Hydrogels Based on Hydrophilic Side-Chain Siloxanes

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SYNOPSIS

Methacrylate end-capped diethylene glycol propyl methyl ether, 5-hexyl-1,2-diol, and 3-propyloxy-1,2-propane diol side-chain siloxanes were evaluated for potential use as hydrogels for contact lens application. The preparation of the methacrylate end-capped ether, hexane diol, and propane diol side-chain siloxanes was accomplished in two relatively simple synthetic steps: The first step consisted of the acid-catalyzed co-ring opening polymerization of octamethylcyclotetrasiloxane, tetramethylcyclotetrasiloxane, and 1-3-bis-methacryloyl-butyltetramethyldisiloxane, followed by a platinum-catalyzed hydrosilation with (in separate experiments) diethylene glycol allyl methyl ether, trimethylsilyl protected 3-allyloxy-1,2-propane diol, and trimethylsilyl protected 5-hexene-1,2-diol. The trimethylsilyl protecting group was removed using a 10% 0.1N HCl solution in 2-propanol. Radical polymerization of the methacrylate end-capped ether, hexane, and propane diol side-chain siloxanes with hydrophilic monomers, such as dimethylacrylamide, and a strengthening agent, isobornylmethacrylate, resulted in transparent hydrogels possessing a wide range of water contents, high oxygen permeability, and a low modulus of elasticity and, for the propane diol side-chain siloxanes, excellent hydrolytic stability. The ether side-chain siloxane-based hydrogels exhibited poor hydrolytic stability. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogels are hydrophilic polymers that absorb water to an equilibrium value and are insoluble in water due to the presence of a three-dimensional network.[1] The hydrophilicity is due to the presence of hydrophilic groups, such as alcohols, carboxylic acids, amides, and sulfonic acids. The swollen equilibrated state results from a balance between the osmotic driving forces that cause the water to enter the hydrophilic polymer and the forces exerted by the polymer chains in resisting expansion.[1]

Hydrogels, both the natural and synthetic, have given rise to a wide variety of materials for biomedical use in diagnostic and therapeutic devices for both short-term and long-term applications. These applications include such uses as catheters,[2] hemodialysis membranes,[3] degradable therapeutic systems,[4] drug-delivery systems,[5] and contact lenses.[1]

To design a successful contact lens material, a number of material characteristics must be optimized[1,6]: optical transparency, chemical and thermal stability, wettability to tears, mechanical properties, biological compatibility, and oxygen permeability.

There exist two basic methods for the preparation of hydrogels with high oxygen permeability. The first approach involves the development of high water content hydrogels. The high water content lens material increases the supply of oxygen to the cornea (the higher the water content, the higher the oxygen permeability of the hydrogel).[7] There are several basic limitations of high water content hydrogels: The first is that it is necessary to design materials having water contents as high as 80% or more in order to achieve a corneal-oxygen supply that is sufficient to eliminate the corneal edemic response associated with extended periods of contact lens wear. High water content materials that have in excess of 80% water, however, typically exhibit poor mechanical properties and, in dry environments, induce epithelia dehydration that may cause several adverse physiological responses.[8]

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The second approach to the development of high oxygen permeable hydrogels involves the copolymerization of methacrylate or vinyl-functionalized polydimethylsiloxanes (PDMS) with hydrophilic monomers. PDMS, due to its low modulus of elasticity, optical transparency, and high oxygen permeability, has been extensively studied for use in contact lens materials.[1,9-11] PDMS possesses an oxygen permeability that is about 70 times higher than the oxygen permeability of the hydrogel poly(HEMA).[12] There are, however, several limitations to overcome before designing hydrogels based on polysiloxanes. The biggest limitation is that silicone is hydrophobic and insoluble in hydrophilic monomers. The copolymerization of methacrylate-functionalized silicones with hydrophilic monomers generally results in opaque, phase-separated materials.

This study describes the development of silicone hydrogels based on methacrylate end-capped siloxanes containing diethylene glycol propyl methyl ether, 5-hexyl-1,2-diol, and 3-propyloxy-1,2-propane diol side chains. The methacrylate end-capped hydrophilic side-chain siloxanes, when copolymerized with hydrophilic monomers, resulted in transparent hydrogels possessing high oxygen permeability, a wide range of water contents, and, for the propane diol side chain siloxanes, excellent hydrolytic stability.

EXPERIMENTAL

Materials

The ultraviolet initiator Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) was purchased from EM Science and was used as received. Isobornylmethacrylate (IBOMA), dimethylacrylamide (DMA), 3-allyloxy-1,2-propane diol (PD), and 5-hexene-1,2-diol (HD) (all from Aldrich Chem. Co.) were distilled prior to use. Tetramethyldisiloxane platinum complex, octamethylcyclotetrasiloxane (D_4), and tetramethylcyclotetrasiloxane (D_4') were purchased from Hüls. The D_4 and D_4' were distilled prior to use. The 1,3-bis-methacryloylbutyl tetramethyldisiloxane (M_2) and methacrylate end-capped silicone hydride prepolymer ($M_2D_{75}D_{25}H$) were prepared according to procedures described in the patent literature.[9] The trimethylsilyl-protected 3-allyloxy-1,2-propane diol and 5-hexene-1,2-diol were prepared using a silyation procedure described in the literature[13] (trimethylsilyl protected propane diol bp 75°C/3 mm Hg, trimethylsilyl-protected hexane diol bp 60°C/

1 mm Hg). The diethylene glycol allyl methyl ether was prepared by the phase transfer-catalyzed reaction of allyl bromide with the corresponding ethylene glycol methyl ether using tetrabutylammonium hydrogen sulfate, methylene chloride, and 50% (w/w) NaOH.[14] All other solvents and reagents were used as received.

Synthesis of a Methacrylate End-capped Poly(25 mol % 3-propyloxy-1,2-propane diol methyl siloxane)-co-(75 mol % dimethylsiloxane) and a Methacrylate End-capped Poly (25 mol % 5-hexyl-1,2-diol methyl siloxane)-co-(75 mol % dimethylsiloxane) (Scheme 1)

Trimethylsilyl protected 3-allyloxy-1,2-propane diol or trimethylsilyl protected 5-hexene-1,2-diol (0.15 mol), $M_2D_{75}D_{25}H$ (30 g, 0.004 mol), 150 mL tetrahydrofuran, 150 mL 1,4-dioxane, and 50 µL of tetramethyldisiloxane platinum complex were added to a 500 mL flask under dry nitrogen and heated to reflux (75°C). The reaction was monitored for loss of silicone hydride by ^{1}H-NMR and FTIR and was complete following a 3 h reaction time. The reaction mixture was placed on a rotary evaporator and the solvents were removed using a vacuum of 40 mmHg at 40°C. The resultant oil was slowly added to a 50/50 (v/v) solution of water and methanol and allowed to separate in a separatory funnel. The oil layer was collected and dissolved in 200 mL of diethyl ether, dried over magnesium sulfate, and filtered through a 5 µ millipore Teflon® filter and the diethylether was removed on a rotary evaporator using a vacuum of 40 mmHg at 40°C.

The purified trimethylsilyl-protected alcohol side-chain siloxane was dissolved in 300 mL of 2-propanol and 30 mL of 0.1N HCL was added. The reaction mixture was allowed to stir 1 h, at which time 30 mL of a saturated sodium bicarbonate solution was added. The solution was vigorously stirred for 15 min and 500 mL of diethyl ether was added. The neutralized solution was placed in a 1 L separatory funnel and allowed to separate. The ether layer was collected, dried over magnesium sulfate, and filtered and the ether removed using a rotary evaporator. The resulting alcohol side-chain siloxane was a viscous, slightly hazy fluid; SEC: propane diol, M_n = 17,051, M_w/M_n = 1.9; hexane diol, M_n = 22,000, M_w/M_n = 2.1; ^{1}H-NMR for propane diol (CDCl$_3$, TMS, δ, ppm): 0.25 (s, 537H, Si—CH$_3$), 0.8 (t, 54H, Si—CH$_2$—), 1.9–2.2 (m, 58H, —Si—CH$_2$—CH$_2$—CH$_2$— and —Si—CH$_2$—CH$_2$—CH$_2$—), 1.95 (s, 6H, —CH$_3$), 3.3–3.4 (m, 150H, —CH$_2$—CH$_2$—O— and —CH$_2$—OH), 3.6 (m,
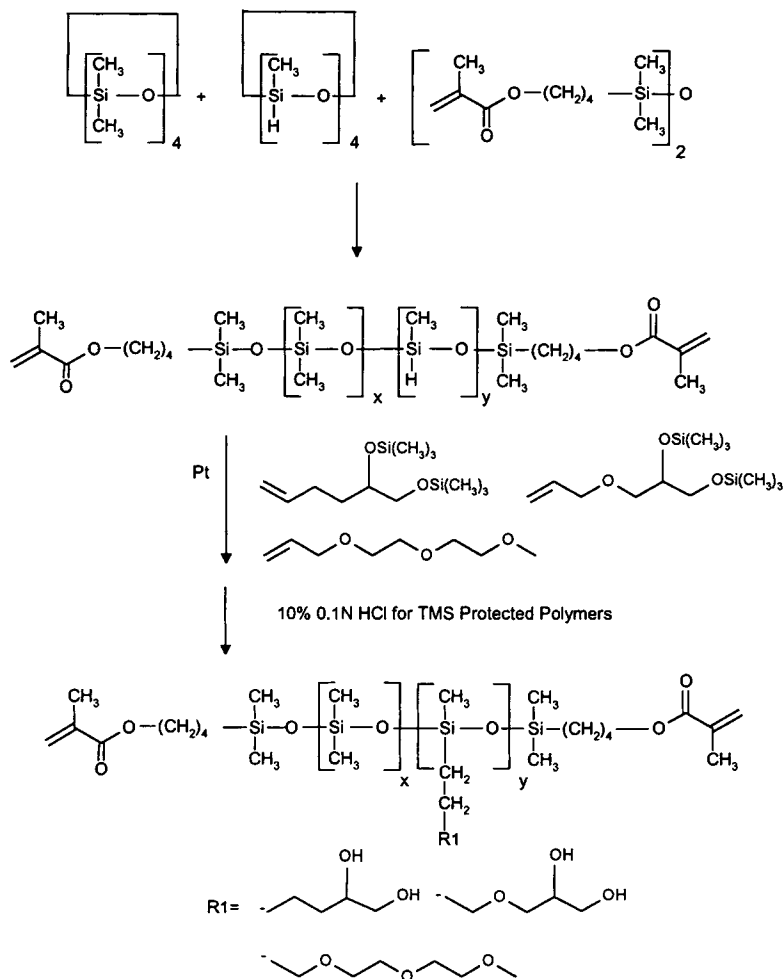
Scheme 1

25H, —CH—OH), 4.1 (t, 4H, —C(O)—O—CH₂—), 4.5–5.0 (broad s, 50H, —OH), 5.6 (s, 2H, =C—H—, 6.2 (s, 2H, =C—H).

Synthesis of a Methacrylate End-capped Poly(25 mol % diethylene glycol propyl methyl ether methyl siloxane)-co-(75 mol % dimethylsiloxane) (Scheme 1)

Diethylene glycol allyl methyl ether (24 g, 0.15 mol), M₂D₇₅D₂₅H (30 g, 0.004 mol), 150 mL tetrahydrofuran, 150 mL 1,4-dioxane, and 50 μL of tetramethyldisiloxane platinum complex were added to a 500 mL flask under dry nitrogen and heated to reflux (75°C). The reaction was monitored for loss of silicone hydride by ¹H-NMR and FTIR and was complete following a 3 h reaction time. The reaction mixture was placed on a rotary evaporator and the solvents were removed using a vacuum of 40 mmHg at 40°C. The resultant oil was slowly added to a 50/50 (v/v) solution of water and methanol and allowed to separate in a separatory funnel. The oil layer was collected and dissolved in 200 mL of diethyl ether, dried over magnesium sulfate, and filtered through a 5 μ Millipore Teflon filter, and the diethylether was removed on a rotoevaporator using a vacuum of 40 mmHg at 40°C. The resulting ether side-chain siloxane was a low viscosity, clear fluid; SEC: M_n = 18,000, M_w/M_n = 2.0; ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.25 (s, 537H, Si—CH₃), 0.8 (t, 54H, Si—CH₂—), 1.9–2.2 (m, 58H, —Si—CH₂—CH₂—CH₂— and —Si—CH₂—CH₂—CH₂—), 1.95 (s, 6H, —CH₃), 3.7 (broad s, 250H, —CH₂—CH₂—O—), 3.3 (m, 25H, —O—CH₃), 4.1 (t, 4H, —C(O)—O—CH₂—), 5.6 (s, 2H, =C—H—, 6.2 (s, 2H, =C—H).

Techniques

Monomer purity was determined on a Hewlett-Packard HP5890A GC using a 6.1 m × 0.32 cm column of 10% SP-1000 80/100 Supelcoport. The

monomer structure was confirmed by 60 MHz ^{1}H-NMR spectroscopy using a Varian EM 360 spectrometer. Films were cast between silanized glass plates using a 0.3 mm Teflon spacer. The cure conditions were established through a thorough investigation of initiators and temperature to optimize vinyl conversion and minimize alcohol extractables. The optimum cure conditions consisted of 30 min of UV (2500 μW/cm^2) at room temperature followed by 45 min of UV at 70°C using 0.5% Darocur 1173 as the initiator. The resultant films were extracted 16 h in 2-propanol and 2 h in distilled water followed by a 16 h hydration in phosphate-buffered saline (pH 7.3). The water content was determined using the following equation:

$$\%H_2O = (\text{hydrated weight}$$

$$- \text{dry weight/hydrated weight}) \times 100$$

The mechanical properties of films were determined on an Instron Model 4500 using ASTM methods 1708 and 1938. The relative molecular weights of soluble polymers were determined by size exclusion chromatography (SEC) with a Waters 820 LC using polystyrene standards (THF/2 mL/min). Oxygen permeability (DK) was determined using the polarographic probe method.[15] The hydrolytic stability test consisted of heating the test films in saline for 3, 5, 7, and 14 days at 80°C and monitoring the weight loss and change in water content (1 year shelf-life equivalency). Following the 14 day stability test, the films were extracted in 2-propanol and total weight loss was determined.

RESULTS AND DISCUSSION

The goal of this study was to design hydrogels with high oxygen permeability suitable for fabricating extended wear contact lenses. Our approach was to design hydrogels based on methacrylate end-capped siloxanes containing hydrophilic side chains, specifically, side chains that contain ethylene oxide and alcohol functionality. The ethylene oxide and alcohol side-chain siloxanes were selected as a first approach based on the relative ease of synthesis of the ether and alcohol side-chain siloxanes and the water-solubility characteristics of the ether and alcohol functionality. This approach would allow for the design of hydrogels with high oxygen permeability through the copolymerization of the hydrophilic side-chain siloxanes with highly hydrophilic monomers without the occurrence of phase separation.

The physical and mechanical properties that we hoped to achieve in this study included a Young's modulus between 20 and 200 g/mm^2, a tear strength greater than 2.0 g/mm, a DK greater than 40 Barrers, and water contents between 20 and 60%. These physical and mechanical property objectives were chosen based on clinical experience from a variety of commercial and experimental lens materials.

Scheme 1 outlines the synthetic procedure used to prepare the methacrylate end-capped ether and alcohol side-chain siloxanes. This synthetic route consisted of two steps (Scheme 1): The first step involved the acid-catalyzed co-ring opening polymerization of octamethylcyclotetrasiloxane (D$_4$), tetramethylcyclotetrasiloxane (D$_4'$),) and 1-3-bis-methacryloylpropyl tetramethyl disiloxane (M$_2$) using trifluoromethane sulfonic acid for 24 h. The 24 h equilibration time was determined by monitoring the reaction using liquid and gas chromatography techniques. In this study, a degree of polymerization of 100 and a side-chain concentration of 25 mol % was selected for evaluation.

The alcohol side chain was attached to the silicone hydride prepolymer by the platinum-catalyzed hydrosilation (0.5% w/w tetramethyldisiloxane platinum complex-Hüls) of an allyloxy or vinyl-functionalized trimethylsilyl-protected alcohol. The two protected alcohols utilized were an allyloxy trimethylsilyl-protected propane diol and a trimethylsilyl-protected 1-hexene diol. The protected alcohol side-chain siloxanes were purified by solution precipitation prior to deprotection to remove the low molecular weight siloxane cyclics and unreacted trimethylsilyl-protected alcohol. The trimethyl silyl-protecting groups were removed using a 0.1N HCl/ 2-propanol solution at room temperature. Following deprotection and a high vacuum devolitilization step, a viscous methacrylate end-capped alcohol side-chain prepolymer resulted. We also investigated alternate protecting agents (pyran and ketal), but it was determined that the trimethyl silyl group was the most effective. Deprotection was fast and quantitative under extremely mild conditions without degradation of the siloxane backbone or methacrylate end cap.

The ether side-chain siloxane was prepared by the hydrosilation of diethylene glycol allyl methyl ether with the methacrylate end-capped 25 mol % silicone hydride prepolymer using conditions identical to the alcohol side-chain synthesis. The crude diethylene glycol side chain siloxane was purified by solution precipitation, resulting in a clear, low viscosity fluid.

The casting of homopolymer films from the ether,

hexane diol, and propane diol-side chain prepolymers was first attempted using the photoinitiator Darocur 1173 (EM Science). It was found advantageous to add 20% of the diluent hexanol to the alcohol side-chain siloxanes to facilitate mixing and handling during film casting. In all films cast, a complete loss of the vinyl (as shown by NIR spectroscopy) was shown to occur following 45 min of UV irradiation (3500 μW/mm^2) at room temperature followed by 45 min of UV irradiation at 70°C. The films were slightly tacky and too weak to determine mechanical properties. We were able to show, however, that both the propane diol homopolymer films absorbed 8–9% water following a 2 h distilled water extraction and overnight hydration in buffered saline. A homopolymer film from a methacrylate end-capped unfunctionalized polydimethylsiloxane contained 0–0.1% water.

Additional films were cast from the ether, propane diol, and hexane diol side-chain siloxanes with varying concentrations of the hydrophilic monomers dimethylacrylamide (DMA), hydroxy propyl acrylate (HPA), and a bulky cyclic strengthening agent, isobornylmethacrylate (IBOMA). The monomers DMA and HPA were chosen because both are extremely hydrophilic (a homopolymer of DMA absorbs greater than 90% water), possess excellent hydrolytic stability, and readily copolymerize with methacrylates.

Table I summarizes the mechanical and physical property results for films cast from the DP 100 methacrylate end-capped 25 mol % propane diol side-chain siloxane with varying concentrations of DMA and IBOMA. A significant increase in water content occurred with an increase in the concentration of DMA with a corresponding decrease in oxygen permeability (DK) (Fig. 1). The DK levels, however, are well above that required for extended lens wear. In addition, the tear strength increased

with an increase in the concentration of IBOMA with a corresponding decrease in water content. The 75/25/5 [propane diol/DMA/IBOMA] formulation resulted in a material possessing a water content of 38%, a DK of 67 Barrers, a modulus of 68 g/mm^2, and a tear strength of 4.0 g/mm. All the films were transparent. In contrast, formulations prepared from a DP 100 methacrylate end-capped polydimethylsiloxane (no alcohol functionality) resulted in phase-separated, opaque films.

Table II summarizes the mechanical and physical property results for two series of films cast from the DP 100 methacrylate end-capped 25 mol % diethylene glycol propyl methyl ether side-chain siloxane. The first film series consisted of copolymers of the ether side-chain siloxane with varying concentrations of the hydrophilic monomer HPA and the strengthening agent IBOMA. The second copolymer series consisted of the ether side-chain siloxane with varying concentrations of DMA and IBOMA. All the films cast were transparent. For both copolymer series, low isopropanol extractables, a wide range in water content, low moduli, excellent tear strengths, and high oxygen permeability values were achieved.

The final phase of testing consisted of determining the hydrolytic stability of the ether, propane, and hexane diol side-chain siloxane hydrogels. The hydrolytic stability of a hydrogel material provides a measure of stability to heat when submerged in buffered saline. This screening is often an indicator of whether or not thermal disinfection of the material can be advised and may also provide an indication of lens shelf life. The test consists of several steps: The material is first extracted separately with isopropanol and distilled water, and the percent water and percent extractables are determined. The test sample is then placed in phosphate-buffered saline and heated for 80°C for 3, 5, 7, and 14 days and analyzed for water content and weight loss. The

Table I   Mechanical and Physical Property Results for the Propane Diol Side-chain Siloxane/DMA/Iboma-based Formulations

Composition (w/w)	% Ext.	% Water	DK	Modulus (g/mm^2)	% Elongation	Tensile (g/mm^2)	Tear (g/mm)
100	6	8.1	100	—	—	—	< 1.0
75/25	5.8	43.4	67	109	50	34	2.9
70/30	4.9	49.4	64	92	44	90	3.1
70/15/15	3.5	21.5	72	60	130	44	13
70/25/5	2.5	38	67	68	77	33	4
60/40	6.2	56.9	50	118	88	54	3.1
60/25/15	2.3	34.2	47	52	130	39	9

DK in units of [cm^3 O$_2$(STP) cm]/(s cm^2 mmHg) $\times$ 10^{-11}. % Ext. = percent isopropanol extractables.
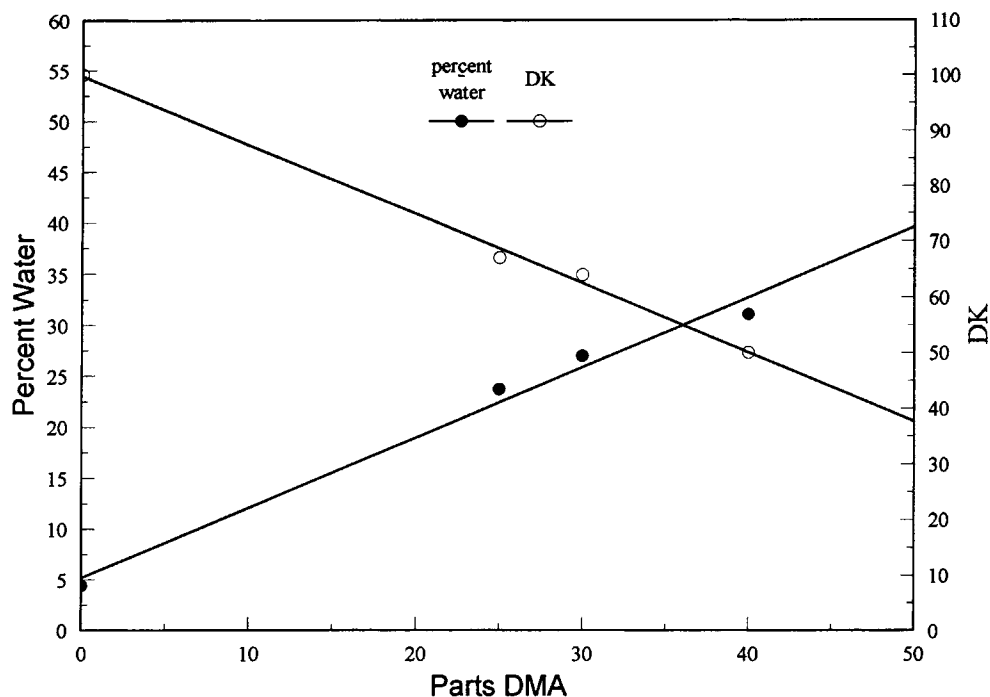
Figure 1 Dependence of percent water and oxygen permeability (DK) vs. concentration of DMA for hydrogel formulations based on the propane diol side-chain siloxane (formulations cast using 0.5% Darocur 1173 and 20 parts of hexanol).

samples are then extracted in 2-propanol to determine the amount of water-insoluble leachables. The standard for this test is poly (HEMA), where, in 14 days, a water content increase of 2% and a weight loss of 1% is observed.

Table III lists the saline weight loss and percent water for the ether, propane diol, and hexane diol/DMA/IBOMA-based formulations following a 3, 5, 7, and 14 day buffered saline heating at 80°C. A significant increase in weight loss and percent water was observed for the ether side-chain siloxane hy-

drogels with, at present, no explanation. Infrared analysis of the films following the 7 and 14 day stability test indicates the loss of ether functionality and a reduction in the concentration of silicone. In contrast, a significant increase in overall stability was observed for the alcohol side-chain siloxane hydrogels. For the propane diol side-chain siloxanes, a modest increase in weight loss and no change in water content was observed following 14 days of testing. Several of the hexane diol-based films, however, showed a somewhat higher increase in weight

Table II   Mechanical and Physical Property Results for the Diethylene Glycol Methyl Ether Side-chain Siloxane-based Formulations

Composition (w/w)	% Ext.	% Water	DK	Modulus (g/mm^2)	% Elongation	Tensile (g/mm^2)	Tear (g/mm)
Ether/HPA/iboma							
10/80/10	6.9	41.3	18.5	40	187	50	1.2
30/60/10	4.7	34.4	32.5	53	134	43	6.1
40/40/20	2.4	16.6	38	71	125	42	5.9
50/40/10	2.0	23.0	55.6	72	78	42	2.5
Ether/DMA/iboma							
70/25/5	6.4	32.6	129	123	22	22	2.0
70/15/5	4.3	11.6	117	111	47	32	4.0
60/25/15	7.6	25.6	83	98	49	31	4

DK in units of $[cm^3\ O_2(STP)\ cm]/(s\ cm^2\ mmHg) \times 10^{-11}$. % Ext. = percent isopropanol extractables.

Table III   Hydrolytic Stability Test Results (Saline Loss and Percent Water) for Formulations Based on the Ether, Propane Diol, and Hexane Diol Side-chain Siloxanes with Dimethylacrylamide and Isobornylmethacrylate

Composition (w/w)	Initial Water	3 Day Loss	3 Day Water	5 day Loss	5 day Water	7 Day Loss	7 Day Water	14 Day Loss	14 Day Water
Ether									
70/25/5	32.6	12	49	17	57	25	61	35	68
70/15/15	11.6	13	25	19	30	29	34	38	32
60/25/15	25.6	11	41	17	50	26	51	35	47
Propane diol									
70/15/15	22.6	1.5	18	1.2	20	2.1	19	2.4	22
60/25/15	33.7	2.2	27	2.6	32	3.1	33	2.9	33
Hexane diol									
80/5/15	6.1	0.5	5	0.8	6	1.6	6	2.0	6
80/15/5	17.4	2.0	19	2.7	20	3.6	19	5.5	23
75/25	32.6	1.6	37.1	3.3	38.8	6.2	41.8	13.5	46.4
70/15/15	18.4	0.7	18	1.2	18	1.5	16	3.0	21
70/25/5	32.0	2.1	35.1	2.0	35.9	3.4	37.2	6.3	41.3
60/25/15	30.8	0.6	31	0.6	30	1.7	31	3.6	35

All formulations contain 0.5% Darocur 1173 as the initiator and the propane diol and hexane diol formulations contain 20 parts hexanol as the diluent. The diluent is removed during the isopropanol extraction process. All samples were tested in phosphate-buffered saline at 80°C.

loss and a significant increase in water content. For example, the 70/25/5 [hexane diol/DMA/IBOMA] formulation showed a 6.3% saline weight loss and a 9.3% increase in water content.

Table IV lists the saline and 2-propanol weight loss results for the hexane diol and propane diol formulations following the 3, 5, 7, and 14 day hydrolytic stability test. The propane diol-based formulations showed only a modest increase in 2-propanol ex-

tractables with time. The hexane diol-based formulations exhibited a nearly twofold increase in 2-propanol extractables when compared to the propane diol films. For example, the 60/25/15 [propane diol/DMA/IBOMA] formulation showed a combined saline and 2-propanol weight loss of 7.0% and the 60/25/15 [hexane diol/DMA/IBOMA] formulation showed a combined saline and 2-propanol weight loss of 13.8%, with at present, no explanation.

Table IV   Water Content and Hydrolytic Stability Test Results for Formulations Based on the Propane Diol and Hexane Diol Side-chain Siloxanes with Dimethylacrylamide and Isobornylmethacrylate

Composition (w/w)	Initial Percent Water	7 Day Saline Loss	7 Day 2-Prop Loss	7 Day Percent Water	14 Day Saline Loss	14 Day 2-Prop Loss	14 Day Percent Water
Propane diol							
70/15/15	22.6	2.1	1.4	19	2.4	4.2	22
60/25/15	33.7	3.1	2.9	33	2.9	4.1	33
Hexane diol							
80/5/15	6.1	1.6	0.9	6.2	2.0	6.7	6.0
80/15/5	17.4	3.6	4.3	18.7	5.4	13.4	23.1
75/25	32.6	6.2	6.8	41.8	13.4	13.4	46.4
70/15/15	18.4	1.5	2.7	16.3	3.0	9.3	21.3
70/25/5	32.0	3.4	6.0	37.2	6.3	13.5	41.3
60/25/15	30.8	1.7	5.2	31	3.6	10.2	34.9

All compositions contain 0.5% Darocur 1173 as the initiator and 20 parts hexanol as the diluent. All samples were tested in phosphate-buffered saline at 80°C.
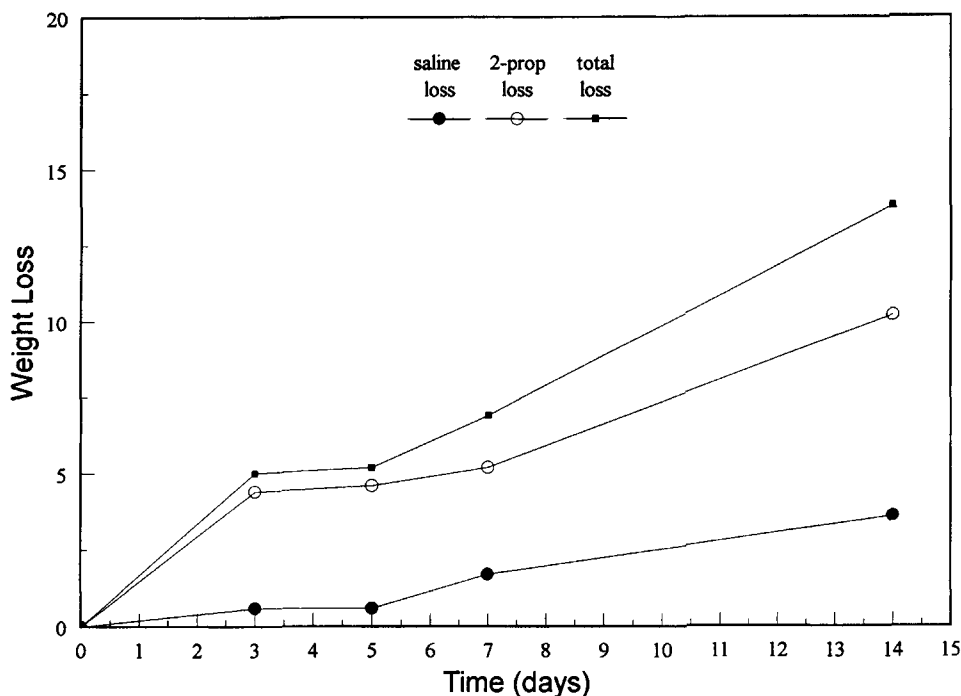
Figure 2 Dependence of saline, 2-propanol, and combined weight loss vs. time for the 60/25/5 [hexane diol/DMA/IBOMA] formulation during hydrolytic stability testing in buffered saline at 80°C.

Figure 2 shows the dependence of saline, 2-propanol, and combined weight loss vs. time for the 60/25/15 [hexane diol/DMA/IBOMA]-based formulation. These results demonstrate the importance of an organic extraction follow-up when evaluating silicone hydrogel stability.

CONCLUSION

In conclusion, methacrylate end-capped ether, hexane diol, and propane diol side-chain siloxanes were evaluated for potential use as hydrogels for contact lens application. The preparation of the ether, hexane diol, and propane diol side-chain siloxanes was accomplished in two relatively simple synthetic steps: ring-opening polymerization of octamethylcyclotetrasiloxane, tetramethylcyclotetrasiloxane, and a methacrylate bis-disiloxane followed by hydrosilation of the resultant silicone hydride polymer with a trimethyl silyl-protected hexene diol, a trimethylsilyl-protected allyloxypropane diol, and an allyl diethylene glycol methyl ether. Deprotection of the trimethylsilyl group was accomplished under mild acidic conditions. Radical polymerization of the ether, hexane diol, and propane diol side-chain siloxanes with hydrophilic monomers and a strength-

ening agent resulted in transparent hydrogels possessing a wide range of water contents, high oxygen permeability, and a low modulus of elasticity and, for the propane diol side-chain siloxanes, excellent hydrolytic stability.

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