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Polyvinylpyrrolidone–polydimethylsiloxane amphiphilic co-networks: Synthesis, characterization, and perm-selective behavior

Li Zhang, Xinzhen Zhao, Dapeng Liu, Haiye Wang, Chunju He

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, 2999 North Renmin Road, Songjiang District, Shanghai, 201620, People's Republic of China

Correspondence to: C. He (E-mail: chunjuhe@dhu.edu.cn)

ABSTRACT: An amphiphilic co-network (APCN) membrane has been synthesized through end-crosslinking of amphiphilic grafts of polyvinylpyrrolidone (PVP) backbone carrying polydimethylsiloxane (PDMS) branches fitted with terminal vinylsilyl groups via free radical polymerization. The synthesis strategy has been carried out by the free radical polymerization of N-vinylpyrrolidone (VP) with methacrylate allyl terminated polydimethylsiloxane (MA-PDMS-V) and dimethacrylate terminated polydimethylsiloxane (MA-PDMS-MA) to form a soluble graft consisting of PVP main chains carrying vinyl terminated PDMS branches, which is crosslinked with polymethylhydrosiloxane through hydrosilylation. The resulting APCN membrane exhibited a combination of unique properties, that is, high transparency, high mechanical properties, and high permeation rate to inulin. Notably, the mechanical properties and inulin permeability of fabric-support APCN membrane were higher than that of pure APCN membrane. As a result of their unique performance, the resulting APCN membranes showed a wide range of potential applications in drug release vectors, soft contact lenses, and biomedical separation materials. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42985.

KEYWORDS: amphiphilic conetwork; membrane; polymethylsiloxane; polyvinylpyrrolidone; semi-permeability

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INTRODUCTION

Amphiphilic co-network (APCN),[1–5] which is composed of hydrophilic and hydrophobic units through covalently interlinking into a three-dimensional (3D) structure, becomes the forefront of polymer science research due to its potential application in many advanced areas, such as intelligent polymer materials,[2] antifouling surface,[3] biomedical materials,[4] and drug-controlled release matrices.[5]

In recent years, the commonly reported APCN, usually consists of polyisobutylene (PIB),[6,7] polydimethylsiloxane (PDMS),[8,9] and various polyacrylates[10,11] as hydrophobic segments. Particularly, PDMS has attracted great attention due to its own characteristics, that is, excellent biocompatibility, high elasticity, heat resistance, low surface free energy, biological inertness as well as the highest oxygen permeability among all the polymers,[12–14] which has been widely associated with other hydrophilic units into block and graft copolymer,[15] so-called PDMS-based amphiphilic copolymer that can further crosslink into PDMS-based APCN.[16] In addition, PDMS-based APCN exhibits channel type structure to allow rapid diffusion of both water and oxygen,[17,18] which has potential application in the area of biocatalysis,[19] ophthalmic applications,[20] soft contact lenses,[21] and especially coating material for islet encapsulation.[22,23] Although one of the most commonly hydrophilic segments used in APCN fabrication is polyethylene glycol (PEG)[24,25] due to its low biotoxicity and well biocompatibility, the PEG segment is prone to oxidative degradation as indicated from accelerated air/moisture degradation tests,[26] which limits its further practical applications. Hydrophilic polyvinylpyrrolidone (PVP) gains much attention due to its physiologically inert, hydrolytic stable, excellent biocompatibility, and safe to human body, which is widely used in the areas of medicine, cosmetics, food packing, and health care.[27–29]

PDMS/PVP typed of polymeric materials have also been reported via surface initiated atom transfer radical polymerization (ATRP),[30] thermodynamical approach,[31] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[32] Although the controlled radical polymerization techniques, that is, ATRP and RAFT polymerization, have been applied in polymeric materials fabrication,[12,24,33] both of them have high selectivity to the monomers, initiators, or chain transfer agents as well as rigorous reaction condition, which limit their application scope. Whereas, the free radical polymerization has the advantages that is suitable for a wide range of monomers and can be used in various media, which provide a convenient and facile method to synthesis a variety of different copolymer

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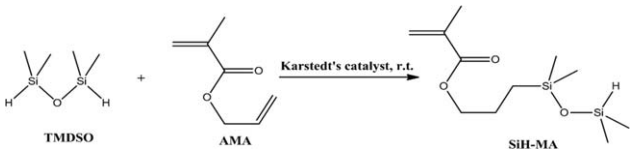


Scheme 1. Synthesis of the end-functionalizing agent SiH-MA.

architectures.[34] Therefore, it is of great interest to fabricate an APCN membrane consisting of PDMS and PVP segments via free radical polymerization. To our knowledge, APCN containing PDMS and PVP has seldom been reported and this is the first attempt to study it.

Our previous work proves that PVP–PDMS polymer conetworks could be synthesized,[35] whose mechanical properties, swelling behavior, and ratio were not satisfactory. In recent years, amphiphilic grafts of PVP backbone carrying PDMS branches fitted with terminal vinylsilyl groups via free radical polymerization were crosslinked into APCN with controllable swelling behavior, good mechanical properties, micro-phase separated morphology as well as favorable inulin permeability, which has potential application in soft contact lenses, drug delivery, and semipermeable membrane for cell encapsulation and immuoisolation of living tissues.

EXPERIMENTAL

Materials

Allyl methacrylate and tetramethyldisiloxane were supplied by Shanghai Jiachen Chemical Co., Ltd. Vinyl-ditelechelic polydimethylsiloxane (V-PDMS-V, $M_w = 17{,}000$ g/mol), polymethylhydrosiloxane (PMHS, $M_w = 2000$ g/mol) and Karstedt's catalyst [3% (wt %) Pt (0) in xylene, low color] were provided by Gelest. N-vinylpyrrolidone was supplied by Wenzhou Ouhai Fine Chemicals Co. Inulin ($M_w = 5184$ g/mol, 99%) and phosphate buffer solution (PBS, pH = 7.4) were supplied by Sigma-Aldrich. All other reagents unless specially stated were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification.

Polymerization

Synthesis of 2-Propenoic Acid-3-(1,1,3,3-tetra-methyldisiloxanyl) Propyl Ester (SiH-MA). Tetramethyldisiloxane (TMDSO, 13.4 g, 0.1 mol) and allyl methacrylate (AMA, 12.6 g, 0.1 mol) were added to a round-bottom flask equipped with a stirring bar and placed in an oil bath at room temperature. The reaction was induced by the addition of Karstedt's catalyst (70 μL) for 3 h. The charge was vacuum distilled (30–50 mbar) at 39°C. And the colorless product was rectified on a spinning band column (70 plates, 0.25 mbar) with purity over 98% determined by GC. Yield: 10.40 g (40%). The process was shown in Scheme 1.

Synthesis of Methacrylate Allyl Terminated Polydimethylsiloxane (MA-PDMS-V). V-PDMS-V (4.0 g, 0.28 mmol), SiH-MA (74 mg, 0.28 mmol), and toluene (toluene) were placed in a 100 mL Erlenmeyer flask. The reaction was started by adding 70 μL Karstedt's catalyst and the charge was heated at 50°C for 1 h. The components of the charge were not separated, which were used for the preparation of the grafts. ^{1}H NMR was applied to analyze the product, which showed MA/PDMS = 1.0, proving an average MA functionality of 1.0.

Synthesis of Graft Consisting of PVP Main Chain Carrying Vinyl Terminated PDMS Branches [PVP (PDMS)]-g-PDMS-V. In a 250 mL Erlenmeyer flask were placed anhydrous THF (20 mL), freshly distilled NVP (5 g, 45.05 mmol) and the mixture of MA-functionalized PDMS (MA/PDMS = 1.0, 5 g in 12 mL toluene). After the flask was deaerated via sparging with N_2 for 20 min, AIBN (7.5 mg, 0.036 mmol) was added, and the charge was heated at 65°C for 5 h, respectively. The bulk of solvent was evaporated under reduced pressure and washed by proper amount of methanol. After drying under vacuum at 70°C for 2 days, a brittle and white material was obtained. Yield: 9.3 g (93%).

Synthesis of Pure Conetwork. [PVP (PDMS)]-g-PDMS-V (0.93 g) and PMHS (0.66 g, 0.33 mmol) were dissolved in $CHCl_3$ before 150 μL Karstedt's catalyst was added. The mixing solution was poured into a Teflon mold (10 × 10 cm) and kept in an oven for curing at 60°C overnight. The product was removed from the mold, exhaustively extracted by $CHCl_3$ (3 × 500 mL/day), and dried under vacuum at room temperature. The resulting membrane was colorless, optically clear, and flexible membrane.

Synthesis of Fabric-Support Conetwork. [PVP (PDMS)]-g-PDMS-V (0.93 g) and PMHS (0.66 g, 0.33 mmol) were dissolved in $CHCl_3$ and 150 μL Karstedt's catalyst was added to the solution at room temperature. The mixing solution was sprayed on a piece of non-woven fabric (10 × 10 cm) and kept in an oven for curing at 60°C overnight. The resulting fabric-support APCN membrane was removed from the mold, exhaustively extracted by $CHCl_3$ (3 × 500 mL/day), and dried under vacuum at room temperature. The resulting fabric-support APCN membrane was colorless and flexible.

Methods

Proton nuclear magnetic resonance (^{1}H NMR) was performed on an Avance 400-MHz Instrument (Bruker, Germany) at 21°C with deuterated chloroform ($CDCl_3$) as the solvent.

Gel permeation chromatography (GPC) eluograms were carried out by a Waters GPC instrument equipped with a series of six Waters Styragel columns (HR 0.5, HR 1, HR 3, HR 4, HR 5, and HR 6), a refractive-index detector (Optilab, Wyatt Technology), a dual ultraviolet absorbance detector (model 2487, Waters), a laser light scattering detector (Minidawn, Wyatt Technology), and a viscometer (Viscostar, Wyatt Technology). The samples were dissolved in THF (chromatography purify, CP) and filtrated before conducting with a 0.2 μm Nylon filter. The GPC traces were then obtained at 35°C by using THF (CP) as the eluent at a flow rate of 0.8 mL/min with a polystyrene standard as the reference.

Atomic force microscopy (AFM) (E-SWEEP, Seiko, Japan) was applied for imaging the micro-phase separation of APCN membranes. The scanning was operated in tapping mode with a scan rate of 1 nm/s and scan area of 500 × 500 nm.

Light transmittance of APCN membranes, either in dry or swollen state, was determined by the photoelectric haze instrument (KEXIN, WGW, China), where air was used as the reference.[36] Each sample was tested on five different spots to calculate its average value.

Tensile strength and elongation at break were measured by Universal Testing Machine (KEXIN, WDW3020, People's Republic of China). Samples were made into rectangle (6 × 2 cm) and tensile speed was set at 10 mm/min. Each sample was measured three times and the average value was obtained. The error was less than 5%.

Swelling Measurements

The soluble content (Sol) of NVP and PDMS was recorded at room temperature when the weight of APCN membranes remained unchanged after extracting with $CHCl_3$ for several times. The following equation was used to express the data[37]:

$$\mathrm{Sol}=\frac{m_{\mathrm{dry}}-m_{\mathrm{ex}}}{m_{\mathrm{dry}}}\times 100\% \quad (1)$$

where m_{ex} is the mass of dry APCN membranes after extracting in $CHCl_3$ and m_{dry} is the original mass of the dry APCNs membrane.

Swelling measurements were performed at room temperature by immersing preweighed samples in excessive distilled water. The swelling extent was measured by periodically moving samples from water, removing the water absorbed to the surface by blotting with tissue paper, and weighing. When the weight of the swollen samples remained unchanged for 24 h, the equilibrium water swelling of APCNs (S_w) was recorded. Following equation was used:

$$S_w=\frac{m_{\mathrm{sw}}-m_{\mathrm{dry}}}{m_{\mathrm{dry}}} \quad (2)$$

where m_{sw} is the mass of water swollen APCN membranes and m_{dry} is the mass of dry APCN membranes after extraction.

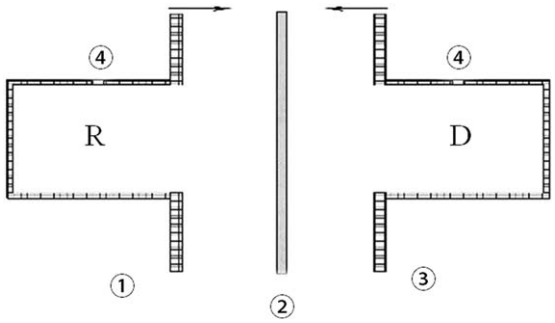
Permeability Performance

Permeability constant to inulin was determined at 37°C by the equipment shown in Scheme 2. Briefly, APCN membrane samples were fixed between two chambers (2 mL), which were marked as D (donor) and R (receiver), respectively. The diffusion area was about 2 cm^2 and the systems were mixed at 100 rpm to wipe off the boundary layer effect. Inulin in PBS buffer (490 μg/mL) was moved to chamber D, while chamber R was placed with PBS buffer. Aliquots were withdrawn from sampling ports at time intervals to detect their current concentration, which was determined by a UV-1800 Spectrophotometer at $\lambda = 620$ nm (SHIMADZU).

Permeability value (P) and diffusion index (D) of APCN membranes can be calculated via eqs. (3) and (4), respectively.[38]

$$\frac{V_2+V_1}{V_2V_1}\cdot\frac{AP}{\delta}=-\ln\left[1-\left(\frac{V_2+V_1}{V_1}\right)\frac{C_r}{C_{d0}}\right] \quad (3)$$

where P, permeability, cm^2/s; δ, thickness of APCN membranes; V_1, volume of permeating solution, cm^3; V_2, volume of buffered solution, cm^3; A, effective permeating area, cm^2; t, permeating time, s; C_r, current concentration in receiver chamber, mg/mL; C_{d0}, original concentration in donor chamber, mg/mL.



Scheme 2. Equipment for permeability test. ①, ③ PTFE chambers; ② APCN membranes; ④ sampling ports.

$$D=\frac{\delta^2}{3t_B} \quad (4)$$

where D, diffusion coefficient; and t_B, burst time.

RESULTS AND DISCUSSION

Synthesis Strategy

Figure 1 helps to visualize the synthetic strategy, the starting materials, and the microstructure of the products. The first step is hydrosilylation of commercially available V-PDMS-V by SiH-MA at a stoichiometric ratio of 1:1 in the presence of Karstedt's catalyst. The reaction produces a statistical three component mixture consisting of MA-PDMS-V (50%, mol %, the macromonomer), MA-PDMS-MA (25%, mol %, the first crosslinker), and unreacted starting material V-PDMS-V (25%, mol %, the second crosslinker). All three moieties are needed and will be utilized during the following steps without further purification. The second step is a free radical terpolymerization of vinylpyrrolidone with MA-PDSM-V and MA-PDMS-MA to yield a high molecular weight slightly crosslinked soluble graft consisting of PVP main chains carrying vinyl terminated PDMS branches. The vinylsilyl termini do not copolymerize with MA groups, so the product remains soluble. The terpolymerization is controlled below the gel point by controlling the molecular weight of the terpolymer. The synthesis is simple and efficient due to the formation of soluble graft of a PVP backbone carrying vinyl terminated PDMS branch, which combines the thermodynamic incompatible hydrophilic PVP segments with hydrophobic PDMS segments. The pendant vinylsilane groups in the resulting amphiphilic grafts are co-crosslinked to yield the target APCN membrane by hydrosilylating with polydimethylhydrosiloxane in the presence of the second crosslinker V-PDMS-V. The amount of PMHS is slightly excessive to ensure the effective crosslinking. And the Si—H in PMHS residual is transformed into Si—OH in the presence of trace amount of moisture to ensure the full crosslinking without dangling linear polymer chain. Therefore, trace amount of moisture is necessary to ensure the full crosslinking of the whole process. The APCN membrane is optically clear, indicating the absence of massive phase coalescence, while the sol content keeps at a low level, which is less than 10% (wt %) after complete swelling in $CHCl_3$, indicating an effective crosslinking.

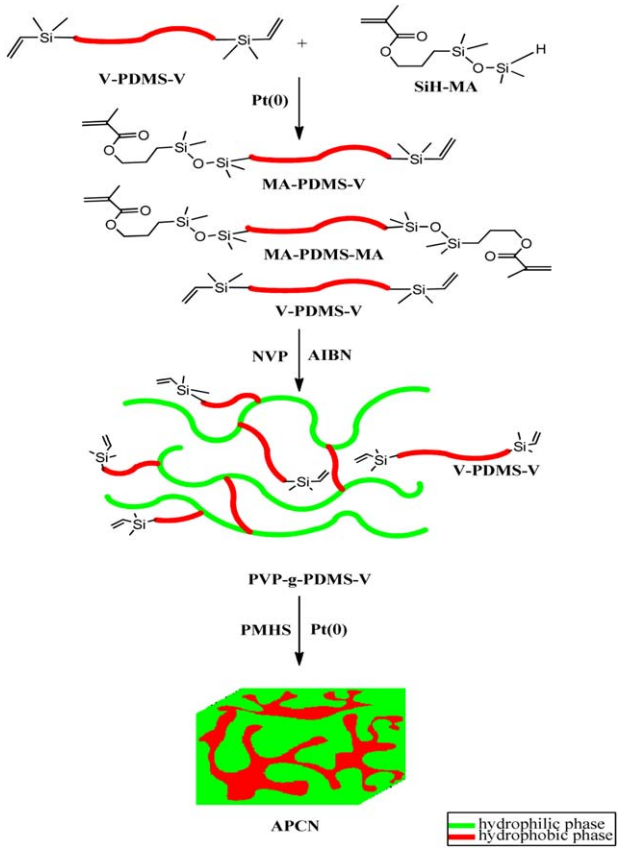


Figure 1. Synthesis strategy of APCN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The amphiphilic character of this network is more stable than that of prior interpenetrating polymer network (IPN) consisting of PDMS and PVP because excessive PVP has to be covered on the PDMS surface in later method, which is easily dissolve in water, leading to unstable hydrophilicity. Besides, as IPN is not fully crosslinked inside by chemical bonds, the thermal incompatibility of segments cannot be overcome, forming a more heterogeneous and larger domain size.[31]

Synthesis of SiH-MA

Our strategy begins with the synthesis of SiH-MA, which converts V-PDMS-V to MA-PDMS-V and MA-PDMS-MA. The ^{1}H NMR spectrum in Figure 2 shows a multiplet at 4.67 ppm, indicating the presence of SiH group, and the characteristic resonances at 6.11 and 5.55 ppm (for the olefinic) and 1.9 ppm (for the methyl protons) are associated with the MA group. All of these verify the successful synthesis of SiH-MA.

^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.00 (m, 6H), 0.15 (s, 6H, —$Si(CH_3)_2$), 0.6 (t, 2H, —CH_2), 1.73 (m, 2H, —CH_2), 1.90 (q, 3H, =$CH(CH_3)$), 4.12 (t, 2H, —CH_2), 4.67 (m, 2H, =CH_2), 5.55 (m, H, =CH_2), 6.11 (m, H, =CH_2).

Synthesis of MA-PDMS-V

MA-PDMS-V is obtained by the hydrosilylation of V-PDMS-V with SiH-MA at a molar ratio of 1:1. The product is a statistical mixture of MA-PDMS-MA, MA-PDMS-V, and unreacted V-PDMS-V. Figure 3 shows the ^{1}H NMR spectrum of the mixture,

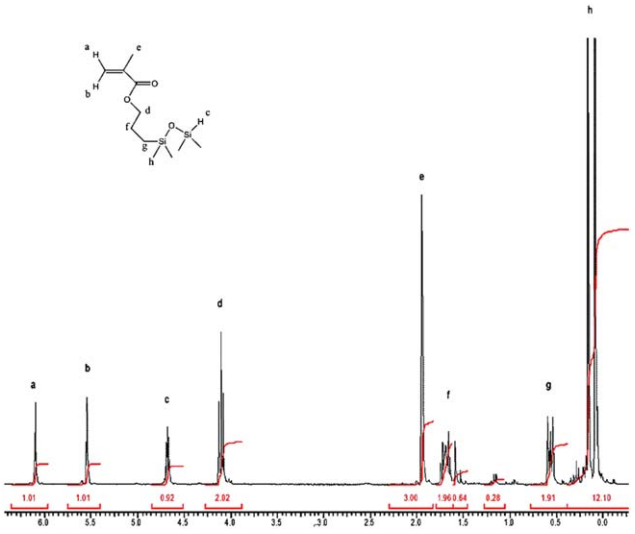


Figure 2. ^{1}H NMR spectrum of SiH-MA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which identifies the resonances characteristic of both the MA groups (a, d, f protons). The resonance associated with the SiH proton (4.67 ppm) completely disappears, while the resonances for the CH_2 protons appear at 0.4 ppm (i, protons) after the hydrosilylation of vinyl groups in PDMS with SiH-MA, suggesting the successful synthesis of MA-PDMS-V.

^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.00 (m, 6H), 0.08 (s, 6H, —$Si(CH_3)_2$), 0.43 (t, 2H, —CH_2), 0.598 (t, 2H, —CH_2), 1.87 (m, 2H, —CH_2), 1.98 (q, 3H, —CH_3), 4.67 (t, 2H, —CH_2), 5.57 (m, 2H, =CH_2), 5.73 (q, H, —CH), 5.92 (q, H, =CH_2), 6.13 (q, H, =CH_2).

Synthesis of [PVP (PDMS)]-g-PDMS

Free-radical terpolymerization of NVP with MA-PDMS-V and MA-PDMS-MA has been adopted to synthesize a high-molecular weight graft consisting of PVP chains carrying -PDMS-V branches. The free radicals originated from thermal decomposition of AIBN initiate the terminal -MA groups, and then the activated -MA groups initiate the polymerization of NVP. In the chain propagation step, the prolonging polymer chains are branched and slightly crosslinked into a soluble graft PVP-g-PDMS-V, whereas the V-PDMS-V segments are unreacted during the polymerization (Figure 4). Since the

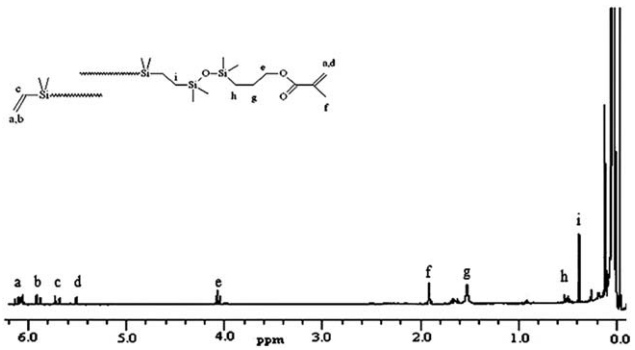


Figure 3. ^{1}H NMR spectrum of MA-PDMS-V.

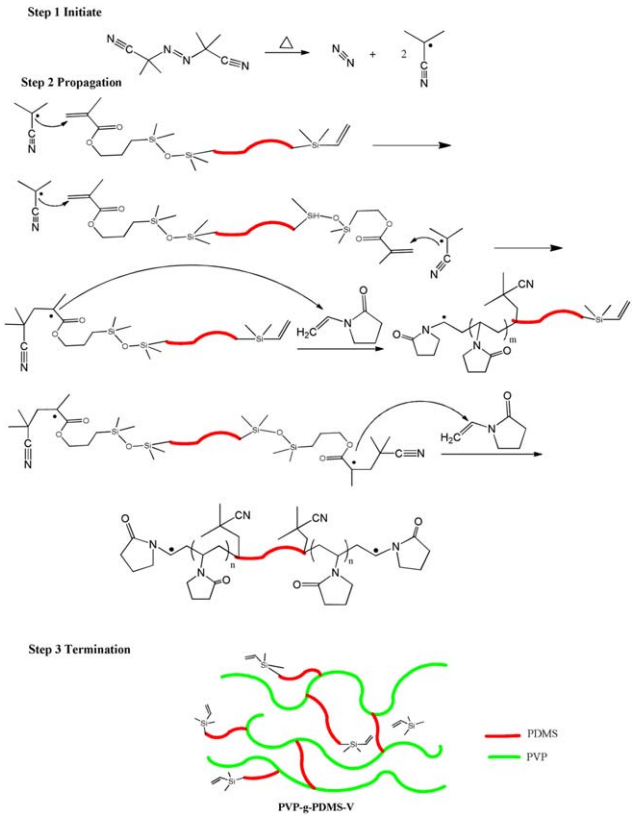


Figure 4. Grafting reaction mechanism of [PVP (PDMS)]-g-PDMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymerization is terminated before the gel point, the product is soluble and can be re-dissolved in various solvents after drying (toluene, chloroform, THF, etc.).

The ^{1}H NMR spectrum of a representative graft in Figure 5 shows the presence of vinylsilyl groups and the absence of MA groups, indicating a complete conversion.

^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.08 (s, 6H, —$Si(CH_3)_2$), 1.51 (m, 2H, CH—CH_2—CH—), 1.91 (m, 2H, CH_2—CH_2CH_2),

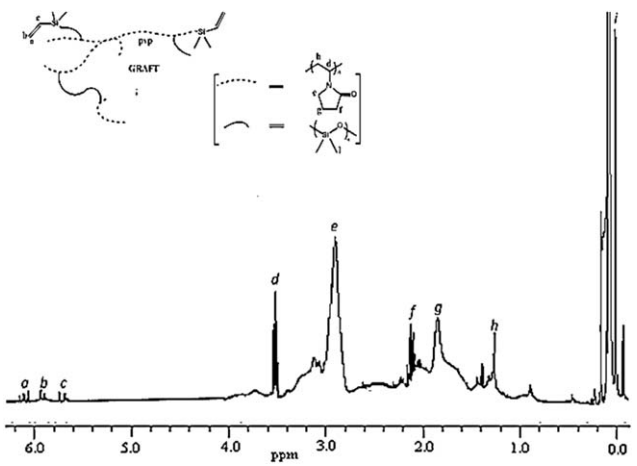


Figure 5. ^{1}H NMR spectrum of [PVP (PDMS)]-g-PDMS.

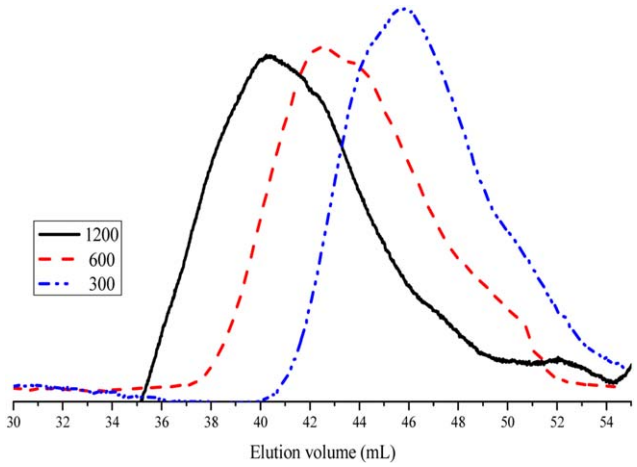


Figure 6. GPC traces of [PVP (PDMS)]-g-PDMS-V grafts [NVP : AIBN ratios (300, 600, and 1200)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2.18 (t, 2H, CH_2CH_2CO), 2.8–3.4 (m, 2H, N—CH_2—CH_2), 3.58 (t, 1H, CH_2—CH—CH_2), 5.73 (q, H, —CH), 5.92 (q, H, =CH_2), 6.13 (q, H, =CH_2).

Although the charge contains approximately 25% MA-PDMS-MA, the graft does not contain gel because the molecular weight of the main chain is controlled by the AIBN concentration. The GPC traces of three representative grafts synthesized with different AIBN concentrations have been shown in Figure 6, which suggests the high molecular weight of heterogeneous products as a result of complexity of the terpolymerization. Soluble grafts of high molecular weight can be formed only if the average arm number of the graft is in the 2–5 range: if the arm number of the grafts is less than 2, co-networks cannot form, and if it is larger than 5, the graft contains gel. Because the molecular weight of PDMS was the same in all charges (17,000 g/mol), the molecular weight of the PVP had to be accommodated to keep the arm number in the 2–5 range. The GPC gives the molecular weight of the soluble grafts, which makes it possible to calculate the arm numbers to keep in the 2–5 range. As AIBN concentration decreases, the position of the main elution peak is shifted to lower elution volume, indicating the high molecular weights of the grafts, that is, greater than 100,000 g/mol, as estimated by polystyrene calibration. Since the relative amount of PVP is not constant in the graft and the product is branched, accurate molecular weight cannot be determined by GPC.

Transmittance Performance

The target pure APCN membrane is obtained by crosslinking of [PVP (PDMS)]-g-PDMS-V with PMHS in the presence of Karstedt's catalyst. The overall sol content is less than 10% (wt %), indicating essentially full crosslinking. The resultant smooth and optically clear membranes with 70% (wt %) PVP content suggest that the domain dimension is well below the wavelength of visible light,[39] indicating no macroscopic phase separation[40] due to the formation of soluble graft of a PVP backbone carrying vinyl terminated PDMS branches, which combines the

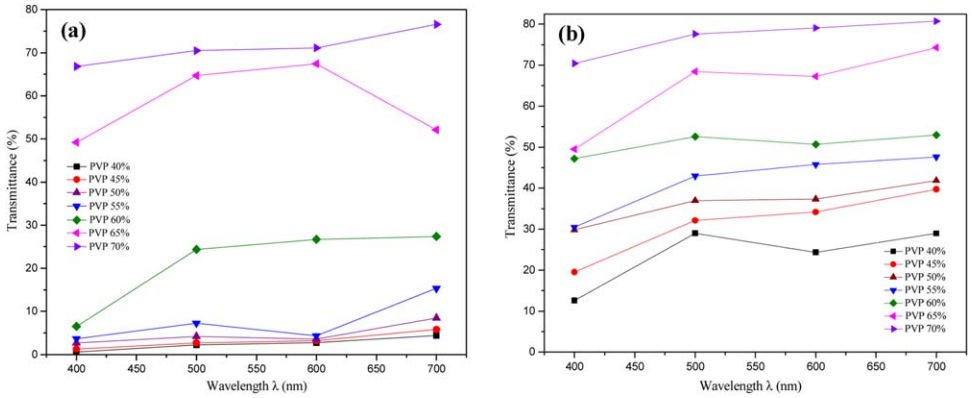


Figure 7. Transmittance of pure APCN membrane with different PVP content (wt %) at (a) dry state and (b) water-swollen state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermodynamic incompatible hydrophilic PVP segments with hydrophobic PDMS segments.

In order to quantitate optical clarity, transmittance of pure APCN membrane has been determined at both dry and swollen state, respectively. As shown in Figure 7, the average transmittance of dry pure APCN membrane is lower than that of corresponding swollen pure APCN membrane. For the dry APCN membrane in Figure 7(a), transmittance of pure APCN membrane is no more than 10% when PVP content is lower than 55%, which goes up sharply to an optically clarified degree of almost 76% as

PVP content is increased to 70% (wt %). For the water-swollen pure APCN membrane in Figure 7(b), when PVP content is increased from 40% to 70%, the transmittance goes up rapidly from approximate 20% to 81%, which shows a better optical clarity than the dry one. Overall, for both dry and swollen pure APCN membrane, transmittance goes up with increasing PVP content since all PDMS chains are wrapped by hydrophilic PVP continuous phase when PVP content is increased to a certain amount and each PDMS chain behaves as isolated phase, whose size is smaller than the wavelength of sunlight, eventually making the APCN membrane optically clear. The swollen membrane behaves more optically clear than the dry one due to the existence of moisture, which enlarges spaces between polymer chains and shows a better clarity where sunlight more easily go through. Therefore, the excellent optical clarity of the resulting APCN membrane with 70% PVP content as shown in Figure 8 indicates its potential use in the area of contact lenses.

Morphology

The phase mode AFM image of pure APCN membrane shows a typical morphology of an amphiphilic conetwork. Thus, a co-continuous distribution of different phases over the whole sample can be seen in Figure 9. The hard PVP phase (bright) is clearly distinguished from the soft PDMS phase (dark) as originally hydrophilic hard PVP segments extend out to form a bright domain, while the hydrophobic soft PDMS segments are extruded to form a dark domain.[41,42] The AFM image reveals the co-connected appearance of the APCN membrane shows a distinct phase separation which is more homogeneous than the PDMS-PVP/IPN reported by A. Hillerström,[43] indicating an more stable and excellent nano-structure for bioapplications.

Swelling

The swelling data is good predictor of glucose and insulin since diffusion rate of insulin and glucose and swelling ratio of the APCN (S_w) are proportional to the volume fraction of the hydrophilic domain in the conetworks.[44] Thus, simple swelling studies provide important guidance for optimizing synthesis conditions. As shown in Figure 10, the overall S_w of APCN

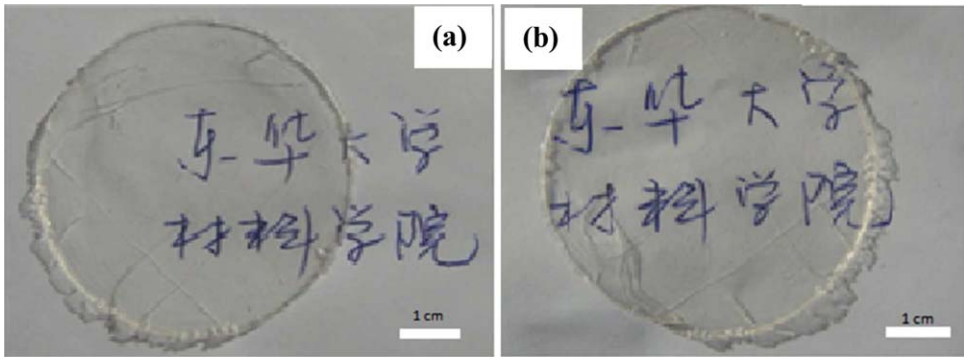


Figure 8. Appearance of pure APCN membrane at (a) dry state and (b) swollen state; APCN composition: $PVP_{70}/PMHS_{10}/PDMS_{20}$ (wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

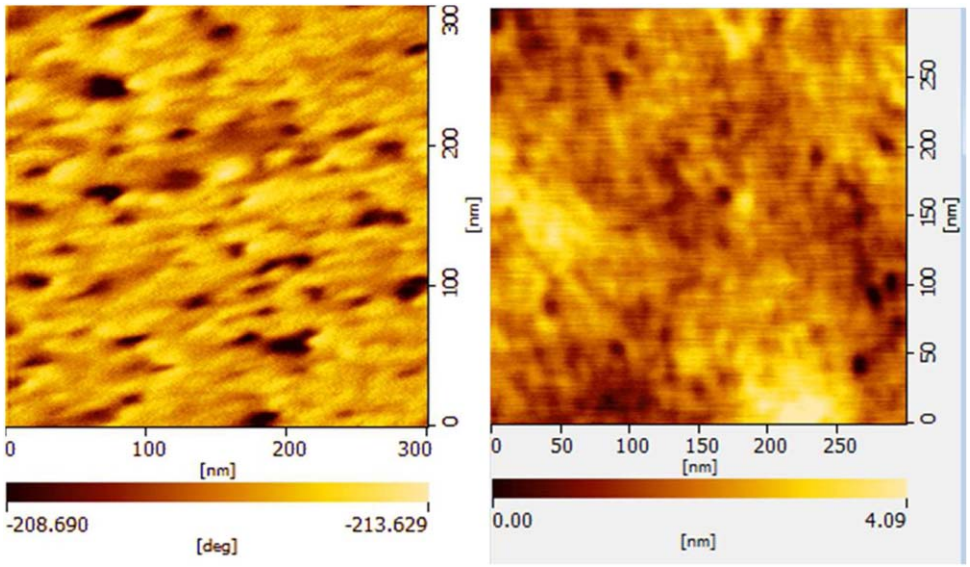


Figure 9. AFM phase images of APCN membranes consisting of 70% PVP and 20% PDMS crosslinked by 10% PMHS [referred as $PVP_{70}/PMHS_{10}/PDMS_{20}$, wt %]. Left, phase; Right, height. Experimental parameters: Taping mode, a scan rate of 1 nm/s, a scan box of 500 × 500 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

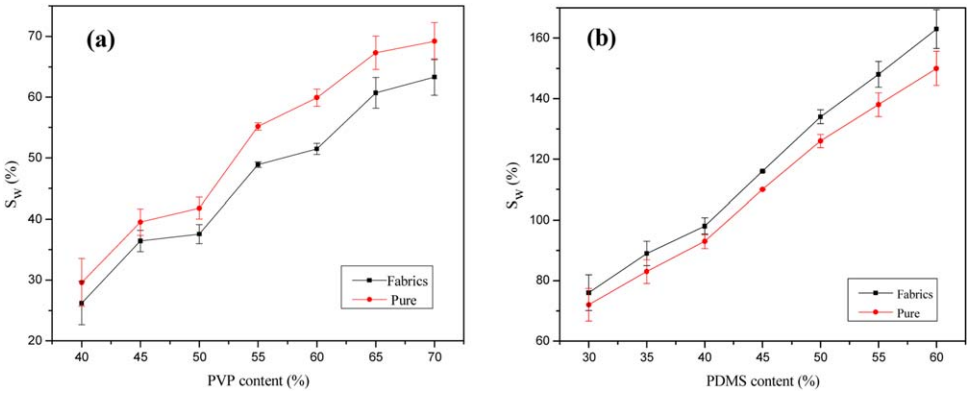


Figure 10. Effects of APCN composition on S_w in water (**a**) and in hexane (**b**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

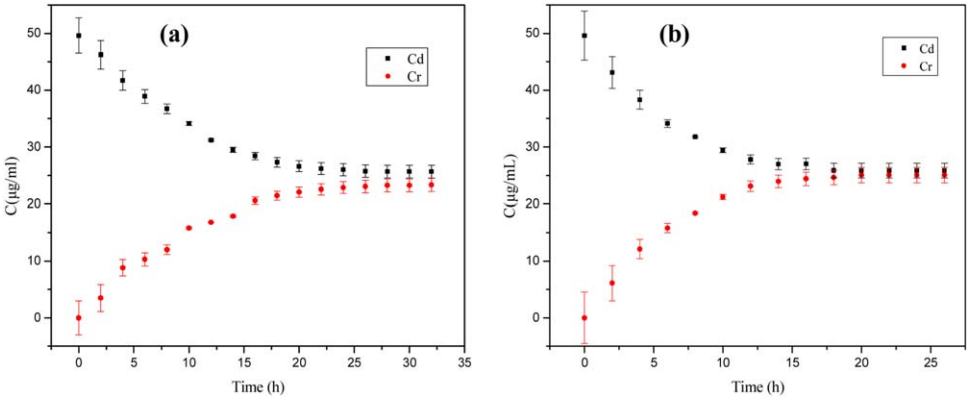


Figure 11. Dependence of inulin concentration on permeation time, (**a**) pure APCN membrane, composition: $PVP_{70}/PMHS_{10}/PDMS_{20}$ (wt %), swollen state, thickness: 195 μm; (**b**) fabric-support APCN membrane, composition: $PVP_{70}/PMHS_{10}/PDMS_{20}$ (wt %), swollen state, thickness: 10.2 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

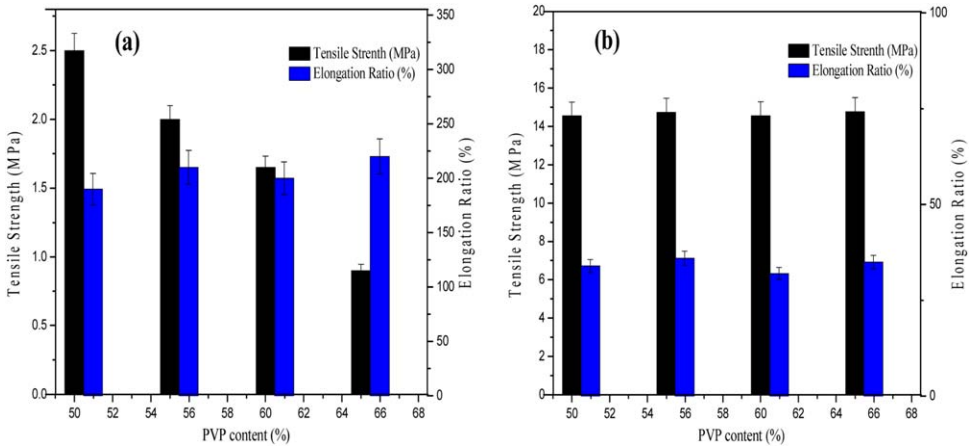


Figure 12. Mechanical properties of (**a**) pure APCN membranes and (**b**) fabric-support APCN membranes with increasing PVP content. (Pure APCN membrane: thickness, 195 μm, water-swollen state; Fabric-support APCN membrane: thickness, 10.2 μm, water-swollen state.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membranes in water goes up with increasing PVP content due to the excellent hydrophilicity of PVP segments. For pure APCN membranes, the water S_w goes up from 30% to 70% when PVP content is increased from 40% to 70%, while the corresponding water S_w for the fabric-support APCN membranes goes up from 22% to 63%. In contrast, the S_w in hexane is increased with increasing PDMS (decreasing PVP) content, which is increased from 72% to 150% for the pure APCN membrane and goes up from 76% to 163% for the fabric one. Therefore, the swelling behavior is intensively associated with the APCN composition and solvent kind, which confirms the amphiphilicity and co-continuous characteristic of the resulting APCN membranes.

Inulin Permeability

In consideration of aggregation property of insulin under shaking conditions as well as the little molecular difference between inulin and insulin, inulin is chosen as a drug model to determine membrane permeability. Equipment has been designed for the investigation of diffusion kinetics as well as quantitative permeating flux. And experiments have been carried out to study the diffusion and permeability of APCN membrane.

As anthrone-sulfuric acid calorimetry is a fast and facile method to determine saccharides concentration, this method has been applied to determine inulin permeability of pure APCN membrane and fabric-support APCN membrane, respectively.

Solution recovery is an important index to determine if there is any seep or solute reduction during permeating process, and the constancy of total concentration ($C_r + C_d$) of samples with the original concentration (C_{d0}) confirms the reliability of the tests.

Apart from constant total concentration, the current concentration is another vital index to evaluate whether the diffusion is fast enough. As shown in Figure 11, the current inulin concentration in chamber D (C_d) is reduced gradually while inulin concentration in chamber R (C_r) is increased accordingly. The concentration of inulin solution through pure APCN membrane becomes stable in 30 h, while fabric-support APCN membrane reaches balance in 20 h, which indicates that permeating balance time (t_B) of pure APCN membrane and fabric-support APCN membrane are 30 h and 20 h, respectively.

According to previous literature, permeability value P and diffusion index D of APCN membrane can be calculated via eqs. (3) and (4), respectively. For pure APCN membrane (PVP_{70}/$PMHS_{10}$/$PDMS_{20}$), the calculated value of P and D is 4.79E-7 cm^2/s and 7.5E-11 cm^2/s, while for the corresponding fabric-support APCN membrane, the calculated value of P and D is 7.99E-7 cm^2/s and 1.25E-10 cm^2/s, respectively, which indicates that fabric-support APCN membrane with a thinner swollen thickness shows a higher value of permeability than that of pure membrane. Both permeability values are higher than that reported by Shamlou *et al.* ($P = 3.1E\text{-}7$ cm^2/s, hydrophilic PDMAAm segments content 70%, wt %),[45] indicating its effective permeability. Therefore, these APCN membranes show a potential application of reliable drug controlled release as well as semipermeable membranes.

Mechanical Properties

The excellent mechanical strength is necessary for swollen membranes when being used in the area of semipermeable membranes. Thus mechanical properties of these APCN membranes have also been investigated and the results are shown in Figure 12. When PVP content is increased from 50% to 65%, the corresponding tensile strength for the swollen pure APCN membrane is deceased sharply from 2.52 to 1.21 MPa and the corresponding elongation ratio remains almost the same at an average of 190%. For the fabric-support APCN membrane, the corresponding tensile strength is decreased from 14.76 to 14.54 MPa, while the corresponding elongation ration almost keeps at an average of 34%. The relatively fine mechanical properties of swollen pure APCN membrane are attributed to high cross-linking density. For fabric-support APCN membrane, the originally fine mechanical properties of non-woven fabric uphold the whole membrane, which behaves independently of PVP content. The fabric-support APCN membrane exhibits higher mechanical properties and better permeability than the PEG/PDMS conetworks[8] and hydrogels[46] and other previous

reports,[47] proving it a good candidate as semipermeable membrane.

CONCLUSIONS

The APCN membranes have been successfully prepared through end-crosslinking of amphiphilic grafts of PVP backbone carrying PDMS branches via free radical polymerization essentially with complete crosslinking efficiency, whose mechanical properties have also been enhanced by non-woven fabrics to form the fabric-support APCN membrane. The light transmittance reaches as high as 80% and behaves as apparently optical clarity. Water swelling of the resultant membrane reaches as high as 70% as the hydrophilic PVP content increases, indicating these membranes possess high permeability. The permeability of the resultant membranes for inulin can reach as high as 7.99E-7 cm^2/s. The microphase separation pure APCN membrane exhibits a combination of properties appropriate for biomaterials applications. The resulting APCN membranes with high mechanical performance and inulin permeability show a wide range of potential applications in drug release vectors, soft contact lenses, medically compatible materials, and biomedical separation materials.

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