

## Preparation and characterization of transparent and foldable polysiloxane-poly(methyl methacrylate) membrane with a high refractive index

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**ABSTRACT:** In this article, carbazole-grafted methacrylic polysiloxane (MA-CZ-PDMS) macromonomer was synthesized and its structure was confirmed by proton nuclear magnetic resonance (<sup>1</sup>H NMR). The polysiloxane macromonomer can homogeneously copolymerize with methyl methacrylate (MMA) to prepare transparent and foldable carbazole-grafted polysiloxane-poly(methyl methacrylate) (PDMS-PMMA) membranes with a high refractive index (RI). The membranes were characterized by light transmittance, RI value, and dynamic mechanical thermal analysis (DMTA). The results indicated that the carbazole-grafted PDMS-PMMA membranes had excellent light transmittance that decreased slightly with increasing carbazole-grafted polysiloxane content. Incorporation of carbazole-grafted polysiloxane in the materials improved its RI value; however decreased the glass transition temperature ( $T_g$ ) that can be adjusted to less than 30°C, enable the membrane foldable at room temperature. The data demonstrate that the carbazole-grafted PDMS-PMMA membranes have a potential application as high RI intraocular lens (IOL) suitable for implantation by minimally invasive surgery. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42491.

**KEYWORDS:** glass transition; membranes; optical properties; ring-opening polymerization; synthesis and processing

Received 1 October 2014; accepted 11 May 2015

DOI: 10.1002/app.42491

### INTRODUCTION

Cataract is one of the main causes of blindness due to opacification in the natural crystalline lens. Its standard treatment procedure is to remove the natural lens contents, and then insert an intraocular lens (IOL) in the capsular bag to restore the ocular refractive power. Poly(methyl methacrylate), a high transparency and excellent biocompatible biomaterial with human body, has been widely used as IOL biomaterial. However, it is so stiff that a large operative incision more than the diameter of IOL is needed to implant it. Ideal artificial IOL materials should have a low modulus, which enables the IOL implant by minimally invasive surgery and change the shape upon action of the ciliary's muscles, so change focus for different viewing distances.

Polysiloxane has been extensively used as contact lens for refractive correction or intraocular lens<sup>1</sup> for the cataract treatment due to its attractive properties such as high oxygen permeability, optical transparency, and good biocompatibility as well. Moreover, polysiloxane has high elasticity and flexibility at extreme low temperatures. Therefore, combination of polysiloxane in

PMMA network decreases the  $T_g$  of PMMA to obtain flexible materials, making it suitable for implantation by minimally invasive surgery. Such combination has been the focus of many research groups around the world. For example, Shuizhu Wu *et al.*<sup>2</sup> prepared polyorganosiloxane/poly(methyl methacrylate) interpenetrating networks via sequential polymerization and studied its damping and mechanical properties. Hideki Sugimoto *et al.*<sup>3</sup> prepared transparent poly(methyl methacrylate)-poly(dimethylsiloxane) hybrid materials by copolymerization of MMA monomer and methacrylic PDMS macromonomer.

Refractive index (RI) is an important parameter of ocular biomaterials as IOL applications because high RI lens materials can be cut thinner, providing a higher refractive power and reduce friction between lens and iris. This will therefore help minimize inferior decentration and increase comfort. Conventional polysiloxane has a relative lower RI value than that of the human natural lens. Combination of PDMS in PMMA network will decrease its RI value, and this may induce significant hyperopia due to RI mismatch.<sup>4</sup> The RI value of polysiloxane can be

**Table I.** Formulations of Carbazole-Grafted Polysiloxane-poly(methyl methacrylate) Membranes with High RI Value

Samples	MA-CZ-PDMS (g) <sup>a</sup>	Methyl methacrylate (g)	BPO (g)
1	0.3 (50 wt %)	0.3000	0.0036
2	0.3 (60 wt %)	0.2000	0.0030
3	0.3 (70 wt %)	0.1286	0.0026
4	0.3 (80 wt %)	0.0750	0.0023

<sup>a</sup>The data in brackets is weight percent of MA-CZ-PDMS macromonomer versus total monomer weight of MA-CZ-PDMS and MMA.

improved by grafting high RI phenyl on its side-chain. For example, Hao *et al.*<sup>4</sup> synthesized polysiloxane with a high RI of 1.46 via re-equilibration of octamethylcyclotetrasiloxane (D<sub>4</sub>) and phenyl-grafted siloxane copolymer, which was suitable for injectable *in situ* curable accommodating intraocular lens. Carbazole, a rigid fused ring molecule with specific photoelectric properties, can be also grafted on the side-chain of polysiloxane to improve RI value. Wang *et al.*<sup>5</sup> synthesized carbazole-bound epoxy tetramethylcyclotetrasiloxane (Ep-Cz-Si) and epoxy methylhydrogen silicone oil (Ep-Cz-SiO), which showed strong self-photosensitizing effects in photopolymerization. The RIs of Ep-Cz-Si and Ep-Cz-SiO improved with increasing carbazole content. The RI value of polysiloxane can also be improved by introducing epithio-group on the side-chain. For example, Lan *et al.*<sup>6</sup> synthesized 1,3,5,7-tetra-(3-glycidoxypropyl)tetramethylcyclotetrasiloxane (TGCS) by hydrosilation reaction of D<sub>4</sub>H and allyl glycidyl ether, and then replaced the oxygen atoms with sulfur atoms using potassium thiocyanate to obtain siloxane episulfide with a higher RI value of 1.51.

In this report, we prepared high RI foldable PDMS-PMMA materials; in which copolymerization of polysiloxane decreased its T<sub>g</sub> and grafting carbazole molecule to compensate the decreased RI value. To achieve the aim, MA-CZ-PDMS macromonomer with high RI value was synthesized, and then copolymerized with methyl methacrylate (MMA). The structure of MA-CZ-PDMS macromonomer was confirmed by proton nuclear magnetic resonance (<sup>1</sup>H NMR) and the properties of the material such as gel fraction, light transmittance, and refractive index were characterized. Moreover, the thermomechanical behaviors were also studied by dynamic mechanical thermal analysis (DMTA).

## EXPERIMENTAL

### Materials

Octamethylcyclotetrasiloxane (D<sub>4</sub>), 2,4,6,8-tetramethylcyclotetrasiloxane (D<sub>4</sub>H), and 1,1,3,3-tetramethyl disiloxane were purchased from Jiangxi Xinghuo Organic Silicone Plant (Nanchang, China) and distilled before used. 2-Allyloxyethanol (99%), trifluoromethane sulfonic acid (98%), dibutyltin dilaurate (DBTDL), and benzoyl peroxide (BPO) were purchased from Aladdin Industrial Corporation (Shanghai, China). Chloroplatinic acid and methyl methacrylate (MMA) were purchased from Shanghai Chemical Regent (Shanghai, China). Carbazole and allyl bromide were purchased from Energy chemical

(Shanghai, China). Methacrylic acid ethyl isocyanide was purchased from Ji'nan Yu East Technology Development Co. (Jinan, China).

### Synthesis of N-Allyl Carbazole (ACZ)<sup>7</sup>

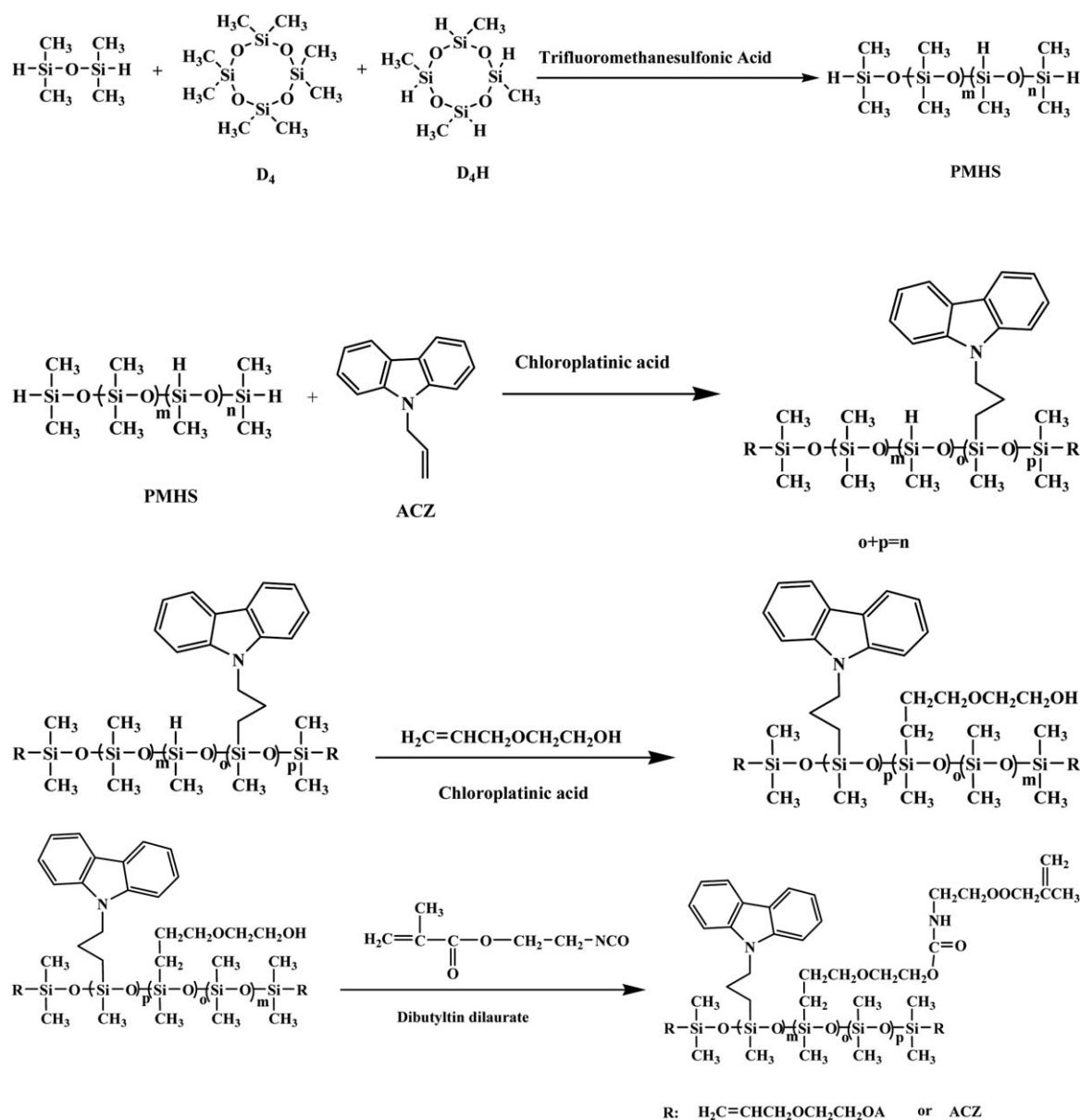
To a 150 mL round-bottom flask, 14 g of KOH was dispersed in 80 mL of N,N-dimethyl formamide (DMF), then 6.6 g of carbazole was added and stirred for 40 min at room temperature. Allyl bromide (7.26 g) was dissolved in 10 mL of DMF and then added to the DMF solution of carbazole by drop-wise over 30 min. The mixture was stirred overnight at room temperature, and then poured into 1 L of water to precipitate followed by filtration to obtain white crude product of N-allyl carbazole (ACZ). The crude ACZ was purified three times by recrystallization in ethanol, and then dried *in vacuo* at 40°C.

### Synthesis of Carbazole-Grafted Methacrylic Polysiloxane Macromonomer (MA-CZ-PDMS)

Carbazole-grafting methacrylic polysiloxane macromonomer (CZPDMS) was synthesized by a four-step reaction. Firstly, 1.65 g (12.28 mmol) of end-capper of 1,1,3,3-tetramethyl disiloxane, 16 g (53.94 mmol) of octamethylcyclotetrasiloxane (D<sub>4</sub>), and 12 g (49.89 mmol) of tetramethylcyclotetrasiloxane (D<sub>4</sub>H) were dispersed in 30 mL of toluene in a 100-mL three-neck boiling flask. After the temperature was increased to 40°C, trifluoromethane sulfonic acid (200 μL) was added, stirred for 24 h under nitrogen atmosphere, and then washed repeatedly with purified water until the pH of the mixture became neutral. After water was separated, the residual liquid was dried with anhydrous magnesium sulfate and then toluene was distilled off under reduced pressure. The residual liquid was dissolved in 20 mL of acetone and then reprecipitated in 40 mL of methanol in a separatory funnel to remove unreacted D<sub>4</sub>, D<sub>4</sub>H, and end-capper of 1,1,3,3-tetramethyl disiloxane. This was followed by the removal of volatile components *in vacuo* to give a transparent liquid polymethylhydrosiloxane (PMHS).

PMHS (5 g) and 3 g (14.95 mmol) of ACZ were dispersed in 25 mL of toluene and heated to 80°C under N<sub>2</sub>; This was followed by drop-wise addition of 5 mL of toluene containing 0.0012 g of chloroplatinic acid. The reaction was monitored by thin layer chromatography (TLC) with petroleum ether as the developing agent. After ACZ completely reacted, 2-allyloxyethanol (3 g) was added dropwise to the mixture, which was then allowed to stand for 6 h at 80°C, and then washed several times with distilled water to remove excess 2-allyloxyethanol. After water was separated, the residual liquid was dried with anhydrous magnesium sulfate and then toluene was distilled off under reduced pressure to obtain a transparent liquid of carbazole-grafted polysiloxane copolymer.

Carbazole-grafted polysiloxane copolymer (3 g) was dispersed in 20 mL of acetone containing 0.002 g of DBTDL. Methacrylic acid ethyl isocyanide (0.1042 g) was dissolved in 2 mL of acetone, and then added to the acetone solution of carbazole-grafted polysiloxane by drop-wise over 10 min by a constant pressure dropping funnel. This was then allowed to stand for 6 h at room temperature. Finally, acetone was removed under reduced pressure to obtain pale yellow viscous liquid of



**Scheme 1.** Synthesis route of carbazole-grafting polysiloxane macromonomer (CZ-MA-PDMS).

carbazole-grafted methacrylic polysiloxane macromonomer (MA-CZ-PDMS).

### Preparation of PDMS-PMMA Membranes with High Refractive Index

MA-CZ-PDMS macromonomer and MMA monomer and BPO initiator were mixed with the formulations as described in Table I, and then ultrasonicated for 10 min to dissolve the initiator of BPO and remove dissolved oxygen. The mixture was injected into the cavity of the polypropylene plate mold separated by polypropylene frame with a thickness of 0.2 mm. The mold was cured in an oven at 60°C for 1 h, and then the temperature was increased to 80°C for another 12 h to obtain bulk copolymer materials.

### Methods and Measurements

**NMR Spectra.**  $^1\text{H-NMR}$  spectra were recorded on a 400-MHz instrument (Bruker AC200) with  $\text{CDCl}_3$  as a solvent. H content

of Si-H in PMHS copolymer, the average number of dimethyl siloxane and Si-H unit of PMHS copolymer were also determined by  $^1\text{H-NMR}$  spectra by adding 0.0288 g of dioxane as internal standard in 0.063 g of PMHS.

**Gel Permeation Chromatography (GPC).** The average molecular weight of PMHS was determined by GPC (Waters, E2695). The injection volume of samples was 80  $\mu\text{L}$  and THF was used as mobile phase at a flow rate of 1.0 mL/min. Calibration was done with polyoxytetramethylene standards with molecular weight from 800 to 90,000 Daltons.

**Gel Fraction (G).** The carbazole-grafted PDMS-PMMA membranes were dried to a constant weight *in vacuo* and weighed before and after extraction in a Soxhlet extractor with acetone for 24 h. G was gravimetrically calculated with the following formula:

$$G = 100 \times W_g / W_0 \quad (1)$$

where  $W_0$  and  $W_g$  are the weights of dry sample before and after extraction, respectively.

**Element Analysis.** N, C, and H content of CZ-MA-PDMS and PDMS-PMMA membranes were carried out on a Vario EL III instrument (Elementar Analysensysteme, Germany).

**Light Transmittance.** The carbazole-grafted PDMS-PMMA membranes were cut into  $10 \times 40 \text{ mm}^2$  strips and attached to the inner surface of a quartz colorimetric cuvette. The transmittance of the membranes were recorded at a wavelength between 200 and 800 nm with an ultraviolet-visible spectrophotometer (Helios, Thermo Electron), with air as a reference.

**Refractive Index (RI).** The refractive index of PDMS-PMMA samples were determined with an abbe's refractometer (WAY, Shanghai Ineas Instrument) equipped with an electric heating constant temperature water cycle box (Thermo Electron Corporation, German) at a constant temperature of  $37^\circ\text{C}$ . The samples were clipped between the measuring prism and the auxiliary prisms for 10 min, and then determined the RI value of carbazole-grafted PDMS-PMMA materials.

**Dynamic Mechanical Thermal Analysis (DMTA).** The dynamical thermomechanical behavior of the samples was followed on a Tritec 2000 (Triton Technology) instrument with  $10 \times 20 \text{ mm}^2$  rectangular bars in single-cantilever bending mode. The storage moduli ( $E'$ ) and loss factor ( $\tan \delta$ ) were registered as a dependence on the temperature ranging from 30 to  $200^\circ\text{C}$  at a  $5^\circ\text{C}/\text{min}$  heating rate and a frequency of 1 Hz.

## RESULTS AND DISCUSSION

### Synthesis of MA-CZ-PDMS Macromonomer

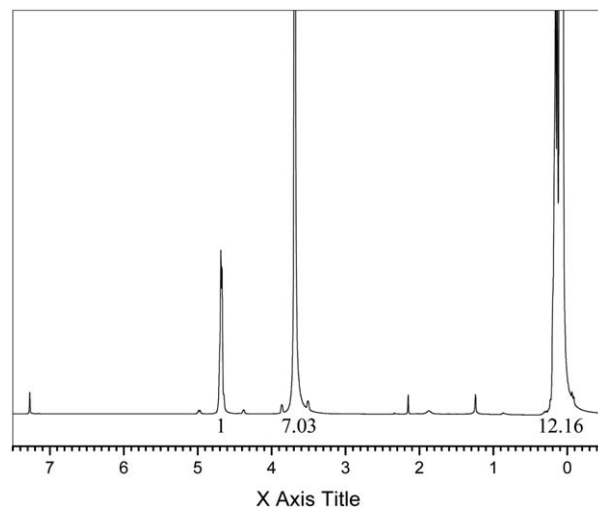
The synthesis route of MA-CZ-PDMS macromonomer is summarized in Scheme 1. First, the PMHS copolymer was synthesized by ring-open polymerization of  $D_4$ ,  $D_4H$ , and end-capper 1,1,3,3-tetramethyl-disiloxane by the acid-catalyzed equilibration. Molecular weight of PMHS determined by GPC was about 2357 Kg/mol. This is consistent with the theoretical molecular weight of PMHS (2414 Kg/mol) calculated from the ratio between the mass of  $D_4$ ,  $D_4H$ , and end-capper and the molar amount of end-capper. H content of Si-H in PMHS copolymer was 0.59 wt % calculated as eq. (2), and the average number ( $m$ ) of dimethyl siloxane unit in the PMHS copolymer was about 23 and the average number ( $n$ ) of Si-H unit was about 14 calculated as eqs. (3) and (4) respectively according to  $^1\text{H}$  NMR spectrum of PMHS/dioxane as shown in Figure 1.

$$H\% = \frac{A_{\text{Si-H}} \times W_{\text{Dioxane}} \times 8}{A_{\text{Dioxane}} \times W_{\text{PMHS}} \times 88} \times 100\% \quad (2)$$

$$\frac{A_{\text{Si-H}}}{A_{\text{Si-CH}_3}} = \frac{n+2}{3n+6m+12} \quad (3)$$

$$\frac{A_{\text{Dioxane}}}{A_{\text{Si-H}}} = \frac{\frac{W_{\text{Dioxane}} \times 8}{88}}{\frac{W_{\text{PMHS}} \times (n+2)}{60n+74m+134}} \quad (4)$$

where,  $A_{\text{Si-H}}$ ,  $A_{\text{Dioxane}}$  and  $A_{\text{Si-CH}_3}$  were the areas of Si-H peak at 4.70 ppm, proton peak area of dioxane and the methyl group peaks connecting to silicone, respectively.  $W_{\text{Dioxane}}$  and  $W_{\text{PMHS}}$  were the weights of internal standard (dioxane) and sample of



**Figure 1.**  $^1\text{H}$  NMR spectra of PMHS with dioxane as internal standard.

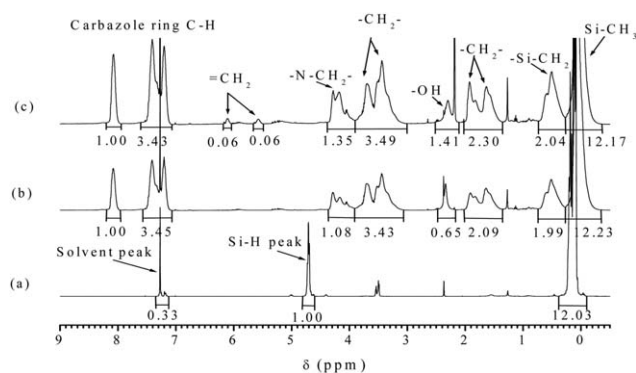
PMHS, respectively.  $m$  and  $n$  were the average number of dimethyl siloxane and Si-H unit in PMHS copolymer.

ACZ was grafted on the side-chain of PMHS by hydrosilation reaction in the presence of Pt-catalyst. However, the product is immiscible with MMA monomer. Therefore, hydrophilic 2-allyloxyethanol was also grafted on the side-chain of PMHS to obtain hydroxyl- and carbazole-grafted polysiloxane copolymer. The hydrosilation reaction of ACZ and PMHS can be determined by TLC with petroleum ether as developing solvent and no free ACZ was observed after 48 h reaction. Carbazole-grafted PMHS was unstable and crosslink occurred when removing solvent of toluene under reduced pressure. This may be ascribed to the instability of the Si-H in the presence of chloroplatinic acid.  $^1\text{H}$  NMR spectrum of hydroxyl- and carbazole-grafted PMHS is shown in Figure 2(b). No obvious resonance peak of allyl group in allyl glycidyl ether ( $\delta = 5.5$  and  $6.0$  ppm) was observed. This indicated that excess 2-allyloxyethanol can be efficiently removed by washing with water. In addition, the resonance peaks at  $\delta = 4.7$  ppm corresponding to Si-H was not observed. This indicated that all the Si-H bond has involved into the hydrosilation reaction. The  $^1\text{H}$  NMR spectra as shown in Figure 2(b) clearly indicated that the hydroxyl- and carbazole-grafted polysiloxane copolymer was successfully synthesized. The ratio of Si-H bonds grafted carbazole and allyloxyethanol was about 51 mol % and 49 mol % calculated by added ACZ weight in synthesis process.  $^1\text{H}$  NMR spectra of final MA-CZ-PDMS macromonomer was shown in Figure 2(c). It can be seen that obvious carbon-carbon double bond peak locating at  $\delta = 6.11$  and  $5.57$  ppm was observed. This indicated that carbazole-grafted polysiloxane macromonomer was successfully synthesized. The ratio of methacrylic acid ethyl isocyanide was about 6.12 mol % according to the area of the carbon-carbon double bond peak locating at  $\delta = 6.11$  and  $5.57$  ppm (0.12) with carbazole peak at  $8.04$  ppm (2H, ArH) as reference (0.12  $\times$  51 mol %).

### Preparation and Characterization of Carbazole-Grafted PDMS-PMMA Membranes with High Refractive Index

Poly(methyl methacrylate) and polysiloxane have good biocompatibility with human body and have widely used as

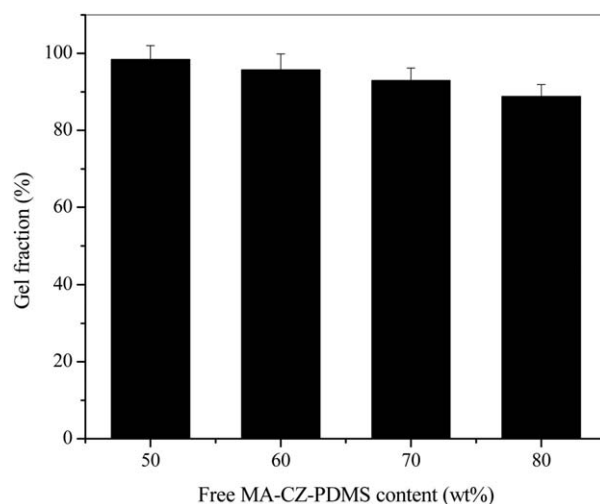




**Figure 2.**  $^1\text{H}$  NMR spectra of (a) PMHS, (b) hydroxyl- and carbazole-grafted polysiloxane copolymer (HO-CZ-PDMS), and (c) carbazole-grafted methacrylic polysiloxane macromonomer (MA-CZ-PDMS).

biomaterials for the eye refractive correction such as contact lens and intraocular lens (IOL). However, pure PMMA material is too stiff to satisfy the demand of minimally invasive implant. Usually, polysiloxane can be combined into PMMA material to decrease its glass transition temperature ( $T_g$ ). However, this will decrease the RI of materials due to low RI value of polysiloxane. The RI value of polysiloxane can be improved by grafting carbazole molecule on its side-chain. Synthesized macromonomer of MA-CZ-PDMS can homogeneously copolymerize with MMA monomer using BPO as initiator. MA-CZ-PDMS macromonomer is soluble in acetone. Therefore, after curing, PDMS-PMMA membranes were extracted 24 h with acetone in a Soxhlet. The gel fractions corresponding to sample 1–4 with free content of MA-CZ-PDMS from 50% to 80% were obtained and are shown in Figure 3. It can be seen that the gel fraction decreased from 98% to 89% with the increase of MA-CZ-PDMS free content in the formulation. The actual content of MA-CZ-PDMS in PDMS-PMMA membranes after extracted by acetone was determined by elemental analysis and the data were listed in Table II. It can be seen that the actual content is lower than the free MA-CZ-PDMS content. For example free MA-CZ-PDMS content of 50%, 60%, 70%, and 80% corresponding to actual content of 42%, 53%, 57%, and 67%.

Transmittance ( $T\%$ ) is an important parameter for the ocular refractive materials, especially for the IOL application, the synthesized silicone hydrogels must be optically transparent.  $T\%$  of the carbazole-grafted PDMS-PMMA is shown in Figure 4. It can be seen that the sample 1, 2, 3, and 4 showed a high  $T\%$



**Figure 3.** Gel fraction of sample 1–4 with MA-CZ-PDMS content of 50–80 wt %, respectively.

at the wavelengths between 500 nm and 800 nm, and increasing the content of carbazole-grafted polysiloxane in the materials decreased slightly its  $T\%$ . Therefore, the  $T\%$  of carbazole-grafted PDMS-PMMA may be suitable for biomaterial used as ocular biomaterials for refractive correction. Moreover, the carbazole-grafted PDMS-PMMA showed a relative low  $T\%$  at the wavelengths between 400 nm and 500 nm. This is consistent with its yellow appearance as shown in Figure 5. The most sensitive wavelength for human eye is about 555 nm corresponding to yellow and green light. Nowadays, yellow-tinted intraocular lenses have been clinically used with additional function of blue light blocking. Therefore, this may be a good thing because high energy purple and blue light (wavelengths from 400 nm to 500 nm) can induce retinal damage.<sup>8</sup>

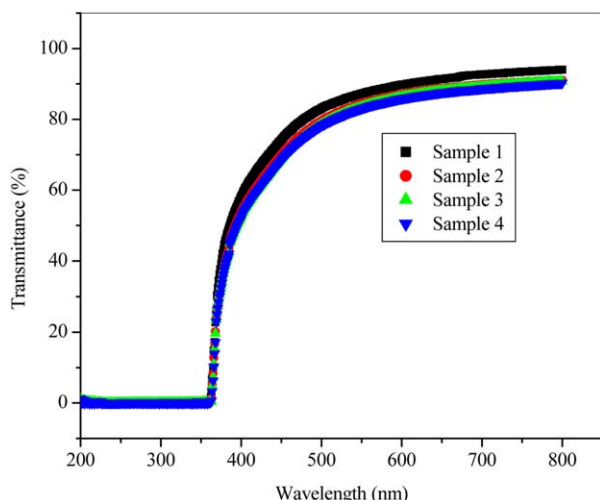
Refractive index is an important parameter for biomaterial application of ocular refractive correction. Lens materials with high refractive index can be cut thinner. This will greatly improve the ocular biocompatible especially for the refractive correction of high myopia. The RI value of the carbazole-grafted PDMS-PMMA membranes was shown in Figure 6. It can be seen that the RI value of all samples was higher than pure PMMA materials (about 1.49) and increasing the high RI carbazole-grafted polysiloxane composition in the materials increased its RI value. This indicated that the high RI value is

**Table II.** Element Analysis Data of PDMS-PMMA Membranes and Actual MA-CZ-PDMS Content in PDMS-PMMA Membranes

Samples	N content (wt %)	C content (wt %)	H content (wt %)	Actual CZ-MA-PDMS content (wt %) <sup>a</sup>
0 <sup>b</sup>	2.981	52.32	8.942	–
1	1.265	55.70	9.152	42
2	1.588	56.07	9.417	53
3	1.712	53.93	8.726	57
4	2.002	52.49	8.752	67

<sup>a</sup> Calculate by the ratio of N content in PDMS-PMMA samples to N content in CZ-MA-PDMS macromonomer;

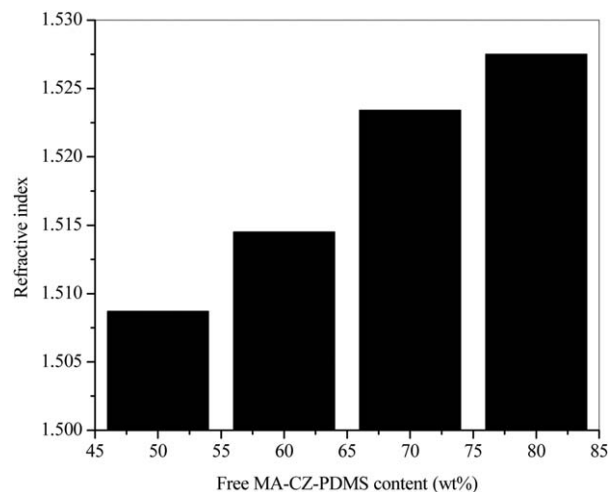
<sup>b</sup> Sample 0 means MA-CZ-PDMS macromonomer.



**Figure 4.** Transmittance of carbazole-grafted PDMS-PMMA membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

mainly ascribed to the carbazole molecule grafted on the side-chain of MA-CZ-PDMS macromonomer. Nowadays, soft IOL, usually made from pHEMA-based hydrogel or polysiloxane rubber, has been widely used in clinic and its RI value is usually about 1.40. The RI value of carbazole-grafted PDMS-PMMA (the RI value for sample 4 is higher than 1.525) was much higher than that of soft IOL materials. Therefore, the material may be used as thinner IOL and improve its biocompatible in eye.

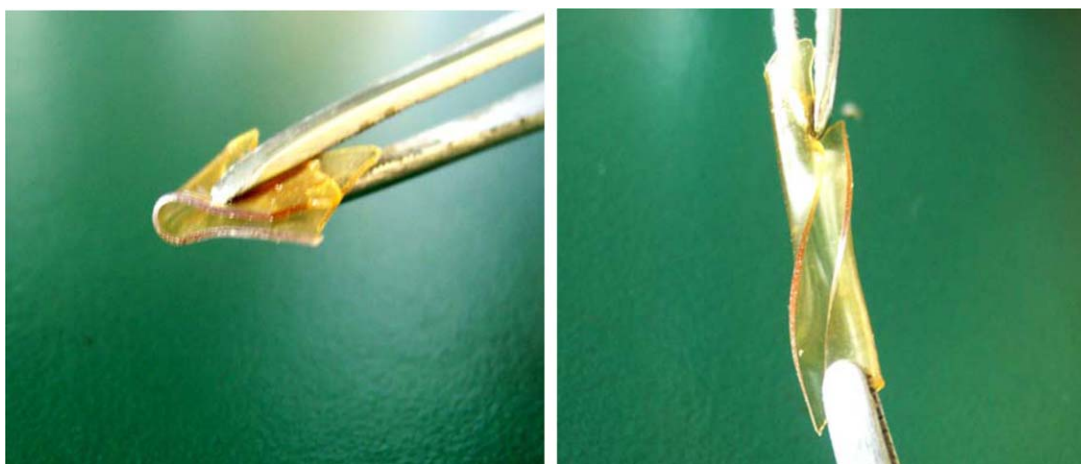
The storage modulus ( $E'$ ) and the loss factor ( $\tan \delta$ ) for a series of carbazole-grafted PDMS-PMMA membranes with different proportion of MA-CZ-PDMS composition are shown as a function of temperature in Figure 7. From the viscoelastic spectra, several parameters,  $E'$ ; rubbery modulus ( $E'_r$ ), the glass transition temperature ( $T_g$ ), and the amplitude of the damping peak ( $\tan \delta$ )<sub>max</sub>, were obtained and are listed in Table III. It can be seen that  $E'$  of copolymerization network with actual MA-CZ-PDMS content of 42 wt % was about  $5.79 \times 10^8$  Pa that



**Figure 6.** Refractive index of carbazole-grafted PDMS-PMMA membranes of sample 1–4.

gradually drops to  $2.77 \times 10^8$ ,  $0.84 \times 10^8$ , and  $0.06 \times 10^8$  Pa with increasing MA-CZ-PDMS content to 53 wt %, 57 wt %, and 67 wt %, respectively. Moreover, the temperature range of glassy state became very short. The glassy state temperature of sample 4 was even lower than  $30^\circ\text{C}$ ; therefore it showed a low  $E'$ .

Increasing the content of MA-CZ-PDMS in the network decreased the  $T_g$ . When the content was more than 57 wt %,  $T_g$  rapidly decreased, even the  $T_g$  of sample 4 with MA-CZ-PDMS of 67 wt % was lower than  $30^\circ\text{C}$ . This indicates that sample 4 was in elastic state, enabled the materials foldable at room temperature as shown in Figure 5.  $T_g$  value can be effected by pendent group of carbazole and the content of Si–O component. Generally,  $T_g$  decreased with the increase of Si–O component in materials. However, there are two main sides about the influence of pendent groups on  $T_g$  of a polymer.<sup>9</sup> One is that pendent groups can reduce the interaction between polymer backbones and this leads to a low  $T_g$ ; the other is that steric effect of pendent groups could decrease flexibility of polymer chains, and make the polymer  $T_g$  increase. The  $T_g$  value of



**Figure 5.** Photograph of transparent and foldable carbazole-grafted PDMS-PMMA membrane with free MA-CZ-PDMS content of 80 wt % (sample 4). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

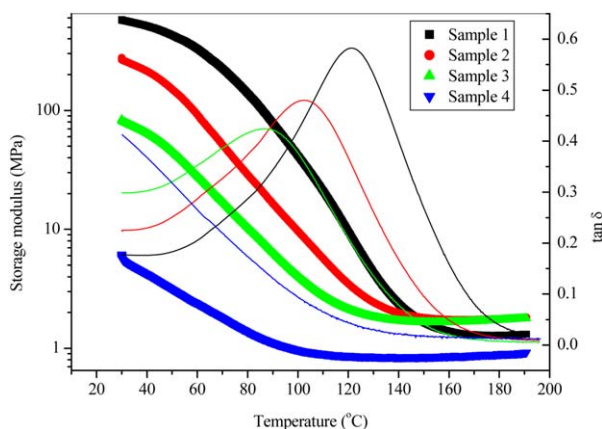
carbazole-grafted PDMS-PMMA was far more than polysiloxane materials (usually lower than 0°C) even MA-CZ-PDMS content reached 57 wt % (sample 3). Therefore, the steric effect of carbazole molecule is a dominant aspect due to its rigidity and big volume, and the  $T_g$  decrease was mainly ascribed to the flexibility of the siloxane bonds in the polymerization network, which decreased the stiffness of the crosslinked networks.

According to the rubber elasticity theory,<sup>10</sup> it may be assumed that the effect of internal energy of the formed network can be neglected above  $T_g$  and by relating the changes in entropy, thus, the variation in the rubbery modulus ( $E'_r$ ) can be expressed as a function of crosslinking density by the following relationship:

$$E'_r = 3\theta\rho RT/M_c \quad (5)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $\rho$  is the density of the crosslinked network,  $\theta$  is the 'front factor', and  $M_c$  is the average molecular weight between crosslinks. The above equation shows that  $E'_r$  is proportional to  $1/M_c$ ; in other words, an increase in the crosslinking density will cause an increase in  $E'_r$ . As shown in Table II, the value of  $E'_r$  increased with increasing the proportion of carbazole-grafted polysiloxane in the PMMA material. This indicates that copolymerization of MA-CZ-PDMS in the materials increased slightly its crosslinking spot, inducing the crosslinking density slightly increased. The crosslinking density can also be seen from the height of the  $\alpha$ -transition  $(\tan \delta)_{\max}$ . In generally, the height of  $(\tan \delta)_{\max}$  becomes lower as the distance between crosslinks decreases.<sup>11</sup> As seen in Table II, the  $(\tan \delta)_{\max}$  decreased with increasing amounts of carbazole-grafted polysiloxane in the crosslinked networks. The result was consistent with the trend obtained from the  $E'_r$  determination; i.e. the higher carbazole-graft polysiloxane content will lead to a more densely crosslinked network. Moreover, all of the maxima of  $\tan \delta$  were less than one. This indicated that the PDMS-PMMA materials had  $E'$  value that was higher than the loss modulus ( $E''$ ).

Further, the widths at the half-height on the relaxation peak are sensitive to the homogeneity of the networks.<sup>12</sup> In Figure 7, it was clear that all samples exhibited a single  $T_g$ . Therefore, the carbazole-grafted polysiloxane composition did not separate from PMMA



**Figure 7.** Storage modulus and  $\tan \delta$  relaxation of PDMS-PMMA membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table III.** DMA Characteristics of the Carbazole-Grafted PDMS-PMMA with High RI Value

Sample	$E'$ (Pa)	$E'_r$ (Pa)	$(\tan \delta)_{\max}$	$T_g$ (°C)
1	$5.79 \times 10^8$	$1.60 \times 10^6$	0.58	121.26
2	$2.77 \times 10^8$	$2.29 \times 10^6$	0.48	102.62
3	$0.84 \times 10^8$	$2.31 \times 10^6$	0.42	86.6
4	$0.06 \times 10^8$	-	-	<30

$E'_r = T_g + 30^\circ\text{C}$ .

$T_g$  was the temperature corresponding to  $(\tan \delta)_{\max}$ .

composition. However, the widths at the half-height on the relaxation peak were broadening with the increase of carbazole-grafted polysiloxane content in the materials. This indicated that there was slight phase separation in the material which increased with the increase of carbazole-grafted polysiloxane content.

## CONCLUSIONS

Carbazole molecule can be grafted on the side-chain of polysiloxane by hydrosilylation reaction to synthesize high refractive index liquid polysiloxane macromonomer, which can homogeneously copolymerize with MMA to prepared transparent high RI materials. The RI value and  $T_g$  of the carbazole-grafted PDMS-PMMA material is tunable and can be controlled by the incorporation ratio of carbazole-grafted polysiloxane macromonomer. Copolymerization of MA-CZ-PDMS macromonomer in the PMMA network increased the crosslinking density and decreased its  $T_g$ . The  $T_g$  of carbazole-grafted PDMS-PMMA membrane is lower than 30°C and is foldable at room temperature when the content of MA-CZ-PDMS macromonomer is about 67 wt %. The data demonstrate that the carbazole-grafted PDMS-PMMA membrane has a potential application as high RI ocular refractive correction biomaterial such as intraocular lens that can implant by minimally invasive surgery.

## ACKNOWLEDGMENTS

The projects were supported by National Nature Science Foundation of China (No. 51163007); Nature Science Foundation of Jiangxi Province (No. 20114BAB206025), Nature Science Foundation of Shandong Province (No. ZR2013BQ014), Science and Technology Development Program of Shandong Province (No. 2014GSF118009), and Nature Science Foundation of Jiangxi Agricultural University (No. 09003332).

## REFERENCES

- Koopmans, S. A.; Terwee, B.; Barkhof, J.; Haitjema, H. J.; Kooijman, A. C. *Invest. Ophthalmol. Vis. Sci.* **2003**, *44*, 250.
- Wu, S.; Yao, S.; Huang, Z.; Xi, H.; Shen, J. *Macromol. Mater. Eng.* **2002**, *287*, 231.
- Sugimoto, H.; Nishino, G.; Koyama, H.; Daimatsu, K.; Inomata, K.; Nakanishi, E. *J. Appl. Polym. Sci.* **2012**, *124*, 1316.
- Hao, X.; Jeffery, J. L.; Le, T. P. T.; McFarland, G.; Johnson, G.; Mulder, R. J. *Biomaterials* **2012**, *33*, 5659.

5. Wang, T.; Ye, H.; Zhang, X.; Cheng, J. *Ind. Eng. Chem. Res.* **2012**, *51*, 15832.
6. Lan, X.; Huang, W.; Yu, Y. *Eur. Polym. J.* **2010**, *46*, 1545.
7. Nishi, H.; Kohno, H.; Kano, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1897.
8. Tanito, M.; Okuno, T.; Ishiba, Y.; Ohira, A. *J. Cataract Refract. Surg.* **2010**, *36*, 299.
9. Liu, Y. Y.; Fan, X. D. *Biomaterials* **2005**, *26*, 6367.
10. Tobolsky, A. V. *Properties and structure of polymers*; Wiley: New York, **1960**.
11. Unsworth, J.; Li, Y. *J. Appl. Polym. Sci.* **1992**, *46*, 1375.
12. Hou, S. S.; Chung, Y. P.; Chan, C. K.; Kuo, P. L. *Polymer* **2000**, *41*, 3263.