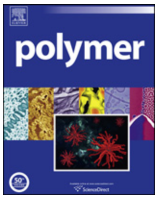
Polymer 50 (2009) 5414–5421

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Hydrogels prepared from polysiloxane chains by end linking them with trifunctional silanes containing hydrophilic groups

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ARTICLE INFO

Article history:
Received 16 July 2008
Received in revised form
31 December 2008
Accepted 10 January 2009
Available online 12 October 2009

Keywords:
Alkoxy silanes
Hydrogel
Hydrophilicity

ABSTRACT

A strongly hydrophobic polymer was converted into a hydrogel by introducing hydrophilic side chains of sufficient lengths and amounts to overcome the hydrophobicity but sufficiently well dispersed to avoid disadvantages such as loss of the transparency required in applications. Specifically, poly(dimethylsiloxane) (PDMS) hydrogels were successfully prepared by end linking a combination of long and short chains to give the bimodal distributions of network chain lengths that generally give unusually good mechanical properties. The end linkers were chosen using trialkoxylsilanes R′Si(OR)$_3$ having R′ side chains that are hydrophilic of variable lengths and of sufficient hydrophilicity to produce the desired hydrogels. The first trialkoxysilane was *N*-(triethoxysilylpropyl)-O-polyethylene oxide urethane (S1) with 4–6 units of ethylene glycol, and the second was [methyoxy(polyethyleneoxy)propyl]-trimethoxysilane (S2) with 6–9 units of ethylene glycol, and they were used to end link hydroxyl-terminated PDMS chains in standard room-temperature condensation reactions. It was possible to introduce the hydrophilic side chains into the hydrophobic networks without discernible phase separation. These linear side chains increase equilibrium water contents, from 0 to 11.2 wt% in the first series and from 0 to 29.8 wt% in the second. Longer hydrophilic chains clearly migrated to the surfaces of the resulting PDMS hydrogels to give reduction in static contact angles from 105° to 40° for the first series, and to 80° for the second. The longer hydrophilic chains were found to give larger decreases in the contact angles and larger equilibrium water contents. The mechanical properties demonstrated that Young's moduli of the hydrogels did not change upon introduction of the S1 hydrophilic cross linker, but did decrease from the presence of the S2. The tensile strength and elongation at break were relatively insensitive to the amounts of either of the hydrophilic groups.

1. Introduction

Poly(dimethylsiloxane) (PDMS), with repeat unit [–Si(CH$_3$)$_2$–O–], has attracted great interest for many years since it can be widely used in microfluidic devices [1–6], microcontact printing technology [6–8], biocompatible devices (e.g. contact lenses) [9], and drug delivery systems [10–13]. These impressive ranges of applications have been due to the many attractive features of PDMS, including (i) high gas permeability, (ii) good optical transparency, (iii) high flexibility and low risk of loss or damage, (iv) nontoxicity and biocompatibility, (v) stability toward heat and chemicals, (vi) low curing temperature, (vii) moldability, and (viii) ease of sealing with other materials. Although PDMS has many advantages, its hydrophobicity has limited its use in some applications, especially those involving biocompatible devices, because other hydrophobic molecules, biopolymers and cells irreversibly absorb to its surface [5,14]. In addition, small hydrophobic molecules can actually be absorbed into the bulk of the PDMS [5]. This has led to the recognition of the need for modifying the surface of such polysiloxane materials to ameliorate problems of this type. Obviously, increasing the hydrophilicity of any polymer surface improves its' wettability and this, in turn, improves its biocompatibility.

There have been a large number of patents and research reports that describe attempts to modify the strongly hydrophobic surfaces of PDMS to make them sufficiently hydrophilic to be useful in a number of biomedical applications. Increased hydrophilicity can be obtained by introducing various polar groups with corona discharges [15,16], ultraviolet irradiation in combination with ozone [17–20], plasma treatments [2,21,22], and grafting or simple adsorption of polar polymers onto the surfaces by oxidation [23]. These methods have indeed given significant improvements in the wettability of PDMS surfaces.

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0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.01.047

Three problems that have arisen, however, are (i) the loss of hydrophilicity from the migration of surface hydroxyl groups into the polymer bulk (to minimize surface free energies), (ii) physical damage to the surface of PDMS including cracks or other defects, and (iii) limited biocompatibility of PDMS surfaces after some of the more aggressive chemical treatments [15,16,20,24]. Similar problems occurred upon either coating the surface with additives, or compounding the additives into the polymer since they would subsequently diffuse to the surfaces. In one case, Binkert covalently immobilized lactic acid-grafted poly(ethylene glycol (PLL-g-PEG) copolymer onto the surfaces of polysiloxane hydrogels-based contact lenses via an intermediate aldehyde plasma polymer to form brush-like, protein-resistant surfaces [23]. More hydrophilic surfaces and good optical quality were achieved, but reproducibility problems and inhomogeneities in the coatings were encountered.

Preparation of amphiphilic polymer conetworks has been a successful way to make the surfaces and interiors of a polysiloxane network more hydrophilic. Such amphiphilic conetworks consist of hydrophilic and hydrophobic chains covalently bonded to each other [25]. The amphiphilic nature of these new cross-linked polymers is indicated by their swelling ability in both aqueous and organic media without losing their dimension stability and without encountering macroscopic phase separation or polymer leaching. Amphiphilic polymer conetworks represent a relatively new class of promising materials for applications such as pervaporation membranes, contact lenses, drug delivery systems, biomedical scaffolds for tissue engineering, and supports for catalysts. The amphiphilic conetworks based on PDMS and some hydrophilic components were shown to at least partly provide co-continuous or interpenetrating phase morphologies for long-term biocompatibility, with the resulting two phases acting as two different routes for transfer of oxygen as well as aqueous materials [26–29].

The hydrophilic component can be poly(ethylene oxide) (PEO) or, nearly equivalently, poly(ethylene glycol) (PEG), both being polyethers already used in numerous applications involving biomaterials. Their advantages are their interfacial energies with water, relative structural stability, lack of binding sites for reactive proteins, high chain mobility, and steric stabilization effects [30–33]. However, because of their incompatibilities with other polymers, phase separation almost always occurs in their mixtures and this can lead to opaqueness as well as reduced mechanical properties [34]. Covalently cross linking the polymer chains at least prevents demixing at the macroscopic level, leading to domains that remain at the nanoscale level [28,35–40].

An earlier part of this series of reports describes using amphiphilic PDMS–PEG block copolymers as both compatizilers for these very different blocks, as well as sources of greatly increased hydrophilicity [41]. The present study involves another novel method to prepare polysiloxane hydrogels by cross linking hydroxyl-terminated PDMS with poly(ethylene oxide) functionalized trialkylsilanes with different chain lengths. Specifically, these materials were [2-methoxy(polyethylenxy)propyl]-trimethoxysilane with 4–6 units of ethylene oxide, and *N*-(triethoxysilylpropyl)-O-polyethylene oxide urethane with 6–9 units of polyethylene oxide (from polycondensations at room temperature) [42]. The hydrophilic chains thus introduced would be dangling from the trifunctional cross links and should have very favorable effects on surface hydrophilicities, equilibrium water contents, and mechanical properties. The bimodal PDMS network is used as the basic network because the network chain length could be controlled through end-linking, at the same time the bimodal network gives unusually good mechanical properties in a variety of elastomers [43–47].

2. Experimental section

2.1. Materials

Samples of linear hydroxyl-terminated PDMS with average number-molecular weights, 22,600 g mol^{-1} and 880 g mol^{-1} (DMS-S31 and DMS-S12) were purchased from the Dow Corning Corporation, Midland, MI. The cross linkers were tetraethoxysilane (TEOS), *N*-(triethoxysilylpropyl)-O-polyethylene oxide urethane (brand name: SIT8192.0, designated here as S1), and [methyoxy-(polyethyleneoxy)propyl]–trimethoxysilane (brand name: SIM6492.7, designated S2), and their structures are shown in Fig. 1. These cross linkers and the catalyst, stannous-2-ethylhexanoate (SNB1100), were all purchased from Gelest Inc, Morrisville, PA. Alcohol and toluene were purchased from the Aldrich–Sigma Company, and were used directly without further purification. Deionized (DI) water was used in the measurements of static contact angles of the hydrogels. Additional details are given elsewhere [48].

2.2. Preparation of the polysiloxane hydrogels

The hydrogels were prepared with the constant mole ratio (5/95) of DMS-S31 (the long chains) to DMS-S12 (the short chains). The samples of hydroxyl-terminated chains were end-linked in the undiluted state with the stoichiometrically-required amounts of cross linkers at the mole ratios (10/0, 8/2, 6/4, 4/6, 2/8) of TEOS to S1 (designated T-0, T-S1-2, T-S1-4, T-S1-6, T-S1-8), and at the mole ratios (10/0, 8/2, 6/4, 4/6, 2/8) of TEOS to S2 (designated T-0, T-S2-2, T-S2-4, T-S2-6, T-S2-8), respectively.

Briefly, the mixtures were first stirred vigorously in air at room temperature for at least 2 h to a transparent state. The stannous-2-ethylhexanoate catalyst was then introduced at 0.6 wt% of the total weight of the other components. The mixtures were then stirred for approximately 10 min before being poured into Teflon™ molds and were left at room temperature for three days. After the by-products such as alcohol and water, and gas bubbles were remove by vacuum, the hydrogel sheets were then extracted with toluene for three days, and subsequently deswelled with methanol and dried under vacuum. Finally, the transparent conetworks films were prepared. The fractions of soluble polymers thus removed were very small, approximately only 2.5 wt%.

2.3. Static contact angles (CA)

Contact angles were used to characterize the hydrophilicities of the surfaces of the hydrogels. The tests were carried out at room temperature with ca. 1 μl deionized water, and angles were visually determines using a VS2000 digital camera with zoom capability. Measurements were taken from at least four areas on the surfaces for each sample.

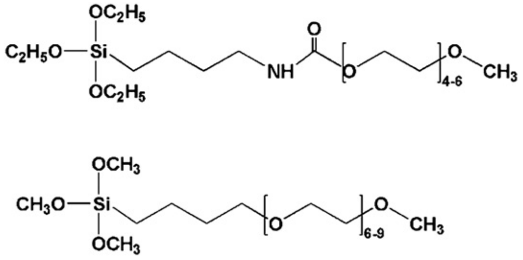

Fig. 1. Structures of end linkers S1 (upper sketch) and S2 (lower sketch).

2.4. Equilibrium water contents (EWC)

Values of the EWC were obtained by immersing a 1 cm × 1 cm × 0.2 cm piece of weighed hydrogel film in a large excess of distilled water at ambient temperature. The weights of the swollen samples were not recorded until they became constant. $S_m = (Wt_s - Wt_d)/Wt_s \times 100\%$, where Wt_s and Wt_d were the swollen and dry weights, respectively.

2.5. Differential scanning calorimetry (DSC)

A TA 1501thermal analyzer (Thermal Analyzer Inc.) was used for determination of the thermal behaviors of the samples in an atmosphere of nitrogen flowing at 30 ml/min. After a 5–10 mg sample of hydrogel film was sealed into an aluminum sample pan, it was then quickly heated above its glass transition temperature T_g to negate its thermal history, and was then quickly cooled to $-150\,^{\circ}C$. After a period for equilibration, the sample was then heated at a scan rate of $10\,^{\circ}C/min$ from -150 to $100\,^{\circ}C$ in a nitrogen environment.

2.6. Mechanical properties

The stress–strain behavior at ambient temperature was determined using a home-built tensile tester on samples of 30 mm × 5 mm × 2 mm, at an elongation rate of 5 mm/min. Of particular interest were Young's modulus, tensile strength, toughness, and elongation at break.

2.7. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy measurements were carried out to identify the functional groups on the surfaces of the pristine hydrogel samples. This could be useful for analyzing the structures and reaction mechanism involved in the processing. The measurements were conducted using a Digilab Excalibur FTIR equipment in the mid-IR range (4000–500 cm^{-1}) at a resolution of 4 cm^{-1}, and sixteen scans per sample were analyzed using the Digilab Resolutions Software.

2.8. Environmental scanning electron microscopy (ESEM)

Sample surfaces were cleaned with alcohol. Samples were immersed in liquid nitrogen and then broken to obtain fresh surface areas. The morphologies of the surfaces and cross sections were measured using a Philips XL30 Environmental Scanning Electron Microscopy under high vacuum.

3. Results and discussion

3.1. Cross linked hydrogels of the poly(ethylene oxide)–trialkoxylsilanes

FTIR was used to monitor the reaction processes of the T-S1 and T-S2 series of hydrogels (Fig. 3a and b), respectively. In the pristine PDMS, the peaks at 2965 cm^{-1}, 1263 cm^{-1} and 792 cm^{-1} were assigned to Si–CH_3 groups, and the peak at 1012 cm^{-1} to Si–O–Si groups (Fig. 3a and b). These peaks were not changed in the resulting hydrogels (Fig. 3a and b), while new peaks appeared in the cross-linking of poly(ethylene oxide)–trialkoxylsilanes. In the T-S1 series at 3357 cm^{-1}, 2871 cm^{-1} and 1074 cm^{-1} in T-S1-2 and T-S1-4, and were assigned to the –NH–, –CH_2– and C–O–C groups (Fig. 3a), respectively. In the T-S2 series of hydrogels 2965 cm^{-1} and 1074 cm^{-1} were assigned to –CH_2– and C–O–C (Fig. 3b), respectively. These results suggested the introduction of the hydrophilic chains, with their PEG sequences, into the resulting hydrogel networks.

The reaction mechanisms were proposed (Fig. 2). The scheme is based on the usual preparation of networks from linear hydroxyl-terminated PDMS end linked by TEOS with stannous 2-ethylhexanoate as catalyst [43,49–51]. When catalyzed by stannous

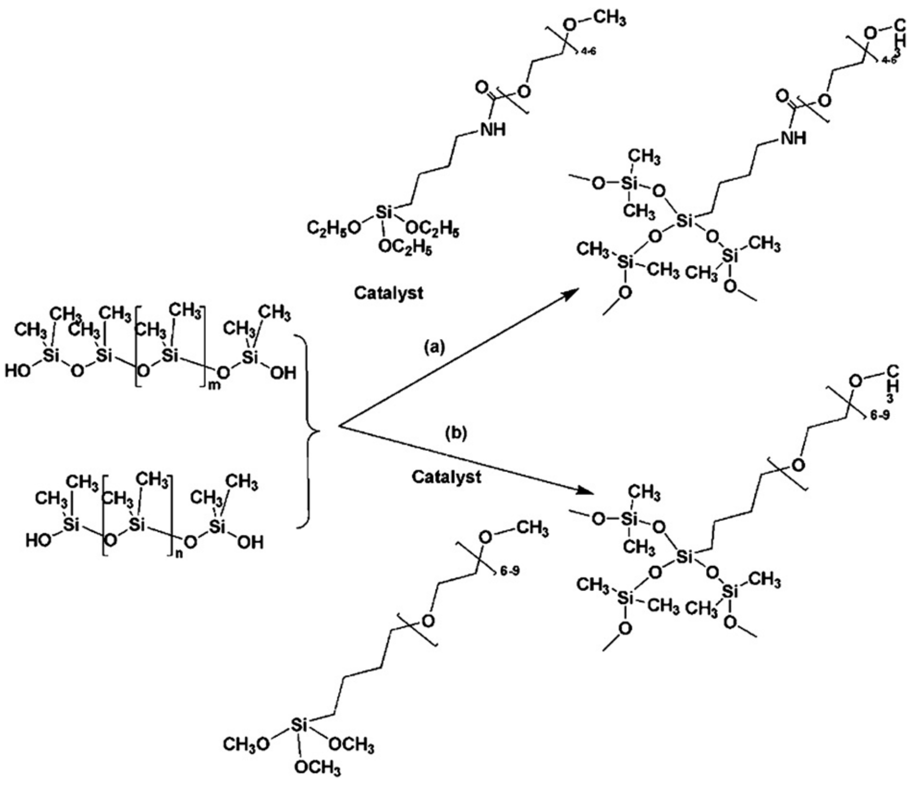

Fig. 2. Schematic reactions for end linking the hydrogels by (a) S1 and (b) S2.

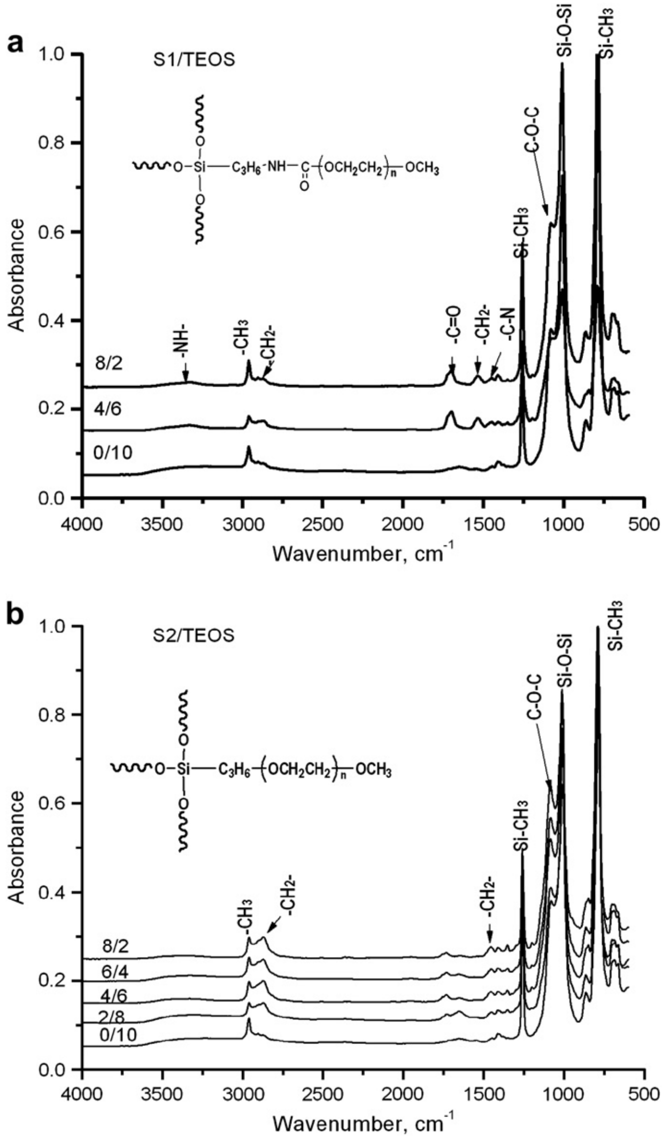

Fig. 3. FTIR results for the (a) T-S1 series and the (b) T-S2 series of hydrogels.

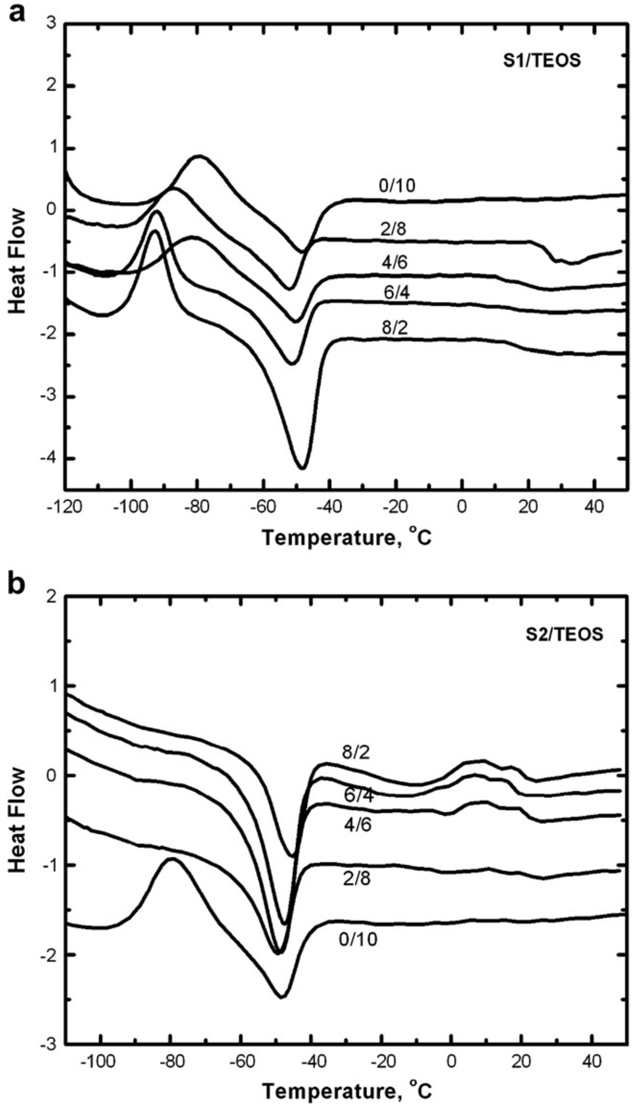

Fig. 4. Differential scanning calorimetry results for the (a) T-S1 series and (b) T-S2 series of hydrogels.

octoate without cross-linker, hydroxyl-terminated PDMS only underwent a linear polycondensation, without network formation. The following reactions can take place during the cross-linking reaction of PDMS: (1) hydrolyzation of cross-linker, (2) condensation of silanol groups between cross-linker and PDM. Based on Warrick's report [52], the former reaction takes place without catalyst, but the latter occurs only if tin or titanium compounds are present as catalysts. In the present case, the cross linkers were TEOS and a poly(ethylene oxide) (PEG) derivative of trialkoxysilane (S1 or S2). Specifically, there was a condensation reaction between hydroxyl end groups of the PDMS and the alkoxy groups on the TEOS and the trialkoxysilane. In this way, the hydrophilic PEG sequences on the S1 or S2, were attached to the cross links as dangling chains.

3.2. Thermal characteristics

The differential scanning calorimetry (DSC) results for the T-0 and T-S1 series of hydrogels, shown in Fig. 4(a), demonstrated that there were two new values of the glass transition temperature, $T_{g1(PEG)}$ and $T_{g2(PEG)}$, in the range 10–30 °C in the T-S1 series. As is also shown in Table 1, comparisons can be made with pristine PDMS networks, whose crystalline temperature $T_{c(PDMS)}$ is -86.6 °C and crystalline melting point $T_{m(PDMS)}$ is -65.0 °C. In the hydrogels, $T_{c(PDMS)}$ decreased slightly, while $T_{m(PDMS)}$ and $T_{m\ peak}$ increased slightly with increase content of S1. $T_{g1(PEG)}$ and $T_{g2(PEG)}$ also decreased with increasing S1 content. These results indicated that the S1 end linker improved the compatibility of the two phases. The results on the T-S2 series of hydrogels, shown in Fig. 4(b), also clearly indicated that there were two new values of the glass transition temperature, $T_{g1(PEG)}$ and $T_{g2(PEG)}$, in the range 10–30 °C. Again, increase in S2 content decreased $T_{g1(PEG)}$ and $T_{g2(PEG)}$ and slightly increased $T_{m(PDMS)}$ and $T_{m\ peak}$. However, the crystalline temperature of PDMS, $T_{c(PDMS)}$, was not discernible, possibly because of improved compatibility obtained from the long dangling chains of PEG in the networks. The longer dangling PEG chains in S2, gave more pronounced improvements in the compatibility between the PDMS and PEG.

3.3. Morphology of the hydrogels

It can be presumed that the hydrophilic PEG dangling chains formed hydrophilic macroscopic phases in PDMS because of their limited compatibility with the hydrophobic matrix in the networks.

Table 1
Some thermal characteristics of the two series of the bimodal hydrogels.

	$T_{c(PDMS)}$ (°C)	$T_{m(PDMS)}$ (°C)	$T_{m\ peak}$ (°C)	C (J/g)	$T_{g1(PEG)}$ (°C)	$T_{g2(PEG)}$ (°C)
T-0	−86.6	−65.0	−51.9	9.2	–	
T-S1-2	−87.3	−65.9	−52.2	10.1	24.9	31.3
T-S1-4	−82.0	−64.8	−50.6	17.9	10.6	16.8
T-S1-6	−92.4	−67.0	−51.7	18.4	8.9	13.7
T-S1-8	−92.6	−62.3	−48.4	20.0	14.5	19.1
T-S2-2	–	−61.3	−49.3	15.1	11.8	20.4
T-S2-4	–	−60.0	−48.9	16.4	9.7	19.4
T-S2-6	–	−58.6	−47.3	15.3	7.8	16.6
T-S2-8	–	−55.9	−45.2	15.1	9.2	18.0

However, the hydrogel films were optically transparent, i.e., no macroscopic or microscopic phase separation has occurred. Both the surface and cross-section morphology of the hydrogels in the dry state were studied by the electron microscopy, which provided direct visualization of the PDMS and PEG phases (Fig. 5). The dark regions are the PEG phases, and PEG phases are well dispersed in the PDMS, at the surface and in the bulk of the hydrogels. There was no discernable difference in the surface and cross-section results, with the PEG forming spherical phases of diameter less than 5 μm. This was much less than the PEG phase diameters in the PDMS–PEG systems cross linked by bis[(3-methyldimethoxysilyl)propyl]-polypropylene oxide [41]. In the T-S1 hydrogels, it was also observed that the PEG phase diameters in T-S1-6 (Fig. 5d–f) were somewhat larger than those in T-S1-2 (Fig. 5a–c) because of the higher contents of PEG in T-S1-6. Similar results were seen in the T-S2 hydrogels, that is, the PEG phase T-S2-6 (Fig. 5j–l) hydrogels, slightly larger than those in T-S2-2 (Fig. 5g–i). The morphologies of T-S1 and T-S2 also depended on the mixing condition during the cross-linking process as well as on the lengths and the amounts of the hydrophilic chains.

3.4. Hydrophilicities

One of the simplest methods available for probing the surface properties of materials involves measuring the contact angles (CA) a water droplet makes on these surfaces. Baier et al. [33,53] have found empirically that minimal fouling of hydrophilic polymer surfaces is obtained for intermediate values of the critical surface tension, obtained from the contact angles of a series of different liquids. In the case of PDMS networks, low contact angles would support that water-miscible polymers at surface probably cause such low values angles. Fig. 6(a) shows the CA values for the T-S1 bimodal hydrogel networks. The results show that (i) the CA values were considerably less than that of pristine PDMS (ca. 105°), and (ii) the CA values of hydrogels on the air-side surface were much lower than those of the mold-side surface, and (iii) the CA values for both sides of the hydrogels decreased with increased amounts of S1 (except for T-S2-6), decreasing up to 40° for the air-side surfaces and up to 15° for the mold-side surfaces. The results certainly confirmed the presence of hydrophilic chains on the surfaces of the polysiloxane networks. In some cases, the Teflon™ molds apparently expelled some hydrophilic dangling chains on the mold side surface into the bulk of the polysiloxane networks, decreasing the hydrophilicity of these surfaces. This result demonstrated that the hydrophilicity of the hydrogels was strongly related to environmental conditions. The corresponding results for the T-S2 series were very similar, as can be seen from Fig. 6(b). Again, the values of the contact angles were lower than that of the pristine PDMS (ca.

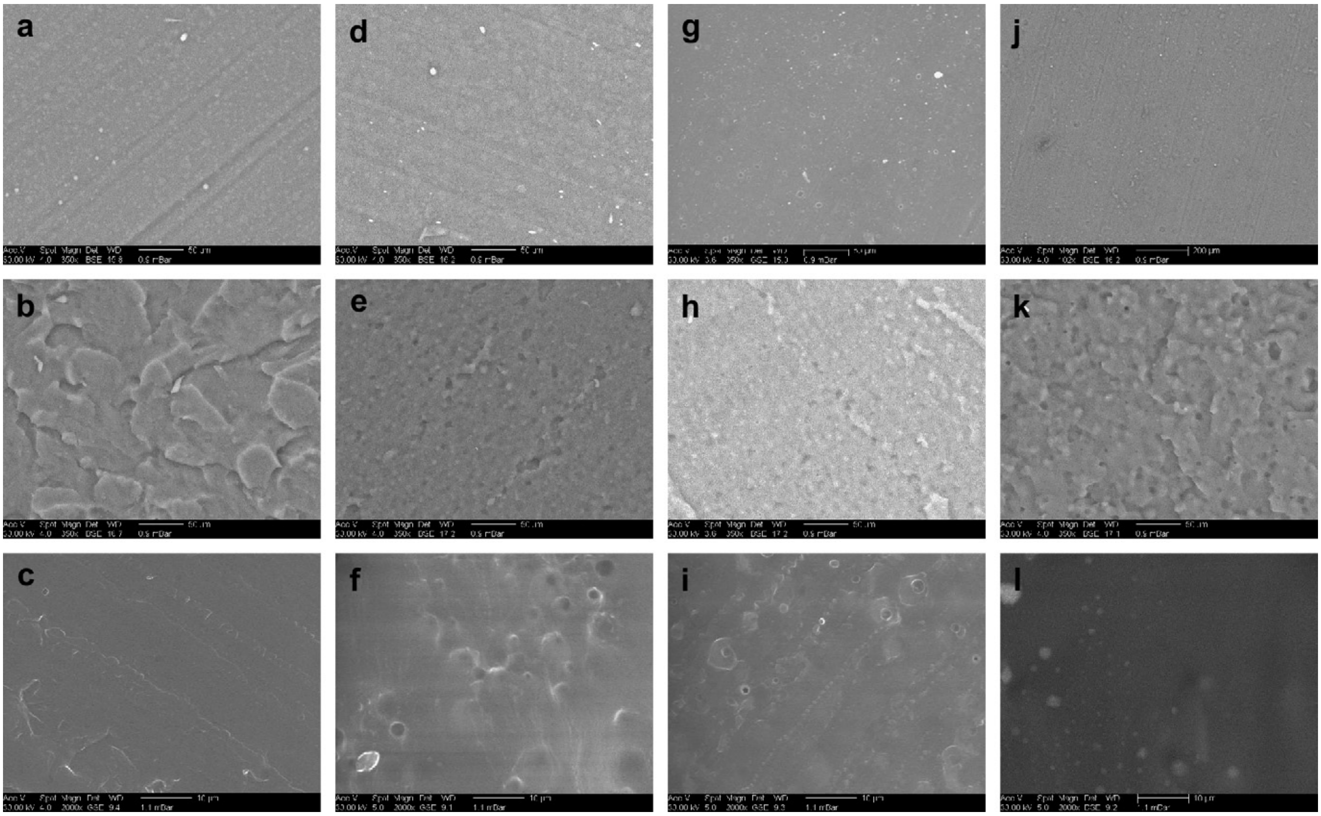

Fig. 5. Scanning electron microscopy images for the hydrogels: (a) surface of T-S1-2, (b and c) cross section of T-S1-2, (d) surface of T-S1-6, (e and f) cross section of T-S1-6, (g) surface of T-S2-2, (h and i) cross section of T-S2-2, (j) surface of T-S2-6, and (k and l) cross section of T-S2-6.

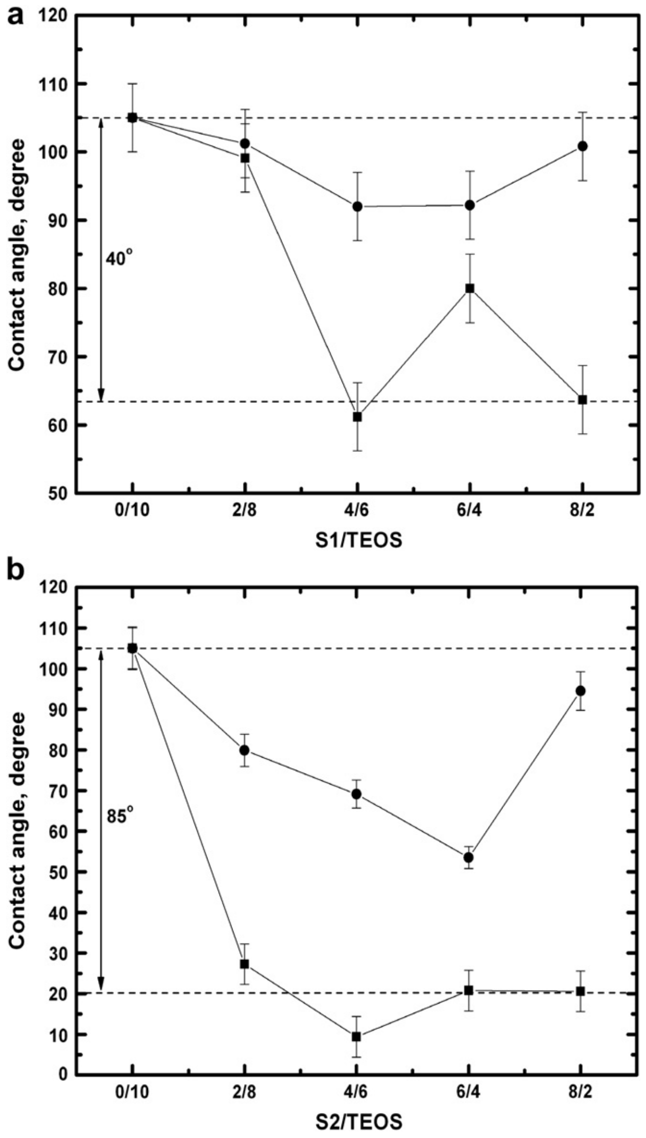

Fig. 6. Effects of the end linkers on the static contact angles with water for the T-S1 and T-S2 hydrogels. -■- the air-side surfaces, -●- the mold-side surfaces; (a) end linker S1 and (b) S2.

105°). Also, the CA values of the air-side surfaces were much lower than those on the mold-side surfaces. The CA value decreased up to 55° for the mold-side surface sand up to 85° for the air-side surfaces. The CA values for the T-S2 series were much lower than those on the T-S1 list, which was mainly due to the larger number of PEG units (6–9) in the end linker S2 than in the S1 one (4–6). This suggests that the longer hydrophilic chains do form hydrophilic layers on the surfaces, but there may be a critical length which, when exceeded, leads to saturation of the desired changes.

3.5. Equilibrium water contents

The equilibrium degrees of swelling of the hydrogels are of obvious importance, since several applications require suitable water contents. It should be noted that attaching a conetwork to the surface of a hydrophobic material confines the swelling volume change to one dimension (normal to the surface), which obviously affects on swelling behavior [33]. In the specific case of the present hydrogels, higher water contents were generally more advantageous because they gave a higher permeability and biocompatibility. However, with increasing water content, the mechanical strengths of the hydrogels decreased and their transparencies could also decrease (as a consequence of a microscopic phase separations). The optimal situation would obviously be high mechanical strength, transparency, and sufficient water content, which is the ultimate goal of these series of investigations [54,55]. The EWC values of the T-S1 series, shown in Fig. 7(a), increased in proportion to the S1/TEOS amount, up to 11.8 wt%. The same trend was observed for the T-S2 series in Fig. 7(b), where the EWC values increased up to 29.8 wt%. These results thus indicate that the larger the number of PEG repeat units in the hydrophilic trialkoxysilane, the higher the hydrophilicity of the resulting hydrogel.

3.6. Mechanical properties

The stress–strain behaviors of the T-S1 series of hydrogels (Fig. 8a) showed that the tensile strengths and elongations at break increased with increased values of S1/TEOS (except T-S1-8), while Young's moduli remained almost the same. In the T-S2 series (Fig. 8b), the tensile strength and elongation at break also increased with increased value of S2/TEOS (except T-S2-8), except that Young's moduli slightly decrease instead of increasing. Comparison

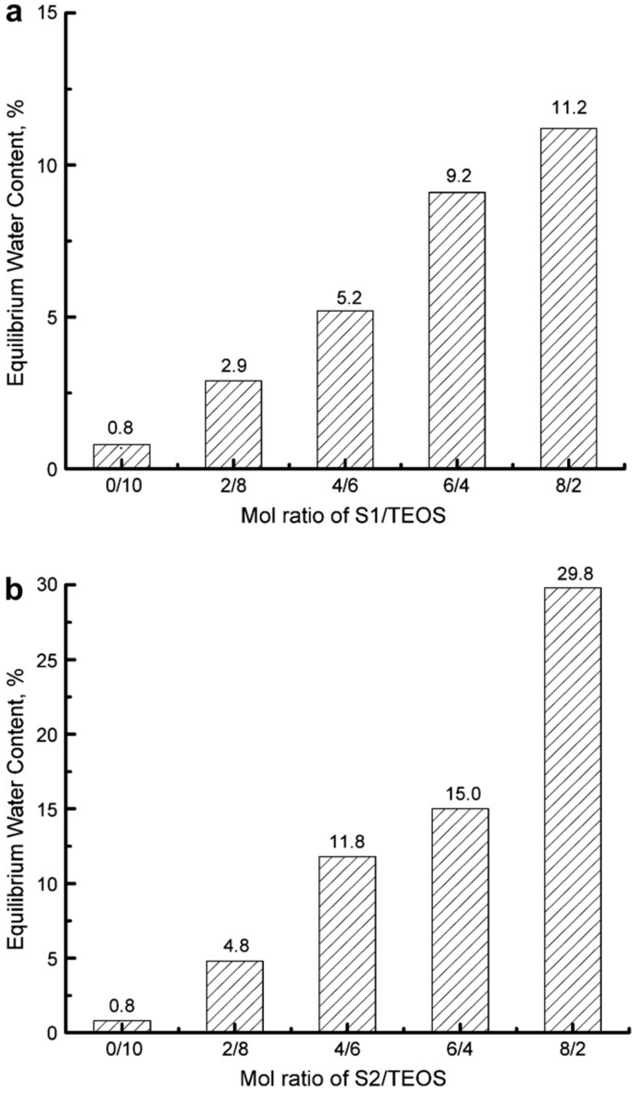

Fig. 7. Effects of the end linkers on equilibrium water contents.

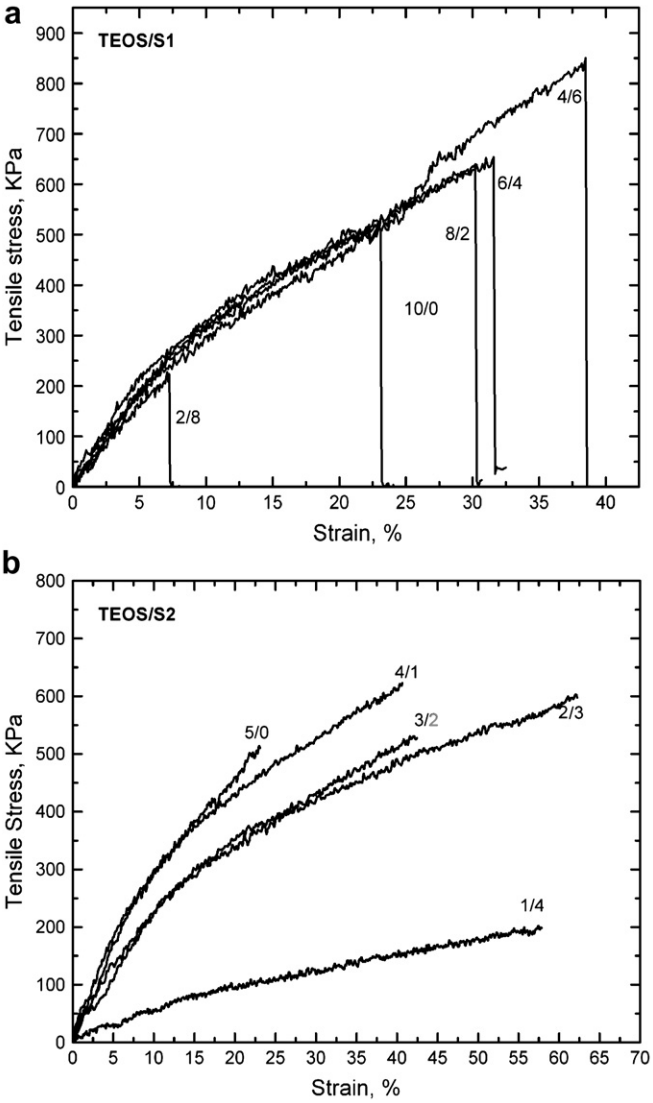

Fig. 8. Dependences of the stress–strain isotherms in elongation on the end linker (a) S1, and (b) S2.

of mechanical properties for the T-S1 and T-S2 series given in Table 2, shows that the dangling hydrophilic chains did not decrease Young's moduli of the hydrogel until their lengths were over a critical value (i.e., 6 units of ethylene glycol). With increased value of the ratio S1/TEOS, more cross links become trifunctional (the functional of S1) from tetrafunctional (the function of TEOS). This could increase the extensibility of the network chains. Moreover, the introduced PEG dangling chains in less than 6 units may act as the small plasticizer among the networks to make the networks easily to transition according to the deformation, which help to improve the elongation, but not long enough to decrease the interaction among the chains entanglements. When the dangling chain length over the critical length the role of dangling chain still help to deform in the network main chains during strain, but the dangling obviously decrease the interaction of networks, which led to the decrease of Young's moduli in T-S2 series.

Table 2
Mechanical properties of the bimodal hydrogels.

	T-0	T-S1-2	T-S1-4	T-S1-6	T-S1-8	T-S2-2	T-S2-4	T-S2-6	T-S2-8
Modulus of elasticity, MPa	3.87	3.72	4.45	3.93	3.93	3.16	2.68	2.20	0.76
Tensile strength, MPa	0.52	0.64	0.65	0.84	0.25	0.62	0.53	0.60	0.20
Elongation at break, %	23.2	30.3	31.6	38.5	7.2	40.6	42.2	62.1	57.5

Some of these results parallel earlier results, particularly on bimodal elastomers [47,56]. The mechanical properties of bimodal elastomers in general could readily be controlled by variation of the ratio of the short to long chains in the end-linked networks [43,47,56]. This suggests the importance of additional work to optimize the mechanical properties of the present hydrogels through changes in the relative amounts of short chains and long chains in the networks. As a specific goal, for example, Young's moduli for biomaterials used in soft contact lenses should be less than 1.0 MPa (preferably less than 0.70 MPa), and elongations at break should be larger than 250% [29]. In this regard, optimization of the present materials is in progress.

4. Conclusions

Bimodal hydrogels were successfully prepared from hydroxyl-terminated long and short chains of poly(dimethylsiloxane) (PDMS), end linked with TEOS and the hydrophilic trialkoxysilane cocross linkers, methoxy(polyethyleneoxy)propyltrimethoxysilane and *N*-(3-triethyoxysilylpropyl)-O-gluconamide. The contact angles observed with water showed that the surface hydrophilicities did greatly increase with increasing proportions of the poly(ethylene oxide) (PEG) sequences of the hydrophilic chains. Equilibrium water swelling results showed the same increases with increasing proportions of the end linkers. The mechanical properties of the bimodal hydrogels did not suffer very much with introduction of the hydrophilicity. The hydrophilic phases were well dispersed but calorimetric results indicated that there was nonetheless some phase separation, into PDMS and PEG phases. The contact angles with water and equilibrium water contents were in the acceptance range of materials used for contact lenses. Further work should focus on increasing the advantages of bimodalities, increasing transparencies and oxygen and water permeability, and decreasing the extents of protein absorptions.

Acknowledgments

It is our pleasure to acknowledge financial support provided JEM by the National Science Foundation through Grants DMR-0314760 and DMR-083454 (Polymers Program, Division of Materials Research) and the use of some facilities in the Department of Electrical and Computer Engineering at the University of Cincinnati to measure the hydrophilicity.

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