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# Supporting Information

SUPPORTING INFORMATION

# In Situ Polymerized Hydrogels for Repairing Scleral Incisions Used in Pars Plana Vitrectomy Procedures

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## Experimental section

**Material.** All solvents were dried and freshly distilled prior to use ($CH_2Cl_2$ with $CaH_2$ and MeOH with Na) or were purchased from Acros (DMF). All chemicals were purchased from Aldrich, Acros, Shearwater or CHEM IMPEX as highest purity grade and used without further purification. All reactions were performed under nitrogen atmosphere. NMR spectra were recorded on a Varian INOVA spectrometer (for $^{1}H$, $^{19}F$, and $^{13}C$ at 400, 376.31, and 100.6 MHz, respectively). Chemical ionization mass spectra were obtained on a Hewlett-Packard HP 5988A spectrometer using $NH_3$. Fast atom bombardment mass spectra (FABMS) were obtained on a JEOL JMS-SX102A spectrometer using a 3-nitrobenzyl alcohol matrix. MALDI-MS spectra were obtained using a PerSeptive Biosystems Voyager-DE BioSpectrometer Workstation with 2-(4-hydroxyphenylazo)-benzoic acid (HABA). Elemental analysis was obtained from Atlantic Microlab, Inc. A TA Instruments RA 1000 was used for the rheological measurements. DPTS = 4-(dimethylamino)pyridinium 4-toluenesulfate, DCC = dicyclohexylcarbodiimide, DMF = *N*,*N*-dimethylformamide, DCU = 1,3-dicyclohexylurea, Pd/C = 10% palladium on activated carbon, PFP = 2,3,4,5,6-pentafluorophenol, DIEA = diisopropylethyl amine, HOBT = hydroxybenzotriazol, TFA = trifluoroacetic acid, Z = benzyloxycarbonyl, Boc = terbutyloxycarbonyl, Isopr = isopropylydene. The buffer pH = 7.4 was prepared from HEPES (100 mM) with NaOH 1M.

### Synthesis of ZLys(Z)OPFP

DCC (5.45 g, 26 mmol) in $CH_2Cl_2$ (20 mL) was added in five portions over 10 minutes to a solution of ZLys(Z)OH (10 g, 24 mmol) and PFP (4.49 g, 26 mmol) in freshly distilled $CH_2Cl_2$ (40 mL). The reaction mixture was stirred under $N_2$ at 25 °C for 2 h, filtered to remove the insoluble DCU, concentrated to ~ 20 mL under reduced pressure, and then

stored at 4 °C for 2 h. An additional filtration removed further urea, and the solution was then diluted with hexane (25 mL) and stored at 4 °C for 4h. The resultant white precipitate was collected by filtration, washed with $CH_2Cl_2$/hexane (1:2, 3x5 mL), and dried under vacuum; yield 13.37 g (98%). $^1$H NMR ($CDCl_3$): δ 1.46 (m, 2, C*H*$_2$-CH$_2$); 1.54 (m, 2, C*H*$_2$-CH$_2$); 1.84 (m, 1, C*H*$_2$-CH); 2.00 (m, 1, C*H*$_2$-CH); 3.19 (m, 2, C*H*$_2$-NH); 4.67 (m, 1, C*H*$_2$-CH); 4.8 (m, 1, N*H*); 5.03 (m, 2, C*H*$_2$-O); 5.11 (s, 2, C*H*$_2$-O); 5.54 (m, 1, N*H*); 7.3 (m, 10, arom C*H*). $^{13}$C NMR ($CDCl_3$): δ 22.63 ($CH_2$); 30.06 ($CH_2$); 32.10 ($CH_2$); 40.72 (C*H*$_2$-NH); 54.33 (CH); 67.44 and 68.04 ($CH_2$-O); 128.78-129.22 (CH arom); 136.61 and 137.13 (C arom); 156.61-157.38 (CO-O-NH); 169.48 (CO ester). $^{19}$F NMR ($CDCl_3$): δ -162.26 (t, 2, C*F*); -157.60 (t, 1, C*F*); -152.72 (d, 2, C*F*). FAB MS: 581.7 *m/z* ($MH^+$) (theory: 580.5 *m/z* ($M^+$)). Elemental analysis: (theory: C, 57.93; H, 4.34) found C, 58.12; H, 4.40.

**Synthesis of BocLys(Boc)OPFP**

BocLys(Boc)OPFP was prepared in a similar manner as ZLys(Z)OPFP starting from BocLys(Boc)OH in 92% yield. $^1$H NMR ($CDCl_3$): δ 1.43 (s, 18, Boc $CH_3$); 1.52 (m, 2, C*H*$_2$); 1.87 (m, 2, C*H*$_2$); 1.95 (m, 2, C*H*$_2$); 3.12 (m, 2, C*H*$_2$-NH)); 4.57 (m, 1, C*H*); 5.24 (m, 1, N*H*). $^{13}$C NMR ($CDCl_3$): δ 22.23 (*C*$H_2$); 28.33 (*C*$H_3$); 29.21-31.12 (*C*$H_2$); 39.70 (*C*$H_2$NH); 53.53 (*C*H); 82.50 and 83.13 (*C*-($CH_3$)$_3$); 157.2-157.5 (*C*ONH); 169.46 (*C*O ester). $^{19}$F NMR ($CDCl_3$): δ -162.22 (t, 2, C*F*); -157.72 (t, 1, C*F*); -152.97 (d, 2, C*F*). FAB MS: 535.7 *m/z* ($M + Na^+$) (theory: 512.4 *m/z* ($M^+$)). Elemental analysis: (theory: C, 51.56; H, 5.70; N, 5.47) found C, 51.49; H, 5.68; N, 5.41.

**Synthesis of ZLys(Z)Lys(ZLys(Z))OMe, 1**

LysOMe•2HCl (1.43 g, 6 mmol) was dissolved in DMF (45 mL) and DIEA (2.35 g, 18 mmol), and HOBT (2.25 g, 14 mmol) were then added. After 5 minutes ZLys(Z)OPFP (12.5 g, 21 mmol) in $CH_2Cl_2$ (30 mL) was added at 0 °C for 10 min. The mixture was stirred for 24 h at RT under $N_2$. After concentration under vacuum the mixture was dissolved again in $CH_2Cl_2$ (50 mL) and washed with $NaHCO_3$ (2x150 mL), water (2x150 mL) and dried over $Na_2SO_4$. The solvent was removed, and the mixture was precipited in ether to afford a pure white compound 5.72 g (98%). $^1$H NMR ($CDCl_3$): δ 1.35-1.79 (m, 18, C*H*$_2$-CH$_2$); 2.87 (m, 1, C*H*$_2$-NH); 3.13 (m, 4, C*H*$_2$-NH); 3.40 (m, 1, C*H*$_2$-NH); 3.63 (s, 3, C*H*$_3$); 4.16 (m, 1, C*H*-NH); 4.34 (m, 1, C*H*-NH); 4.38 (m, 1, C*H*-NH); 4.88-5.02 (4 x s, 8, C*H*$_2$-O); 5.13 (m, 1, CH$_2$-N*H*); 5.28 (m, 1, CH$_2$-N*H*); 5.94 (d, 1, CH-N*H*); 6.25 (d, 1, CH-N*H*); 6.88 (m, 1, CH$_2$-N*H*);7.19-7.27 (m, 20, arom C*H*). 7.43 (d, 1, CH-*NH*). $^{13}$C NMR ($CDCl_3$): δ 22.78-41.06 ($CH_2$); 52.95 ($CH_3$); 54.79-55.33 (CH); 67.19 and 67.70 ($CH_2$-O); 128.60-129.11 (CH arom); 136.81 and 137.33 (C arom); 157.23-157.45 (CO-O-NH); 173.16 (CO ester); FAB MS: 953.4 *m/z* ($MH^+$) (theory: 952.4 *m/z* ($M^+$)). Elemental analysis: (theory: C, 64.27; H, 6.77; N, 8.82) found C, 63.98; H, 6.79; N, 8.81.

**Synthesis of ZLys(Z)Lys(ZLys(Z))OH**

ZLys(Z)Lys(ZLys(Z))OMe (5 g, 5.2 mmol) was dissolved in methanol (200 mL) then NaOH 1M (200 ml) was added. The mixture was stirred for 24 h at RT under $N_2$. After acidification until pH 1 by HCl 1M, and concentrated under vacuum the mixture was dissolved again in $CH_2Cl_2$ (200 mL) and washed with HCl 1M (2x150 mL), water (2x150 mL) and dried over $Na_2SO_4$. The solvent was removed and the mixture was precipitate in

ether to afford a pure white compound 4.2 g (85%). $^{1}$H NMR (DMSO-$d_6$): δ 1.26-1.64 (m, 18, C$H_2$); 3.84, 3.95, 4.08 (m, 3, C*H*); 4.95 (m, 8, C$H_2$O); 7.20-7.33 (m, 20, C*H* Arom); 7.83, 8.03 (m, 6, N*H*). $^{13}$C NMR ($CDCl_3$): δ 22.48-32.33 (*C*$H_2$); 40.72 (*C*$H_2$NH); 52.48-53.72 (*C*H); 66.80-67.16 ($CH_2O$); 128.07-128.70 (*C*H Arom); 136.39-136.72 (*C* Arom); 157.05 (*C*O acid). FAB MS: 939.5 *m/z* ($MH^+$) (theory: 938.4 *m/z* ($M^+$)). Elemental analysis: (theory: C, 63.95; H, 6.65; N, 8.95; O, 20.45) found C, 63.70; H, 6.45; N, 9.02.

**Synthesis of ZLys(Z)Lys(ZLys(Z))OPFP**

ZLys(Z)Lys(ZLys(Z))OPFP was prepared in a similar manner as ZLys(Z)OPFP starting from ZLys(Z)Lys(ZLys(Z))OH in 95% yield. $^{1}$H NMR ($CDCl_3$): δ 1.21-2.01 (m, 18, $CH_2$); 3.17 (m, 4, C$H_2$NH); 3.55 (m, 2, C$H_2$NH); 3.90, 4.41, 4.75 (m, 3, C*H*); 5.01-5.22 (m, 8, C$H_2$Z); 5.56, 5.73, 5.90, 6.82, 7.21, 7.50 (m, 6, N*H*); 7.21-7.38 (m, 20, Arom). $^{13}$C NMR ($CDCl_3$): δ 22.27-31.12 (*C*$H_2$); 31.91-35.95 (*C*$H_2$NH); 47.62-52.43 (*C*H); 62.01-65.84 (*C*$H_2$-O); 122.45-123.99 (*C*H arom); 131.65-137.98 (*C* arom); 153.36-154.00 (*C*O-O-NH); 168.54-170.23 (*C*O-NH). $^{19}$F NMR ($CDCl_3$): δ -162.27 (t, 2, C*F*); -157.62 (t, 1, C*F*); -152.86 (d, 2, C*F*). FAB MS: 1105.4 *m/z* ($MH^+$) (theory: 1104.4 *m/z* ($M^+$)). Elemental analysis: (theory: C, 60.86; H, 5.56; F, 8.60; N, 7.60; O, 17.37) found C, 60.70; H, 5.74; N, 7.55.

**Synthesis of LysLys(Lys)OMe• 4HCl, 2**

Pd/C (10% w/w) was added to a solution of ZLys(Z)Lys(ZLys(Z))OMe (1 g, 1 mmol) in MeOH (50 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 50 psi of $H_2$ before shaking for 10 h. The catalyst was removed by filtration and the catalyst was washed with MeOH (20 mL). The solution containing the product was acidified with HCl 1M. The solution was then evaporated to give 578 mg of the white compound (98%). $^{1}$H NMR (DMSO-$d_6$): δ 1.36-1.81 (m, 18, C$H_2$-$CH_2$); 2.75 (m, 4, C$H_2$-$NH_3^+$); 3.12 (m, 2, C$H_2$-NH); 3.65 (s, 3, C$H_3$); 3.82 (m, 1, C*H*-NH); 3.98 (m, 1, C*H*-NH); 4.25 (m, 1, C*H*-NH); 8.20-8.45 (m, 12, $NH_3^+$); 8.88 (t, 1, $CH_2$-N*H*); 9.18 (d, 1, CH-N*H*). $^{13}$C NMR ($CD_3OD$): δ 23.40-41.23 ($CH_2$); 50.32 ($CH_3$); 53.80-55.10 (CH); 170.80-171.18 (CO-NH); 174.61 (CO ester); FAB MS: 417.4 *m/z* ($MH^+$- 4HCl) (theory: 560 *m/z* ($M^+$)). Elemental analysis: (theory: C, 40.65; H, 7.72; Cl, 25.26; N, 14.97) found C, 40.31; H, 7.87; Cl, 25.10; N, 14.97.

**Synthesis of BocLys(Boc)Lys(BocLys(Boc))Lys(BocLys(Boc)Lys(BocLys(Boc)))OMe**

BocLys(Boc)Lys(BocLys(Boc))Lys(BocLys(Boc)Lys(BocLys(Boc)))OMe was prepared in a similar manner as ZLys(Z)Lys(ZLys(Z))OMe but starting from LysLys(Lys)OMe•4HCl. **2** (300 mg, 0.53 mmol) was dissolved in DMF solution (45 mL), and then DIEA (330 mg, 2.5 mmol), HOBT (390 mg, 2.5 mmol), and (Boc)Lys(Boc)OPFP (1.6 g, 3.2 mmol) were added. The reaction was run for 24h at room temperature. The solution was concentrated and the product purified by silica gel chromatography ($CH_2Cl_2$/MeOH = 95/5): yield 650 mg (70 %). $^{1}$H NMR (DMSO-$d_6$): δ 1.16-1.62 (m, 42, C$H_2$-$CH_2$); 1.32 (s, 72, Boc C$H_3$); 2.81 (m, 8, C$H_2$-NH Boc); 2.96 (m, 6, C$H_2$-NH); 3.56 (s, 3, C$H_3$-O); 3.76 (m, 4, C*H*-NH Boc); 4.12 (m, 2, C*H*-NH); 4.25 (m, 1, NH-C*H*-$CO_2CH_3$); 6.43, 6.67, 6.85, 7.69, 7.84 and 8.24 (m, 14, N*H*). $^{13}$C NMR (DMSO-$d_6$): δ 28.10 (*C*$H_2$); 33.41-37.12 (*C*$H_2$ and *C*$H_3$); 52.80 (O*C*$H_3$); 56.95 (*C*H);

59.59 (*C*H); 82.53-83.13 (*C*-$(CH_3)_3$); 157.23-158.10 (*C*ONH); 160.75 (*C*O ester); 177.05-177.51 (*C*O-NH). FAB MS: 1730.1 *m/z* ($MH^+$) (theory: 1729.1 *m/z* ($M^+$)). Elemental analysis: (theory: C, 57.62; H, 8.85; N, 11.33) found C, 57.37; H, 8.94; N, 11.10.

**Synthesis of LysLys(Lys)Lys(LysLys(Lys))OMe• $8CF_3CO_2H$, 3**

TFA (5 mL) was added in 10 portions over 10 minutes to a solution of BocLys(Boc)Lys(BocLys(Boc))Lys(BocLys(Boc))Lys(BocLys(Boc))OMe (100 mg, 0.057 mmol) in freshly distilled $CH_2Cl_2$ (30 mL) at 0 °C. The reaction mixture was stirred under $N_2$ at 25 °C for 1 h. The product was isolated after evaporation of the solvent to give a pure white compound 104 mg (99 %). $^1$H NMR (DMSO-$d_6$): δ 1.26-1.64 (m, 48, C*H*$_2$-$CH_2$); 2.76 (m, 8, C*H*$_2$-NH); 3.04 (m, 6, C*H*$_2$-NH); 3.57 (s, 3, C*H*$_3$); 3.65 and 3.76 (m, 4, C*H*-$NH_3^+$); 4.12 (m, 2, C*H*-NH); 4.25 (m, 4, NH-C*H*-$CO_2CH_3$). 7.82, 8.15, and 8.50 (m, 30, NH and $NH_3^+$). $^{13}$C NMR (DMSO-$d_6$): δ 21.12-31.25 (*C*$H_2$); 52.53-52.77 (*C*H and *C*$H_3$); 159.74 (*C*O ester); 168.80-173.04 (*C*ONH). FAB MS: 929.2 *m/z* ($MH^+$ -$8CF_3CO_2H$) (theory: 140.6 *m/z* ($M^+$)). Elemental analysis: (theory: C, 55.58; H, 9.55; N, 21.10) found C, 55.30; H, 9.59; N, 21.00.

**Synthesis of Bis(2-amido-Zlys(Z))-poly(ethylene glycol)**

Polyethylene glycol diamino Mw=3400 g/mol (1 g, 0.3 mmol) was dissolved in DCM (5 mL) followed by the addition of HOBT (112 mg, 0.7 mmol), and DIEA (113 mg, 0.9 mmol). After 5 min the ZLys(Z)OPFP (500 mg, 0.9 mmol) in $CH_2Cl_2$ (5 mL) was added at 0 °C. The reaction mixture was stirred for 24 h at 25 °C under $N_2$. After concentration under vacuum the mixture was dissolved in DCM (100 mL) and washed with $NaHCO_3$ (2x100 mL), water (2x100 mL), and then dried over $Na_2SO_4$. Evaporation of the organic solvent gave an oil that was purified by precipitation in cool ether to give a white powder 1.14 g (95 %). $^1$H NMR ($CDCl_3$): δ 1.33, 1.48, 1.61-1.77 (m, 12, C*H*$_2$-$CH_2$); 3.13 (m, 4, C*H*$_2$-NH); 3.41 (m, 4, C*H*$_2$-NH); 3.55-3.80 (m, 340, PEG); 4.10 (m, 2, C*H*); 4.99 (m, 2, N*H*); 4.99-5.04 (m, 8, $CH_2$Z); 5.61 (m, 2, N*H*); 6.60 (m, 2, N*H*); 7.24-7.30 (m, 20, Arom). $^{13}$C NMR ($CDCl_3$): δ 22.30, 29.37, 32.42 (*C*$H_2$); 39.31, 40.42 (*C*$H_2$NH); 54.81 (*C*H); 66.52 (*C*$H_2$O); 69.60-70.62 (*PEG*); 128.19-128.63 (*C*H Arom); 136.47, 136.82 (*C* Arom); 156.31-156.75 (*C*ONH); 171.85 (*C*O-NH PEG). MALDI MS: $M_W$ 4153 (theory: 4164 $M_W$) g/mol.

**Synthesis of Bis(2-amido-lysine)-poly(ethylene glycol), 4**

Pd/C (10% w/w) was added to a solution of bis(2-amido-Zlys(Z))-poly(ethylene glycol) (1 g, 0.24 mmol) in MeOH (50 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 50 psi of $H_2$ before shaking for 10 h. The catalyst was removed by filtration and the catalyst was washed with MeOH (20 mL). The solution containing the product was neutralized with HCl 1M until pH=7. The solution was evaporated and then the compound was precipitated in cool ether to give 780 mg of the white compound (99%). $^1$H NMR (DMSO-$d_6$): δ 1.29-1.46 (m, 12, C*H*$_2$-$CH_2$); 2.69 (m, 4, C*H*$_2$-NH); 3.18 (m, 2, C*H*-$NH_3^+$); 3.28 (m, 4 , C*H*$_2$-$NH_3^+$); 3.40-3.62 (m, 340, C*H*$_2$ of PEG); 8.01 (m, 2, NH). $^{13}$C NMR (DMSO-$d_6$): δ 22.40, 30.32, 32.01 ($CH_2$); 53.00 (CH); 170.00-172.34 (CO-NH). MALDI MS: $M_W$ 3620) (theory: $M_W$ 3632) g/mol.

**Synthesis of Bis(2-amido-ZLys(Z)Lys(ZLys(Z)))-poly(ethylene glycol)**

Bis(2-amido-ZLys(Z)Lys(ZLys(Z)))-poly(ethylene glycol) was prepared in a similar manner as bis(2-amido-Zlys(Z))-poly(ethylene glycol) but starting from polyethylene glycol diamino Mw=3400 g/mol (2 g, 0.6 mmol), HOBT (224 mg, 1.4 mmol), DIEA (275 mg, 1.8 mmol), and ZLys(Z)Lys(ZLys(Z))OPFP (1.8 g, 1.8 mmol). The reaction was run for 24h at RT. The solution was concentrated and purified by precipitation in cool ether to give a white powder 2.96 g (96 %). $^{1}$H NMR ($CDCl_3$): δ 1.16-1.84 (m, 36, C*H*$_2$-CH$_2$); 3.12 (m, 12, C*H*$_2$-NH); 3.46 (m, 4, C*H*$_2$NH of PEG); 3.60-3.63 (m, 340, C*H*$_2$ of PEG); 4.02-4.30 (m, 6, C*H*); 5.00-5.05 (m, 16, C*H*$_2$OCO); 5.80-6.60 (m, 12, N*H*); 7.23-7.28 (m, 40, Arom). $^{13}$C NMR ($CDCl_3$): δ 22.13-40.89 (*C*H$_2$); 51.95-55.92 (*C*H); 67.02-67.95 (*C*H$_2$O); 127.98-129.21 (*C*H Arom); 136.72-137.41 (*C* Arom); 157.10-157.67 (*C*O-O-NH); 172.01 (*C*ONH of PEG). MALDI MS: $M_W$ 5198 (theory: $M_W$ 5242) g/mol.

**Synthesis of Bis(2-amido-LysLys(Lys))-poly(ethylene glycol), 5**

Was prepared in a similar manner as bis(2-amido-lysine)-poly(ethylene glycol) but starting from bis(2-amido-ZLys(Z)Lys(ZLys(Z)))-poly(ethylene glycol), yield 99 %. $^{1}$H NMR (DMSO-$d_6$): δ 1.19-1.69 (m, 36, C*H*$_2$-CH$_2$); 2.70 (m, 8, C*H*$_2$NH); 3.10 (m, 4, C*H*$_2$NH of PEG); 3.24-3.63 (m, 340, C*H*$_2$ of PEG); 3.80-4.20 (m, 6, C*H*); 8.02-8.53 (m, 16, N*H*). $^{3}$C NMR (DMSO-$d_6$): δ 23.13-40.48 (*C*H$_2$); 52.80-54.92 (*C*H); 170.00-172.07 (*C*ONH). MALDI MS: $M_W$ 4150 (theory: $M_W$ 4170) g/mol.

**Rheology.**

Rheological measurements were performed on a RA 1000 controlled strain rheometer from TA Instrument equipped with a peltier temperature control. Cylindrical hydrogel samples of 8 mm diameter and 3 mm thickness were prepared for each type of dendron in triplicate in a precast teflon mold (n =3). Before swelling each sample was allow reaching the equilibrium at 25 °C for 24 hours and 8 mm steel plate diameter geometry was used to measure the rheological properties. The swelling equilibrium for each type of dendron at different concentration was determinate as 24 hours by weight measurement. After swelling at 25 °C for 48 hours we used either a 12 mm diameter steel plate or a 20 mm aluminum plate geometry to measure the rheological properties according the diameter of the sample. Care was always taken to use a bigger geometry than sample. All rheological measurements were performed with a cover and at 25 °C to avoid evaporation. The insensitive to temperature of each hydrogel was check at different temperature (25 °C and 37 °C) on one sample of each group. Each rheological measurement was performed at 25 °C to prevent dehydration as follow. First to determine the Pseudo-Linear Viscoelastic Region (LVR) an oscillatory strain sweep (strain amplitude from 0.01 to 10%) at fixed frequency (1 Hz) was perform. Secondly, a normal force (enough to obtain a flat surface) was applied to the gel using either geometry and a strain-rate compression test (maximum compression as 10% of the height) was realized to determine the compress modulus, E. After equilibrium (15 min at zero strain) an oscillatory frequency sweep (from 0.1 to 10 Hz) with a controlled strain for a linear response (as determine in the LVR test) was performed at 25 °C. This measures the storage modulus G', the lost modulus G'' and the complex modulus G*. All data are reported at a frequency of 1 Hz.

**Reaction kinetics.**
We investigated the rate of crosslinking with a React IR 4000 (Mettler Teledo). The concentrations used for this experiment was the same as for the *in vitro* experiment (18% w/w). Almost all spectral features of the polymerization are obscured by water absorbances. Therefore, the spectrum of the starting mixture in water was subtracted from the spectra to display the absorbance changes of monomer as it was consumed in the formation of the hydrogel. The reaction was monitored at 1733 $cm^{-1}$ for the starting material .

**Swelling ratio.**
Cylindrical hydrogels (d = 8 mm, h = 3 mm) were immersed in buffer HEPES 100 mmol for two (2) days, equilibrium diameters, heights, and weights were measured using either a digital micrometer or a milligram precision scale. The equilibrium conditions were obtained after three consecutive measurements, 6 hours between each measurement, yielded the same results. The swelling ratio was calculated by dividing the weight of the hydrogels at equilibrium swelling minus the weight just after gelation by their weight just after gelation.

$$Q=(Weq-Wo)/Wo$$

**Vitrectomy**

All extraocular muscle, fat, subconjunctiva and tenon were removed from the 17 porcine globes. The globes were cut in half, bisecting the cornea. Uvea, viteous and lens were removed from each hemiglobe and the corneal/scleral shells were individually mounted on a watertight artificial anterior chamber with two-port access. One port was used to infuse balanced salt solution and the other port was attached to a transducer to monitor pressure. Using a 19-guage MVR blade, a pars plana, full-thickness sclerotomy wound was made in each shell perpendicular to the limbus. Seven wounds were left unrepaired. Six wounds were closed using a traditional 3-pass running configuration with 7-0 vicryl suture. Four wounds were sealed using the biodendritic adhesive. For the hydrogel sealant treatment group, the solution of the adhesive was applied to the wound and the adhesive cured in less than one minute. BSS was then infused into the chamber at a rate of 5mL/hour. Infusion was continued until the wound leaked, at which point the pressure was noted (designated as the leaking pressure). If the wound had not leaked with a pressure greater than 250 mm Hg, the recording of the pressure was halted.

To test if the adhesion of the polymer at the wound surface of the sclera involves covalent attachment with the amines of the proteins the following experiment was carrying out. First, the surface the sclera was basified with phosphate buffer at pH = 9 to activate the amines. Next, 50 µl of a solution of 20 % w/w of PEG-NHS, **6**, in buffer (HEPES pH = 7.4) was added to the site wound. The solution was let to react for 15 min before to perform the leaking experiment to conform than the PEG-NHS, **6**, alone did not seal the

laceration. Then the wound site was washed 3 times with phosphate buffer at pH = 9 to hydrolyze all the remaining unreacted hydroxy-succinimide functions followed by washing the surface with neutral buffer (HEPES pH = 7.4). The adhesive was applied to the wound and the pressure was monitored as previously to determine at which point leakage occurs. The wound had not leak up to 250mm/Hg