Supporting Information

A Self-healable and Antifouling Hydrogel Based on PDMS Centered ABA Tri-block Copolymer Polymersomes: A Potential Material for The Therapeutic Contact Lens

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Preparation of PDMS based macro-RAFT reagent

Synthesis of bromine terminated PDMS (Br-PDMS-Br):

In a typical synthesis process, OH-PDMS$_{65}$-OH (5g, 8.92 x 10^{-4}mol) and triethylamine (1.25 ml, 1.23 x 10^{-2} mol) were dissolved in dry DCM (50 ml) at 0°C. Into this cold reaction mixture, BPBr (1.05 ml, 4.84 x 10^{-3} mol) was added drop-wise for 1 h and the mixture was allowed to react at room temperature for 48 h. After completion of the reaction, the reaction product was washed with 5% $NaHCO_3$ solution for three times to neutralize followed by washing with deionized water. The formed organic layer after the treatment of $NaHCO_3$ and water was separated using a separating funnel and the resultant solution was treated with dry $MgSO_4$ to remove the remaining trace amount of water. The product solution was filtered and concentrated using a rota-evaporator followed by precipitation in diethyl ether. The required product was isolated via filtration and successive vacuum drying for 24 h at 40°C followed by analysis with ^{1}H NMR analysis carried out using $CDCl_3$ as a solvent (For pristine PDMS, characteristic peaks have been appeared at δ = 0.07 ppm (Si-C**H**$_3$), δ = 0.56 ppm (Si-C**H**$_2$-CH$_2$-), δ = 1.64 ppm (Si-CH$_2$-C**H**$_2$-), δ = 3.55-3.45 ppm (-C**H**$_2$-O-) and δ = 3.76 ppm (C**H**$_2$-OH) (Figure S1). After modification with BPBr, characteristic resonance peaks have been appeared at δ = 1.93 ppm (-CH(C**H**$_3$)Br) and δ = 4.48 ppm (-C**H**(CH$_3$)Br).

Synthesis of potassium O-ethyl xanthate

Potassium O-ethyl xanthate was prepared using our previously reported method[28]. Melting point of the prepared solid product was analyzed (210 °C) along with the ^{1}H NMR (D_2O, δ = 4.40 ppm (-CH$_2$-) and at δ = 1.27 ppm (-CH$_3$)), ^{13}C NMR (D_2O, δ = 207.17 ppm (C=S), δ = 70.17 ppm (-CH$_2$-) and δ = 13.65 ppm (-CH$_3$)), and mass spectra analyses (combined weight for xanthate and potassium was obtained at 198.8) to ensure the purity of the light yellow colored product.

Synthesis of PDMS based macro-RAFT reagent

In a typical synthesis process, 5 g [8 x 10^{-4} mol, calculated on the basis of $M_{n/GPC}$ =6000 g mol^{-1}] of Br-$PDMS_{65}$-Br and 0.8 g of potassium O-ethyl xanthate (5 x 10^{-3}mol) were taken into a round bottom flask and then degassed by three freeze-pump-thaw cycles under nitrogen atmosphere. After that 1.25 ml (1.58 x 10^{-2} mol) of degassed pyridine was mixed with 30 ml of degassed DCM in a round bottom flask under nitrogen atmosphere. The as obtained solution was dropwise added to the previously prepared solution (PDMS-xanthate mixture) under vigorous stirring condition at 0°C and under nitrogen atmosphere. The reaction mixture was stirred for 36 h at room temperature. The reaction was stopped by addition of excess (50 ml) DCM. The as obtained solution was washed with 50 ml of saturated NH_4Cl solution for 4 consecutive times followed by treatment with 60 ml deionized water for 4 times. The organic layer was separated out using a separating funnel and the obtained solution was treated with anhydrous $MgSO_4$ to make the solution free from water. The final pale yellow colored viscous PDMS based macro RAFT reagent was obtained via rotary evaporation of the organic solvent. The obtained product was analysed with ^1H NMR analysis using d_6-DMSO as a solvent. [δ = 0.07 ppm (Si-C**H**$_3$), δ = 0.56 ppm (Si-C**H**$_2$-CH$_2$-), δ = 1.64 ppm (Si-CH$_2$-C**H**$_2$-), δ = 1.66 ppm (C**H**$_3$-CH$_2$-O-), δ = 1.93 ppm (S-CH(C**H**$_3$)), δ = 3.55-3.45 ppm (-C**H**$_2$-O-), δ = 4.48 ppm (S-C**H**(CH$_3$)) and δ = 4.66 ppm (CH$_3$-C**H**$_2$-O-)].

Characterization:

The prepared samples were characterized by using Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, model spectrum-2) at the scanning range of 500 cm^{-1}-4000 cm^{-1}. ATR mode was used to analyze all the samples. The prepared samples were further characterized using ^1H NMR analysis on Bruker, 600 MHz instrument at ambient temperature using D_2O and $CDCl_3$ as NMR solvent and Tetramethylsilane (TMS) as an internal standard. The molecular weight and the dispersity (*Đ*) of the prepared homopolymer and the block copolymers were analyzed using Gel permeation chromatography (GPC) analysis. For the GPC analysis, Viscotek Gel Permeation Chromatography equipped with a VE 1122 solvent delivery system was used and the data was analyzed with OmniSEC 4.2 software. For all the GPC analysis, HPLC grade tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 ml/min in room temperature. Narrow dispersed polystyrene (Viscotek, LT4000L, Mixed, Low, Org 300 x 8. 0

mm, No. A1830071) having a reference molecular weight of 2 x 10^3 g/mol – 7 x 10^5 g/mol was used as an internal standard. The particle size of the triblock zwitterionic block copolymer and the amine modified PDMS based BCP was determined using dynamic light scattering (DLS) instrument (Malvern Nano ZS). A scattering angle of 90° and a He-Ne (4 mW, λ = 632.8 nm) laser was used for this experiment. ZEISS Field emission scanning electron microscopy (FESEM) was used to study the surface morphology of the polymer samples. The machine was operated at an accelerating voltage of 5kV. AFM (Agilent 5500 (USA) analysis, carried out in tapping mode was further utilize to study the surface morphology. The morphology of the BCP samples was analyzed using FESEM and AFM analyses. The zwitterionic tri block copolymer samples were dispersed into water at a concentration of 1 mg/ml and sonicated for 1 h. After that the solution was spin coated over the glass side and dried in vacuum chamber at 30°C. For the hydrogel sample, the dried sample was mounted over the stab and coated with gold before taking the image. The bulk morphology of the BCPs was studied using transmission electron microscopy (TEM) (JEOL, JEM-2000E7) instrument which was operated at an accelerating voltage of 200 kV. The zwitterionic BCP solution (1 mg/ml) was drop-cast over the TEM grid and dried at ambient temperature before imaging. All the experiments were carried out at room temperature. The hydrophilicity of the formed PDMS based hydrogel was measured by analyzing the water contact angle (WCA) of synthesized hydrogel at ambient temperature using a Rame-Hart 260 F4 standard Goniometer. For the analysis, a drop of water was placed over the surface of dried hydrogel and the image of the contact angle was taken within 5-10 Sec. Differential scanning calorimetry (DSC) of the synthesized BCPs was carried out to confirm the formation of the BCP. The experiment was carried out in DSC 200 F3 instrument (Netzsch, Germany). During the analysis, samples were heated from -100°C to 200°C under nitrogen atmosphere at a heating rate of 20°C/min and nitrogen flow rate of 50 ml/min. The temperature against the heat flow was recorded.

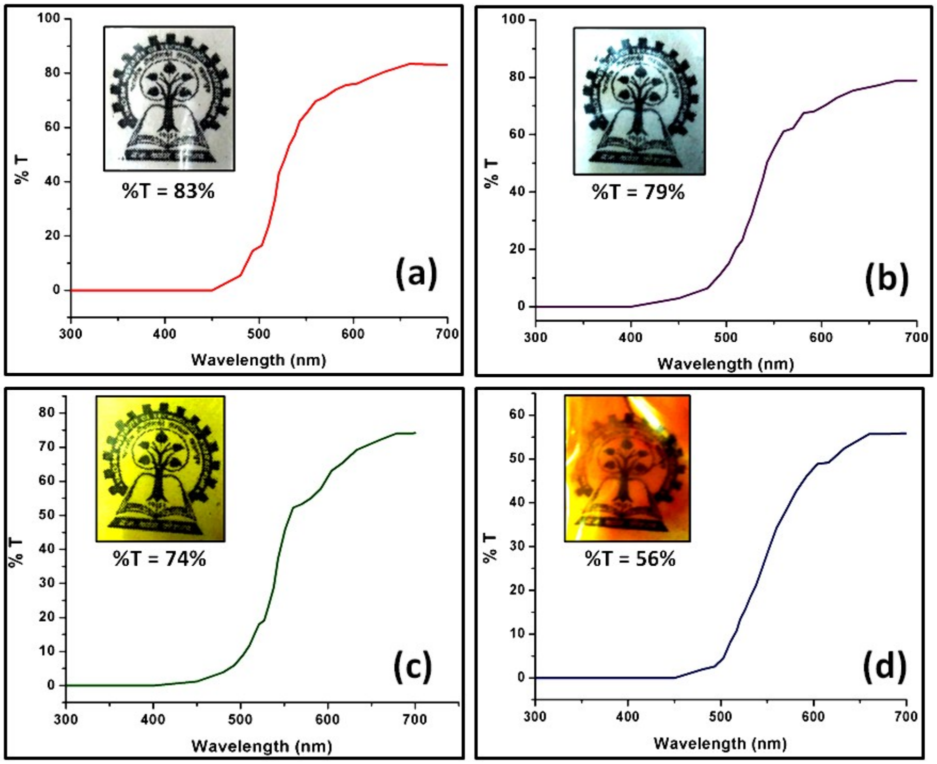
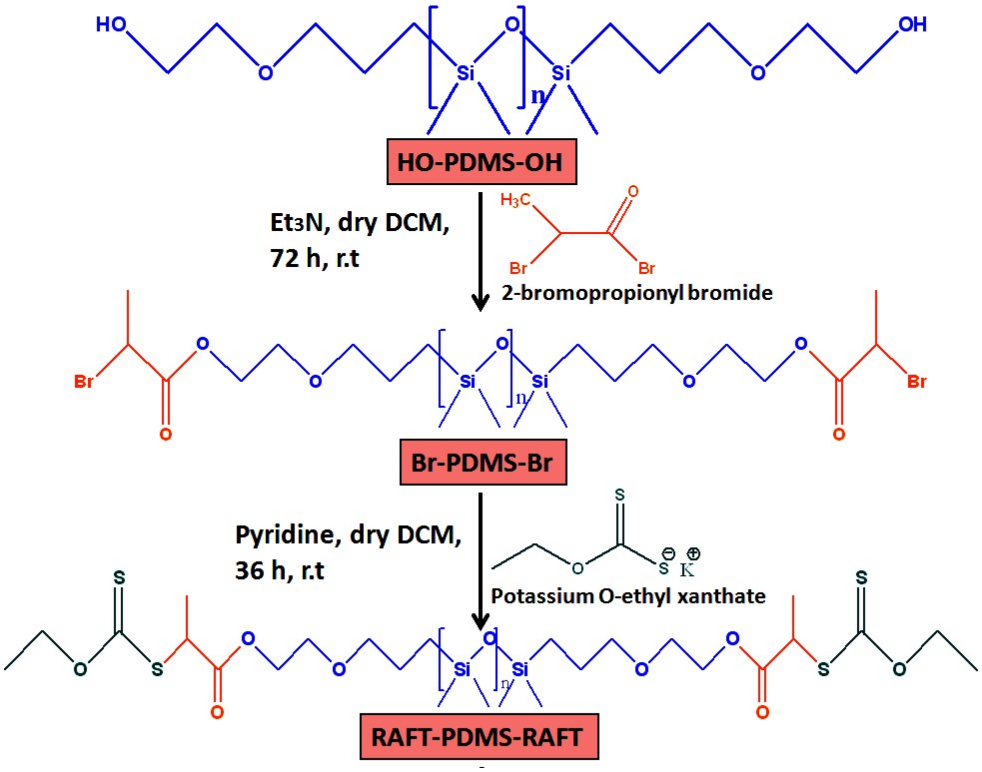


Fig. S1. Determination of % Transmittance of **(e)** as prepared PDMS hydrogel (thickness 1.5 mm), **(f)** polyzwitterionic polymersome incorporated PDMS hydrogel (thickness 1.5 mm), **(g)** curcumin loaded polyzwitterionic polymersome incorporated PDMS hydrogel (thickness 1.5 mm) and **(h)** curcumin loaded polyzwitterionic polymersome incorporated PDMS hydrogel (thickness 2.5 mm).



Scheme S1. Preparation of PDMS based macro-RAFT reagent.

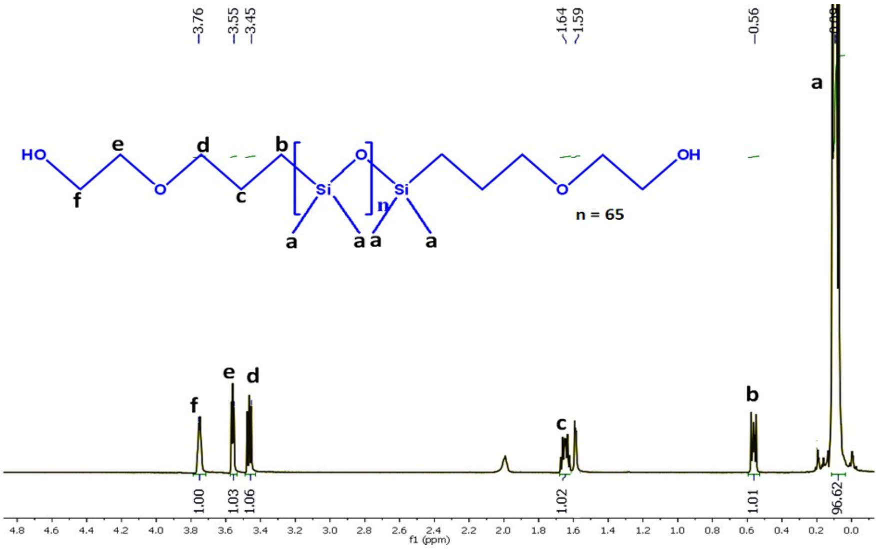


Fig. S2. ^{1}H NMR of poly(dimethyl siloxane) (PDMS) (Mn = 5600 g mol^{-1}).

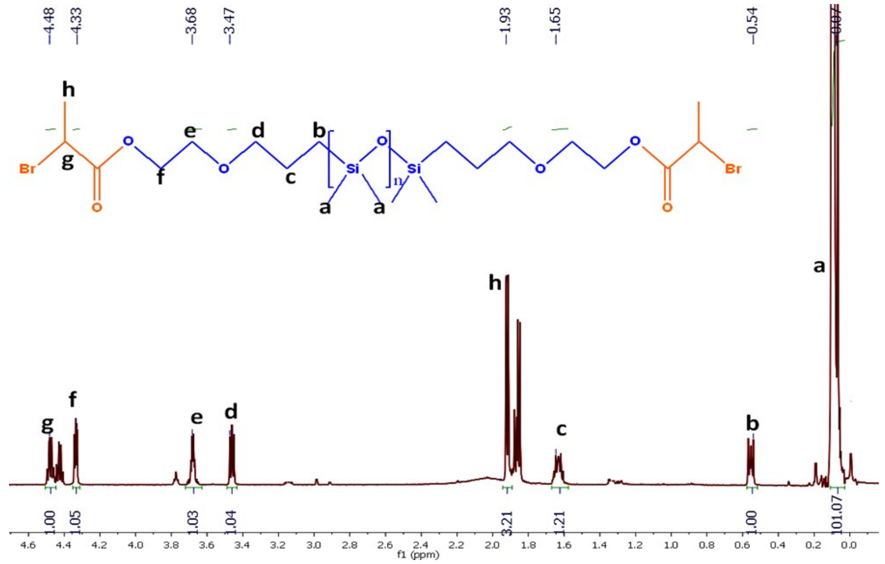


Fig. S3. ^{1}H NMR of brominated poly(dimethyl siloxane) (Br-PDMS-Br).

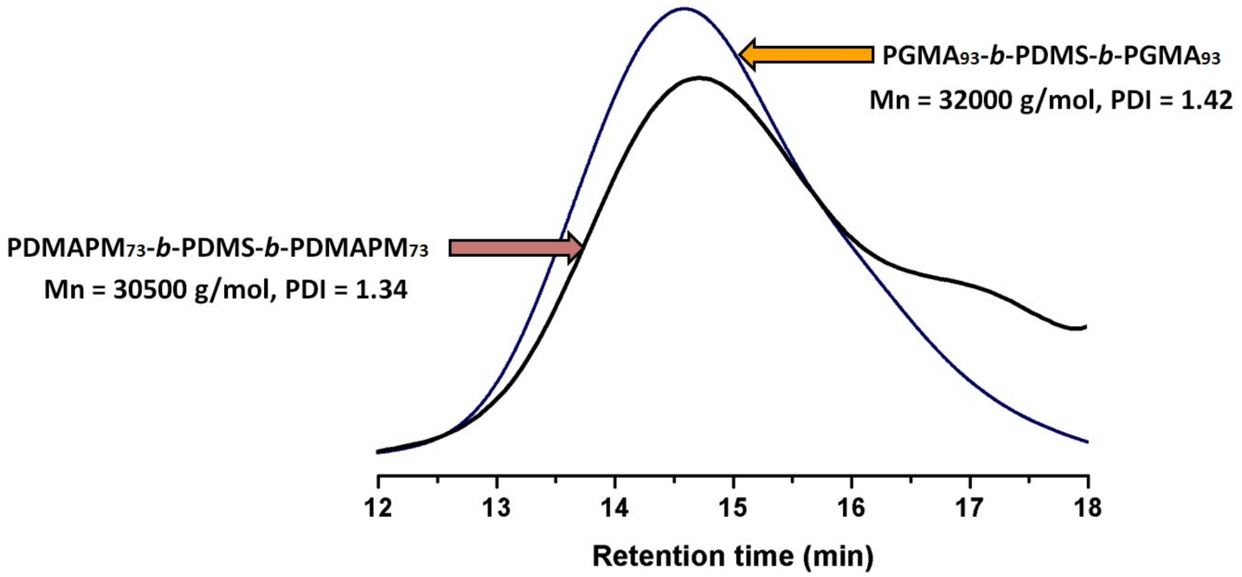


Fig. S4. GPC analysis of the block copolymers.

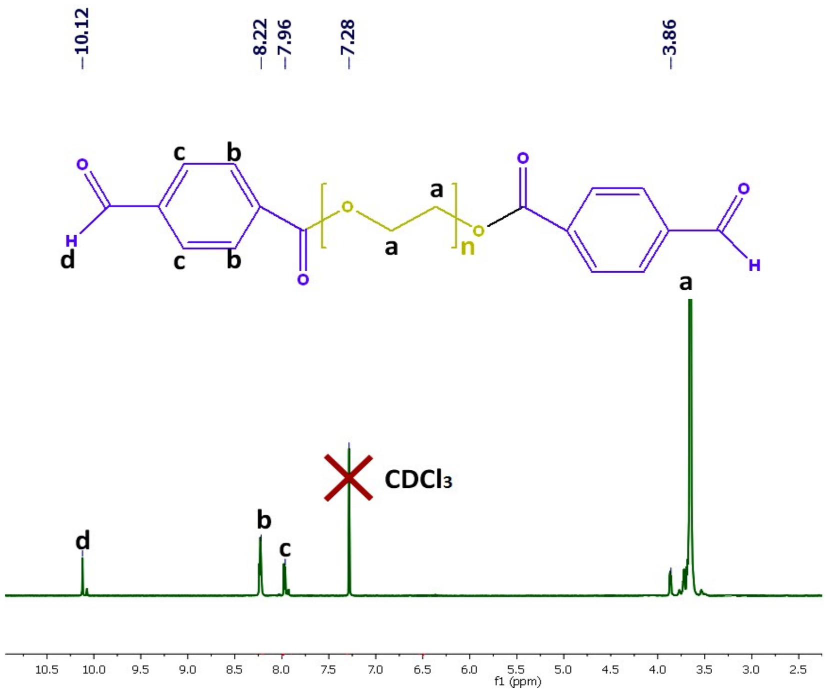


Fig. S5. ^{1}H NMR of poly(ethylene glycol)-dialdehyde (Ald-PEG-Ald).

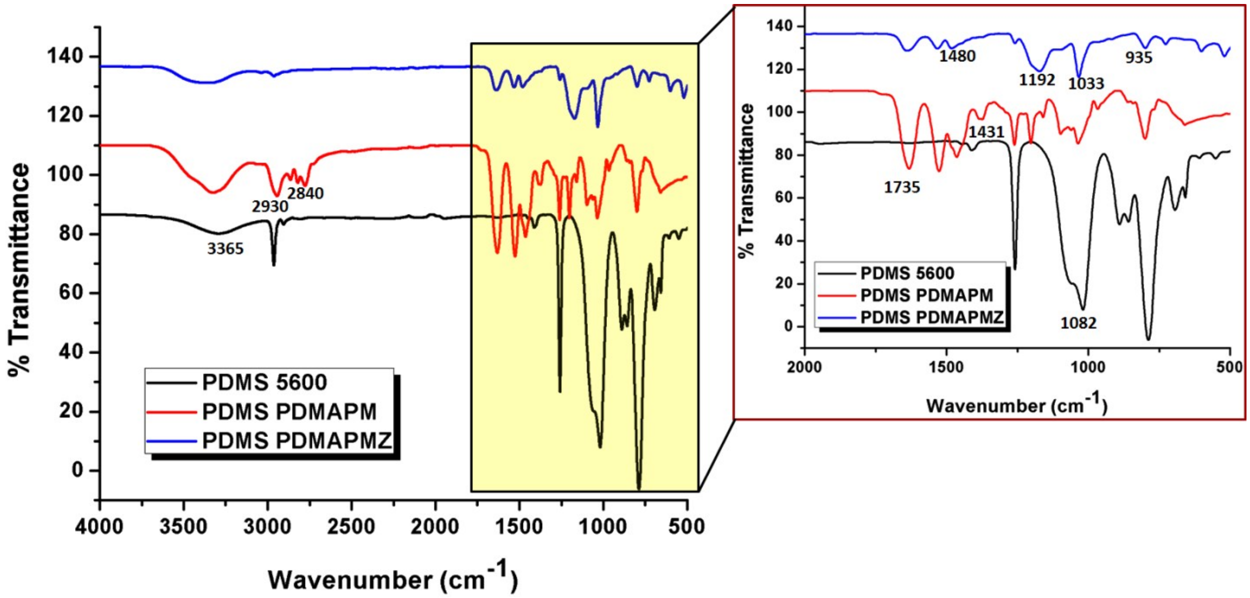


Fig. S6. FTIR analysis of PDMS, PDMAPM-*b*-PDMS-*b*-PDMAPM tri-block copolymer and ZPDMAPM-*b*-PDMS-*b*-ZPDMAPM tri block copolymer.

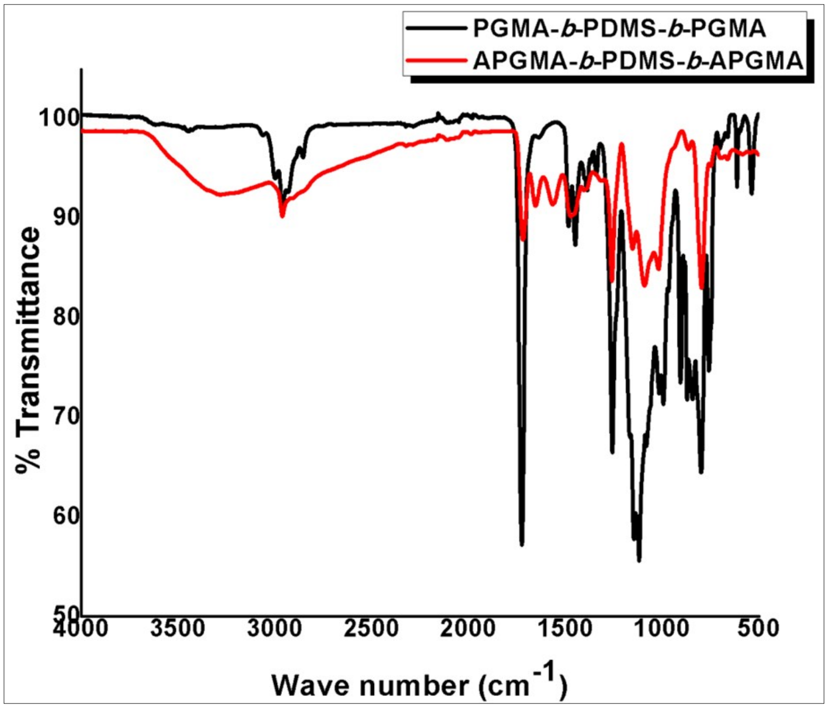


Fig. S7. FTIR analysis of PGMA-*b*-PDMS-*b*-PGMA tri-block copolymer and AmPGMA-*b*-PDMS-*b*-AmPGMA tri block copolymer.

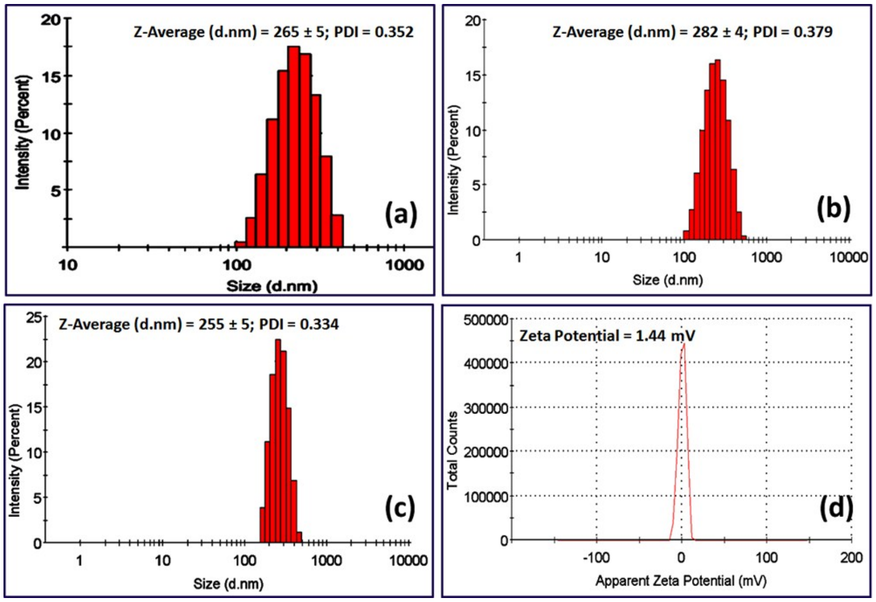


Fig. S8. Dynamic light scattering analysis of **(a)** zwitterionic tri block copolymer based polymersome (ZPDMAPM-*b*-PDMS-*b*-ZPDMAPM), **(b)** curcumin loaded ZPDMAPM-*b*-PDMS-*b*-ZPDMAPM, **(c)** amine modified tri block copolymer based polymersome (AmPGMA-b-PDMS-b-AmPGMA) and **(d)** zeta potential analysis of ZPDMAPM-*b*-PDMS-*b*-ZPDMAPM.

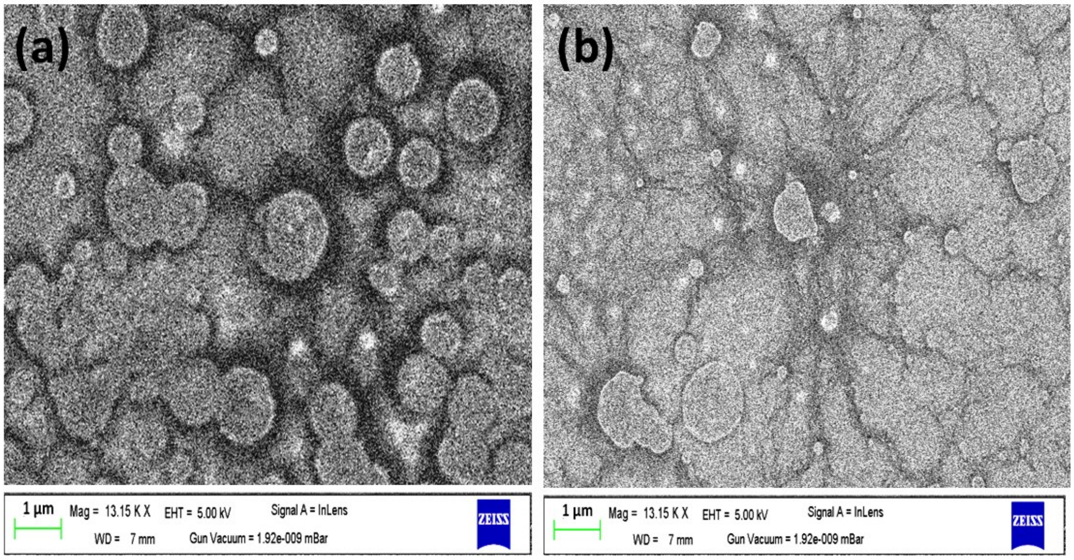


Fig. S9. FESEM images of **(a)** PDMS-NH_2 polymersome crosslinked hydrogel and **(b)** polyzwitterionic polymersome incorporated PDMS-NH_2crosslinked hydrogel.

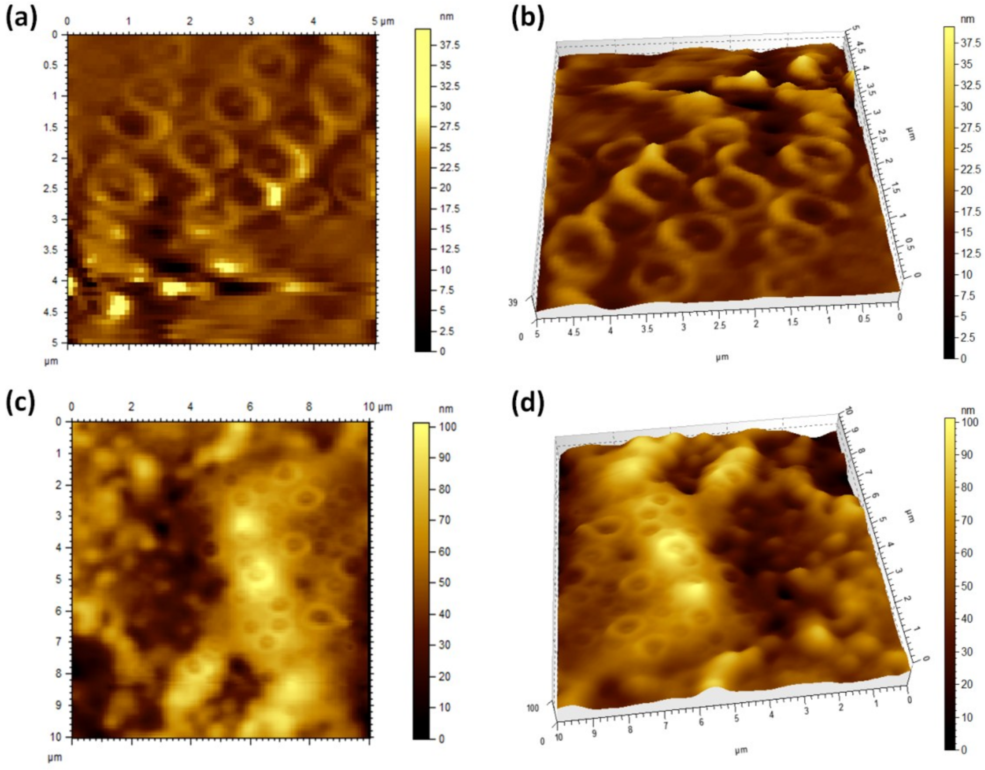


Fig. S10. AFM images of ZPDMAPM-*b*-PDMS-*b*-ZPDMAPM tri-block copolymer based polymersome in **(a)** 2D and **(b)** 3D profile; AFM image of AmPGMA-*b*-PDMS-*b*-AmPGMA tri-block copolymer based polymersome in **(c)** 2D and **(d)** 3D profile.

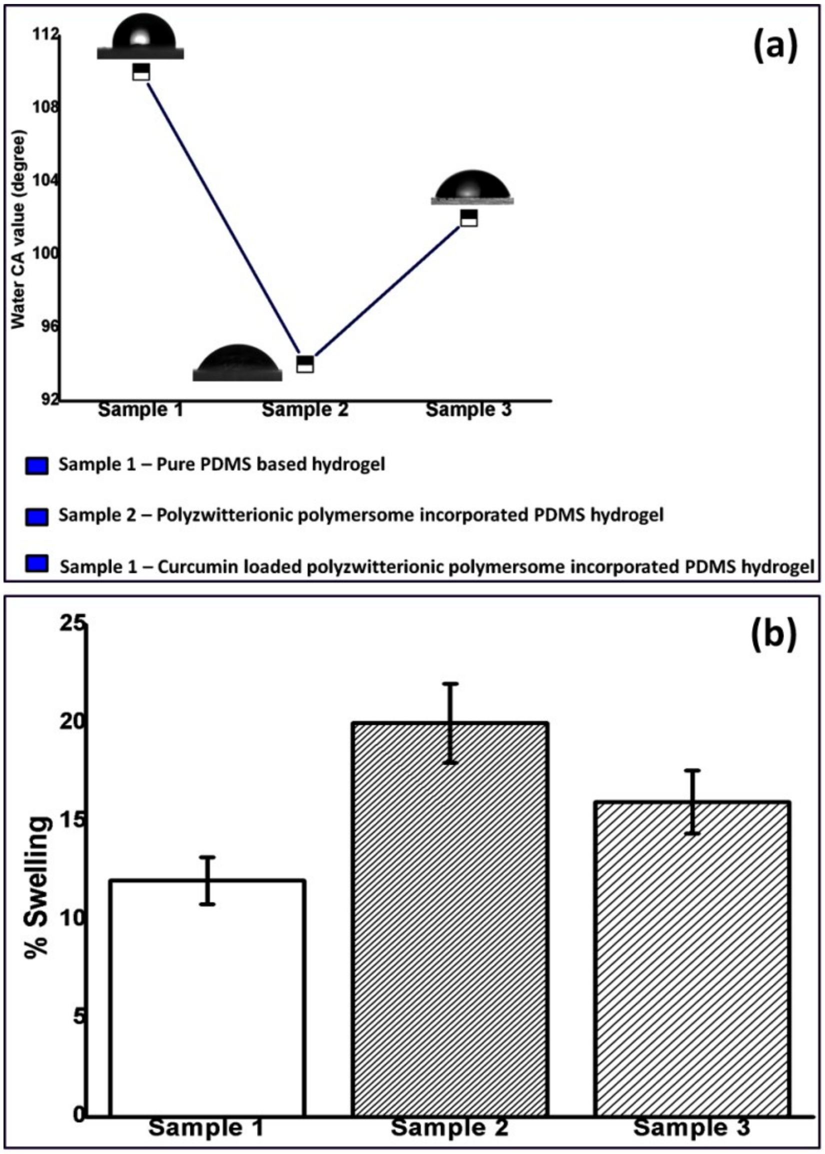


Fig. S11. **(a)** Water contact angle analysis and **(b)** swelling study of the synthesized hydrogels.

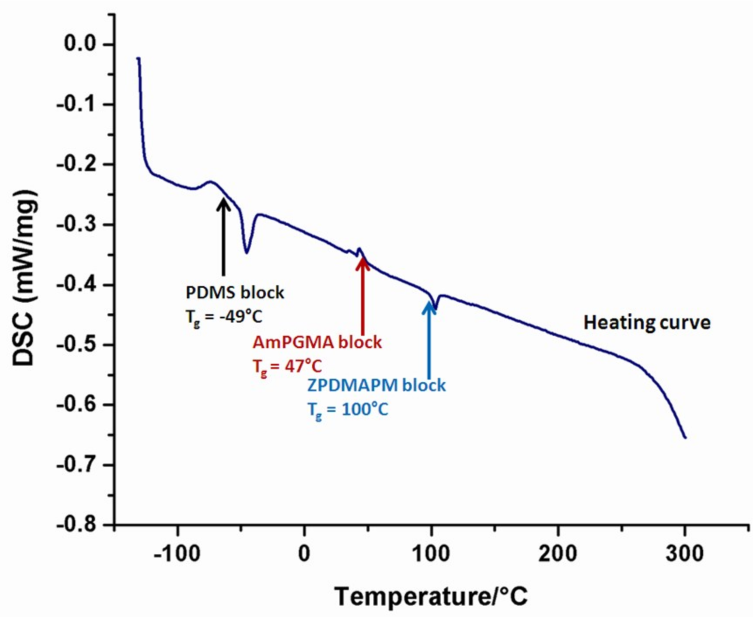


Fig. S12. DSC traces of the zwitterionic PDMS based hydrogel.

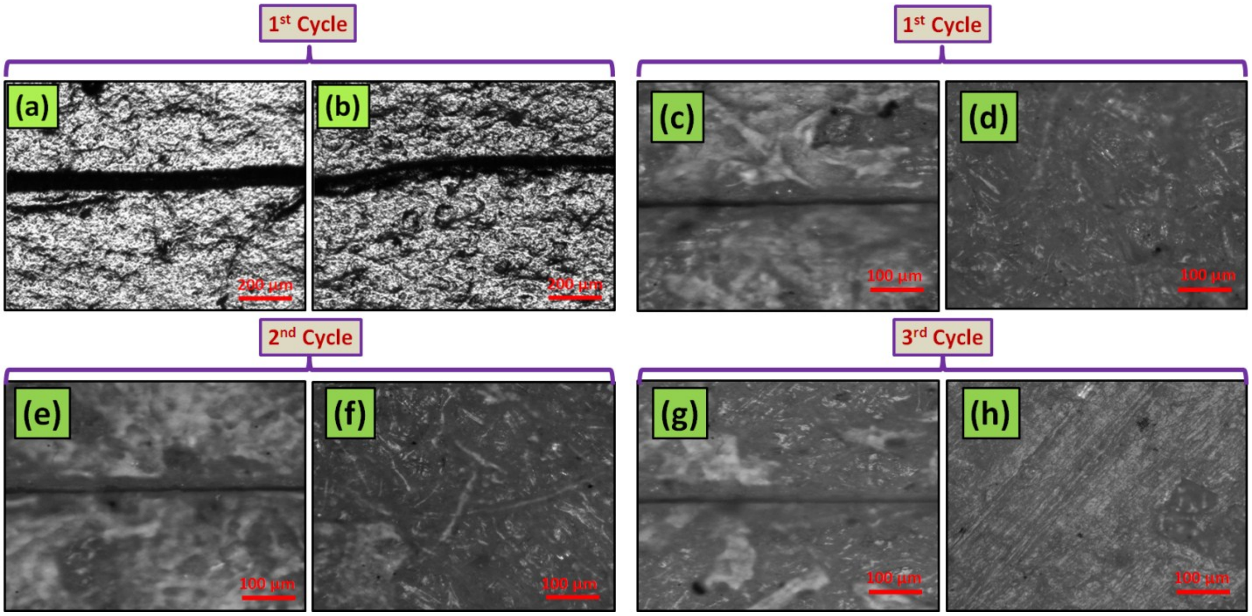


Fig. S13. Optical microscopic images of the self-healing study over the PDMS based hydrogel without polyzwitterionic polymersome **(a)** and **(b)** (1st cycle); with polyzwitterionic polymersome **(c)** and **(d)** (1st cycle), **(e)** and **(f)** (2nd cycle) and **(g)** and **(h)** (3rd cycle).

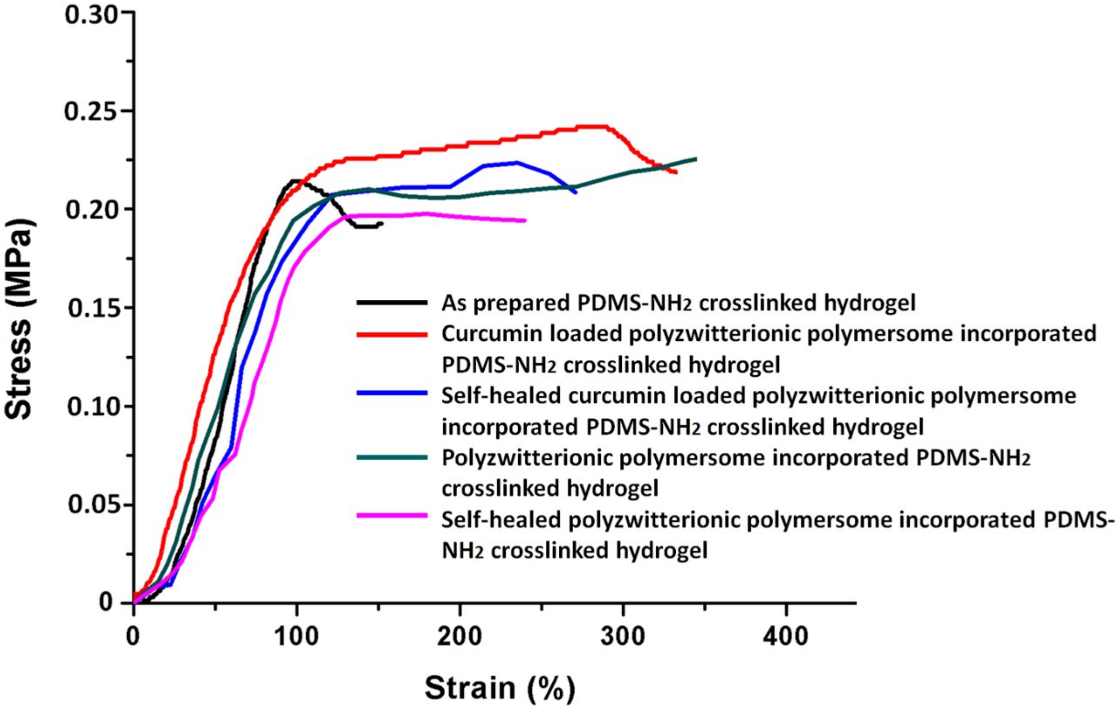


Fig. S14. Tensile study of the prepared hydrogels.

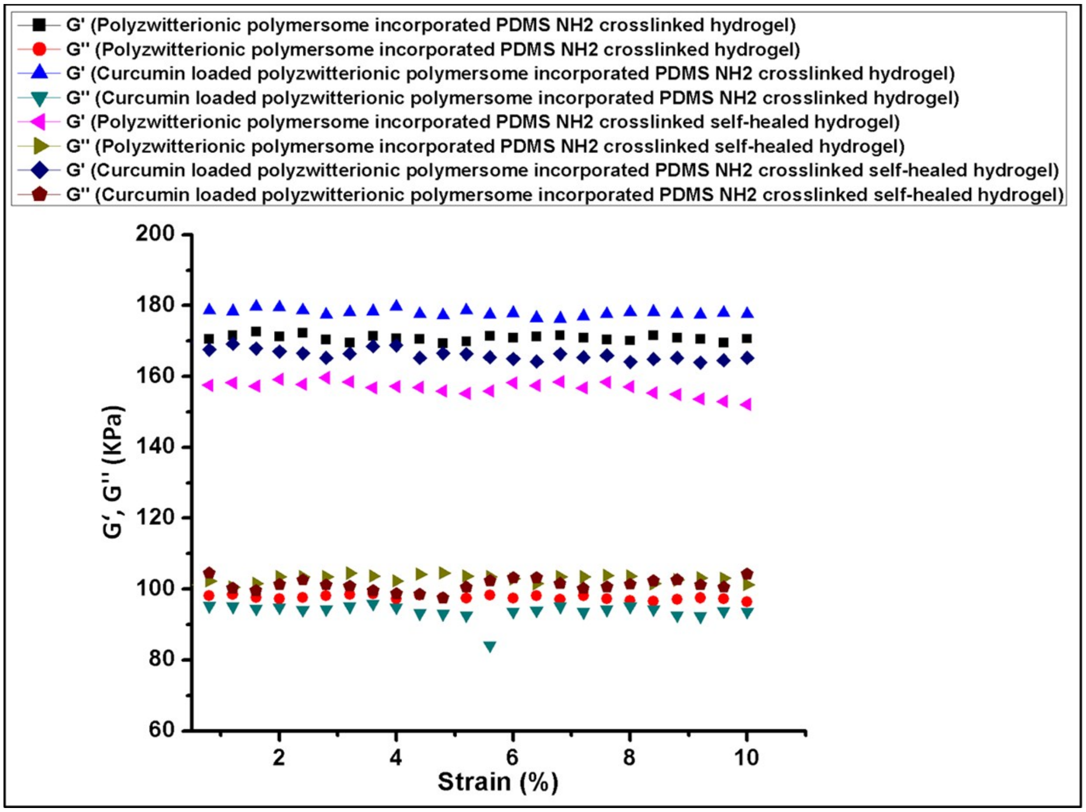
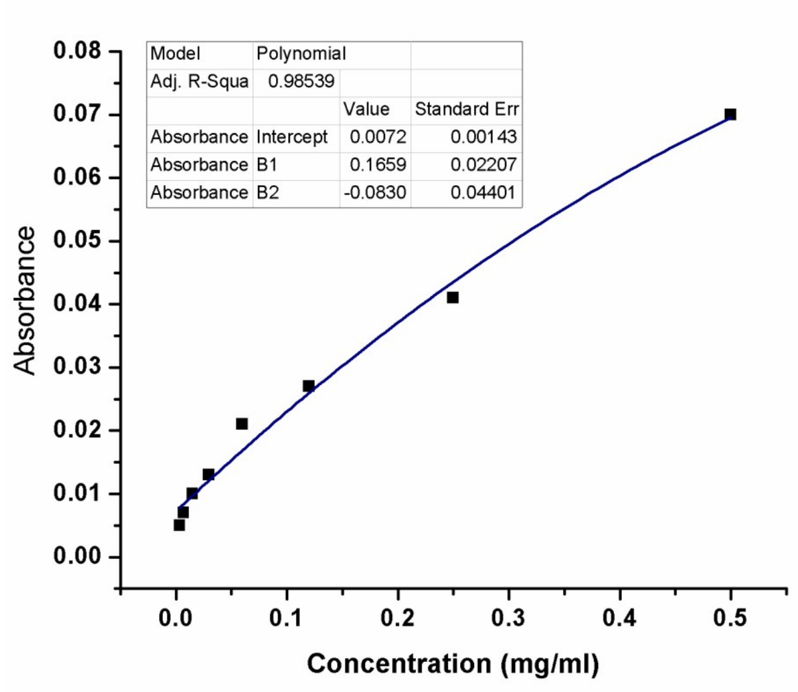


Fig. S15. Study of the self-healing behavior using rheology analysis.



Model	Polynomial		
Adj. R-Squa	0.98539		
		Value	Standard Err
Absorbance	Intercept	0.0072	0.00143
Absorbance	B1	0.1659	0.02207
Absorbance	B2	-0.0830	0.04401

Fig. S16. Calibration curve of 0.154M NaCl solution of BSA.