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"Near Perfect" Amphiphilic Conetwork Based on End-Group Cross-Linking of Polydimethylsiloxane Triblock Copolymer via Atom Transfer Radical Polymerization

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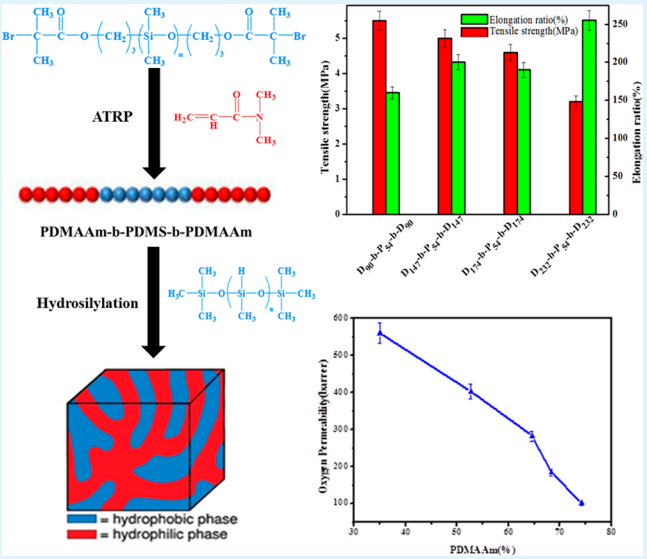
ABSTRACT: Novel amphiphilic conetworks (APCNs) with uniform channel size were synthesized through end-cross-linking of well-defined amphiphilic triblock copolymers via atom transfer radical polymerization (ATRP). A new ditelechelic polydimethylsiloxane macroinitiator was synthesized to initiate the polymerization of *N*,*N*-dimethylacrylamide. The resulting triblock copolymers show well-defined molecular weight with narrow polydisperisty, which are telechelic modified by allylamine and fully cross-linked with polyhydrosiloxanes through hydrosilylation. Transmission electron microscopy shows that the APCN has the behavior of microphase separation with small channel size and uniform phase domain. The resulting APCNs with idealized microstructure exhibit a combination of excellent properties, i.e., superhigh mechanical strength (4 ± 1 MPa) and elongation ratio (175 ± 25%), outstanding oxygen permeability (350 ± 150 barrers), a high water uptake property, and excellent biocompatibility, indicating that in this way, "near perfect" networks are obtained. These results are better than those reported in the literature, suggesting a promising semipermeable barrier for islet encapsulation in relative biomaterial fields.



KEYWORDS: *polydimethylsiloxane, amphiphilic conetwork, atom transfer radical polymerization, oxygen permeability, membrane*

INTRODUCTION

The bioartificial pancreas is a promising device for diabetes treatment, which is designed to protect transplanted islets from recipient immune responses by encapsulation with a semipermeable barrier, where water and oxygen permeability and regular nanostructure of the membrane barrier are the key parameters to ensure the survival of transplanted pancreas cells and to allow insulin release in response to blood glucose level.[1] However, the relatively low oxygen permeability or mechanical property of existing polymers or hydrogels[2,3] cannot meet the requirement for the survival of high loading density cells. Therefore, it is of great importance to develop new coating membranes for islet encapsulation.

Amphiphilic conetwork (APCN),[4−7] which is composed of hydrophilic and hydrophobic units through covalently interlinking into three-dimensional structure, recently came to the forefront of biomaterials research because of its microphase separation characteristics.[8−10] The APCNs prepared from polyisobutylene (PIB)[11,12] and polydimethylsiloxane (PDMS),[13,14] which own high oxygen permeability among other materials, have received great attention as controlled drug release matrixes because they provides channel-type structure which allows rapid diffusion of water.[15] PDMS-based APCN has received special attention due to its own characteristics, i.e., excellent biocompatibility, high elasticity, heat resistance, low surface free energy, and biological inertness as well as the highest oxygen permeability among all polymers, which shows a wide range of potential applications in intelligent polymer materials, soft contact lenses, biomedical materials, antifouling surfaces, and biochemical sensors.[16−21] Therefore, PDMS-based APCN is a perfect coating material for islet encapsulation developed in recent years.[22,23]

Most APCNs are synthesized by free radical polymerization,[24−26] which inevitably leads to poor conformation regularity, structure defects, or even loss of performance when regular nanostructure is required; especially, body immunity to the cell encapsulation coating membrane will occur. Therefore, it is urgent to prepare APCN with controlled size and narrow molecular weight distribution for the purpose of islet encapsulation. Generally, such special networks are obtained

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by cross-linking polymer chains of well-defined length through quasiliving carbocationic polymerization (QLCCP), reversible addition−fragmentation chain transfer (RAFT) polymerization, group transfer polymerization (GTP), and atom transfer polymerization (ATRP)[27−31] since Iván first prepared PIB-based APCN by radical copolymerization of *N,N*-dimethylacrylamide (DMAAm) and well-defined telechelic PIB macromonomer by QLCCP and quantitative chain end derivatization.[32] Among these methods, ATRP is a well-developed method, and the use of macroinitiator has received much attention because it simplifies the synthesis step.[33]

In the present work, we report a novel approach to the synthesis of amphiphilic triblock copolymer polydimethylacrylamide-*b*-polydimethylsiloxane-*b*-polydimethylacrylamide with controllable chain length through ATRP, where PDMS was incorporated as difunctional macroinitiator. The APCNs were synthesized by controlled end group cross-linking of ditelechelic PDMAAm-*b*-PDMS-*b*-PDMAAm, leading to consistent channel length aperture of the APCNs. Importantly, the resulting APCNs exhibited a combination of excellent properties, i.e., high mechanical property and elasticity, a combined high swelling ratio in water, and high oxygen permeability, indicating that some "near perfect" networks are obtained. The resulting APCNs with idealized microstructure avoid the major obstacles for islet encapsulation coating material, i.e., conformation irregularity and the imbalance between swelling ratio and oxygen permeability, and could be a promising coating material for islet encapsulation.

EXPERIMENTAL SECTION

Materials. *N,N*-Dimethylacrylamide (DMAAm) was purified by distillation and stored in the freezer. Hydroxypropyl polydimethylsiloxane (M_n = 4000 g/mol, PDI = 1.41), polymethylhydrosiloxane (M_n = 6000 g/mol, PDI = 1.40), and Karstedt's catalyst (3% Pt(0) in xylene) were purchased from Gelest Co. and were used as received. Copper(I) bromide (CuBr; Aldrich, 98%) was purified according to a standard procedure.[34] 2-Bromoisobutyryl bromide, anhydrous magnesium sulfate ($MgSO_4$), sodium bicarbonate, calcium hydride (CaH_2, 90−95%), potassium carbonate (K_2CO_3), potassium iodide (KI), and tris(2-(dimethylamino)ethyl)amine (Me_6TREN) were used without further purification. Tetrahydrofuran (THF), triethylamine, and toluene were evaporated, and aluminum oxide was activated at 120 °C for 6 h. L929 cells were obtained from the Shanghai Institute of Biochemistry Cell Biology. The nutrient solution RPMI-1640 medium for cell culture and phosphate buffer solution (PBS) were purchased from Sigma.

Synthesis of Macroinitiator Br-PDMS-Br. Hydroxypropyl polydimethylsiloxane (30 g, 7.5 mmol) and triethylamine (1.59 g, 15.76 mmol) were dissolved in 200 mL of anhydrous THF in a three-neck round bottomed flask and immersed in an ice bath for 30 min before 2-bromoisobutyryl bromide (3.45 g, 15 mmol) was added dropwise to the stirred solution. The resulting heterogeneous mixture was stirred at room temperature for 12 h, filtered to remove the triethylamine hydrobromide byproduct, and evaporated under vacuum. The resulting oil was redissolved in hexane (80 mL) and washed two times with saturated sodium bicarbonate solution (200 mL). The organic layer was separated and dried with anhydrous magnesium sulfate. The final PDMS macroinitiator (Br-PDMS-Br) was obtained as a slightly yellow liquid. Yield: 28.5 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ): 0.00 (m, 6H), 0.079 (s, 6H, Si(CH_3)$_2$), 0.87 (m, 2H, SiCH_2CH$_2$CH$_2$), 1.6 (m, 2H, SiCH$_2$$CH_2CH_2$), 4.33 (m, 2H, SiCH$_2CH_2$$CH_2$), 1.96 (s, 6H, BrC($CH_3$)$_2$).

Synthesis of PDMAAm-*b*-PDMS-*b*-PDMAAm Amphiphilic Copolymer. A series of triblock copolymers was synthesized by ATRP. For example, a mixture of Br-PDMS-Br macroinitiator (1.00 g, 0.25 mmol), DMAAm (25 g, 250 mmol), Me_6TREN (0.115 g, 0.5 mmol), and THF (100 mL) were added to a Schlenk flask equipped with a magnetic stirring bar and subjected to one freeze−pump−thaw cycle. Then CuBr (0.072 g, 0.5 mmol) was added into the flask under argon atmosphere. After three freeze−pump−thaw cycles, the polymerization was carried out at 70 °C for 24 h. The reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove the metal salts. The polymerization mixture was diluted with THF and precipitated into cold *n*-hexane, and the obtained precipitate was filtered and dried for 24 h in a vacuum oven at room temperature. PDMAAm-*b*-PDMS-*b*-PDMAAm triblock copolymer was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ): 0.00 (m, 6H), 0.079 (s, 6H, Si(CH_3)$_2$), 1.8 (m, 1H, CH_2CHCON(CH_3)$_2$), 1.4 (m, 2H, CH_2CHCON(CH_3)$_2$), 2.1 (m, 6H, C(CH_3)$_2$), 3.0 (m, 6H, N(CH_3)$_2$).

Synthesis of Allyl-Telechelic Amphiphilic Copolymer. PDMAAm-*b*-PDMS-*b*-PDMAAm (3.86 g, 0.1 mmol) amphiphilic copolymer was dissolved in dichloromethane (50 mL), and equivalent K_2CO_3 (0.0138 g, 0.1 mmol) and KI (0.0166 g, 0.1 mmol) were added and stirred at room temperature for 30 min. Allylamine (0.285 g, 5 mmol) was added and heated at 50 °C for 24 h. The solution was dialyzed against distilled water in a dialysis tube (MwCO: 7000) for purification for 7 days. The allyl functionality (f) of the triblock copolymer was around 1.98. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ): 0.00 (m, 6H), 0.079 (s, 6H, Si(CH_3)$_2$), 1.8 (m, H, CH_2CHCON-(CH_3)$_2$), 1.4 (m, 2H, CH_2CHCON(CH_3)$_2$), 2.1 (m, 6H, C(CH_3)$_2$), 3.0 (m, 6H, N(CH_3)$_2$), 5.9 (m, 1H, CH_2=CH), 5.17 (m, 2H, CH_2=CH).

Conetwork Preparation. The allyl triblock copolymer (1.9 g, 0.05 mmol), polymethylhydrosiloxane (0.6 g, 0.1 mmol), and Karstedt's catalyst (0.05 mL) were dissolved in 20 mL of toluene. The solution was poured in a Teflon mold and placed in an oven at 60 °C for 24 h for cross-linking.

CHARACTERIZATION TECHNIQUES

Proton Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR was performed on a Bruker Avance 400 instrument with deuterated chloroform as the solvent.

Gel Permeation Chromatography. GPC was performed on a BI-MwA Gel Permeation Chromatography (Waters, Milford, MA), equipped with a light scattering instrument (Brookhaven, Holtsville, NY) at room temperature, using THF as the eluent at a flow rate of 0.8 mL/min with a polystyrene standard as the reference.

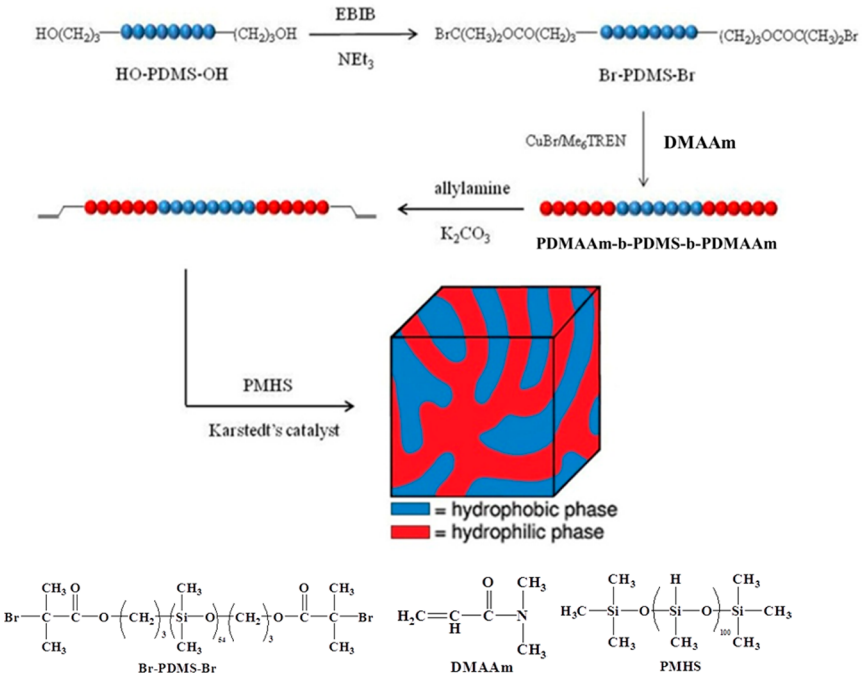
Determination of the Sol Fraction of the Conetworks. The sol fraction of the conetworks was extracted with THF (3 × 500 mL/day, 25 °C for 72 h). The sol fraction was calculated as the ratio of the dry mass of the extractables divided by the virgin conetwork.

Measurements of the Contact Angle. Static water contact angles (WCA) of the APCN were measured on a telescopic goniometer (OCA40, Dataphysics, Germany). A 5 μL drop of pure distilled water was placed on the APCN surface, using a syringe with a 22-gauge needle. The surface contact angles were the mean of five determinations

Transmission Electron Microscope. TEM was performed on a JEOL JEM-2010 high-resolution transmission electron microscope at an acceleration voltage of 120 kV. The samples were trimmed using an ultrathin microtome machine.

Measurement of the Swelling Ratio. Swelling experiments were carried out at room temperature by immersing a preweighed sample in an excess of distilled water and hexane, respectively. The extent of swelling was determined by periodically taking the samples from the solvent, removing the solvent adsorbed to the surfaces by blotting with tissue paper, and weighing. Equilibrium swelling ratio (S_w) was recorded when the weight of the swollen samples remained

Scheme 1. Synthesis Strategy of APCN



unchanged for 24 h. The swelling ratio was calculated with the following equation:

$$S_w = \frac{m_t - m_0}{m_0} \times 100\%$$

where m_t is the mass of the swollen sample and m_0 is the mass of the dry sample.

Tensile Strength and Elongation at Break. The tensile strength and elongation at a break of APCN were measured by Universal Testing Machine (KEXIN, WDW3020, China) in the water-swollen state. The samples were formed into rectangles (6 cm × 2 cm), and the tensile speed was set at 10 mm/min. Each sample was measured three times, respectively, and the average value was obtained. The error is less than 5%.

Oxygen Permeability. Apparent oxygen permeability of APCN was determined at 35 °C. The instrument used together with specifications and the operational principle were described in detail.[35] To obtain comparable results with different compositions, the membranes were of the same dimensions (8 cm × 8 cm × 0.2 mm) and measurements were carried out under the same conditions.

Cell Culture. L929 cells were cultured in a culture flask in RPMI-1640 medium supplemented with 10% fetal bovine serum, 1% L-glutamine, and 1% penicillin/streptomycin and then grown at 37 °C with 5% CO_2 for 3 days. Prior to cell culture, all conetworks (15 × 15 × 2 mm) were placed in 12-well plates and washed with PBS. Then the cell suspension was incubated with conditioned media for 3 days at 37 °C with 5% CO_2.

Scanning Electron Microscopy. SEM was performed on a JEOL JSM5600 scanning electron microscope using an accelerating voltage of 15 kV. The samples were then mounted on aluminum specimen stubs and sputter coated with gold before being examined.

RESULTS AND DISCUSSION

Synthesis Methodology. Scheme 1 outlines the synthetic strategy for a novel family of APCNs. The first step is the synthesis of PDMS macroinitiator by coupling commercially available PDMS diol with 2-bromoisobutyryl bromide. Thionyl bromide PDMS materials provide an excellent starting point for the synthesis of block copolymers with hydrophobic vinyl monomers such as styrene, methyl methacrylate, and butyl methacrylate[36−41] by ATRP. However, a few examples of hydrophilic monomers are known to date. Here the PDMS-based macroinitiator initiates the ATRP polymerization of *N*,*N*-dimethylacrylamide in combination with CuBr/Me_6TREN catalytic complex, which also acts as the hydrophobic segment in the resulting amphiphilic triblock copolymer with well-defined molecular weight and narrow polydisperisty. The bromine end of the triblock copolymer is then transformed to an active allyl group through nucleophilic substitution. The present research concerns the synthesis of APCN by combining amphiphilic triblock copolymers with polymethylhydrosiloxane (PMHS) through hydrosilylation. There exist an average of 100 Si−H pendant bonds per PMHS chain available for hydrosilylation, which means that the PDMAAm-PDMS-PDMAAm acts as a cross-linker for the PMHS chains. Therefore, the important difference between the conetworks obtained by free radical copolymerization of functional macromonomers, and the present work is the specific average chain length and relatively narrow molecular weight distribution of the PDMAAm-PDMS-PDMAAm chains in comparison with the broad distribution of the cross-linked chains in the conetworks prepared by conventional free radical copolymerization of telechelic macromonomers with low molecular weight monomers. The APCN is optically clear, indicating the absence of macroscopic phase separation. Domain aggregation during cross-linking/membrane casting is absent because the PDMAAm and PDMS are already covalently linked in the triblock polymer stage. Scheme 1 shows an idealized microstructure of the amphiphilic conetwork.

Table 1. Characterization of PDMAAm$_x$-*b*-PDMS$_{54}$-*b*-PDMAAm$_x$

no.	polymer structure[a]	reaction time (h)	conversion (%)	$M_{n,NMR}$[b] (kDa)	$M_{n,GPC}$[c] (kDa)	$M_{n,calc}$[d] (kDa)	PDI
block-1[e]	D_{44}-*b*-P_{54}-*b*-D_{44}	3	7.6	12.5	12.7	11.5	1.33
block-2	D_{90}-*b*-P_{54}-*b*-D_{90}	6	13.5	17.2	21.8	17.5	1.30
block-3	D_{147}-*b*-P_{54}-*b*-D_{147}	12	21.2	26.0	33.2	25.2	1.24
block-4	D_{158}-*b*-P_{54}-*b*-D_{158}	18	31.3	31.4	35.4	29.0	1.14
block-5	D_{174}-*b*-P_{54}-*b*-D_{174}	24	35.7	39.1	38.6	32.5	1.12
block-6	D_{205}-*b*-P_{54}-*b*-D_{205}	30	39.8	44.9	44.7	43.0	1.18
block-7	D_{232}-*b*-P_{54}-*b*-D_{232}	36	42.5	63.1	49.9	46.5	1.21

[a]D and P are further abbreviations for DMAAm and PDMS, respectively. The subscript means the number of the unit, calculated from the GPC. [b]Calculated from ^{1}H NMR-based PDMS unit (6H at 0.079 ppm) and DMAAm unit (6H at 3.0 ppm). [c]Determined by GPC measurement using polystyrene standards. [d]Theoretical M_n = [monomer]/[initiator] × (monomer conversion) × (monomer molecular weight) + (initiator molecular weight). [e]Block-1 is synthesized specially for the preparation of APCN with low DMAAm repeating unit to show the oxygen permeability over a wide PDMAAm content range so as to compare its oxygen permeability with the reference, which has low PDMAAm content.

Synthesis of PDMAAm-*b*-PDMS-*b*-PDMAAm Triblock Copolymer. As shown in Scheme 1, PDMAAm-*b*-PDMS-*b*-PDMAAm triblock copolymer was synthesized via ATRP using Br-PDMS-Br as macroinitiator and CuBr/Me$_6$TREN as catalyst. Well-defined PDMAAm$_x$-*b*-PDMS$_{54}$-*b*-PDMAAm$_x$ copolymers with different hydrophilic lengths are summarized with the data in Table 1, where the number-average molecular weight (M_n) and monomer conversion rate increase with prolonged reaction time. Their GPC traces are all symmetrical monomodal (Figure 1), and their polydispersity indices (PDIs)

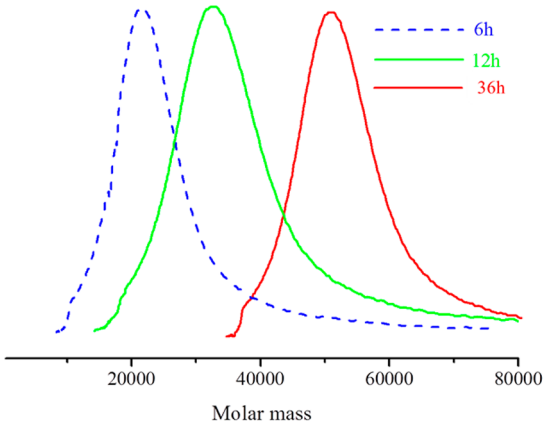


Figure 1. GPC traces of PDMAAm$_x$-*b*-PDMS$_{54}$-*b*-PDMAAm$_x$ triblock copolymers.

are less than 1.30 (Table 1), indicating that no self-polymerization of the monomer occurred. The relatively wide PDI of PDMS macroinitiator, i.e., 1.41, does not influence the low PDI of the resulting copolymer, which narrows with increasing PDMAAm chain length, indicating that the polymerization of DMAAm proceeds in a controlled manner. As the ATRP process occurs at a rate balance between activation (K_{act}) and deactivation (K_{deact}), the rate of reaction is not as high as the radical polymerization reaction. When the conversion reaches a high level, the rate of propagation is slowed considerably and the rate of any side reaction increases, leading to an increasing PDI of the final polymer. PDMAAm$_x$-*b*-PDMS$_{54}$-*b*-PDMAAm$_x$ was also studied by ^{1}H NMR analysis (Figure 2). The signal at 3.0 ppm is assigned to the protons of the N(CH$_3$)$_2$ group, indicating the successful incorporation of the PDMAAm segment.

Figure 3 reveals that M_n of the polymer is increased with the monomer conversion. The M_n of PDMAAm is increased

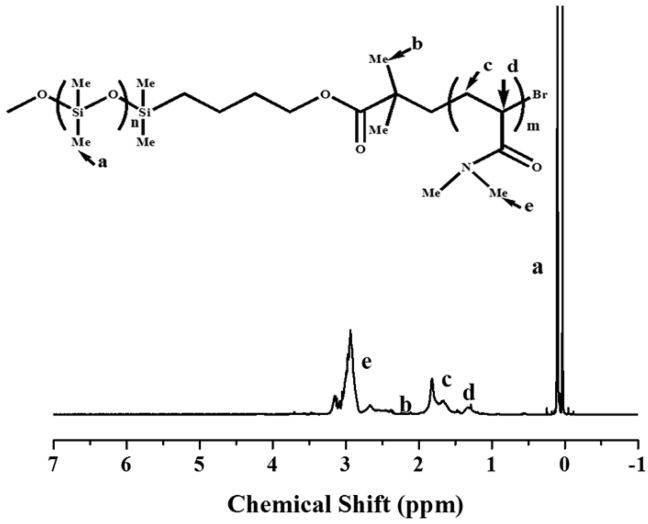


Figure 2. ^{1}H NMR spectrum of PDMAAm$_{174}$-*b*-PDMS$_{54}$-*b*-PDMAAm$_{174}$. The subscript means the number of repeat units.

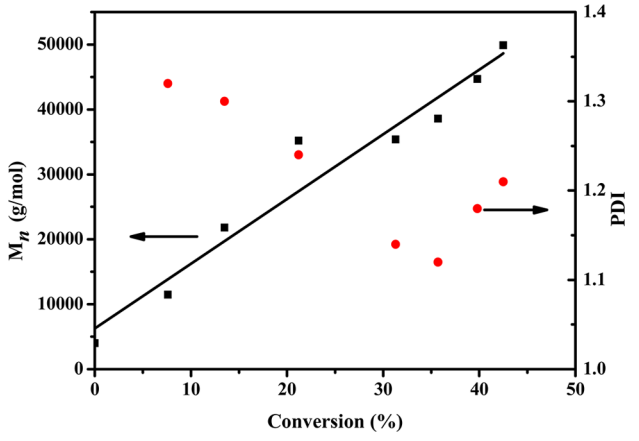


Figure 3. Number-average molecular weight and polydispersity index of the triblock copolymer as a function of conversion.

linearly with the monomer conversion. Moreover, the PDI of the copolymer is comparatively narrow. Therefore, this polymerization is living and controllable.

Synthesis of Allyl-Telechelic Amphiphilic Copolymer. According to some former reports, the halogen end groups of polymers prepared by ATRP are active, which can be substituted by nucleophiles, i.e., sulfhydryl compounds and azides.[42,43] Therefore, the active Br end of the copolymers is

transformed to functional allyl end groups with allylamine. The ^{1}H NMR of allyl-telechelic PDMAAm$_{174}$-*b*-PDMS$_{54}$-*b*-PDMAAm$_{174}$ is shown in Figure 4. The triplet at δ = 5.17 and 5.9 assigned to the allyl group provides evidence of the successful nucleophilic reaction.

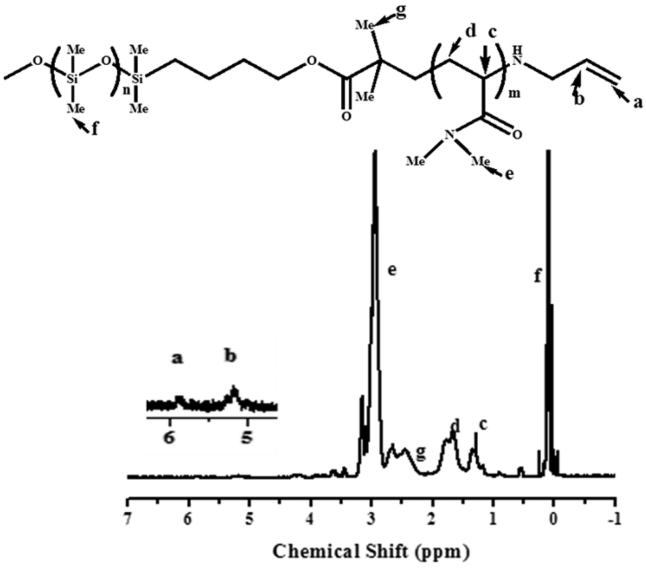


Figure 4. ^{1}H NMR spectrum of allyl-telechelic PDMAAm$_{174}$-*b*-PDMS$_{54}$-*b*-PDMAAm$_{174}$.

Sol Fraction of the Conetworks. Table 2 shows the sol fraction extracted from each conetwork. The sol fraction

Table 2. Fabrication Composition of Conetworks and Corresponding Sol Fraction Percentage

block used (g)	PMHS cross-linker (g)	total DMAAm (w %)	sol fraction (w/w %)
block-1, 0.63	0.60	35.1	4.5
block-2, 1.10	0.60	52.8	5.1
block-3, 1.62	0.60	64.2	5.2
block-4, 1.80	0.60	66.5	6.0
block-5, 1.96	0.60	68.6	5.4
block-6, 2.26	0.60	71.9	5.6
block-7, 2.50	0.60	74.2	6.8

percentage is no more than 10%, indicating essentially complete cross-linking and control over the conetwork structure.

Mechanical Properties of the Conetworks. High mechanical strength is of crucial importance for immunoisolatory membranes. As shown in Figure 5, the conetwork of PDMAAm$_{147}$-*b*-PDMS$_{54}$-*b*-PDMAAm$_{147}$/PMHS presents excellent mechanical properties in the water-swollen state, i.e., 5 MPa tensile strength and 190% elongation ratio, while the conetwork with similar PDMAAm and PDMS segments through free radical polymerization by Kang et al.[44] is only 1.3 MPa and 45% elongation ratio, respectively. The mechanical performance of our conetworks is almost 300% superior to that of other PDMS-based conetworks reported in the literature.[45−47] The high mechanical performance of our APCN is mainly due to the characteristic of ATRP, avoiding the formation of inhomogeneity throughout the conetwork structure as usually encountered through an uncontrolled

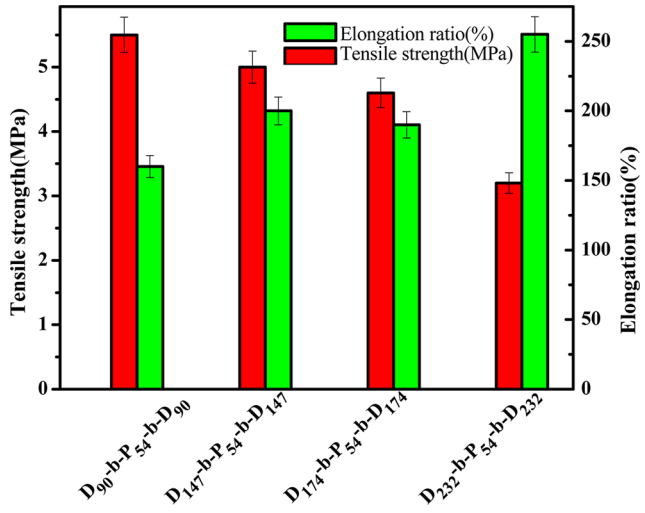


Figure 5. Mechanical properties of APCNs with different PDMAAm segment chain lengths.

polymerization. Figure 5 shows a decrease in tensile strength and an increase in elongation ratio with increasing PDMAAm block length into APCN.

Oxygen Permeability. High oxygen permeability is a key requirement for an immunoisolatory device, and we focus on this requirement when constructing the APCN. Figure 6 shows

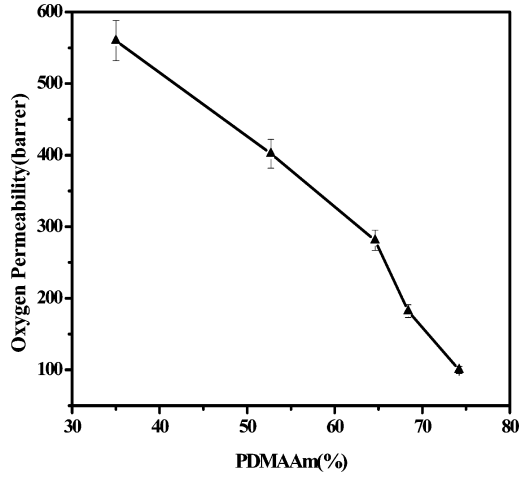


Figure 6. Oxygen permeability of PDMAAm$_x$-*b*-PDMS$_{54}$-*b*-PDMAAm$_x$/PMHS membranes as a function of PDMAA content (1 barrer = 10^{-11}(cm^2/s)(mL of O_2 (STP))/(mL mmHg).

the apparent oxygen permeability of water-swollen PDMAAm$_x$-*b*-PDMS$_{54}$-*b*-PDMAAm$_x$/PMHS membranes as a function of PDMAAm segment chain length. The data are collected by using 0.2 mm thick membranes, and the boundary layer effect is not taken into account. Therefore, the true permeability is slightly higher than those test values.

As shown in Figure 6, oxygen permeability is decreased from 560 to 100 barrers by increasing the PDMAAm content from 35 to 74%. This trend is not surprising in view of the high gas permeability of PDMS and low oxygen permeability of hydrogels. It is noteworthy that the oxygen permeability of the present APCN, even those containing relatively large amounts of PDMAAm, are far superior to even the best commercial extended-wear soft contact lenses, i.e., 195 ± 4

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barrers.[48] Therefore, the novel APCN exhibits very high oxygen permeability, which is higher than that of the reported PDMAAm/PMHS/PDMS amphiphilic conetwork with 20% PDMAAm content, i.e., 250 barrers.[44]

Surface Hydrophilicity of APCN. To probe the surface properties of APCN, the contact angle measurements are used to characterize the surface hydrophilicity, as shown in Figure 7.

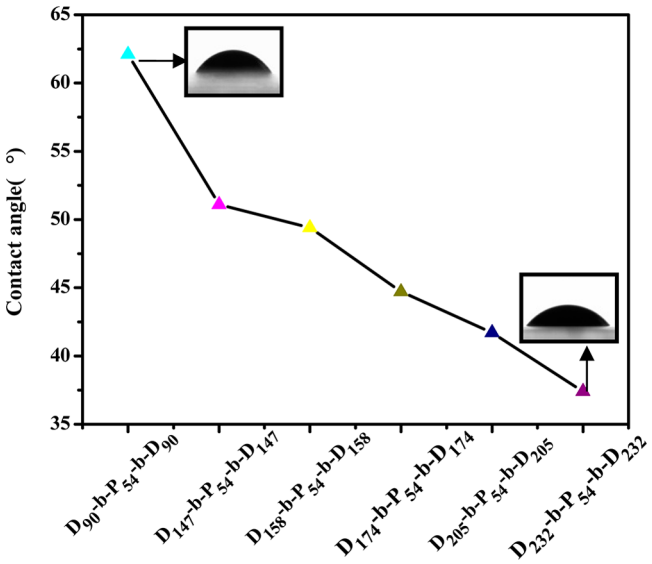

Figure 7. Influence of PDMAAm segment chain length on contact angle.

The water contact angle is decreased gradually with increasing PDMAAm block length, which decreases from 62° to 37.4° as the molecular weight of the hydrophilic segment is increased from 18000 g/mol to 45000 g/mol. This result indicates that with the increase of hydrophilic content, the hydrophilicity of APCN increases correspondingly. It will be helpful to avoid protein deposition on the APCN surface and to further improve its properties.

Swelling in Water and Hexane. The swelling data are a good predictor of glucose, insulin, and oxygen permeability because the diffusion rate of glucose and insulin and swelling ratio of the PDMAAm ($S_{w,PDMAAm}$) are proportional to the volume fraction of the hydrophilic domain in the conetwork, and the oxygen permeability is proportional to the volume fraction of PDMS in water-swollen membranes.[49] Therefore, a simple swelling study provides important guidance for optimizing synthesis conditions. As shown in Figure 8, the S_w of the conetworks in water increases with increasing PDMMAm units because of the excellent hydrophilicity of the PDMMAm unit. Even for the PDMAAm$_{90}$-*b*-PDMS$_{54}$-*b*-PDMAAm$_{90}$/PMHS membrane, the swelling reaches 180%. In hexane, the S_w of the conetworks reaches a balance, i.e. 188% after 28 h. Therefore, the architecture of the conetworks varies with its compositions in different solvents. This fact is attributed to the strong chemical bonds between HI and HO segments, which also confirm the cocontinuous characteristic of the resulting APCN.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) was used to visually investigate the morphology of the APCN. Figure 9 displays a typical TEM image of the APCN prepared from PDMAAm$_{174}$-*b*-PDMS$_{54}$-*b*-PDMAAm$_{174}$, which reflects a two-phase bicontinuous structure with small channel size and uniform phase domain. The high electron density of the PDMS microphase gives sufficient contrast without the need for staining, where the soft PDMS

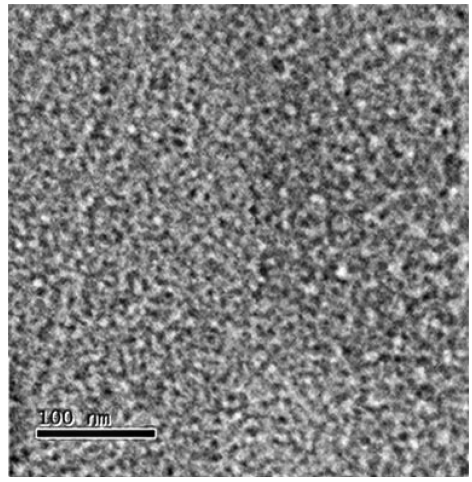

Figure 9. TEM images of the PDMAAm$_{174}$-*b*-PDMS$_{54}$-*b*-PDMAAm$_{174}$/PMHS conetwork.

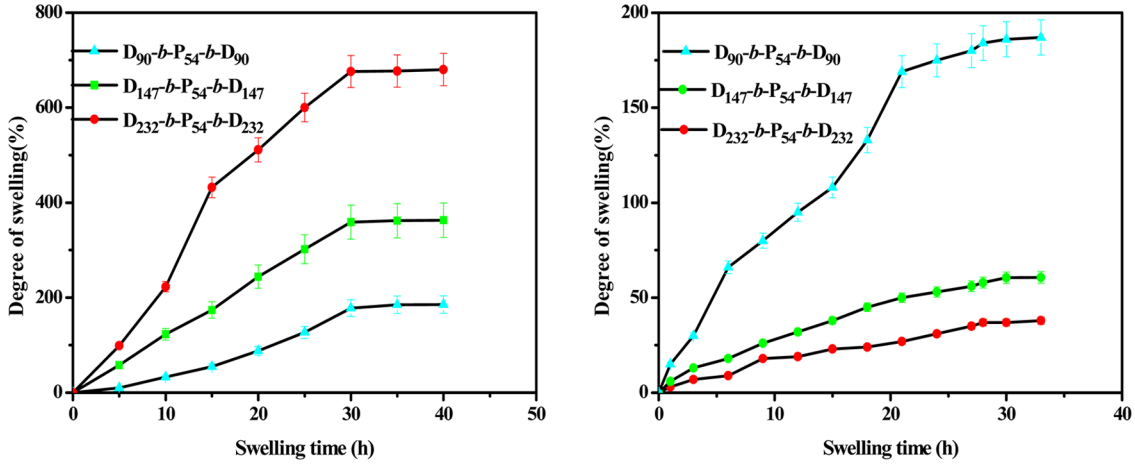

Figure 8. Effect of hydrophilic segment length on the degrees of swelling of conetworks in water (left) and hexane (right).

appeared darker and the brighter structure was related to the PDMAAm segment.

As we know, hydrophilic segments in APCN provide channels[15] through which nutrient substances reach the transplanted pancreas cell, and waste products can be sent out. Therefore, uniform channel size is important to guarantee that each transplanted pancreas cell grows well at almost the same rate, to avoid possible death due to an uneven transportation rate of nutrient and waste substances. As shown in Figure 9, the dimension of PDMAAm segments is uniform with the size around 10 nm, which will not cause a systemic immune response and will guarantee the living efficiency of transplanted cells because of the narrow hydrophilic size distribution. Therefore, the present APCN with such a homogeneous hydrophilic channel will guarantee the future success of encapsulation.

Cell Culture. In our present work, the $PDMAAm_{174}$-*b*-$PDMS_{54}$-*b*-$PDMAAm_{174}$/PMHS network is an excellent substrate for the culture of L929 cells. Figure 10 shows the

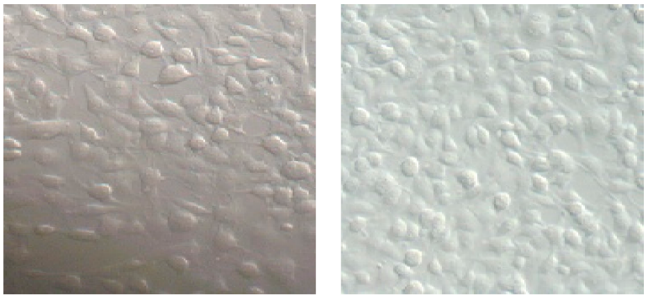

Figure 10. SEM images of L929 cells cultured (for 72 h) on APCN and control experiment.

SEM analysis of the morphology of cells on the surface of APCN. The cell viability of APCN reaches almost 100% after being cultured for 72 h, which is comparable to that of the control experiment. Therefore, the prepared APCN shows excellent biocompatibility with L929 cells, which will meet the urgent requirement for transplanted islets and other cell encapsulations as a promising semipermeable barrier.

CONCLUSIONS

Novel amphiphilic conetworks with uniform channel size are synthesized through in-one-step end-cross-linking of well-defined allyl ditelechelic amphiphilic triblock copolymers via ATRP, which show well-defined molecular weight with narrow polydispersity. The resulting APCN with two-phase bicontinuous structure and uniform phase domain exhibits a combination of excellent properties, i.e., superior mechanical properties, outstanding oxygen permeability, a high water uptake property, and excellent biocompatibility, indicating that "near perfect" networks are obtained in this way. The APCN with idealized microstructure and excellent biocompatibility is a promising semipermeable barrier due to the uniform distribution of hydrophilic channels, which will have potential applications in relative biomaterial fields.

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Notes

The authors declare no competing financial interest.

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