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Radical/Addition Polymerization Silicone Hydrogels with Simultaneous Interpenetrating Hydrophilic/Hydrophobic Networks

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ABSTRACT: Transparent silicone hydrogels with interpenetrating hydrophilic/hydrophobic networks were simultaneously synthesized on the basis of the radical polymerization of the methacrylic monomer of 3-methacryloxypropyl tris(trimethylsiloxy) silane (TRIS)/*N*,*N*-dimethylacrylamide (DMA) and the addition polymerization of hydroxyl-grafted polysiloxane (HPSO)/isophorone diisocyanate. The curing temperature was set at 80°C by a differential scanning calorimetry study. The polymerization process was studied by *in situ* Fourier transform infrared spectroscopy. The results indicate that the curing time was about 4.5 min, and the addition polymerization had a faster rate than radical polymerization. Then, the radical polymerization rate increased rapidly, and this led to instant curing. The interpenetrating polymer network (IPN) silicone hydrogels were characterized by swelling kinetics and dynamic mechanical thermal analysis. The results show that all of the hydrogels reached swelling equilibrium at about 4 h in water, and the IPN silicone hydrogels with a hydrophobic network of HPSO indicated a slower water transport than that of the copolymerization hydrogel of DMA and TRIS. The hydrophobic network was finely dispersed in the hydrophilic network, and the increasing hydrophobic network of HPSO decreased the glass-transition temperature of the IPN silicone hydrogels. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41399.

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INTRODUCTION

Polysiloxane rubbers are well-known to possess attractive properties of high oxygen permeability, optical transparency, and high elasticity and flexibility at extreme temperatures, particularly in the low range. Moreover, polysiloxane has a good biocompatibility with the human body[1] and has been extensively used in biomedical applications, especially for contact lenses. Nevertheless, polysiloxane materials exhibit high hydrophobic properties. This may lead to binding or adherence to the cornea, and therefore, these materials can never deliver comfort characteristics to hydrogels.[2–4] To enlarge the field of applications of polysiloxane as biomaterials, polysiloxane materials have been combined with hydrophilic polymers (usually called silicone hydrogels) that enable them to swell in water, so they possess a better biocompatibility with the human body. The challenge lies in not impairing their oxygen permeability and optical transparency. Such combinations can be achieved by the copolymerization of methacrylate-functionalized siloxane macromers and hydrophilic comonomers, such as 2-hydroxyethyl methacrylate, *N*,*N*-dimethylacrylamide (DMA), and *N*-vinyl pyrrolidone.[5,6] The copolymerization method has been applied extensively for the preparation of contact lenses.[7]

Another possibility for obtaining silicone hydrogels is combining them with hydrophilic polymers and hydrophobic polysiloxane into an interpenetrating polymer network (IPN). IPNs are most generally defined as mixtures of two or more crosslinked polymers; their entanglement leads to forced miscibility compared with usual blends, and the resulting materials exhibit a good dimensional stability. IPN hydrogels can be prepared by either sequential or simultaneous IPNs. In sequential IPNs, the hydrophilic network is polymerized in the presence of swollen siloxane rubber. In simultaneous IPNs, both of the networks are synchronously synthesized at a similar rate by independent and noninterfering routes. Simultaneous IPN techniques usually prove to be the most convenient, highly efficient, and cost saving. They are key to controlling the formation of two networks at a similar rate. Otherwise polymerization will further enlarge the difference in the hydrophilic/hydrophobic composition and lead to phase separation.

Silicone hydrogels based on the sequential IPN technique have been developed and studied for applications, including diagnostic, therapeutic, and implantable devices, for example, controlled drug-delivery systems, which have been studied extensively;[8–10] contact lenses;[7] and tissue engineering applications.[11] Shimizu et al.[12] prepared silicone hydrogels with interpenetrating poly(2-methacryloyloxyethyl phosphorylcholine) networks, which had a superhydrophilic surface achieved by the surface enrichment of poly(2-methacryloyloxyethyl phosphorylcholine) units. Its optical and mechanical properties are suitable for use as a material for preparing contact lenses. Liu and Sheardown[13] developed IPNs based on poly(dimethyl siloxane) (PDMS) and poly(*N*-isopropyl acrylamide); the networks exhibited good oxygen/glucose permeability and improved wettability compared to the PDMS homopolymer and greater mechanical strength than the poly(*N*-isopropyl acrylamide) homopolymer. However, to date, simultaneous IPN silicone hydrogels have rarely been reported in the literature. Indeed, Wang and Li[14] recently developed a simultaneous IPN silicone hydrogel based on polysiloxane and poly(*N*-vinyl pyrrolidone) by a hybrid free-radical/cationic photopolymerization mechanism, but in this material, the polysiloxane chains were crosslinked through a methacrylate-terminal difunctional PDMS macromer via free-radical polymerization. The assumed formation of two networks was based on the difference in the reactivity ratios for the copolymerization of methacrylate in the PDMS macromere and vinyl in *N*-vinyl pyrrolidone.[15]

In this report, silicone hydrogels with simultaneous interpenetrating hydrophilic/hydrophobic networks were prepared by radical/addition polymerization. This involved an *in situ* strategy, in which hydroxyl-grafted polysiloxane (HPSO) was synthesized, and all of the components were first mixed together, and the networks were then formed more or less simultaneously according to different reaction mechanisms. The polymerization temperature was studied by differential scanning calorimetry (DSC), and the polymerization rate before curing was monitored by *in situ* Fourier transform infrared (FTIR) spectroscopy. To examine the extent of network interpenetration, the thermomechanical properties of the resulting materials were studied by dynamic mechanical thermal analysis. Moreover, the relevant characterizations, including the swelling kinetics and light transmittance, were also observed.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane (D_4), tetramethylcyclotetrasiloxane (D_4H), 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%), isophorone diisocyanate (IPDI), and dibutyltin dilaurate were purchased from Aladdin Industrial Corp. (Shanghai, China). Chloroplatinic acid was purchased from Shanghai Chemical Regent (Shanghai, China). 3-Methacryloxypropyl tris(trimethylsiloxy) silane (TRIS) and DMA were purchased from Sigma-Aldrich. Ethylene glycol dimethacrylate (EGDMA) and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Energy Chemical (Shanghai, China). Dibutyltin dilaurate (DBTDL) was purchased from Kermel Chemical Regent (Tianjin, China).

Synthesis of the HPSO Copolymer

HPSO was synthesized by a ring-opening polymerization and hydrosilylation reaction as described in our previous work.[16] Briefly, a 1.0385-g (0.00775 mol) end capper of 1,1,3,3-tetramethyl disiloxane, 15.76 g (0.0532 mol) of D_4, and 2.25 g (0.0094 mol) of D_4H were dispersed in 30 mL of toluene. After the temperature was increased to 40°C, trifluoromethane sulfonic acid (200 μL) was added, stirred for 24 h under a nitrogen atmosphere, and then washed repeatedly with purified water until the pH of the mixture became neutral. After water was separated, toluene was distilled off under reduced pressure. The residual liquid was dissolved in 20 mL of acetone and then precipitated in 40 mL of methanol; this was followed by the removal of volatile components *in vacuo* to give a transparent liquid polymethylhydrosiloxane (PMHS).

PMHS (10.45 g) and 2-allyloxyethanol (5 g) were dispersed in 25 mL of toluene and heated to 70°C under N_2; this was followed by the dropwise addition of 5 mL of toluene containing 0.0012 g of chloroplatinic acid. The reaction mixture was maintained for 6 h and then washed several times with distilled water. 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 HPSO.

IR (cm^{-1}): 3439 (O—H stretching), 2962 (C—H stretching), 1421 (Si—CH_2 stretching), 1261 (CH_2—O—CH_2 stretching), 1092 (Si—O—Si stretching), and 800 (Si—CH_3 rocking).

Preparation of the Simultaneous Interpenetrating Network Silicone Hydrogels

All of the components were mixed with the formulations, as described in Table I. The mixture was injected into the cavity of the polypropylene plate mold separated by polypropylene frame with a thickness of 0.1 mm and then cured at 80°C for 24 h. IPN silicone hydrogels were obtained as transparent membranes.

Methods and Measurements

NMR Spectra. ^{1}H-NMR spectra were recorded on a 400-MHz instrument (Bruker AC200) with $CDCl_3$ as a solvent.

FTIR Analysis. The IR spectra of HPSO were recorded over the range of 400–4000 cm^{-1} with a Bruker Vector 22 FTIR spectrometer (Germany).

DSC. The DSC curves were registered on a Netzsch DSC 204 F1 Phoenix instrument at a heating rate of 5°C/min under a constant nitrogen flow rate (20 mL/min).

***In Situ* FTIR Spectrometry.** The polymerization ratio before curing was monitored with *in situ* FTIR spectrometry (React IR IC10, Mettler Toledo). The scan region was 4000–650 cm^{-1}.

Gel Fraction (*G*). The IPN silicone hydrogels 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 calculated gravimetrically with the following formula:

Table I. Formulations of the Simultaneous IPN Silicone Hydrogels

	Hydrophobic network (g)			Hydrophilic network (g)			
Sample	HPSO	IPDI	DBTDL	DMA	TRIS	EGDMA	AIBN
1	—	—	—	0.15	0.15	0.0015	0.0015
2	0.1	0.003	0.0003	0.15	0.15	0.0015	0.0015
3	0.2	0.005	0.0005	0.15	0.15	0.0015	0.0015
4	0.3	0.008	0.0008	0.15	0.15	0.0015	0.0015
5	0.4	0.01	0.0010	0.15	0.15	0.0015	0.0015
6	0.5	0.0125	0.0013	—	—	—	—

$$G = 100 \times W_g / W_0$$

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

Swelling Kinetics. The swelling kinetics of the dried discs (three replicates) were estimated as the relative weight gain when the samples were immersed in water at 25°C. The samples were weighed at various times (ts) after the moisture on the surface was carefully sucked up with filter paper. The degree of swelling of the hydrogel sample at time t (Q_t) was calculated as follows:

$$Q_t = 100(W_t - W_0)/W_0$$

where W_0 is the weight of the dry sample and W_t is the weight at time t.

Light Transmittance. The IPN silicone hydrogel membranes were cut into 10 × 40 mm^2 strips and attached to the inner surface of a quartz colorimetric cuvette that was full of distilled water. The transmittance of the hydrogel membranes were recorded at a wavelength between 200 and 800 nm with an ultraviolet–visible spectrophotometer (Helios, Thermo Electro), with distilled water as a reference solution.

Dynamic Mechanical Thermal Analysis. The dynamical mechanical behavior of the samples was followed on a Tritec 2000 (Triton Technology) instrument with 10 × 20 mm^2 rectangular bars in single-cantilever bending mode. The storage modulus (E') and loss factor (tan δ) were registered as a dependence on the temperature ranging from −100 to 200°C at a 5°C/min heating rate at a frequency of 1 Hz.

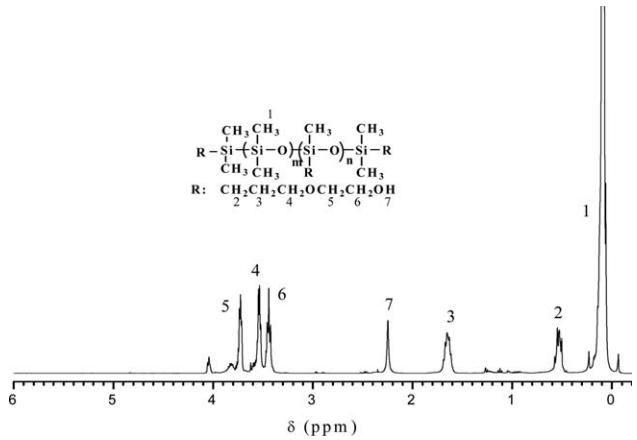


Figure 1. ^{1}H-NMR spectra of HPSO in $CDCl_3$.

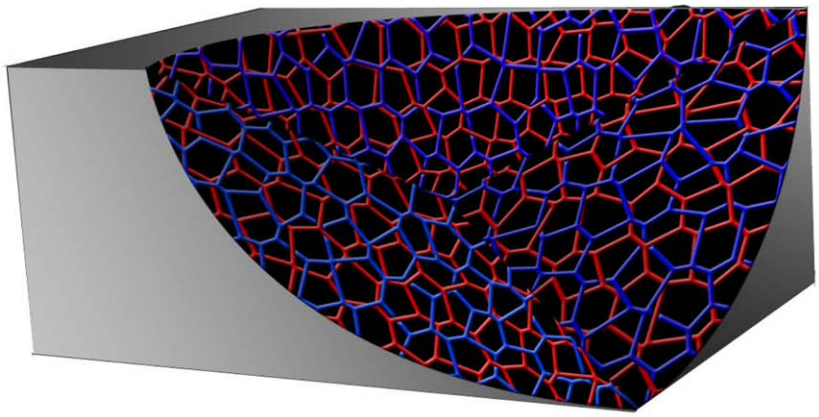
RESULTS AND DISCUSSION

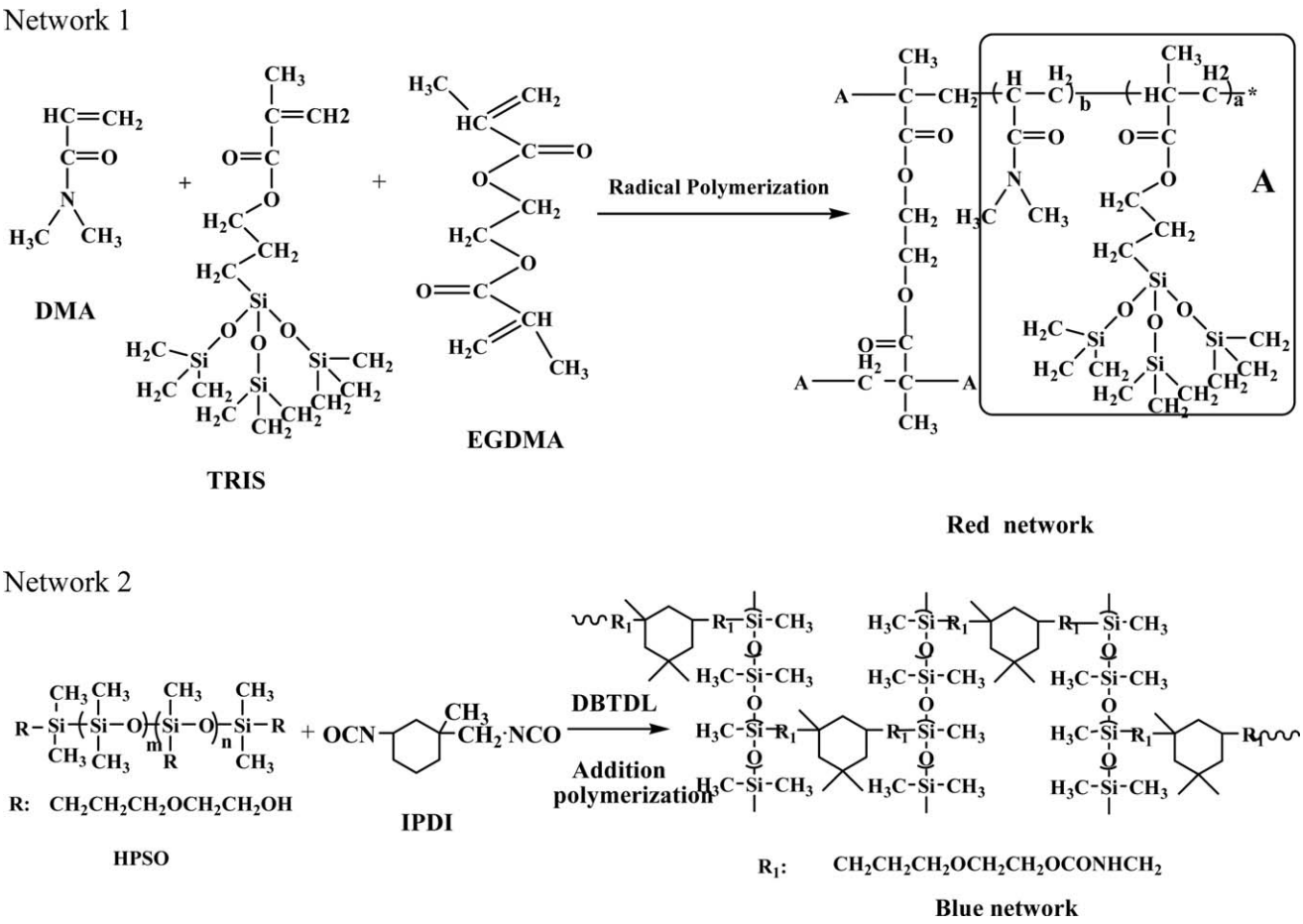
Synthesis of the HPSO Copolymer

HPSO was synthesized by a ring-opening polymerization and hydrosilylation reaction.[16] The ^{1}H-NMR spectra, as shown in Figure 1, clearly indicated that the hydroxyl-grafting polysiloxane copolymer was successfully synthesized. The peak area corresponding to the methyl group connecting to silicone in the ^{1}H-NMR spectra was 29.5, with the area of peak 5 as a reference. So, the average number of the dimethyl siloxane unit in the PMHS copolymer was about 27, and the average number of the Si—R unit was about 1. Therefore, the weight average molecular mass of the HPSO copolymer was about 2480.

Preparation of the Simultaneous IPN Silicone Hydrogels

Silicone hydrogels have widely used as biomaterials, especially for contact lenses, in which the hydrophilic compositions, usually from the polymerization from the monomer of DMA,[17] help to accelerate the percolation of water, and the hydrophobic segments of polysiloxane provide the needed high oxygen permeability essential for the healthy eye.[18] Additionally, small molecular silicon monomer of TRIS is usually copolymerized in the silicone hydrogel contact lens network to maintain oxygen permeability and reduce the modulus of the final polymer.[19] Therefore, we chose DMA and TRIS as methacrylic monomers to form the hydrophilic network and polysiloxane for the hydrophobic network to prepare IPN silicone hydrogels. The hydroxyl-grafted siloxane had good compatibility with TRIS and DMA. The assumed curing mechanism is summarized in Scheme 1. AIBN was used as the initiator for the radical polymerization of the methacrylic monomers (DMA, TRIS, and crosslinker of EGDMA) and dibutyltin dilaurate (DBTDL) was used as a catalyst for the addition polymerization of HPSO and IPDI. HPSO was a hydrophobic polymer, and DMA was a hydrophilic monomer. Therefore, it was key to control the formation of two networks at a similar rate. Otherwise, the polymerization of HPSO and DMA further enlarged the difference of the hydrophilic/hydrophobic composition and, therefore, led to phase separation. The temperature is an important parameter for thermocuring; it influences the curing rate of radical/addition polymerization. Here, the curing temperature was studied by DSC, and the results are shown in Figure 2. IPDI had two isocyanate groups connecting the primary and secondary





Scheme 1. Curing process of the simultaneous interpenetrating silicone hydrogel networks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carbons, respectively. The one on the primary carbon showed a greater reactivity than that on secondary carbon because of steric effects.[20] Therefore, as shown in Figure 2, the chemical reaction of HPSO and IPDI exhibited two endothermic peaks at 43.3 and 62.5°C in the presence of the catalyzer DBTDL, whereas DMA/TRIS/EGDMA/AIBN showed an exothermic peak at 96°C, which was assigned to the maximum polymerization enthalpy of the methacrylic groups from the monomers. Moreover, the exothermic peak from DMA/TRIS/EGDMA/AIBN was higher and narrower than the endothermic peak from HPSO/IPDI. All of the difference, the values of the temperatures, and the peak shape corresponding to the endothermic/exothermal peaks were due to the mechanisms of reaction in the two cases. The addition polymerization of HPSO and IPDI reacted step by step at a lower reaction temperature, and the methacrylic monomer polymerized rapidly once enough radicals emerged. The IPN polymerization solution showed three distinct peaks corresponding to addition and radical polymerization, and the peak of radical polymerization appeared to be slightly shifted from 96 to 106°C. This was due to the dilution effect of the

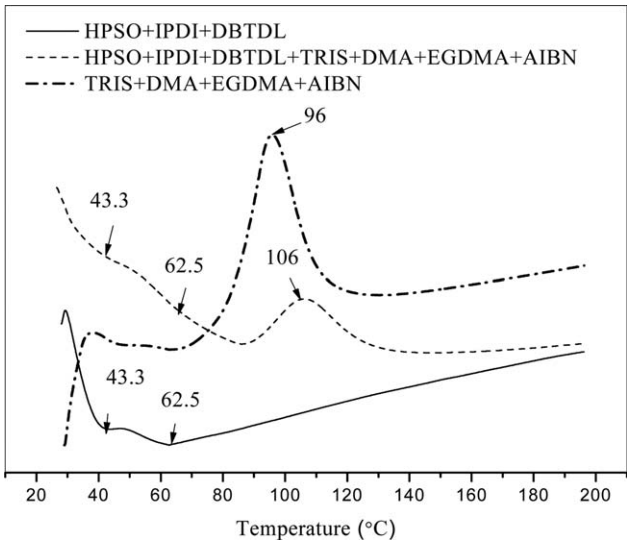


Figure 2. DSC curves of the pure hydrophilic network, hydrophobic network, and IPN systems.

reactants. The starting point of the three peaks was lower than 80°C; therefore, in this study, 80°C was used as the curing temperature for the preparation of the IPN silicone hydrogels.

The radical/addition polymerization rate in the IPN solution before curing was monitored by *in situ* FTIR spectroscopy, and the result is shown in Figure 3. Radical/addition polymerization was initiated simultaneously, and the addition polymerization had a faster polymerization rate than the radical polymerization before the IPN hydrogel was formed. The absorbance of isocyanate groups at a wave number of 2265 cm^{-1} dropped from the initial 0.139 to 0.102 at a polymerization time of 4.5 min, and the double bond of methacrylic monomer at 1619 cm^{-1} [21] dropped from 0.399 to 0.345. Therefore, the convergent ratio of isocyanate groups was about 26.6%, and the double bonds were about 13.5% before curing. Furthermore, the rate of radical/addition polymerization was determined in the absence of the initiator AIBN and crosslinker IPDI/catalyst DBTDL. The curing hydrogel was also obtained at about 4.5 min for radical polymerization, and the hydrogel was opaque ones. The addition polymerization had a longer curing time of about 31 min, and the obtained hydrogel was transparent, as shown in Figure 3(B). This indicated that the curing of the IPN solution was mainly due to the radical polymerization of the methacrylic monomer, and this prolonged curing time may have been a way to obtain the transparent IPN silicone hydrogel. Moreover, the convergent ratio of isocyanate groups in the absence of initiator (AIBN) of radical polymerization was about 27.1%, that is, almost same as that in the IPN solution (26.6%). This indicated that the radical polymerization of the methacrylic monomer hardly influenced the addition polymerization before 4.5 min of curing. The whole IR spectra between 650 and 4000 cm^{-1} of the addition polymerization is shown in Figure 3(C). The IR absorbance of the methacrylic monomer showed no change during the time of the addition polymerization of 31 min. This indicated that the IPDI molecular could not react with the methacrylic monomer, so the two networks of the hydrophilic/hydrophobic ones were formed by independent and noninterfering routes.

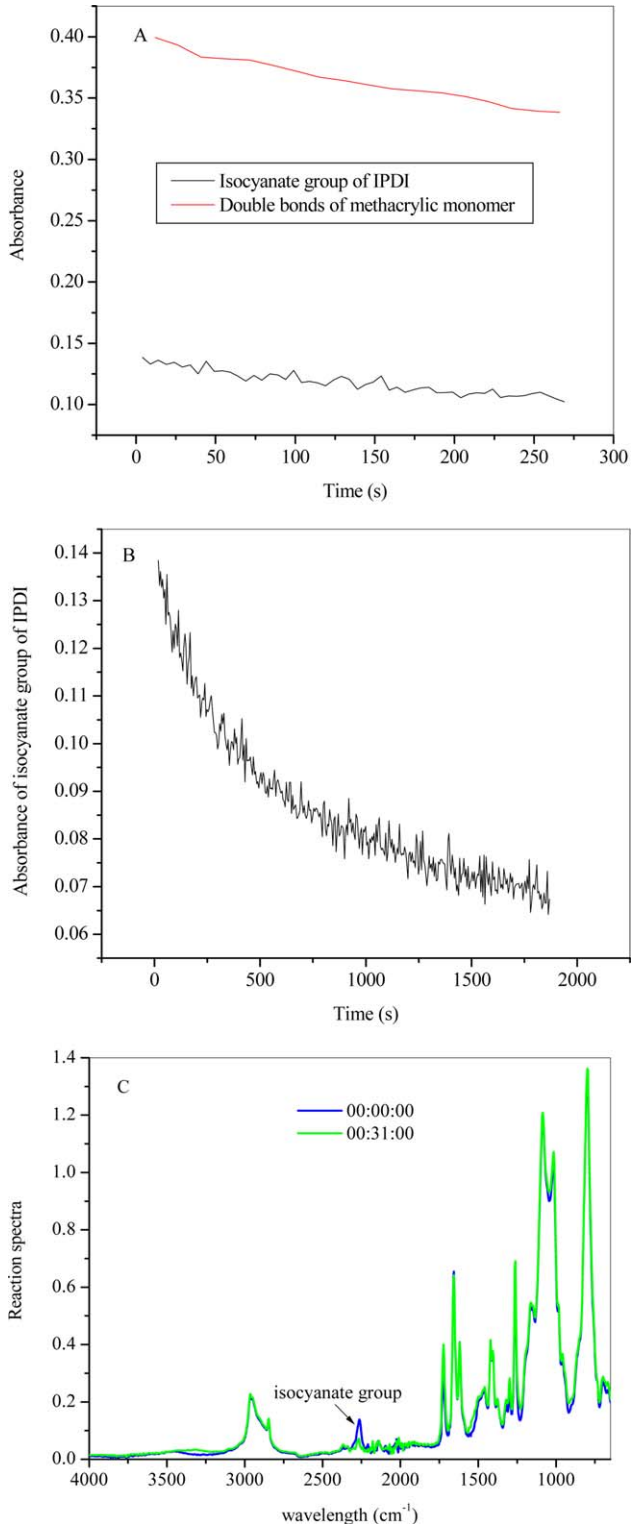


Figure 3. Absorbance changes determined by *in situ* FTIR spectroscopy: (A) isocyanate group of the IPDI and double bonds of methacrylic monomer in the polymerization process of the IPN solution, (B) isocyanate group of IPDI in the addition polymerization process of the IPN solution without the AIBN initiator for radical polymerization, and (C) initial/final FTIR spectra in the addition polymerization process of the IPN solution without the AIBN initiator for radical polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. *D* into the IPN Silicone Hydrogels

Sample	*D* (m^2/s, $\times 10^{-8}$)
1	2.01
2	0.86
3	0.19
4	0.21
5	0.30

HPSO was soluble in acetone. Therefore, after 12 h of curing, the IPN silicone hydrogel was extracted for 24 h with acetone in a Soxhlet extractor. The *G* values corresponding to samples 1–6 were obtained and are listed in Table II. The pure copolymerization hydrogel of TRIS, DMA, and the polysiloxane network had the highest and lowest *G* compared to the IPN hydrogels. This indicated that the polymerization efficiency of radical polymerization was higher than that of the addition polymerization of HPSO and IPDI. The *G*s of all of the IPN silicone hydrogels were over 80%. This indicated that the formation of the cross-linked hydrophilic network hindered the reaction between hydroxyl connections on HPSO and isocyanate groups on IPDI.

Characterization of the Simultaneous IPN Silicone Hydrogels

Water transport through hydrogel membranes is an importance parameter for soft contact lenses.[22] Too-rapid water transport will enable the lens capture the postlens tear film in the evaporative–dehydration process and, therefore, will lead to corneal desiccation[23,24] and even lens adherence to the cornea.[25] The swelling kinetics of the IPN silicone hydrogels was determined, and the results are shown in Figure 4. All of the hydrogels reached equilibrium swelling at about 4 h once they were immersed in water. The IPN silicone hydrogels with a hydrophobic network of polysiloxane indicated a slower water transport than the copolymerization hydrogel of DMA and TRIS. Pure polysiloxane rubber is a highly hydrophobic material that cannot swell in water. The addition of the hydrophobic network of polysiloxane to the fixed hydrophilic network of poly[3-methacryloxypropyl tris(trimethylsiloxy) silane–*N*,*N*-dimethylacrylamide] decreased the water content of the IPN hydrogel, and the more hydrophobic the network was, the lower the water content was.

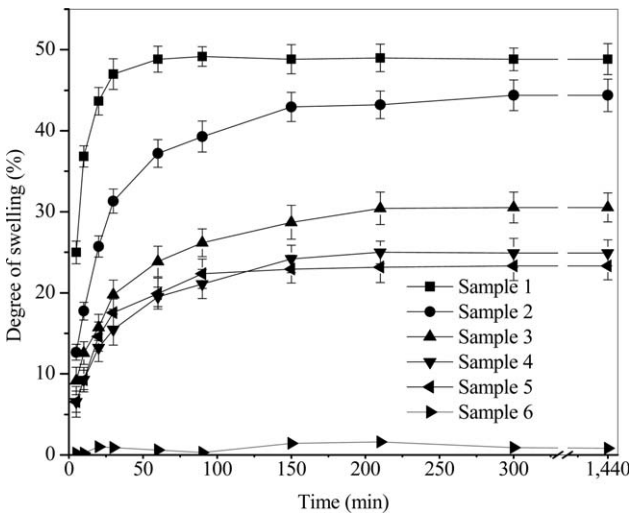


Figure 4. Curve of R_D versus time of the IPN silicone hydrogels immersed in water.

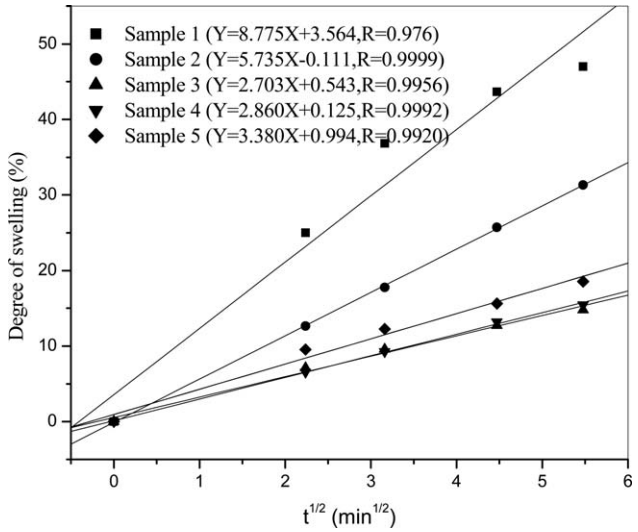


Figure 5. Plot of the linear regression of R_D of water into the IPN silicone hydrogels versus the square root of swelling time ($t^{1/2}$).

The swelling degree of the hydrogels (R_D) in water could be fit to the Higuchi equation in the initial short time limit, as follows:

$$R_D(\%) = \sqrt{\frac{4Dt}{\pi h^2}} \times 100$$

where *D* is the diffusivity of water into the hydrogels, and *h* is the half-thickness of the hydrogels.

According to equation, we calculated *D* by carrying out a linear regression for the original R_D versus $\sqrt{t}$. The fitted results are shown in Figure 5. The slope of the plot was used to obtain *D*, and the calculated value of *D* is shown in Table II. The initial R_D in water fit the Higuchi equation well. *D* into the IPN

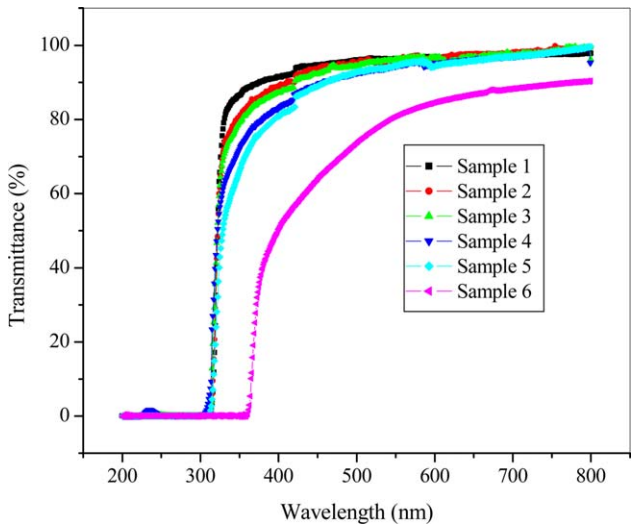


Figure 6. Transmittance of the hydrated IPN hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

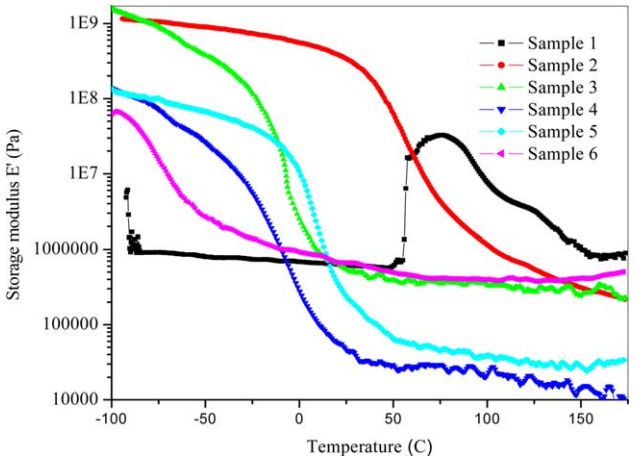


Figure 7. E' of the cured IPN silicone hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

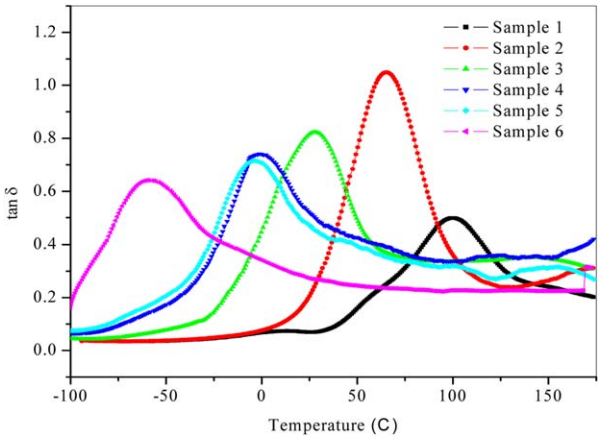


Figure 8. Tan δ relaxation of the cured IPN silicone hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogels was lower than that of the hydrogel from copolymerization of TRIS and DMA. This could be ascribed to the migration of the hydrophobic polysiloxane chain to the surface of the IPN hydrogel, and this hindered *D*.

The transmittance of the swollen silicone hydrogels is shown in Figure 6. It seemed that the increase in the hydrophobic network of polysiloxane slightly decreased the transmittance at wavelengths between 310 and 500 nm. The transmittance of the pure polysiloxane network was lower than the IPN silicone hydrogel, especially at wavelengths between 300 and 400 nm. This may have been due to phase separation because the HPSO possessed a hydrophilic segment from the hydrosilylation reaction of 2-allyloxyethanol on the side chain. All of the IPN silicone hydrogels had good transmittance in the visible light region. This revealed that the two networks of the hydrophilic and hydrophobic ones had homogeneous phase structures.

The E' and tan δ values for a series of IPN silicone hydrogels with different proportions of the hydrophobic network of polysiloxane are shown as a function of the temperature in Figures 7 and 8. From the viscoelastic spectra, several parameters, E', rubbery modulus (E'_r), glass-transition temperature (T_g), and amplitude of the damping peak [$(\tan \delta)_{max}$], were determined and are listed in Table III. E' of the copolymerization network of DMA and TRIS was about 1.0×10^6; this increased to 1.58×10^9 when the addition of the hydrophobic network from HPSO/IPDI was about 25.6 wt % of the total monomers (sample 3); it then gradually dropped to 0.13×10^9 when the amount of the hydrophobic network of HPSO increased to 57.6 wt % (sample 5). The pure polysilicone network had the lowest E' among all of the silicone hydrogels. Moreover, it was interesting to note that the copolymerization hydrogel of TRIS and DMA (sample 1) was an exception to the E' trend; that is, it had the lowest E', which showed little change in the glassy state and then increased rapidly to a peak near T_g. The addition of the hydrophobic network decreased T_g, and the greater the addition of the hydrophobic network was, the lower the T_g was. Even the T_g of the pure hydrophobic network was at -59°C. These observations could be explained by the flexibility of the siloxane chain in the IPN silicone hydrogel; this decreased the friction force between the network of addition polymerization and the network of radical polymerization.

We assumed that the effect of the internal energy of the formed network could be neglected above T_g, and by relating the changes in entropy, we could thus express the variation in E'_r as a function of the crosslinking density with the following relationship:

$$E'_r = 3\theta RT/M_c$$

where R is the gas constant, T is the absolute temperature, ρ is the density of the crosslinked network, θ is the front factor, and M_c is the average molecular weight between crosslinks.

Table III. DMA Characteristics and Gs of the IPN Silicone Hydrogels

Sample	E' (Pa)	E'_r (Pa)	$(\tan \delta)_{max}$	T_g (°C)	G (%)
1	1.0×10^6	7.06×10^5	0.50	100.08	93
2	1.15×10^9	5.94×10^5	1.05	65.17	89
3	1.58×10^9	1.56×10^5	0.82	27.57	86
4	0.17×10^9	2.18×10^4	0.74	−1.17	81
5	0.13×10^9	9.88×10^4	0.72	−3.78	83
6	0.07×10^9	6.37×10^5	0.64	−58.85	79

$E'_r = T_g + 30$°C. T_g was the temperature corresponding to $(\tan \delta)_{max}$.

The previous 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, increasing the proportion of the hydrophobic network in the IPN silicone hydrogel decreased the value of E'_r for samples 1–4; it then increased when the hydrophobic network continued to increase. This result shows that the crosslinking density of the hydrophobic network was lower than that of the hydrophilic network from the copolymerization of TRIS and DAM at a low hydrophobic network proportion than at a higher proportion. This may be attributed to the reason that the curing of the methacrylate monomer of TRIS and DMA hindered the crosslinking of the addition polymerization of HPSO and IPDI. When the hydrophobic proportion was higher than 50.5 wt % (sample 4), the influence of the curing hydrophilic network on the polymerization of the hydrophobic network decreased.

The loss spectra (tan δ vs temperature, Figure 8) of the IPN silicone hydrogel decreased with increasing hydrophobic network, and all of the maxima of tan δ were less than 1, except for in sample 2. This indicated that samples 1 and 3–6 had E' values that were higher than the loss modulus (E''). The IPN silicone hydrogel samples exhibited a single T_g. This indicated that the hydrophobic network of siloxane domains did not separate from the continuous network formed from the polymerization of the methacrylic monomers of TRIS and DMA.[26]

CONCLUSIONS

HPSO soluble with the methacrylic monomer of TRIS and DMA was synthesized, and simultaneous IPN silicone hydrogels were successfully prepared by radical/addition polymerization. At a curing temperature of 80°C, the addition polymerization showed a faster reactive rate than radical polymerization before 4.5 min; then, the radical polymerization rate increased rapidly and led to curing. In the IPN hydrogels, the hydrophobic network was finely dispersed in the hydrophilic network. The hydrated IPN silicone hydrogels showed a high light transmittance. Thus, the simultaneous IPN based on radical/addition polymerization may be an effective method for preparing silicone biomaterials because the siloxane macromer (HPSO) can be synthesized more easily than the conventional methacrylate-functionalized siloxane macromer.

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