Methacrylate-Capped Fluoro Side Chain Siloxanes: Synthesis, Characterization, and Their Use in the Design of Oxygen-Permeable Hydrogels

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ABSTRACT: Methacrylate end-capped 3-(2,2,3,3,-tetrafluoropropoxy)propyl, 3-(2,2,3,-3,4,4,5,5-octafluoropentoxy)propyl, and 3-(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorotridecoxy)-propyl side chain siloxanes were evaluated for potential use in hydrogels for contact lens application. The preparation of the methacrylate end-capped perfluoro 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*-methacryloxybutyltetramethyldisiloxane, followed by a platinum-catalyzed hydrosilation with the tetrafluoro-, octafluoro-, and dodecafluoro-substituted allylic ethers. The incorporation of the terminal [— CF$_2$—H] functionality had a dramatic effect on the increased solubility of the fluoro siloxane with hydrophilic monomers. Radical bulk polymerization of the methacrylate-capped fluoro side chain siloxanes with hydrophilic monomers, such as dimethylacrylamide and *N*-vinyl pyrrolidinone, resulted in transparent hydrogels possessing a wide range of water contents, high oxygen permeability, and a low modulus of elasticity. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1081–1089, 1997

Key words: silicone-hydrogel; fluoro side chain siloxanes; oxygen permeability; mechanical properties; contact lens

INTRODUCTION

To design a successful hydrogel for contact lens application, the candidate polymer must satisfy a number of material requirements.[1–3] The material must be optically transparent, possess chemical and thermal stability, and be biologically compatible with the ocular environment. The material must also possess a low modulus of elasticity for patient comfort and a high tear strength for lens-handling durability. In addition, it is important that the material can be bulk polymerized and processed utilizing current contact lens manufacturing techniques.[4] Finally, the material must be permeable to oxygen. Due to a lack of blood vessels within the corneal framework, the cornea obtains oxygen from the atmosphere. Without an adequate supply of oxygen, corneal edema may occur, resulting in a number of adverse physiological responses.[5] The key intrinsic material property that is a measure of oxygen diffusion is oxygen permeability (Dk, where D is the diffusion coefficient and k is a proportionality coefficient called the Henry's law coefficient). There is currently no generally accepted level of Dk for extended wear application. Many practitioners believe, however, that for a 0.1-mm-thick lens, a Dk of 100 barrers [$(cm^3\,O_2(STP)\,cm)(sec^{-1}\,cm^{-2}\,mm\,Hg^{-1})$] is suitable for extended-wear application.[6]

There exist two basic methods for the development of hydrogels with high oxygen permeability. The first approach involves the development of

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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).[1] The second approach for the development of high-oxygen-permeable hydrogels involves the design of silicone-based hydrogels. Polydimethylsiloxane (PDMS), due to its low modulus of elasticity, optical transparency, and high oxygen permeability, is an ideal candidate for use in contact lens materials. PDMS possesses an oxygen permeability that is about 50 times higher than the oxygen permeability of the hydrogel poly(HEMA) and 15 times higher than the high-water-content hydrogels.[7]

There are, however, several limitations to overcome before designing hydrogels based on PDMS. The primary obstacle is that PDMS is hydrophobic and insoluble in hydrophilic monomers. Thus, when attempts are made to copolymerize methacrylate-functionalized siloxanes with hydrophilic monomers, opaque, phase-separated materials are usually obtained. In many cases, a cosolvent such as hexanol or isopropanol can be used to solubilize the siloxane and hydrophilic monomer. In addition, the copolymerization of methacrylate-functionalized silicones with hydrophilic monomers results in materials with a reduction in water content, a loss of surface wettability, and an increase in lipophilic character. Lipid uptake can lead to a loss in material wettability. Several approaches in the design of silicone hydrogels for biomedical applications have been pursued.[8]

The goal of this study was to design hydrogels for extended contact lens wear application based on methacrylate-functionalized polydimethylsiloxanes. In previous work, we had shown that copolymers of methacrylate end-capped fluoro-substituted siloxanes with varying concentrations of fluorinated methacrylates resulted in transparent, oxygen-permeable, low-water ($<1\%$) materials possessing a low affinity for lipids.[9] The higher concentration of fluoro side chain and fluoro methacrylate in the copolymer formulation, resulted in a dramatic reduction in lipid uptake.

Further, we showed that the copolymerization of methacrylate end-capped siloxanes containing hydrophilic side chains, with high concentrations of hydrophilic monomers, resulted in transparent hydrogels possessing high levels of oxygen permeability without the use of a solubilizing cosolvent.[10] The copolymerization of methacrylate end-capped polydimethylsiloxanes (without a hydrophilic side-chain) with hydrophilic monomers, such as dimethylacrylamide (DMA) and 2-N-vinyl pyrrolidinone (NVP), lead to phase separated materials.

Our original approach in this study was to design methacrylate-functionalized siloxanes containing both hydrophilic functionality, for improved solubility with hydrophilic monomers, and fluorine functionality, for improved resistance to lipids. In our investigation into the design of a "hydrophilic-fluorinated" siloxane, we discovered that the incorporation of a fluoro-substituted side chain containing a terminal [—CF_2—H] functionality alone dramatically improved the solubility characteristics of the resultant fluorosiloxane polymer with polar solvents and hydrophilic monomers.

This article describes the development of oxygen-permeable silicone hydrogels based on the [—$(CF_2)_x$—H] functionalized fluoro side chain siloxanes. The fluorinated side chain siloxanes, when copolymerized with hydrophilic monomers, such as DMA, resulted in transparent, wettable, and oxygen permeable hydrogels.

EXPERIMENTAL

Materials

The ultraviolet (UV) initiator Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) was purchased from EM Science and was used as received. DMA, NVP, tetrafluoro-1-pentanol (TFP), octafluoro-1-pentanol (OFP), dodecafluoro-1-nonanol (DDN), and allyl bromide (AB) were purchased from Aldrich Chemical Co. The TFP, OFP, and DDN were used as received. The DMA, NVP, and AB were distilled under nitrogen prior to use. Octamethylcyclotetrasiloxane (D_4), tetramethylcyclotetrasiloxane (D_4H), and 1,3-tetramethyl disiloxane platinum complex (2% platinum in xylenes) were purchased from Hüls. The D_4H was distilled prior to use under dry nitrogen. The fluorinated allylic ethers, allyloxy tetrafluoropentane, allyloxy octafluoropentane, and allyloxy dodecafluorotridecane, were prepared by the phase transfer catalyzed reaction of AB with the corresponding fluorinated alcohol using tetrabutylammonium hydrogen sulfate, tetrahydrofuran, and 50% (w/w) NaOH.[11] All other solvents and reagents were used as received.

Synthesis of 1,3-*bis*(4-Methacryloyloxybutyl)-Tetramethyl Disiloxane (M₂)

To a 5-L four-neck resin flask equipped with a mechanical stirrer, Dean-Stark trap, heating
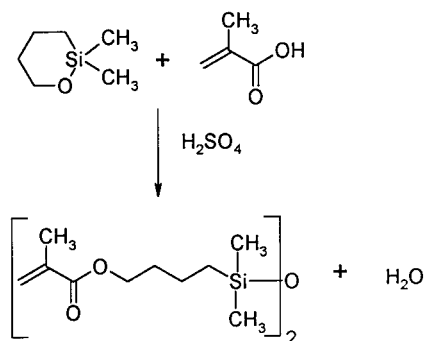
Scheme 1   Synthetic route used to prepare M_2.

mantle, water-cooled condenser, and thermometer was added 1,1-dimethyl-1-sila-2-oxacyclohexane (521 g, 4.0 mol), methacrylic acid (361 g, 4.2 mol), and concentrated sulfuric acid (25.5 g). To the reaction mixture was then added 1 L of cyclohexane and hydroquinone (0.95 g, 8.6 mmol) as a polymerization inhibitor. The reaction mixture was heated to reflux for 5 h, during which time 28 mL of water was collected. The reaction mixture was then cooled, divided, and passed through two chromatography columns filled with 1 kg of alumina (packed using cyclohexane as eluant). The cyclohexane was removed with a rotary evaporator, and the resultant M_2 (Scheme 1) was placed under vacuum (0.2 mm Hg) for 1 h at 80°C (yield, 80%; purity by gas chromatography, 96%). ^{1}H nuclear magnetic resonance (NMR) (CDCl$_3$, TMS, ∂, ppm): 0.1 (s, 12H, Si—CH$_3$), 0.5 (t, 4H, Si—CH$_2$—), 1.5–1.8 (m, 8H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$ and Si—CH$_2$—CH$_2$—C$\underline{H}_2$), 1.95 (s, 6H, =C—CH$_3$), 4.1 [t, 4H, —CH$_2$—O—C(O)], 5.6 (s, 2H, =C—H), 6.2 (s, 2H, =C—H).

Synthesis of Methacrylate End-Capped Poly (25 mol % Methyl Siloxane)-*co*-(75 mol % Dimethylsiloxane)(M$_2$D$_{75}$D$_{25}$H)

To a 1,000-mL round-bottom flask under dry nitrogen was added D$_4$ (371.9 g, 1.25 mol), D$_4$H (100.4 g, 0.42 mol), and M$_2$ (27.7 g, 0.7 mol). Trifluoromethane sulfonic acid (0.25%, 1.25 g, 8.3 mmol) was added as initiator. The reaction mixture was stirred for 24 h with vigorous stirring at room temperature. Sodium bicarbonate (10 g, 0.119 mol) was then added, and the reaction mixture was again stirred for 24 h. The resultant solution (Scheme 2) was filtered through a 0.3-μm-pore-size Teflon® filter. The filtered solution was vacuum stripped and placed under vacuum (>0.1 mm Hg) at 50°C to remove the unreacted silicone

cyclics. The resulting silicone hydride–functionalized siloxane was a viscous, clear fluid; yield, 70%; size exclusion chromatography (SEC): M_n = 7,500, M_w/M_n = 2.2; ^{1}H NMR (CDCl$_3$, TMS, ∂, ppm): 0.1 (s, 525H, Si—CH$_3$), 0.5 (t, 4H, Si—CH$_2$—), 1.5–1.8 (m, 8H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$ and Si—CH$_2$—CH$_2$—C$\underline{H}_2$), 1.95 (s, 6H, =C—CH$_3$), 4.1 [t, 4H, —CH$_2$—O—C(O)], 4.5 (s, 25H, Si—H), 5.6 (s, 2H, =C—H), 6.2 (s, 2H, =C—H).

General Procedure for the Synthesis of the Fluoro Side Chain Siloxanes: Synthesis of Methacrylate End-Capped Poly {25 mol % [3-(2,2,3,3,4,4,5,5-Octafluoropentoxy)Propyl Methyl Siloxane]-*co*-[75 mol % Dimethylsiloxane]}

To a 500-mL round-bottom flask equipped with a magnetic stirrer and water condenser was added M$_2$D$_{75}$D$_{25}$H (15 g, 0.002 mol), allyloxyoctafluoropentane (27.2 g, 0.1 mol), tetramethyldisiloxane platinum complex (2.5 mL of a 10% solution in xylenes), 75 mL of dioxane, and 150 mL of anhydrous tetrahydrofuran under a nitrogen blanket. The reaction mixture was heated to 75°C, and the reaction was monitored by infrared and ^{1}H NMR spectroscopy for loss of silicone hydride. The reaction was complete in 4–5 h of reflux. The resulting solution was placed on a rotoevaporator to remove tetrahydrofuran and dioxane. The resultant crude product was diluted with 300 mL of a 20% methylene chloride in pentane solution and passed through a 15-g column of silica gel using a 50% solution of methylene chloride in pentane as eluant. The collected solution was again placed on the rotoevaporator to remove solvent, and the resultant clear oil was placed under vacuum (>0.1 mm Hg) at 50°C for 4 h. The resulting octafluoro-functionalized side chain siloxane was a viscous, clear fluid; yield, 65%; SEC: M_n = 18,000, M_w/M_n = 2.3; ^{1}H NMR (CDCl$_3$, TMS, ∂, ppm): 0.1 (s, 525H, Si—CH$_3$), 0.5 (t, 54H, Si—CH$_2$—), 1.5–1.8 (m, 58H, Si—CH$_2$—C$\underline{H}_2$—CH$_2$ and Si—CH$_2$—CH$_2$—C$\underline{H}_2$), 1.95 (s, 6H, =C—CH$_3$), 4.1 [t, 4H, —CH$_2$—O—C(O)], 5.6 (s, 2H, =C—H), 5.8 (t, 17H, —CF$_2$—H), 6.1 (m, 35H, —CF$_2$—H and =C—H), and 6.3 (t, 17H, —CF$_2$—H).

Techniques

Monomer purity was determined on a Hewlett-Packard HP5890A gas chromatograph using a 15 m × 0.53 mm (inner diameter) × 1.2 μm column of Alltech EC-5 (SE-4). The monomer and pre-
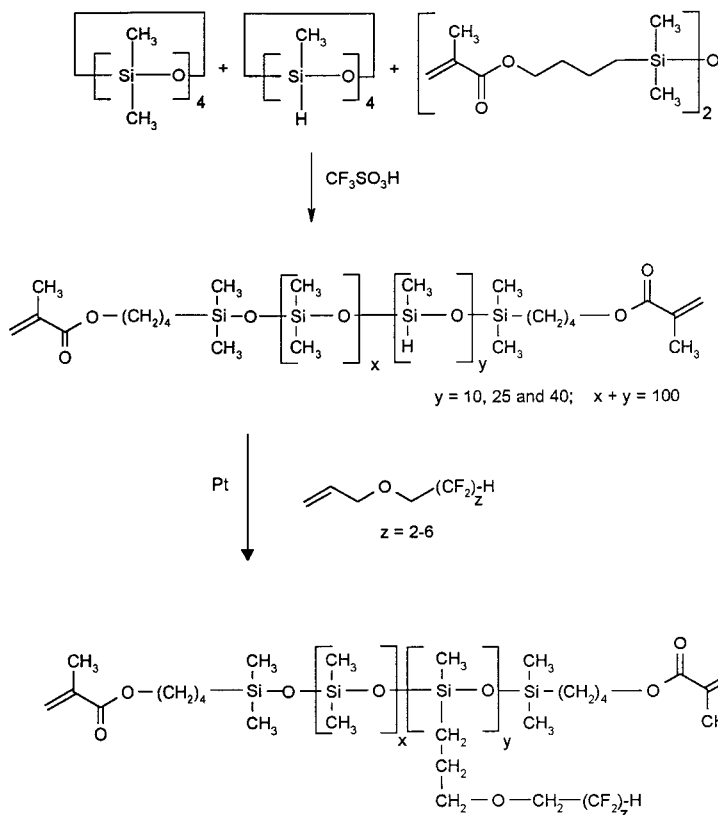
Scheme 2   Synthetic procedure used to prepare the methacrylate end-capped fluoro side chain siloxanes.

polymer structure was confirmed by 200 MHz ^{1}H NMR spectroscopy using a Varian 200 spectrometer. Films were cast between silanized glass plates with a 0.3-mm Teflon® spacer. The optimal cure conditions consisted of 1-h UV at room temperature using a UV intensity of 3,500 μW/cm^2 and 0.5% Darocur 1173 as the initiator. The resultant films were extracted for 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:

$$\% \, \text{H}_2\text{O} = \frac{(\text{hydrated weight} - \text{dry weight})}{\text{hydrated weight}} \times 100$$

(1)

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 SEC with a Waters 820 LC using polystyrene standards (THF/2 mL per min). Oxygen perme-

ability (Dk) was determined using the polarographic probe method.[12] The hydrolytic stability test consisted of heating the test films in phosphate-buffered saline for 14 days at 80°C and monitoring the weight loss and change in water content (2-year shelf-life equivalency).

RESULTS AND DISCUSSION

Synthesis

Scheme 1 shows the synthetic scheme used to prepare the methacrylate M$_2$. This reaction consisted of the acid-catalyzed reaction of 1,1-dimethyl-1-sila-2-oxacyclohexane with methacrylic acid. This reaction proceeded smoothly, providing a glass passivation step was used prior to the M$_2$ reaction to prevent premature polymerization. The passivation step consisted of refluxing a 1,000-ppm xylene solution in the resin pot for 30 min, followed by an air dry to remove the xylenes. It is important to note that several additional approaches to the synthesis of M$_2$ were explored with limited

success, including the platinum-catalyzed reaction (hydrosilation) of allyl methacrylate with tetramethyldisiloxane and the reaction of methacryloyl chloride with 1,3-*bis*(4-hydroxybutyl)tetramethyldisiloxane.

Scheme 2 outlines the synthetic procedure used to prepare the methacrylate end-capped fluorinated side chain siloxanes (F—Si). The perfluorinated allylic ethers were prepared by the phase transfer catalyzed reaction of AB with the corresponding fluoro alcohol. In this study, we synthesized allyl ethers containing a tetrafluoro, an octafluoro, and a dodecafluoro functionality. In general, high yields of high-purity allylic fluoro ethers were obtained. The octafluoro and dodecafluoro allylic ethers were prepared using a THF reflux, but for the tetrafluoro ethers, we were unable to effectively separate by distillation or column chromatography the tetrafluoro ether from THF. Diethyl ether reflux in this reaction was then successfully used. A longer reaction time was required, but high yields of high-purity tetrafluoro ether could be obtained by distillation.

The methacrylate end-capped silicone hydride prepolymers were prepared by the acid-catalyzed co-ring opening polymerization of D_4, D_4H, and M_2 using trifluoromethane sulfonic acid. 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 silicone hydride concentration of 25 and 40 mol % were evaluated. The hydride prepolymer was stored under dry nitrogen and used immediately following preparation to avoid silicone hydride hydrolysis. In addition, it was found necessary to wash all glassware with a mild acid solution ($2N$ HCl) to avoid reaction of the silicone hydride with base-contaminated glassware.

The perfluorinated side chain was attached to the silicone hydride prepolymer by the platinum-catalyzed hydrosilation of the perfluorinated allyl ethers.[13–16] The ideal reaction conditions consisted of a 20% molar excess of allylic ether (based on silicone hydride), a platinum concentration of 0.0025 mol/mol of silicone hydride, and a 50/50 dioxane/THF reaction solvent mixture to give a reflux temperature of 75°C. These conditions lead to a short reaction time with a minimum of color formation and a low rate of premature gelation. Using these conditions, the reaction proceeded smoothly with the loss of silicone hydride typically observed at 4–5 h of reflux.

Our first approach at purification of the fluori-

nated side chain siloxanes consisted of precipitation from a nonsolvent to remove the unreacted allylic ether and cyclic siloxanes formed during the hydride preparation. A typical siloxane fractionation consists of the slow addition of the unpurified siloxane to a rapidly stirred solution of methanol. The siloxane precipitates and is collected, and the cyclic siloxanes remain in the methanol. In our attempts at fractionation of the fluorinated side chain siloxanes, we discovered that the fluorinated side chain siloxanes were readily soluble in methanol. A methacrylate end-capped 25 mol % octafluoropentylpropyloxy [—(CH_2)—O—CH_2—$(CF_2)_4$—H]-functionalized polydimethylsiloxane was readily soluble in methanol. In contrast, a methacrylate end-capped 25 mol % nonafluoropentylpropyloxy [—$(CH_2)_3$—O—CH_2—$(CH_2)_4$—F]-functionalized polydimethylsiloxane was completely insoluble in methanol. This was our first indication of the unusual solubility characteristics of the [—CF_2—H] functionalized fluorinated side chain siloxanes.

A combination column chromatography–vacuum devolitilization purification procedure was then successfully developed. The fluorinated side chain siloxanes were passed through an activated silica column using a 50/50 pentane methylene chloride mixture to remove the platinum(0) precipitate. The eluant was collected and devolatilized under vacuum to remove the excess allylic perfluorinated ether and solvent. Analysis of the final product by both ^{13}C NMR and ^{1}H NMR confirmed the expected prepolymer structure. Figure 1 shows the ^{1}H NMR spectrum from a DP 100 methacrylate end-capped 25 mol % octafluoro side chain siloxane measured in $CDCL_3$. The most important chemical shifts δ (ppm) include the triplet of triplets at 5.8, 6.1, and 6.3 for the terminal (—CF_2—H) functionality and the singlets at 5.6 and 6.1 for the methacrylate vinyl protons. Integration of these signals versus the Si—CH_3 and Si—CH_2 signal agrees well with the accepted structure. Excellent lot-to-lot reproducibility has to date been obtained.

Hydrogel Formulation

With the discovery that the incorporation of the terminal [—CF_2—H] functionality significantly changed the solubility characteristics compared with conventional linear polydimethylsiloxanes, the evaluation of these materials for use in the design of fluorinated siloxane hydrogels was ex-
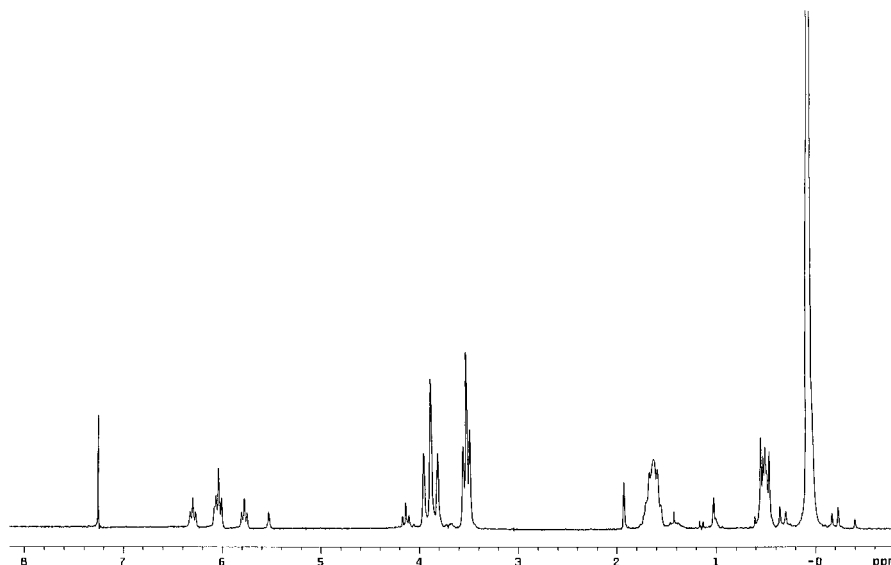
Figure 1 ^{1}H NMR of a methacrylate end-capped 25 mol % [3-(2,2,3,3,4,4,5,5-octaflu-oropentoxy]propyl side chain polydimethylsiloxane (25°C, CDCl$_3$, δ, ppm).

plored. Films were cast from the methacrylate end-capped fluorinated side chain siloxanes with varying concentrations of the hydrophilic monomers DMA and NVP using the photoinitiator Darocur 1173. In all films cast, a complete loss of vinyl (as shown by NIR spectroscopy) was shown to occur following 1 h of irradiation (3,500 μW/cm^2) at room temperature. In cases where noted, the solvent hexanol was added to reduce the viscosity of the formulation and, for the fluorosilicone-*co*-NVP based polymers, to improve film clarity.

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 50 barrers, and water contents between 20 and 60%. These physical and mechanical property objectives were chosen on the basis of clinical experience from a variety of commercial and experimental lens materials.[17]

Table I summarizes the mechanical and physical property results for copolymer films prepared from a DP 100 methacrylate end-capped 25 mol % tetrafluoro side chain, a 25 and 40 mol % octafluoro side chain, and a 40 mol % dodecafluoro side chain siloxane with DMA. All of the films were transparent without the use of a solubilizing cosolvent. Hydrogels possessing a wide range in water content and *Dk* were obtained. The 70/30 (25-octa/DMA) formulation resulted in a transparent material possessing a tear strength of 3.1 g/mm, a modulus of 210 g/mm^2, and a *Dk* of 138

barrers. In contrast, when attempts were made to copolymerize a methacrylate end-capped nonfunctionalized polydimethylsiloxane or a methacrylate end-capped fully fluorinated side chain [—(CH$_2$)$_3$—O—CH$_2$—(CF$_2$)$_4$—F] siloxane with DMA, only phase-separated, opaque films resulted. No morphological data are presently available on the fluoro side chain-DMA copolymer hydrogels, but the data strongly indicate that the incorporation of the terminal [—CF$_2$—H] functionality reduces or eliminates the phase separation that occurs with conventional polydimethylsiloxanes. We attribute this to the hydrogen bond interactions between the terminal [—CF$_2$—H] functionality and the amide linkage of DMA and/or NVP.

Figure 2 shows the relationship between parts of DMA versus water content and *Dk* for the octafluoro side chain siloxane-DMA copolymers. Similar trends were observed for the tetrafluoro and dodecafluoro side chain siloxanes. An increase in the concentration of DMA resulted in a significant increase in water content and a corresponding decrease in *Dk*, due to the lower concentration of fluorosiloxane with higher water content copolymers. No significant changes were observed for modulus, tensile strength, or tear strength properties with concentration of DMA or mol % side chain substitution and side chain length; however, a significant decrease in *Dk* occurred with both an increase in fluoro substitution and an increase in fluoro side chain length. Figure

Table I   Mechanical and Physical Property Results for Copolymers Based on the DP 100 Methacrylate End-Capped Tetrafluoro, Octafluoro, and Dodecafluoro Side Chain Siloxanes (F-Si) with DMA

Composition F-Si/DMA	% Loss	% Water	Dk	Modulus (g/mm²)	Tensile (g/mm²)	Tear (g/mm)
25 mol % Tetra						
80/20	6.3	18	222	191	30	3.2
70/30	2.0	31	150	166	46	3.3
65/35	3.3	39	137	161	40	3.6
60/40	8.9	45	115	160	57	3.8
25 mol % Octa						
100/0	12.0	0.1	530	55	18	1.5
90/10	8.6	6	397	188	48	1.5
80/20	7.2	18	223	219	48	3.3
75/25	6.8	26	134	222	44	4.1
70/30	5.7	31	138	210	68	3.1
40 mol % Octafluoro						
80/20	8.4	28.7	90	146	57.5	3.7
75/25	9.9	26.8	93	146	49.2	3.6
70/30	8.5	34.1	68	160	49.0	3.8
65/35	9.1	38.0	67	131	50	4.2
60/40	8.3	44.0	56	126	57	4.0
40 mol % Dodecafluoro						
100	7.5	0.1	130			
80/20	10.7	22.7	94	138	34	2.3
70/30	10.3	34.4	59	163	57	2.7
60/40	9.5	49.8	58	142	63	3.1

Dk in units of $(cm^3 \; O_2(STP) \; cm)/(sec \cdot cm^2 \; mmHg) \times 10^{-11}$. All formulations contains 0.5% Darocur 1173 as UV initiator.

3 shows the relationship between *Dk* and parts DMA for formulations based on the tetrafluoro, octafluoro, and dodecafluoro side chain siloxanes. The *Dk* levels for these formulations are well above that required for extended wear.
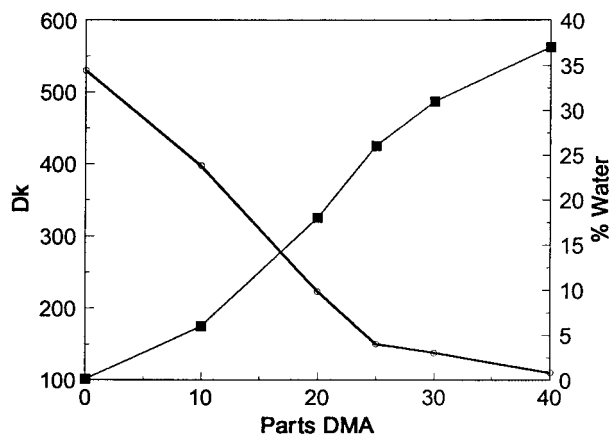
Table II summarizes the mechanical and physical property results for films prepared from the DP 100 methacrylate end-capped 25 mol % octafluoro side chain siloxanes with DMA and NVP.

Figure 2   Dependence of *Dk* (○) and % water (■) versus parts DMA for formulations based on the 25 mol % octafluoro side chain siloxanes with DMA.
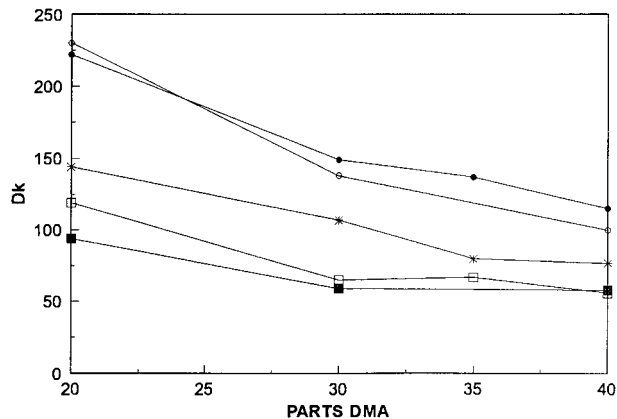

Figure 3   Dependence of *Dk* versus parts DMA for formulations based on the 25 mol % tetra (●), octa (○), and dodeca (∗) fluoro side chain siloxanes and the 40 mol % octa (□) and dodeca (■) fluoro side chain siloxanes with DMA.

Table II   Mechanical and Physical Property Results for Copolymers Based on the DP 100 Methacrylate End-Capped Octafluoro Side Chain Siloxanes (F-Si) with DMA and NVP

Composition F-Si/DMA/NVP	% Loss	% Water	Dk	Modulus (g/mm^2)	Tensile (g/mm^2)	Tear (g/mm)
80/20/0	22	17	186	155	55	1.8
80/15/5	23	16	212	170	60	1.9
80/10/10	21	15	183	195	53	2.4
80/5/15	23	16	186	190	45	2.0
70/0/30	19	28	108	173	52	2.1
70/20/10	20	25	97	180	58	2.7
70/10/20	21	25	105	170	46	2.3
70/1/29	31	19	173	154	35	1.8
70/0/30	34	17	186	146	27	1.5
60/40/0	16	38	76	204	57	2.2
60/30/10	15	35	75	222	64	2
60/20/20	18	34	72	215	53	1.9
60/10/30	19	32	80	213	45	2.3
50/10/40	24	46	44	170	45	2.3

All formulations contain 0.2% hydroxyethyl vinylcarbonate and 20 parts of hexanol.

In these formulations, the total fluorosilicone content was varied from 50 to 80 parts and the total hydrophilic monomer concentration was varied from 20 to 50 parts. For each formulation series, DMA was replaced with NVP in decreasing amounts. It is important to note that, in these formulations, it was necessary to add a cosolvent. Without a cosolvent, an increase in film cloudiness (incompatibility) occurred with an increase in the concentration of NVP. The cosolvent hexanol was added to all formulations in a 20% concentration. In addition, in these formulations, the cross-linker hema vinyl carbonate was added to better incorporate NVP.[18] This is necessary due to the slow polymerization and poor reactivity characteristics of NVP-methacrylate-based copolymerizations. For these DMA/NVP-based copolymer systems, an increase in water content occurred with an increase in the concentration of hydrophilic monomer. DMA and NVP appear to give similar water absorption characteristics. No significant trends in modulus, tensile strength, or tear strength were observed with concentration of DMA or NVP; however, isopropanol extractables increased and water content decreased with an increase in the concentration of NVP due to the poor polymerization characteristics of NVP. The 70/0/30 formulation possessed isopropanol extractables of 34%. The majority of the extractables as determined by ^{1}H NMR consists of unreacted NVP and NVP-based oligomers.

The final phase of testing consisted of determining the hydrolytic stability of the fluoro side chain siloxane hydrogels. The hydrolytic stability of hydrogel materials 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 borate-buffered saline, heated at 80°C for 3, 5, 7, and 14 days, and analyzed for water content and weight loss. The samples are then extracted in isopropanol 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 water content and hydrolytic stability results for formulations based on the DP 100 methacrylate end-capped 25 mol % tetrafluoro, 25 mol % octafluoro, and dodecafluoro side chain siloxanes and DMA. The hydrolytic stability results for both series of formulations were acceptable: minimal weight loss and little change in water content. The 80/20 (25 mol % tetrafluoro/DMA) formulation showed a 2.7% weight loss with only a 2% increase in water content following 14 days in buffered saline at 80°C.

Table III   Hydrolytic Stability Test Results for the 25 mol % Tetrafluoro and Octafluoro Side Chain Siloxane/DMA Formulations

Composition (w/w)	Initial % Water	3-Day Loss (% Water)	7-Day Loss (% Water)	14-Day Loss (% Water)
25 Tetrafluoro				
80/20	18	0.5 (18)	0.8 (18)	2.7 (20)
70/30	31	1.0 (33)	1.1 (33)	2.3 (36)
65/35	39	0.5 (38)	1.2 (41)	2.4 (43)
25 Octafluoro				
80/20	23	0.6 (19)	1.4 (20)	1.8 (21)
75/25	27	0.8 (26)	2.7 (27)	1.3 (27)
70/30	34	0.4 (31)	1.26 (35)	1.8 (37)
40 Dodecafluoro				
80/20	29	1.9 (31)	3.9 (34)	7.2 (37)
75/25	27	2.2 (28)	4.6 (31)	7.2 (34)
70/30	34	3.2 (34)	4.8 (38)	7.1 (41)
60/40	44	3.3 (45)	3.8 (48)	4.2 (50)

CONCLUSIONS

In summary, methacrylate end-capped fluoro side chain siloxanes containing a terminal $-CF_2-H$ group were synthesized and evaluated for potential use as hydrogels for contact lens application. The preparation of the fluoro side chain siloxanes was accomplished in two relatively simple synthetic steps: ring-opening polymerization to prepare a methacrylate end-capped silicone hydride containing polydimethylsiloxane, followed by hydrosilation of a perfluorinated allylic ether. Radical polymerization of the fluoro side chain siloxanes with DMA resulted in transparent hydrogels possessing high oxygen permeability, excellent hydrolytic stability, and mechanical properties suitable for contact lens wear. The incorporation of the terminal $-CF_2-H$ had a dramatic effect on the solubility of the fluoro side chain siloxanes with hydrophilic monomers, such as DMA.

REFERENCES

1. Y. Lai, A. Wilson, and S. Zantos, in *Kirk-Othmer Encyclopedia of Chemical Technology,* Wiley, New York, 1993, 4th Ed., Vol. 7.
2. J. F. Künzler and J. M. McGee, *Chem. Indus.,* **16,** 651 (1995).
3. G. D. Friends, J. F. Künzler, and R. M. Ozark, *Macromol. Symp.,* **98,** 619 (1995).
4. D. V. Ruscio, *Polym. Prep. Am. Chem. Soc. Div. Polym. Mater. Sci. Eng.,* **69,** 221 (1993).
5. P. White, *Contact Lens Spect.,* **February,** 46 (1990).
6. B. Holden, G. Mertz, and J. McNally, *Invest. Ophthalmol. Vis. Sci.,* **24,** 218 (1983).
7. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook,* Wiley, New York, 1989, 3rd Ed.
8. J. F. Künzler, *Trends Polym. Sci.,* **4,** 52 (1996).
9. G. Friends, J. Künzler, R. Ozark, and M. Trokanski, in *ACS Symposium Series No. 540, Polymers of Biological and Biomedical Significance,* S. W. Shalaby, J. Williams, Y. Ikada, and R. Langer, Eds., American Chemical Society, Washington, DC, 1993.
10. J. Künzler and R. Ozark, *J. Appl. Polym. Sci.,* **55,** 611 (1995).
11. E. V. Dehmlow and S. S. Dehmlow, in *Phase Transfer Catalysis,* H. Ebel, Ed., Verlag Chemie, Weinheim, 1983.
12. I. Fatt, J. E. Rasson, and J. B. Melpolder, *ICLC,* **14,** 38 (1987).
13. L. G. Britcher, D. C. Kehoe, J. G. Matisons, and A. G. Swincer, *Macromolecules,* **28,** 3110 (1995).
14. L. N. Lewis, *J. Am. Chem. Soc.,* **112,** 5998 (1990).
15. J. L. Speier, *Adv. Organomet. Chem.,* **17,** 407 (1979).
16. B. Marciniec, J. Gulinski, W. Urbaniak, and Z. Kornetka, in *Comprehensive Handbook on Hydrosilation,* B. Marciniec, Ed., Pergamon Press, Oxford, 1992.
17. Bausch and Lomb in-house clinical data.
18. Y. C. Lai and E. Quinn, *Polym. Prep., Proc. Am. Chem. Soc. Div. Polym. Mater. Sci.,* **73,** 508 (1996).