poly(Glycerol-*co*-Glutaric Acid) Films at 0.22% Strain

Angular frequency (rad/s)	G'' (Viscous modulus, Pa)									
	Dry (1 : 1)	Dry (2 : 1)	DMSO (1 : 1)	DMSO (2 : 1)	THF (1 : 1)	THF (2 : 1)	MeOH (1 : 1)	MeOH (2 : 1)	Water (1 : 1)	Water (2 : 1)
1	18,330	4337	1717	472.3	1942	1086	32,570	976.7	341	971
1.259	16,210	4353	1900	508.1	1817	1015	20,680	839.8	348.6	886
1.586	15,780	4572	1722	532.6	1675	976.5	19,250	891.4	375.7	856.1
1.995	15,610	4858	1646	606.9	1643	940.2	17,860	878.9	392.2	889.7
2.512	15,610	5271	1588	564.9	1569	904.3	16,520	898.2	429.2	930.6
3.163	15,190	5677	1532	532.4	1300	835.3	14,730	840.8	463.6	952.2
3.98	15,360	6232	1464	651.5	1172	779.6	13,340	794.2	498.8	1020
5.011	15,670	6985	1397	910	1091	718.8	12,310	757.7	550.2	1047
6.309	16,000	7881	1332	1432	961.0	660.4	11,090	647.8	607.3	1138
7.943	16,640	8967	1268	2150	883.2	601.0	10,340	636.9	672.4	1247
10.00	17,460	10,270	1200	2418	802.2	524.3	9553	614.5	748.4	1392
12.59	18,470	11,810	1141	2502	740.9	478.3	8924	598.1	835.8	1568
15.84	19,700	13,620	1085	2551	729.3	435.1	8335	573.6	937.4	1770
19.95	20,870	15,790	1041	2449	686.8	409.2	7761	561.9	1068	2013
25.12	22,400	18,330	974.1	2382	636.7	384.3	7204	608.4	1215	2294
31.63	24,340	21,290	927.3	2343	608.9	371.9	6872	696.3	1392	2623
39.81	26,410	24,720	881.7	2300	604.2	339.7	6262	702.8	1593	3013
50.11	28,930	28,670	842.6	2281	524.3	329.1	5763	666.7	1831	3477
63.09	31,870	33,200	812.7	2219	505.3	319.6	5403	673.4	2107	4032
79.43	35,220	38,330	770.5	2190	461.7	297.3	5288	692	2429	4686
100.0	39,180	44,290	756.2	2182	465.2	271.4	4961	664.1	2807	5486

TABLE V
Frequency Sweep Step Data for the Complex Viscosity |η*| of Hyperbranched Poly(Glycerol-*co*-Glutaric Acid) Films at 2% Strain

Angular frequency (rad/s)	|η*| (Complex viscosity, Pa s)									
	Dry (1 : 1)	Dry (2 : 1)	DMSO (1 : 1)	DMSO (2 : 1)	THF (1 : 1)	THF (2 : 1)	MeOH (1 : 1)	MeOH (2 : 1)	Water (1 : 1)	Water (2 : 1)
1	1.36E ± 05	1.25E ± 05	7132	7144	11,230	21,780	95,630	29,510	21,870	67,180
1.259	1.12E ± 05	99,700	5187	5711	8525	16,780	85,390	23,510	17,410	53,370
1.586	89,250	79,360	4207	4570	6583	13,070	68,440	18,650	13,840	42,470
1.995	71,220	63,210	3415	3660	5176	10,260	54,990	14,830	11,020	33,780
2.512	56,790	50,330	2764	3005	4124	8058	44,130	11,790	8768	26,870
3.163	45,260	40,080	2231	2291	3134	6306	35,320	9360	6977	21,380
3.98	36,080	31,940	1803	1808	2446	4941	28,290	7431	5556	17,010
5.011	28,730	25,450	1454	1349	1944	3880	22,580	5905	4426	13,530
6.309	22,900	20,290	1177	936.4	1529	3045	18,040	4702	3525	10,760
7.943	18,270	16,190	950.5	635.7	1215	2390	14,390	3735	2808	8561
10	14,590	12,930	766.1	424.4	957.0	1867	11,480	2964	2238	6811
12.59	11,650	10,340	616.3	316.7	756.6	1462	9150	2354	1785	5424
15.84	9313	8280	495.5	257.5	598.3	1145	7283	1866	1423	4318
19.95	7499	6640	398.3	215.1	471.1	897.3	5799	1474	1136	3438
25.12	6009	5340	320.3	179.1	372.2	704.1	4616	1163	907.5	2739
31.63	4828	4304	257.8	147.5	293.9	554.7	3674	929.2	725.8	2183
39.81	3888	3482	207.4	121.2	231.5	436.2	2919	750.9	581.1	1742
50.11	3135	2827	167.6	101.2	180.4	343.7	2323	599.5	465.8	1390
63.09	2533	2305	135.6	85.19	141.4	272.1	1848	476.4	374.4	1110
79.43	2052	1888	111.1	72.03	114.0	212.6	1472	380.4	302.1	887.2
100	1665	1554	91.75	62.38	91.85	168.4	1173	303.0	245.0	710.3

cause the materials to permanently deform or break. Therefore, all of our materials were evaluated at 0.2% strain to ensure adequate sample torque response.

Before describing the details of how the viscosity and elasticity of each polymer responded to torque, Figures 2 and 3 should be observed. Owing to the scale, the changes in G' and G'' may not be immediately obvious. However, the tan δ parameter describes the dynamic between the two. A perfect viscoelastic polymer has a tan δ of 1 because in that instance, the elastic modulus (G') and viscous modulus (G'') are the same. When the viscous component is higher than the elastic component, tan δ > 1 and

TABLE VI
Frequency Sweep Step Data for tan δ of Hyperbranched Poly(Glycerol-*co*-Glutaric Acid) Films at 2% Strain

| Angular frequency (rad/s)	tan δ (G''/G')									
	Dry (1 : 1)	Dry (2 : 1)	DMSO (1 : 1)	DMSO (2 : 1)	THF (1 : 1)	THF (2 : 1)	MeOH (1 : 1)	MeOH (2 : 1)	Water (1 : 1)	Water (2 : 1)
1	0.1362	0.0347	0.248	0.0663	0.1756	0.0499	0.3622	0.0331	0.0156	0.0145
1.259	0.1159	0.0347	0.3041	0.0708	0.1718	0.0481	0.1961	0.0284	0.0159	0.0132
1.586	0.1122	0.0363	0.2672	0.0737	0.1625	0.0472	0.1803	0.0302	0.0171	0.0127
1.995	0.1105	0.0385	0.249	0.0834	0.1612	0.0460	0.165	0.0297	0.0178	0.0132
2.512	0.1101	0.0417	0.2349	0.0751	0.1533	0.0447	0.1507	0.0303	0.0195	0.0138
3.163	0.1067	0.0448	0.2224	0.0737	0.1323	0.0419	0.1331	0.0284	0.0210	0.0141
3.98	0.1075	0.0491	0.2083	0.0909	0.1213	0.0397	0.1193	0.0269	0.0226	0.0151
5.011	0.1095	0.0549	0.1954	0.1358	0.1127	0.037	0.1095	0.0256	0.0248	0.0154
6.309	0.1114	0.0617	0.1822	0.2499	0.1001	0.0344	0.0980	0.0218	0.0273	0.0168
7.943	0.1154	0.0699	0.1704	0.4706	0.0919	0.0317	0.0908	0.0215	0.0302	0.0183
10.00	0.1206	0.0796	0.1586	0.6932	0.0841	0.0281	0.0835	0.0207	0.0335	0.0204
12.59	0.1270	0.0911	0.1487	0.806	0.0780	0.0260	0.0777	0.0202	0.0372	0.0230
15.84	0.1347	0.1044	0.1395	0.8008	0.0772	0.0240	0.0724	0.0194	0.0416	0.0259
19.95	0.1408	0.1201	0.132	0.6948	0.0733	0.0229	0.0672	0.0191	0.0472	0.0294
25.12	0.1501	0.1379	0.1219	0.6243	0.0683	0.0217	0.0622	0.0208	0.0534	0.0334
31.63	0.1615	0.1583	0.1144	0.5807	0.0657	0.0212	0.0593	0.0237	0.0607	0.0380
39.81	0.1731	0.1812	0.1074	0.5425	0.0657	0.0196	0.0540	0.0235	0.0690	0.0435
50.11	0.1873	0.2066	0.1008	0.5033	0.0581	0.0191	0.0496	0.0222	0.0787	0.0500
63.09	0.2035	0.2344	0.0954	0.4534	0.0567	0.0186	0.0464	0.0224	0.0896	0.0577
79.43	0.2213	0.2644	0.0877	0.4144	0.0511	0.0176	0.0453	0.0229	0.1017	0.0667
100.0	0.2421	0.2972	0.0827	0.3734	0.0507	0.0161	0.0423	0.0219	0.1153	0.0774
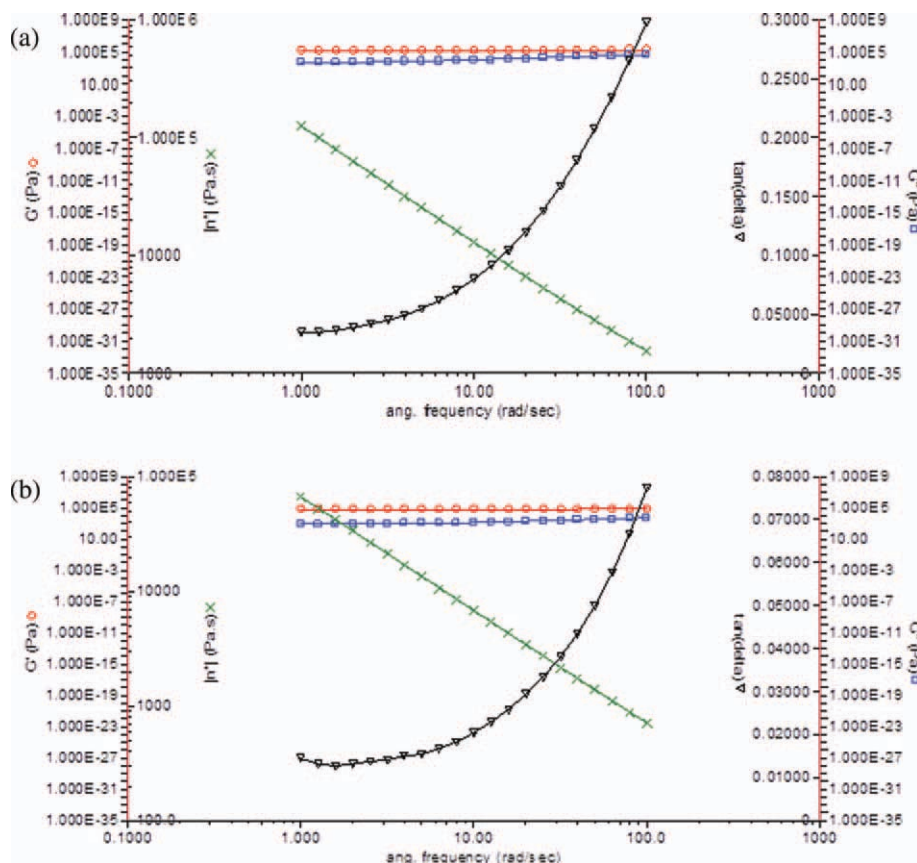
Figure 2 Representative viscoelastic data for a dry polymeric film (top) and a polymeric film immersed in water for 24 h (bottom). Material produced with a 2 : 1 molar ratio (glutaric acid : glycerol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

when the elastic component is dominant, tan δ < 1. Figures 2 and 3 describe the general response shown by all of the polymers as angular frequency increased. For all of the polymers, the elastic modulus (G') was higher than the viscous modulus (G''). Therefore, all of the polymers were highly elastic in character even after they absorbed various solvents.

In Figure 2, the viscous modulus (G'') for the dry polymer and water-absorbed polymer increased with angular frequency and began to converge toward the values of the elastic modulus (G'). Although the viscous modulus (G'') never became greater than the elastic modulus (G'), the material became less elastic and more viscoelastic as the
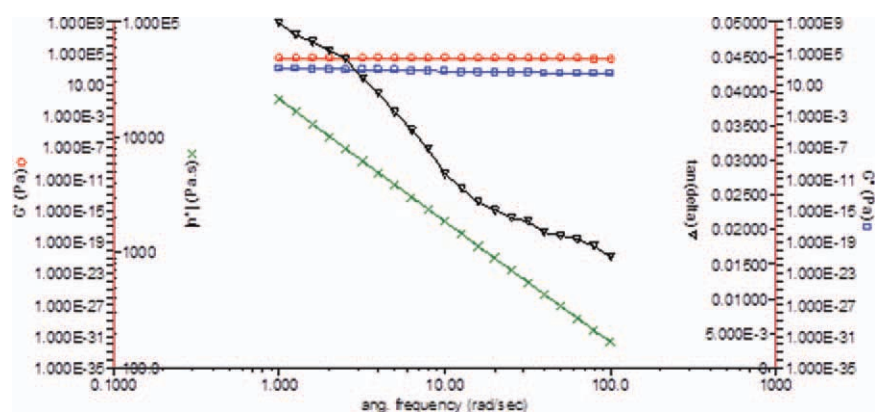

Figure 3 Representative viscoelastic data for a polymeric film immersed in THF for 24 h Material produced with a 2 : 1 molar ratio (glutaric acid : glycerol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

angular frequency increased as shown by an increase in tan δ (G''/G'). Figure 3 shows that the viscous modulus (G'') for a THF-absorbed film decreased with angular frequency and diverged away from the values of the elastic modulus (G''). This increased the elastic component of the polymer, and consequently, resulted in a decrease in the viscoelastic character of the material as shown by a decrease in tan δ. The complex viscosity (η*) decreased linearly with angular frequency for all polymers. These results are very similar to the studies performed by Bose® on agarose hydrogels for use as implantable scaffold materials with tissue-like viscoelasticity.[36]

The results in Table III summarize that the elastic modulus, G', decreased upon absorption of solvent as the dry polymers have significantly higher G' values than the swollen polymers. However, the elasticity of each polymer varied with angular frequency. G' increases linearly with frequency for the dry samples and samples that have absorbed methanol and water. The polymer samples exposed to methanol and water had moderately lower G' values than the dry polymer. However, solvent absorption was not very high for water or methanol which could explain the reason why the polymers exposed to them retain elastic character. G' values were low relative to the dry polymer for the THF- and DMSO-absorbed polymers. The large amounts of solvent infused into the polymer gel greatly decreased the elastic character of the polymer and the elasticity (G') continued to decrease with increased angular frequency. The exception was the G' values for DMSO-absorbed polymer (1 : 1 molar ratio glycerol: glutaric acid). Its G' value was significantly lower than that of the analogous dry polymer. However, it showed an increase in elasticity as the frequency increased. Regardless of this unexpected observation, when comparing the elastic modulus for all of the samples at 100 rad/s, the correlation between elasticity and degree of absorption is obvious as, on average, larger amounts of solvent uptake resulted in a decrease in elasticity.

Table IV summarizes that the viscous modulus (G'') generally increases linearly for the dry and water-absorbed polymer. Once again, the sample with absorbed water appears to behave similarly to the dry polymer. This observation suggests that the relatively small percentage of water absorbed into the polymer matrix is not enough to increase the viscous character of the material. The G'' values for five of the six polymer gels swelled with DMSO, THF or methanol decrease with increasing angular frequency. The lone exception was the DMSO-swelled polymer gel (2 : 1; glutaric acid : glycerol) which increases with increasing angular frequency. When these data are compared at 100 rad/s to the dry

polymer, it is clear that regardless of increasing or decreasing trends, the solvent-absorbed polymers behave less like fluids than the dry sample. Moreover, when comparing the elastic modulus data in Table III, none of the increases in viscosity resulted in a viscous modulus (G'') that was higher than the elastic modulus (G').

The tan δG''/G' is an indicator of how efficiently a material loses energy to molecular rearrangements and internal friction. In this study, all of the tan δ values are very low. This indicates that the polymers all have overwhelming elastic character (Table V). A closer look at the data shows that tan δ directly correlates to the trends of viscous modulus (G'') values. Although the ratio of the G''/G' never got close to 1, the tan δ for the dry and water-absorbed polymers did increase with angular frequency. All other polymers, except the DMSO-absorbed polymer made using a 2 : 1 (glutaric acid: glycerol) molar ratio saw a decrease in tan δ, indicating that their elastic character increased with increasing angular frequency revealing a decrease in the viscoelastic property of the polymers.

The complex viscosity (η*) is a frequency-dependent viscosity function. The η* values for the swelled or unswelled polymers were inversely proportional to frequency (Table VI). This suggests that as the frequency is increased, the solid materials are affected by shear thinning and become more fluid in composition and structure. This is typical behavior for semisolid materials when the rate of shear stress is increased. The linear relationship between complex viscosity and angular frequency illustrates the non-Newtonian behavior of these viscoelastic materials.

These experiments were reasonably reproducible. Across the entire data set, the average percent errors for the elastic modulus (2.09%) and complex viscosity η* (2.04%) were low. The change in values for the viscous modulus (G'') and tan δ as angular frequency increased was greater than the change for other parameters, resulting in average percent errors of 17.12 and 15.09%, respectively. Percent error increased with increasing amounts of solvent absorbed. Variations in amounts of absorbed solvent (Table II) for each polymer likely contribute to viscoelastic differences.

CONCLUSIONS

This research shows that polymer films made from glycerol and diacids can be used as organogels and, to a lesser degree, hydrogels. Our polymers were able to absorb various amounts of a variety of solvents without compromising their elasticity. The information acquired herein opens the door to many new areas of research with polymers of this type,

including hyperbranched polymers with lower degrees of gelation.

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