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Silicone Hydrogels Based on a Novel Amphiphilic Poly(2-methyl-2-oxazoline)-*b*-poly(dimethyl siloxane) Copolymer

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A novel amphiphilic hydrogel based on poly(2-methyl-2-oxazoline)-*b*-poly(dimethyl siloxane) (PMeOx–PDMS) block copolymer was developed. First of all, PMeOx–PDMS macromonomer was synthesized by coupling mono-hydroxylated PMeOx with PDMS followed by end-capping with methacrylate group. The structures of each step were characterized by NMR and titration. After that, silicone hydrogels were prepared by UV-initiated copolymerization of PMeOx–PDMS macromonomer with monomers such as 2-hydroxyethyl methacrylate in the presence of a crosslinker. Measurements of the hydrogels' water contact angle, equilibrium water content, and tensile properties showed that the hydrogels possessed better hydrophilic surface, higher water content, and better ion permeability with the increase of the content of the macromonomer PMeOx–PDMS. Meanwhile, the tensile strength and Young's modulus of the hydrogels decreased slightly. Protein adsorption tests showed that the hydrogels had strong antifouling ability after the incorporation of PMeOx. This newly described hydrogel demonstrated attractive properties to serve as ophthalmic biomaterial. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39867.

KEYWORDS: biomaterials; hydrophilic polymers; silicone hydrogel; photopolymerization

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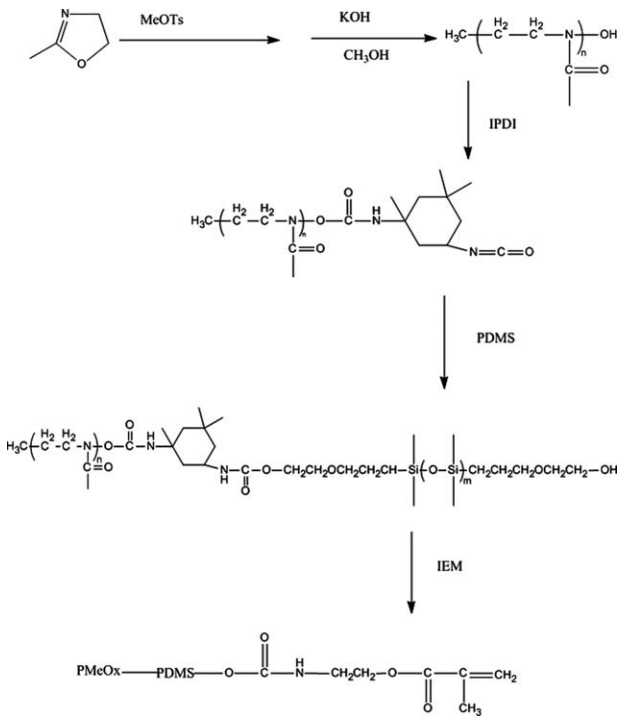
INTRODUCTION

During the past several decades, poly(dimethyl siloxane) (PDMS)-based silicone rubbers have been used successfully as wound dressing, scar gels, implants and drug delivery due to their high oxygen permeability, biocompatibility, ease of fabrication, moderate Young's modulus, and durability. [1,2] However, the extreme hydrophobicity of PDMS limits the wide application in medical area.[3] Surface modification is one common approach to achieve hydrophilicity as reported in the literature. [4,5] The strategies for surface modification of silicone rubbers involve oxygen plasma, ultraviolet light irradiation, corona discharge, and chemical vapor deposition. [6,7] Because of the surface enrichment of siloxane, surface modification, such as, plasma treatment often results in a short-lived hydrophilicity, and the modified hydrophilic surface can revert back to its native hydrophobic state.[8]

Another approach to achieve hydrophilicity is the incorporation of PDMS derived amphiphilic macromer. Actually, silicone hydrogels can be obtained by using amphiphilic PDMS macromers, which are widely used as contact lenses. Künzler and Ozark[9] reported the preparation of silicone hydrogels with amphiphilic PDMS macromers bearing hydrophilic side-chains, such as, PEG and glycol moieties. These PDMS derived amphiphilic macromers had enhanced compatibility with hydrophilic monomers.[10] They reported problems of significant instability when the side chains are polyethylene glycol (PEG) in contrast to when glycols are incorporated. Another class of A–B–A amphiphilic macromer with backbone A of PEG is often used to prepare silicone hydrogels. The instability of PEG was also reported by Nicolson[11] in A–B–A lens polymers, and the materials manifested a poor shelf life whereas when A is polyoxazoline, no such problems were observed.[12]

Polyoxazoline is a class of water-soluble peptide-like polymer. It can be terminated at one end or both with functional groups such as double bond, tosylate, hydroxyl and amine using either initiators or quenchers. Thus, polyoxazoline is such a chemical versatile polymer that a variety of molecules such as proteins, liposome, drugs, and antibacterial composition can be attached onto it.[13] A broader search of the literature revealed the numerous potential uses of polyoxazolines in medical areas.[14] Interestingly, the peptide like polyoxazoline may work as a perfect constituent in applications like antifouling, self-assembling, drug delivery, temperature-sensitive materials,[15] because of its higher hydrophilicity than that of PEG.[16]

Poly(2-methyl-2-oxazoline) (PMeOx) is a typical polyoxazoline which attracts much attention in the development of biomaterials. It can be readily synthesized by living cationic ring-opening polymerization of 2-methyl-2-oxazoline[17] with high batch to



Scheme 1. Preparation of poly(2-methyl-2-oxazoline)-*b*-poly(dimethyl siloxane) macromer.

batch reproducibility and low polydispersity. Usually, PMeOx can be obtained without chain transfer byproducts up to around 40 kDa and high molecular weight species. In this article, a novel amphiphilic poly(2-methyl-2-oxazoline)–poly(dimethylsiloxane) (PMeOx–PDMS) macromer was designed, and silicone hydrogels based on the macromer were developed to extend their applications in medical areas.[18–21] The hydrogels were prepared with different PMeOx–PDMS macromer content by copolymerization with 3-bis(trimethylsilyloxy) methylsilylpropyl glycerol methacrylate (SiMA) and hydrophilic monomer 2-hydroxyethyl methacrylate (HEMA). Furthermore, the hydrophilicity, water content, ion permeability and mechanical strength of the hydrogels were investigated in detail. The protein resistance of the hydrogels was determined by bicinchoninic acid assay. It was showed that the hydrogels had strong antifouling ability after the incorporation of PMeOx. The silicone hydrogels based on the amphiphilic PMeOx–PDMS macromer may have potential medical applications.

MATERIALS AND METHODS

Materials

2-Methyl-2-oxazoline and 2-isocyanatoethyl methacrylate (IEM) were purchased from J&K Scientific Co. and used as received. 3-Bis (trimethylsilyloxy) methylsilylpropyl glycerol methacrylate (SiMA) and hydroxyl-terminated PDMS(with approximate M_n = 2500 g mol^{-1}) were synthesized with the method as described in the literature. [22,23] 2-HEMA was purchased from Aldrich chemical Co. and purified by distillation under reduced pressure before use. Ethylene glycol dimethacrylate (EGDMA) was purchased from Aldrich chemical Co. and used without further purification. Free radical photoinitiator Darocur 1173 (D1173) was obtained from Ciba Co. Dibutylamine was purchased from TCI (Shanghai) Development. Methyl *p*-toluene sulfonate (MeOTs); isophorone diisocyanate (IPDI) and other solvents were purchased from Sino Pharm Chemical Reagent Co.

NMR Characterization

^{1}H-NMR measurement was performed in D_2O or $CDCl_3$ by a Bruker-DPX500 MHz nuclear magnetic resonance spectrometer at room temperature with a TMS internal standard.

Synthesis of PMeOx–PDMS Macromer

PMeOx–PDMS was prepared by the following typical procedure which is schematically illustrated in Scheme 1.

Preparation of Hydroxyl-Terminated Poly(2-methyl-2-oxazoline). 2-Methyl oxazoline 17.28 g (0.2 mol), acetonitrile 50 mL, and methyl *p*-toluene sulfonate 2.92 g (0.017 mol) were successively added to a dry pear shaped flask. Nitrogen gas was bubbled via syringe needle at room temperature for 15 min to remove oxygen. After that, the needle was sealed with wax, and ring opening polymerization was carried out with stirring at 80°C for 30 h. After cooling, the 0.1*N* KOH methanol solution (~17 mL) was added to the reaction flask and the reaction was continued for 4 h to obtain a terminal hydroxyl polyoxazoline. After the reaction, the product was filtrated and passed through silica gel column to remove methyl *p*-toluene sulfonate with eluent of acetonitrile. After concentration, polyoxazoline was obtained by precipitation in cold diethyl ether. The polyoxazoline was further purified by dissolving in acetonitrile and precipitating in diethyl ether twice. After drying a white powder of 10.23 g was obtained with the yield 59.01%.The chemical structure of poly(2-methyl-2-oxazoline) was confirmed by ^{1}H-NMR (500 MHz, D_2O, δ) as follows: 2.27 ppm (s, 3H, CH_3 terminal groups), 3.41 ppm (m, 4H, NCH_2CH_2), and δ 1.99 ppm (s, 3H, $COCH_3$). The molecular weight (M_n) of poly(2-methyl-2-oxazoline) was determined by hydroxyl group titration.[24] It was calculated to be 1067.

Preparation of Isocyanate-Terminated Poly(2-methyl-2-oxazoline). The reaction atmosphere was first exchanged with high-purity nitrogen gas. A total of 5.01 g (0.0047 mol) poly-2-methyl oxazoline (PMeOx, M_n: 1067) was dissolved in mixed solvent comprised 20 mL acetone and 5 mL DMSO coupled with two to three drops of additional dibutyl tin dilaurate as a catalyst. Then, 1.05 g (0.00472 mol) IPDI was added via syringe. The mixture was stirred at room temperature for 12 h. The crude isocyanate-terminated PMeOx was obtained after removal of solvent. Unreacted PMeOx and the impurity of PMeOx-IPDI-PMeOx which are insoluble in CH_3Cl can be removed in the next step of treatment.

Synthesis of PMeOx–PDMS Macromer. Under nitrogen atmosphere, 28.26 g α,ω-bishydroxylethyoxyl propyl polydimethylsiloxane (average molecular weight 2500 determined by ^{1}H-NMR) was dissolved in 50 mL acetone, the stoichiometry is based on four times the equivalent of isocyanate-terminated PMeOx. The solution was added via syringe to the three-necked flask followed by addition of two to three drops of dibutyl tin dilaurate as catalyst. The mixture was stirred at room temperature for 12 h to complete the reaction. The mixture was

Table I. The Formulation for the Preparation of Hydrogels

Sample	PDMS-PMeOx (%)	SiMA (%)	HEMA (%)	TEGDMA[a] (%)	D1173[a] (%)	Hexanol[a] (%)
0	0	70	30	0.6	0.5	20
1	10	60	30	0.6	0.5	20
2	20	50	30	0.6	0.5	20
3	30	40	30	0.6	0.5	20
4	40	30	30	0.6	0.5	20
5	50	20	30	0.6	0.5	20

[a] Weight percent of total monomers including PMeOx–PDMS, HEMA, and SiMA.

concentrated and washed with cold diethyl ether three times to remove excess polydimethylsiloxane (hydroxyl-terminated PMeOx–PDMS didn't dissolve in cold diethyl ether). The remaining mixture was dialyzed against water for 3 days to remove organic solvent like DMSO. The crude hydroxyl-terminated PMeOx–PDMS was obtained after lyophilization. It was further purified by dissolving in $CHCl_3$ and centrifugation. This treatment can remove the insoluble impurity of PMeOx-IPDI-PMeOx which is derived from the potential side reaction during the reaction of PMeOx with IPDI in the former step. After removal of solvent, the final hydroxyl-terminated PMeOx–PDMS was obtained as a white paste like solid (yield: 5.1129 g; 39.0%).The chemical structure of hydroxyl-terminated PMeOx–PDMS was confirmed by ^{1}H-NMR (500 MHz, $CDCl_3$, δ) as follows: 3.41 ppm (m, 4H, NCH_2CH_2), 1.99 ppm (s, 3H, $COCH_3$), 0.09 ppm (m, Si $(CH_3)_2$), δ 0.52 ppm (m, 2H, CH_2Si), 1.63, 3.5, and 3.7 ppm (m, 3H, $CH_2OCH_2CH_2$), 0.88 ppm (m, 6H, C $(CH_3)_2$), 1.26 ppm (m, 2H, CH_2).

The hydroxyl-terminated PMeOx–PDMS (2.48 g) was dissolved in 20 mL dried chloroform. Under a nitrogen atmosphere, IEM 0.26 g (0.00167 mol, 1.5 times' excess) and two drops of dibutyl tin dilaurate were added. The sealed reaction flask was then immersed into an oil bath of 40°C. After 8 h, the reaction was quenched with addition of 10 mL methanol. The solution was washed with 30 mL mixture solvent of H_2O/CH_3OH (1:1) three times. The polymer was then precipitated in diethyl ether (200 mL) and collected by filtration, dried in vacuum for 24 h (yield: 1.89 g, 71.86%).The chemical structure of PMeOx–PDMS macromer was confirmed by ^{1}H-NMR (500 MHz, $CDCl_3$, δ) as follows: 6.1 and 5.6 ppm (s, 2H, CH_2═C), 4.3 (m, 4H, OCH_2CH_2), and 2.0 (s, 3H, CH_3).

Table II. The Equilibrium Water Content, CA, and Mechanical Properties of Silicone Hydrogels with the Formulations as Cited in Table I

Sample	EWC (%)	CA (°)	Mechanical properties	
			S_b (MPa)	E (MPa)
0	6.8	81.0	-	-
1	15.9	73.0	1.37	6.27
2	17.7	74.0	1.17	5.66
3	23.8	72.0	1.01	4.80
4	25.5	67.0	0.95	4.30
5	29.4	61.5	0.72	3.22

Preparation of Silicone Hydrogels Based on PMeOx–PDMS Macromer

PMeOx–PDMS macromer cannot dissolve properly in either siloxane monomer or hydrophilic monomer alone. So, a mixture of siloxane monomer SiMA and hydrophilic monomer HEMA was used to dissolve PMeOx–PDMS macromer, and a transparent solution was obtained. Hydrogels were prepared with the formulations as shown in Table I using TEGDMA as a crosslinker and Darocur 1173 as a free radical initiator.

The mixture of each formulation was introduced between two glass plates (7.5 cm × 2.5 cm) and cured under a high-pressure mercury lamp emitting UV light centered at 365 nm for 1 h (Spectroline SB-100 PC, America SP Corporation) with distance from the lamp to the sample 30 cm, and polymer film is obtained. The film thickness is controlled by a Teflon gasket which gives a fairly consistent thickness of 0.2 mm. The film was then extracted with water/ethanol (1:1) for 48 h. Silicone hydrogel was obtained after immersed in water and stocked in normal saline.

Characterization of Silicone Hydrogels

Transmittance. The transmittance of the silicone hydrogels was measured using a Hελios UV–Visible Spectrophotometers (Thermo Electro Corporation) at 25°C.

Water Content. The equilibrium water content (EWC) was determined by using the following equation:

$$\mathrm{EWC} = \frac{W_S - W_D}{W_S} \times 100\% \quad (1)$$

where W_S is the weight of the hydrogel at swollen state and W_D is the dry weight of the hydrogel. All measurements were triplicated for each sample, and the average EWC was recorded as shown in Table II.

Contact Angle. Static water contact angles (CA) of silicone hydrogel membranes were measured by goniometer using a sessile drop method (Model JC2000C1, Shanghai Zhongchen Technology Company) after wiping free water on the surface with filter paper. Redistilled water was used for the measurement of static constant angles. All measurements were triplicated for each sample, and the average CA was recorded as shown in Table II.

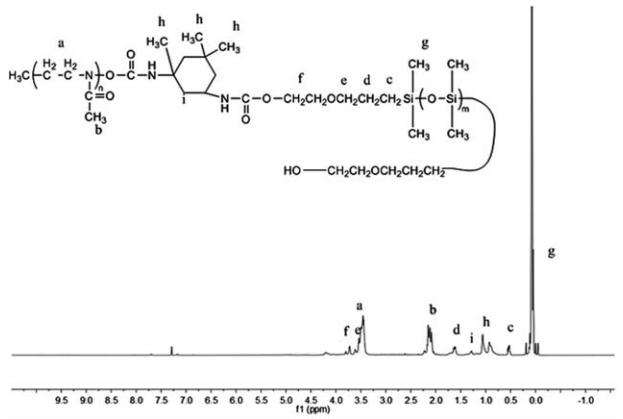


Figure 1. ^{1}H-NMR spectrum of hydroxyl-terminated PMeOx–PDMS.

Mechanical Test. Stress–strain measurements of hydrogels derived from the formulations as cited in Table I were carried out using an Instron series IX materials testing system at room temperature. Samples are cut from the silicone hydrogels (6-mm wide and 30-mm length). Thickness of the samples is measured with a digital micrometer with a precision of 1 μm. The speed of crosshead is 10 mm min^{-1} and at least three samples are tested for each type of hydrogel. The average stress at break (S_b) and Young's modulus (E) were recorded as shown in Table II.

Ion Diffusion Coefficient. Experimental installation was designed with a glass chamber immersed in a beaker. The silicone hydrogel film was sealed at the bottom of the glass chamber. Inside the glass chamber the solution of 0.1N NaCl was filled while the beaker contained 100 mL ultrapure water. The film thickness and surface area were measured by micrometer. The conductivity of water in the beaker was measured every 30 min till 6 h. The concentration of ions was calculated by a standard relationship between the concentration and conductivity of NaCl solutions. The ion diffusion coefficient, D_{ion}, was determined as follows[25]:

$$D_{ion} = \frac{n'}{A \times (dc/dx)} \quad (2)$$

where D_{ion} was ionic flux diffusion coefficient (mm^2/min), n' was the rate of ion transport (mol/min), A was the area of ion transport (mm^2), dc was concentration difference (mol/mm^3), and dx was the thickness of membrane (mm).

Protein Adsorption. Bovine serum albumin (BSA) adsorption on silicone hydrogel in PBS was determined by bicinchoninic acid assay (BCA Assay Kit K3000, Shanghai Biocolor BioScience & Technology Company). Silicone hydrogel membrane of length 3 cm × width 1 cm was equilibrated in phosphate-buffered saline (PBS) for 24 h and then immersed in 3 mL of BSA solution with concentration 5.00 mg mL^{-1} in PBS (pH 7.4) for 24 h at room temperature. The membrane was rinsed three times (10 min each) in PBS to remove loosely bound BSA. It was then transferred into a glass tube containing 3 mL of aqueous solution of sodium dodecyl sulfate (SDS, 1 wt %) and shaken for 4 h at room temperature to release protein on the hydrogel surface. The absorbance of the SDS solution was recorded at 562 nm by a microplate Reader (Bio-Rad 680, USA). The amount of adsorbed protein on the hydrogel surface was calculated by the concentration of protein in the SDS solution compared to a standard curve predetermined. Three repeats were carried out and the average amount of protein adsorption was obtained.

RESULTS AND DISCUSSION

Synthesis of PMeOx–PDMS Macromer

PMeOx–PDMS macromer endcapped with methacrylate group was prepared following the procedure as shown in Scheme 1. The cationic ring-opening polymerization of 2-methyl-2-oxazoline was carried out using MeOTs as an initiator. The hydroxyl-terminated PMeOx was obtained as white powder and the structure was confirmed by ^{1}H-NMR. The single peak centered at δ 3.41 ppm can be attributed to the side group —$COCH_3$, and another single small peak centered at δ 2.27 ppm can be attributed to the terminal group —CH_3. Multiple peaks at about δ 1.99 ppm can be ascribed to —NCH_2CH_2. The molecular weight of the hydroxyl-terminated poly(2-methyl-2-oxazoline) was measured to be 1067 by titration method.

The isocyanate-terminated PMeOx was obtained by converting the hydroxyl end groups of the terminated PMeOx to isocyanate groups by the reaction with IPDI in the second step. We noticed that there are two types of isocyanate groups in IPDI, and the by-product with PMeOx attached at both types of isocyanate groups of IPDI may exist in the crude isocyanate-terminated PMeOx. Fortunately, the by-product can be removed in the next step because it is unsolvable in $CHCl_3$.

The isocyanate-terminated PMeOx was further attached to the hydroxyl-terminated PDMS in the presence of dibutyl tin dilaurate as a catalyst. The PDMS had only one side hydroxyl group converted to carbamate by controlling the mole ratio. The crude hydroxyl-terminated PMeOx–PDMS was dissolved in $CHCl_3$ for purification. The insoluble impurity of PMeOx-IPDI-PMeOx which may derive from the side reaction during the former step of the reaction of PMeOx with IPDI can be removed via centrifugation. The hydroxyl-terminated PMeOx–PDMS was obtained as a white paste like solid. The structure was confirmed by ^{1}H-NMR as indicated in Figure 1. The result was analyzed as follows: δ 3.41 ppm (m, 4H, NCH_2CH_2), δ 1.99 ppm (s, 3H, $COCH_3$), δ 0.09 ppm (m, Si $(CH_3)_2$), δ 0.52 ppm (m, 2H, CH_2Si), δ 1.63, 3.5, and 3.7 ppm (m, 3H, $CH_2OCH_2CH_2$), and hydrogen in IPDI group had some manifestations in the figure at 0.88 ppm (m, 6H, C $(CH_3)_2$), 1.26 ppm (m, 2H, CH_2).

PMeOx–PDMS macromer endcapped with methacrylate was finally synthesized by the reaction of the hydroxyl hydroxyl-terminated PMeOx–PDMS with IEM. The structure of PMeOx–PDMS macromer was confirmed by ^{1}H-NMR as shown in Figure 2 which was analyzed as follows: δ 6.1 and 5.6 ppm (s, 2H, CH_2═C), δ 4.3 (m, 4H, OCH_2CH_2) and δ 2.0 (s, 3H, CH_3). The result indicates that the end-group hydroxyl was converted to double bond. So, the well-defined PMeOx–PDMS amphiphilic macromer was synthesized successfully.

Preparation of Silicone Hydrogels Based on PMeOx–PDMS Macromer

Silicone hydrogels were prepared by the copolymerization of PMeOx–PDMS macromer with HEMA and SiMA using

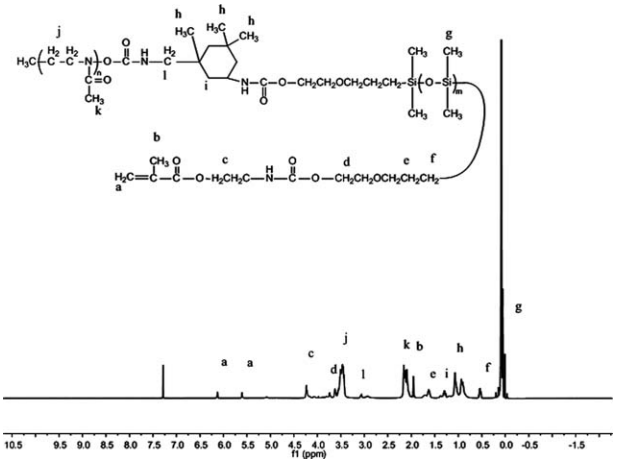


Figure 2. [1]H-NMR spectrum of PMeOx–PDMS monomer.

TEGDMA as a crosslinker in the presence of initiator under UV radiation with the formulations as shown in Table I. The content of TEGDMA of 0.6% was applied in all of hydrogel formulations because high gel fraction more than 90% was reached according to our previous trial. SiMA was used to enhance the compatibility of hydrophilic monomer and PMeOx–PDMS macromer. After extraction and hydration, the silicone hydrogels were obtained. The hydrogels were further characterized by light transmittance, water content, CA, mechanical properties and protein resistance as follows to investigate the role of polyoxazoline in the silicone hydrogels.

Characterization of Silicone Hydrogels

Transmittance. The transmittance of the silicone hydrogel materials based on PMeOx–PDMS macromer was shown in Figure 3. It was indicated that the hydrogel materials have the light transmittance of above 92% in the visible range of 370–780 nm. The silicone hydrogels were prepared by the copolymerization of PMeOx–PDMS macromer, SiMA and hydrophilic monomer. The different nature of PDMS and hydrophilic components are easy to cause phase separation thus affecting optical properties. As we know, phase separated materials don't generate any image

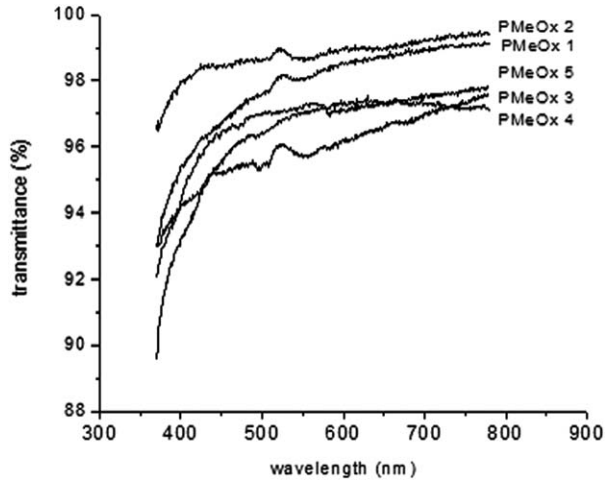


Figure 3. Transmittance of the silicone hydrogel materials with the formulations as cited in Table I.

deformation if the micro phase size is <100 nm (less than the wavelength of visible light).[26] So, the silicone hydrogel materials based on PMeOx–PDMS macromer should be in the state of micro phase separation.

Water Content and CA. The water content of the silicone hydrogels was shown in Table II. It was revealed that the water content increased with the increase of the content of PMeOx–PDMS. The water content of the hydrogel is only 16% when the PMeOx–PDMS content is 10%, while the water content increases to 30% when the PMeOx–PDMS content is 50%. Apparently, polyoxazoline content play an important role in increasing the water content of the hydrogels. Due to the introduction to the hydrophilic chain of PMeOx, the CA of the silicone hydrogels decreases gradually as the PMeOx–PDMS content increases. It is assumed that the hydrophilic chain of polyoxazoline works as a moisture part which balances the surface properties.

Mechanical Properties. The strength at break (S_b) and Young's modulus (E) of the hydrogels based on PMeOx–PDMS macromer were shown in Table II. It was found that the hydrogels have down trends in tensile strength and Young's modulus with the increase of PMeOx–PDMS content. The hydrogels with PMeOx–PDMS content <30% have tensile strength above 1.0 MPa. When PMeOx–PDMS content is >40%, the tensile stress of hydrogel decreased to 0.95 MPa and 0.72 MPa, respectively. With the increase of PMeOx–PDMS content, the hydrogels possess higher water content as indicated above. The silicone hydrogel materials with higher water content showed lower strength and modulus than those with small water content. So, the incorporation of PMeOx induces the increase of water content, and the decrease of tensile strength and modulus.

Ion Diffusion Coefficient. The diffusion of ions in the silicone hydrogel membrane can be ascribed to the thermal motion of molecules caused by the concentration difference of both sides.[27] If ions are uniformly distributed in hydrogel membrane and a steady state diffusion is reached, we could treat it with Fick's first law of diffusion. The ion diffusion coefficient of the hydrogel material can be calculated as shown in Figure 4 according to the formula:

$$D_{\text{ion}} = \frac{n'}{A \times (dc/dx)} \tag{3}$$

where D_{ion} was ionic flux diffusion coefficient (mm^2/min), n' was the rate of ion transport (mol/min), A was the area of ion transport (mm^2), dc was concentration difference (mol/mm^3), and dx was the thickness of membrane (mm).

The ion permeability of the silicone hydrogels mainly derived from the hydrophilic part. The hydrophilic part in the silicone hydrogel works as water osmosis phase and water has strong interaction with these parts. As soon as the hydrophilic part binds with water, the water molecules begin to penetrate, stretch and expand the network of hydrogel. At the same time, ion dissolved in water would migrate under the impetus of concentration difference. Ion transfer from the high concentration side to the low concentration side and achieve concentration equal eventually. With the increase of PMeOx–PDMS content the

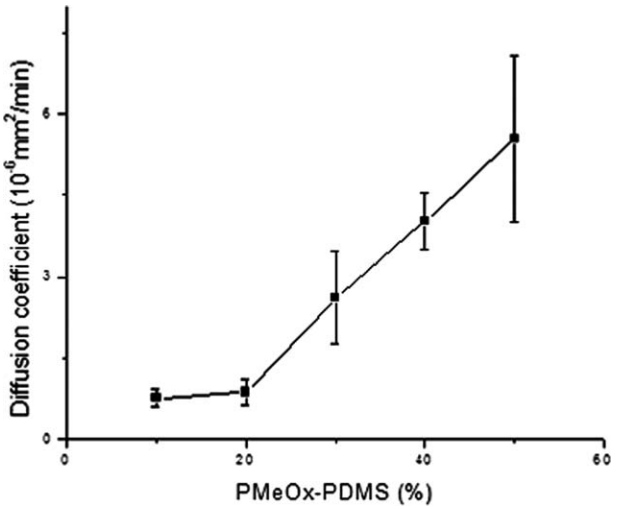


Figure 4. Ion diffusion coefficient of the silicone hydrogels with the formulations as cited in Table I.

hydrophilic part inside the hydrogel begin to feed through. The amount of water absorbed by polyoxazoline can form channels thus ions could move through hydrogels without the hindrance of hydrophobic siloxane. When PMeOx–PDMS content is below 20%, the hydrogel internal hydrophilic portion has not formed a continuous phase and the ions could hardly diffuse through the film. More effective water channels formed in the hydrogel with the increase of the hydrophilic component and more ions can pass through the hydrogel film effectively. And thus ion diffusion coefficient D rises according to the increase of the PMeOx–PDMS content.

Protein Resistance. Previous studies in the literature have highlighted many theoretical approaches to understand protein–polymer interactions. [28,29] It has been concluded that the hydrophilicity, chain length, and density of polymer are important in antiadhering proteins. Herein, to obtain an excellent protein resistance, hydrophilicity is of vital importance. Michel et al found that the PEG architecture and conformation affect the protein adsorption.[30] It was showed that protein adsorption increased as the PEG layer density decreased and the lowest adsorption was reached on the surface with the highest PEG chain surface density.

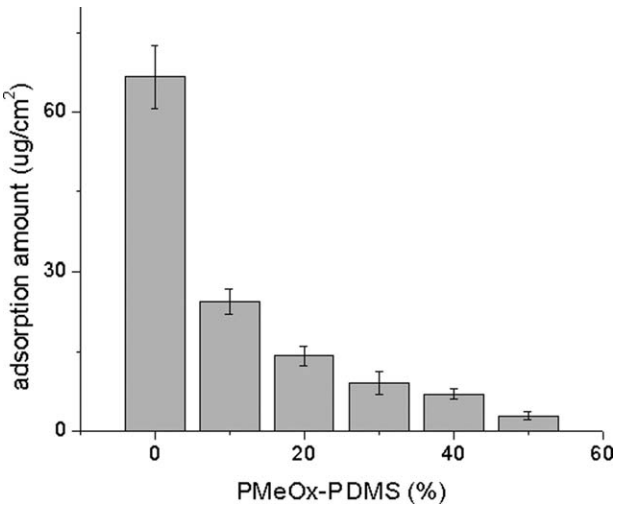


Figure 5. Protein adsorption of silicone hydrogels with the formulations as cited in Table I.

PMeOx could also reduce and even eliminate protein adsorption to surfaces because of its hydrophilicity. As PMeOx–PDMS content increases, the amount of the protein absorption dramatically decreased as shown in Figure 5. The adsorption on hydrogel surface with 50% PMeOx–PDMS is nearly negligible (about 3.76 μg cm^{-2}), whereas the gel without the incorporation of PMeOx–PDMS copolymer has the highest BSA deposition on the surface. The protein adsorption data demonstrated polyoxazolines efficient in rejecting protein adsorption.

CONCLUSION

A strategy has been developed for the efficient synthesis of amphiphilic PMeOx–PDMS macromer. Based on the amphiphilic PMeOx–PDMS macromer, silicone hydrogels were prepared successfully by UV-initiated copolymerization with HEMA and SiMA in the presence of crosslinker of TEGDMA. Property evaluations for these hydrogels have shown good mechanical strength and hydrophilic surfaces. The escalating water content and ion permeability mean that polyoxazoline can alter the hydrophobicity of PDMS. Protein adhesive assessment also suggests that it's a potential material to serve as ophthalmic biomaterials applications.

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