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Functional porous membranes from amorphous linear dendritic polyester hybrids

Surinthra Mongkhontreerat,[a] Marie V. Walter, [a] Yanling Cai,[a] Hjalmar Brismar, [b] , Anders Hult, [a] and Michael Malkoch*[a]

[a] KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Fibre and Polymer Technology, SE-100 44, Stockholm, Sweden.
[b] KTH Royal Institute of Technology, Science for Life Laboratory, School of Engineering Sciences, Division of Cell Physics,SE-106 91 Stockholm, Sweden

Corresponding author:
Dr. Michael Malkoch

Contact info:
KTH Royal Institute of Technology
School of Chemical Science and Engineering
Department of Fibre and Polymer Technology
Teknikringen 56-58, SE-100 44 Stockholm, Sweden
Fax: (+) 46 (0)8 790 8283
E-mail: malkoch@kth.se
www.kth.se

Contents

Materials

2-hydroxyethyl methacrylate (HEMA) (95 %) and anisole were purchased from Fluka. 4-dimethylaminopyridine (DMAP) (99 %), 2-hydroxyethyl 2-bromoisobutyrate (HO-EBiB), 2,2'-bipyridyl (99 %), Cu(I)Cl (99 %), Cu(II)Cl2 (97 %), tetraethylene glycol (TEG), 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heneicosafluoro-1-undecanol and rhodamine-B were purchased from Sigma-Aldrich. Succinic anhydride, dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate (EtOAc), heptane and methanol were purchased from Merck. Pyridine was purchased from VWR. 2,2-Dimethoxy-2 phenylacetophenone (DMPA, Irgacure 651)was purchased from Ciba. All chemicals were used as received.

Analysis and equipment

NMR spectroscopy was conducted on a Bruker AM NMR. 1H-NMR and 13C-NMR spectroscopies were performed at 400 MHz and 100 MHz respectively using CDCl3 or MeOD as solvent.

DMF-SEC measurements were conducted on a TOSOH EcoSEC HLC-8320GPC system equipped with an EcoSEC RI detector and three columns (PSS PFG 5µm; Microguard, 100Å, and 300Å) (MW resolving range: 300-100 000 Da) from PSS GmbH, using DMF as mobile phase (0.2 mL min-1 with 0.01 M LiBr) was conducted at 50 °C on a TOSOH EcoSEC HLC-8320GPC system equipped with an EcoSEC RI detector and three columns (PSS PFG 5 µm; Microguard, 100 Å, and 300 Å) from PSS GmbH. A conventional calibration method was created using narrow linear poly(methyl methacrylate) standards. Toluene was used as an internal standard for correction of flow rate fluctuation. The data were processed with the software PSS WinGPC Unity version 7.2.

DSC measurements were conducted on a Mettler Toledo DSC. The heating and cooling rate were fixed at 10 °C/min. The temperature was increased from 25 °C to 120 °C, stabilized for 2 min, decreased to -60 °C, stabilized 2 min and increased again to 120 °C. The glass transition temperature was obtained from the second heating.

FE-SEM images were acquired on a Hitachi S-4300 FE-SEM. The samples were coated with 5 nm of platinum before imaging.

Thiol-ene coupling reactions were performed using a UVP Black-Ray® B-100AP High Intensity UV Lamp at a wavelength of 365 nm.

Optical microscope was conducted on a Leica DM IRM opical microscopy.

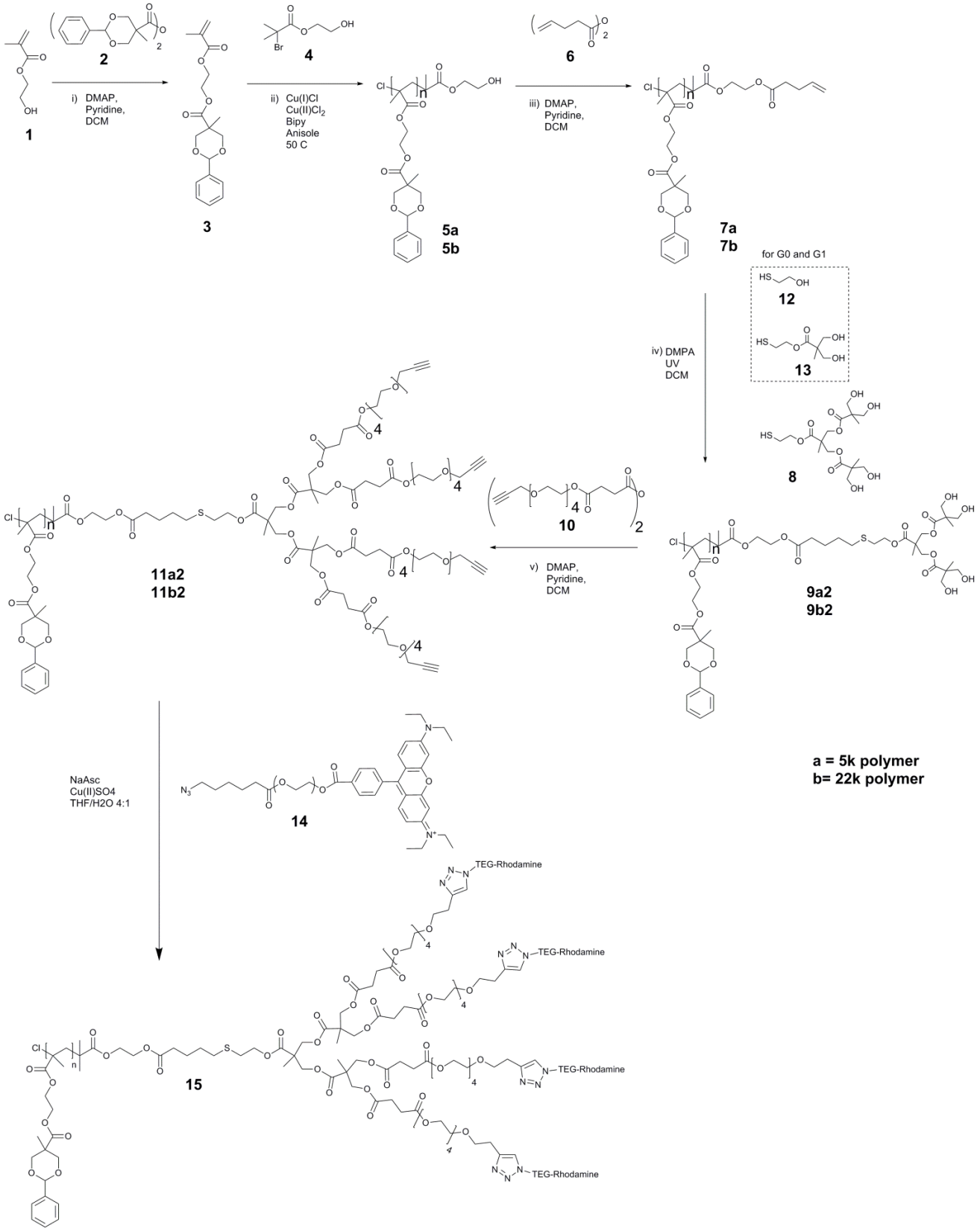
For confocal microscopy analysis the honeycomb films were mounted and coverslipped by applying 50 µl of aqueous non-fluorescing mounting medium (Shandon Immu-Mount). Confocal fluorescence microscopy was performed using a Zeiss LSM5 Pascal microscope equipped with a 63X/1.4 NA oil immersion objective. Rhodamine-B fluorescence was excited at 543 nm and emission was detected with a long pass 570 nm filter. Field of view was set to 18 µm, Z-stacks were recorded with a spacing

of 0.4 μm between optical sections.

Contact angle measurement was analyzed by KSV Instrument CAM 200 equipped with a Basler A602F camera. All the measurements were performed under controlled temperature (25 °C) and relative humidity (RH=60%)

Material Synthesis

Synthesis route for linear dendritic hybrid



Scheme S1 Synthesis route for linear dendritic hybrid

Synthesis of HEMA-benzylidene monomer (HEMA-B_z) (3)

2-hydroxyethyl methacrylate (HEMA) **(1)** (18 ml, 148 mmol) and 4-dimethylaminopyridine (3.62 g, 30 mmol) were dissolved in pyridine (33 ml, 444 mmol) and dichloromethane (100 ml). The solution was placed on ice bath and benzylidene protected bis-MPA anhydride **(2)** (70 g, 164 mmol) dissolved in dichloromethane (100 ml) was slowly added to the solution. The reaction was monitored by ^{13}C NMR. After completion, the residual anhydride was quenched with water. The solution was then extracted 5 times with a 10 % $NaHSO_4$ solution and 2 times with a 10 % Na_2CO_3 solution. The organic phase was dried on $MgSO_4$ and evaporated. The product was collected as a white powder. Yield: 48.5 g, 98 %. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.04 (3H, s, -C-C**H$_3$**), 1.90 (3H, s, CH_2=C(C**H$_3$**)-C=O), 3.65 (2H, d, J = 11.4 Hz, -C-C**H$_2$**-O-), 4.40 (2H, m, -C**H$_2$**-O-C=O-), 4.46 (2H, m, -C**H$_2$**-O-C=O-), 4.66 (2H, d, J = 11.4 Hz, -C-C**H$_2$**-O-), 5.45 (1H, s, Bz-C**H**-), 5.51 (1H, s, -C(CH_3)=C**H$_2$**), 6.09 (1H, s, -C(CH_3)=C**H$_2$**), 7.31-7.43 (5H, m, Benzyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 18.1, 18.4, 42.7, 62.5, 62.9, 73.7, 102.0, 126.3, 126.4, 128.4, 129.2, 136.0, 137.9, 167.3, 173.9.

Synthesis of poly(HEMA-Bz)5k-OH (5a)

In a round bottom flask HEMA-Bz **(3)** (12 g, 36 mmol), HO-EBiB **(4)** (250 mg, 1.2 mmol), 2,2'-bipyridyl (371 mg, 2.4 mmol) were dissolved in anisole (12 ml). The flask was sealed with a rubber septum and degassed with vacuum for 5 min and argon for 5 min. The flask was opened and Cu(I)Cl (118 mg, 1.2 mmol) and Cu(II)Cl_2 (16 mg, 0.1 mmol) were added to the system. The flask was sealed, degassed by two cycles of 5 min vacuum followed by 5min argon, and immersed in a thermostated oil bath at 50 °C. The reaction was monitored by ^1H NMR and when a monomer conversion of 50 % was reached, the reaction solution was exposed to air and diluted with DCM. The solution was passed through a neutral aluminum oxide column to remove the copper. The solvent was evaporated and the polymer was precipitated twice from THF to cold MeOH. The product was collected as a white powder. Yield: 4g, 65%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.86-1.11 (6H, m, **CH$_3$** backbone and -C(=O)-C(**CH$_3$**)-(CH_2-O-)$_2$), 1.76 (2H, m, **CH$_2$** backbone), 3.58 (2H, m, -C(CH_3)-(**CH$_2$**-O-)$_2$), 4.08 (2H, m, -O-**CH$_2$-CH$_2$**-O-), 4.28 (2H, m, -O-**CH$_2$-CH$_2$**-O-), 4.55 (2H, m, -C(CH_3)-(**CH$_2$**-O-)$_2$), 5.39 (1H, m, -**CH**-Bz), 7.31-7.41 (5H, m, **Bz**).

Synthesis of poly(HEMA-Bz)22k-OH (5b)

The polymerization was performed using a similar procedure with HEMA-Bz **(3)** (12 g, 36 mmol), HO-EBiB **(4)** (42 mg, 0.2 mmol), 2,2'-bipyridyl (62 mg, 0.4 mmol) Cu(I)Cl (20 mg, 0.2 mmol), Cu(II)Cl2 (3 mg, 0.02 mmol) and anisole (12 ml) except that the temperature was raised to 55°C and the reaction was stopped at 36 % conversion. Yield: 2.7 g, 90 %. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.94-1.04 (6H, m, **CH$_3$** backbone and -C(=O)-C(**CH$_3$**)-(CH_2-O-)$_2$), 1.89 (2H, m, **CH$_2$** backbone), 3.56 (2H, m, -C(CH_3)-(**CH$_2$**-O-)$_2$), 4.07 (2H, m, -O-**CH$_2$-CH$_2$**-O-), 4.27 (2H, m, -O-**CH$_2$-CH$_2$**-O-), 4.55 (2H, m, -C(CH_3)-(**CH$_2$**-O-)$_2$), 5.36 (1H, m, -**CH**-Bz), 7.29-7.39 (5H, m, **Bz**).

Synthesis of poly(HEMA-Bz)5k-allyl (7a)

poly(HEMA-Bz)5k-OH **(5a)** (3.5 g, 0.70 mmol), DMAP (17 mg, 0.14 mmol), pyridine (156 µl, 2.1 mmol) and DCM (3 ml) were introduced in a round bottom flask and the flask was placed on an ice bath. 4-pentenoic anhydride **(6)** (191 µl, 1.05 mmol) was dissolved in DCM (2 ml) and the solution was slowly added to the round bottom flask. The reaction was left to react over night at room temperature. The product was purified by precipitation from THF to cold methanol. Yield: 2.2 g, 61 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87-1.01 (m, **CH_3** backbone and -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$), 1.75 (m, **CH_2** backbone), 2.37-2.40 (4H, m, C(=O)-**CH_2-CH_2**-=), 3.57 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.28 (m, -O-**CH_2-CH_2**-O-), 4.53 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 4.99-5.07 (2H, m, -CH=**CH_2**), 5.37 (1H, m, -**CH**-Bz), 5.80 (1H, m, -CH=**CH_2**), 7.30-7.40 (m, **Bz**).

Synthesis of poly(HEMA-Bz)22k-allyl (7b)

In a round bottom flask were introduced poly(HEMA-Bz)22k-OH **(5b)** (2.5 g, 0.11 mmol), DMAP (2 mg, 0.022 mmol), pyridine (27 µl, 0.33 mmol) and DCM (5 ml) and the flask was placed on an ice bath. 4-pentenoic anhydride (31 µl, 0.17 mmol) was dissolved in DCM (5 ml) and the solution was slowly added to the round bottom flask. The reaction was left to react over night at room temperature. The product was purified by precipitation from THF to cold methanol. Yield: 1.6 g, 59 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.82-0.92 (m, **CH_3** backbone and -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$), 1.77 (m, **CH_2** backbone), 2.31-2.35 (4H, m, C(=O)-**CH_2-CH_2**-=), 3.56 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 4.03 (m, -O-**CH_2-CH_2**-O-), 4.29 (m, -O-**CH_2-CH_2**-O-), 4.55 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 4.95-5.02 (2H, m, -CH=**CH_2**), 5.34 (m, -**CH**-Bz), 5.76 (1H, m, -CH=**CH_2**), 7.26-7.36 (m, **Bz**).

Synthesis of poly(HEMA-Bz)5k-G0-OH, P5-2 (9a0)

In a vial were dissolved poly(HEMA-Bz)5k-allyl **(7a)** (350 mg, 0.07 mmol), mercaptoethanol **(12)** (16 mg, 0.2 mmol) and DMPA (2 mg, catalytic amount) in DCM (1 ml). The vial was then exposed to 365 nm UV for 30 min. The product was purified by precipitation in cold methanol. Yield: 261 mg, 74 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87-1.09 (m, **CH_3** backbone and -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$), 1.77 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.33 (2H, m, -O-C(=O)-**CH_2**-), 2.50 (2H, m, -CH_2-**CH_2**-S-), 2.69 (2H, m, -S- **CH_2**- CH_2-OH), 3.59 (m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2-**CH_2**-OH), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.29 (m, -O-**CH_2-CH_2**-O-), 4.59 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.38 (m, -**CH**-Bz), 7.29-7.39 (m, **Bz**).

Synthesis of poly(HEMA-Bz)5k-G1-OH, P5-2 (9a1)

In a vial were dissolved poly(HEMA-Bz)5k-allyl **(7a)** (500 mg, 0.1 mmol), HS-G1-OH **(13)** (58 mg, 0.3 mmol) and DMPA (2 mg, catalytic amount) in DCM (1 ml). The vial was then exposed to 365 nm UV for 30 min. The product was purified by precipitation in cold methanol. Yield: 499 mg, 95 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.77-1.07 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$ and **CH_3** dendron), 1.77 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.33 (2H, m, -O-C(=O)-**CH_2**-), 2.54 (2H, m, -CH_2-**CH_2**-S-), 2.76 (2H, m, -S- **CH_2**- CH_2-OH), 2.89 (2H, m, -O**H**), 3.60 (m, -

C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-OH), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.29 (m, -O-**CH_2-CH_2**-O-), 4.56 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.38 (m, -**CH**-Bz), 7.31-7.40 (m, **Bz**).

Synthesis of poly(HEMA-Bz)5k-G2-OH, P5-2 (9a2)

In a vial, poly(HEMA-Bz)5k-allyl **(7a)** (500 mg, 0.1 mmol), HS-G2-OH **(8)** (256 mg, 0.6 mmol) and DMPA (2 mg, catalytic amount) were dissolved in DCM (1 ml). The vial was then exposed to 365 nm UV for 30 min. The product was purified by precipitation in cold methanol. Yield: 339 mg, 63 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87-1.03 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$ and **CH_3** dendron), 1.76 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.33 (2H, m, -O-C(=O)-**CH_2**-), 2.53 (2H, m, -CH_2-**CH_2**-S-), 2.72 (2H, m, -S- **CH_2**- CH_2-OH), 3.08 (4H, m, -O**H**), 3.57 (m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-OH), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.29 (m, -O-**CH_2-CH_2**-O-), 4.55 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.37 (m, -**CH**-Bz), 7.31-7.41 (m, **Bz**).

Synthesis of poly(HEMA-Bz)22k-G0-OH, P22-0 (9b0)

In a vial were dissolved poly (HEMA-Bz)22k-allyl **(7b)** (400 mg, 0.02 mmol), mercaptoethanol **(12)** (14 mg, 0.3 mmol) and DMPA (1 mg, catalytic amount) in DCM (1 ml). The vial was then exposed to 365 nm UV for 30 min. The product was purified by precipitation in cold methanol. Yield: 293 mg, 73 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87-1.07 (m, **CH_3** backbone and -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$), 1.84 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.34 (2H, m, -O-C(=O)-**CH_2**-), 2.49 (2H, m, -CH_2-**CH_2**-S-), 2.67 (2H, m, -S- **CH_2**- CH_2-OH), 3.60 (m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S-CH_2- **CH_2**-OH), 4.09 (m, -O-**CH_2-CH_2**-O-), 4.30 (m, -O-**CH_2-CH_2**-O-), 4.56 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.37 (m, -**CH**-Bz), 7.30-7.40 (m, **Bz**).

Synthesis of poly(HEMA-Bz)22k-G1-OH, P22-1 (9b1)

In a vial were dissolved poly(HEMA-Bz)22k-allyl **(7b)** (400 mg, 0.02 mmol), HS-G1-OH **(13)** (34 mg, 0.2 mmol) and DMPA (2 mg, catalytic amount) in DCM (2 ml). The vial was then exposed to 365 nm UV for 30 min. The product was purified by precipitation in cold methanol. Yield: 364 mg, 91 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88-1.07 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$ and **CH_3** dendron), 1.76 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.34 (2H, m, -O-C(=O)-**CH_2**-), 2.54 (2H, m, -CH_2-**CH_2**-S-), 2.76 (2H, m, -S- **CH_2**- CH_2-OH), 3.56 (m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-OH), 4.07 (m, -O-**CH_2-CH_2**-O-), 4.30 (m, -O-**CH_2-CH_2**-O-), 4.55 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.36 (m, -**CH**-Bz), 7.29-7.40 (m, **Bz**).

Synthesis of poly(HEMA-Bz)22k-G2-OH, P22-2 (9b2)

In a vial, poly(HEMA-Bz)22k-allyl **(7b)** (300 mg, 0.02 mmol), HS-G2-OH **(8)** (60 mg, 0.2 mmol) and DMPA (2 mg, catalytic amount) were dissolved in DCM (2 ml). The vial was then exposed to 365 nm UV for 30 min. The product was purified by precipitation in cold methanol. Yield: 266 mg, 89 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87-1.04 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$ and **CH_3** dendron), 1.76 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.36 (2H, m, -O-C(=O)-**CH_2**-), 2.53 (2H, m, -CH_2-**CH_2**-S-), 2.77 (2H, m, -S- **CH_2**- CH_2-OH), 3.56 (m, -C(CH_3)-(**CH_2**-O-)$_2$

and -S- CH_2- **CH_2**-OH), 4.07 (m, -O-**CH_2-CH_2**-O-), 4.29 (m, -O-**CH_2-CH_2**-O-), 4.55 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.37 (m, -**CH**-Bz), 7.29-7.39 (m, **Bz**).

Synthesis of poly(HEMA-Bz)5k-G0-TEG-Alk, P5-3 (11a0)

In a round bottom flask were introduced poly(HEMA-Bz)5k-G0-OH **(9a0)** (200 mg, 0.04 mmol), DMAP (1 mg, 0.008 mmol),pyridine (9 µl, 0.12 mmol) and DCM (1 ml) and the flask was placed on an ice bath. Acetylene-TEG-anhydride **(10)** (39 mg, 0.06 mmol) was dissolved in DCM (1 ml) and slowly added to the round bottom flask. The reaction was stirred at room temperature overnight. The DCM was evaporated and the product was precipitated from THF to cold methanol. Yield: 150 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87-1.09 (m, **CH_3** backbone and -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$), 1.84 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.31 (2H, m, -O-C(=O)-**CH_2**-), 2.43 (1H, m, -C≡**CH**), 2.50(2H, m, -CH_2-**CH_2**-S-), 2.66 (4H, m, -C(=O)-**CH_2-CH_2**-C(=O)), 3.57(m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-O-), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.28 (m, -O-**CH_2-CH_2**-O- and -O-**CH_2**-C≡CH), 4.60(m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.38 (m, -**CH**-Bz), 7.31-7.41 (m, **Bz**).

Synthesis of poly(HEMA-Bz)5k-G1-TEG-Alk, P5-4 (11a1)

In a round bottom flask were introduced poly(HEMA-Bz)5k-G1-OH **(9a1)** (250 mg, 0.048 mmol), DMAP (2 mg, 0.019 mmol),pyridine (23 µl, 0.29 mmol) and DCM (1 ml) and the flask was placed on an ice bath. Acetylene-TEG-anhydride **(10)** (74 mg, 0.11 mmol) was dissolved in DCM (1 ml) and slowly added to the round bottom flask. The reaction was stirred at room temperature overnight. The DCM was evaporated and the product was precipitated from THF to cold methanol. Yield: 160 mg, 60 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87-1.09 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$ and **CH_3** dendron), 1.59-1.69 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.30 (2H, m, -O-C(=O)-**CH_2**-), 2.44 (2H, m, -C≡**CH**), 2.53 (2H, m, -CH_2-**CH_2**-S-), 2.63 (8H, m, -C(=O)-**CH_2-CH_2**-C(=O)), 2.70 (2H, m, -S- **CH_2**- CH_2-OH), 3.60 (m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-O-), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.28 (m, -O-**CH_2-CH_2**-O-), 4.59 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.35 (m, -**CH**-Bz), 7.30-7.40 (m, **Bz**).

Synthesis of poly(HEMA-Bz)5k-G2-TEG-Alk, P5-5 (11a2)

poly(HEMA-Bz)5k-G2-OH **(9a2)** (250 mg, 0.046 mmol), DMAP (4 mg, 0.037 mmol), pyridine (44 µl, 0.55 mmol) and DCM (1 ml) were introduced in a round bottom flask and the flask was placed on an ice bath. Alkyne-TEG-anhydride **(10)** (142 mg, 0.22 mmol) was dissolved in DCM (1 ml) and slowly added to the round bottom flask. The reaction was stirred at room temperature overnight. The DCM was evaporated and the product was precipitated from THF to cold methanol. Yield: 130 mg, 48 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.86-1.09 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$ and **CH_3** dendron), 1.57-1.80 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.31 (2H, m, -O-C(=O)-**CH_2**-), 2.44 (4H, m, -C≡**CH**), 2.60 (2H, m, -CH_2-**CH_2**-S-), 2.67 (16H, m, -C(=O)-**CH_2-CH_2**-C(=O)), 2.72 (2H, m, -S- **CH_2**- CH_2-O-), 3.65 (m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-OH), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.25 (m, -O-**CH_2-CH_2**-O-), 4.57 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.38 (m, -**CH**-Bz), 7.30-7.41 (m, **Bz**). $Đ_M$: 1.04..

Synthesis of poly(HEMA-Bz)22k-G0-TEG-Alk, P22-3 (11b0)

In a round bottom flask were introduced poly(HEMA-Bz)22k-G0-OH **(9b0)** (200 mg, 0.04 mmol), DMAP (0.2 mg, 0.002 mmol),pyridine (2 µl, 0.03 mmol) and DCM (0.5 ml) and the flask was placed on an ice bath. Acetylene-TEG-anhydride **(10)** (9 mg, 0.02 mmol) was dissolved in DCM (0.5 ml) and slowly added to the round bottom flask. The reaction was stirred at room temperature overnight. The DCM was evaporated and the product was precipitated from THF to cold methanol. Yield: 85 mg, 42 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88-1.08 (m, **CH_3** backbone and -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$), 1.78 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.33 (2H, m, -O-C(=O)-**CH_2**-), 2.44 (1H, m, -C≡**CH**), 2.50(2H, m, -CH_2-**CH_2**-S-), 2.61 (4H, m, -C(=O)-**CH_2-CH_2**-C(=O) and -S-**CH_2**- CH_2-O-), 3.64(m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-OH), 4.09 (m, -O-**CH_2-CH_2**-O-), 4.30(m, -O-**CH_2-CH_2**-O- and -O-**CH_2**-C≡CH), 4.57(m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.39 (m, -**CH**-Bz), 7.31-7.41 (m, **Bz**).

Synthesis of poly(HEMA-Bz)22k-G1-TEG-Alk, P22-4 (11b1)

In a round bottom flask were introduced poly(HEMA-Bz)22k-G1-OH **(9b1)** (250 mg, 0.011 mmol), DMAP (0.5 mg, 0.0044 mmol),pyridine (5 µl, 0.066 mmol) and DCM (1 ml) and the flask was placed on an ice bath. Acetylene-TEG-anhydride **(10)** (22 mg, 0.034 mmol) was dissolved in DCM (1 ml) and slowly added to the round bottom flask. The reaction was stirred at room temperature overnight. The DCM was evaporated and the product was precipitated from THF to cold methanol. Yield: 210 mg, 82 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88-0.97 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$ and **CH_3** dendron), 1.77 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.32 (2H, m, -O-C(=O)-**CH_2**-), 2.44 (2H, m, -C≡**CH**), 2.53 (2H, m, -CH_2-**CH_2**-S-), 2.64 (8H, m, -C(=O)-**CH_2-CH_2**-C(=O)), 2.70 (2H, m, -S- **CH_2**- CH_2-O-), 3.58 (m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-OH), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.29 (m, -O-**CH_2-CH_2**-O-), 4.55 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.37 (m, -**CH**-Bz), 7.30-7.40 (m, **Bz**).

Synthesis of poly(HEMA-Bz)22k-G2-TEG-Alk, P22-5 (11b2)

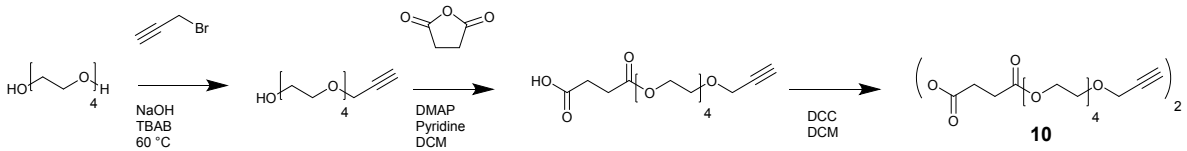
Poly(HEMA-Bz)22k-G2-OH **(9b2)** (266 mg, 0.012 mmol), DMAP (1.2 mg, 0.0096 mmol), pyridine (11 µl, 0.14 mmol) and DCM (1 ml) were introduced in a round bottom flask and the flask was placed on an ice bath. Alkyne-TEG-anhydride **(10)** (47 mg, 0.073 mmol) was dissolved in DCM (1 ml) and slowly added to the round bottom flask. The reaction was stirred at room temperature overnight. The DCM was evaporated and the product was precipitated from THF to cold methanol. Yield: 157 mg, 56 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88-1.09 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$ and **CH_3** dendron), 1.77 (m, **CH_2** backbone and-O-C(=O)- CH_2- **CH_2-CH_2**- CH_2-), 2.36 (2H, m, -O-C(=O)-**CH_2**-), 2.44 (4H, m, -C≡**CH**), 2.54 (2H, m, -CH_2-**CH_2**-S-), 2.65 (16H, m, -C(=O)-**CH_2-CH_2**-C(=O)), 2.72 (2H, m, -S- **CH_2**- CH_2-O-), 3.57 (m, -C(CH_3)-(**CH_2**-O-)$_2$ and -S- CH_2- **CH_2**-OH), 4.08 (m, -O-**CH_2-CH_2**-O-), 4.29 (m, -O-**CH_2-CH_2**-O-), 4.55 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.38 (m, -**CH**-Bz), 7.31-7.41 (m, **Bz**).

Synthesis of poly(HEMA-Bz)22k-G2-TEG-Rh, P22-6 (13)

Poly(HEMA-Bz)22k-G2-TEG-Alk **(11b2)** (50 mg, 0.002 mmol), rhodamine-TEG-N3 **(14)** (7 mg, 0.009 mmol), sodium ascorbate (0.3 mg, 0.0016 mmol) and THF (400 µl) were added in a round bottom flask. Cu(II)SO_4 (0.1 mg, 0.0008 mmmol) was dissolved in H_2O (100 µl) and the solution was added to the round bottom flask. The solution was stirred over night at room temperature. The solvents were evaporated and the product was purified by precipitation from THF to cold MeOH. The product was collected as a pink powder. Yield: 32 mg, 59 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88-0.95 (m, **CH_3** backbone, -C(=O)-C(**CH_3**)-(CH_2-O-)$_2$), 1.25 (m, **CH_3** dendron, -**CH_2**-CH_2-CH_2-N_3 and -N-(CH_2-**CH_3**)$_2$), 1.76 (m, -**CH_2**-CH_2-**CH_2**-CH_2-N_3, **CH_2** backbone and-O-C(=O)-CH_2-**CH_2**-**CH_2**-CH_2-), 2.27 (m, , -O-C(=O)-**CH_2**- CH_2-), 2.40-2.71 (m, -O-C(=O)-**CH_2**-, -CH_2-**CH_2**-S-, -C(=O)-**CH_2**-**CH_2**-C(=O), -S- **CH_2**- CH_2-O-), 3.56 (m, -C(CH_3)-(**CH_2**-O-)$_2$, -N-(**CH_2**-CH_3)$_2$ and -**CH_2**- TEG), 4.07 (m, -O-**CH_2**-**CH_2**-O-), 4.28 (m, -O-**CH_2**-**CH_2**-O-), 4.55 (m, -C(CH_3)-(**CH_2**-O-)$_2$), 5.37 (m, -**CH**-Bz), 6.76-7.10 (m, -N-C=C**H**-C-, -N-CH=**CH**-C-, -N-**CH**=CH-C-), 7.30-7.40 (m, **Bz** and -C=**CH**-HC=CH-HC=C-C(=O)-), 7.70- 7.80 (m, -C=CH-HC=**CH**-HC=C-C(=O)-, -C=CH-**HC**=CH-HC=C-C(=O)- and triazine), 8.34 (1H, m, -C=CH-HC=CH-**HC**=C-C(=O)-).

Synthesis of functionalized molecules

Synthesis of tetra ethyleneglycol alkyne (TEG-Alk) anhydride (10)



Scheme S2 Synthesis route of TEG-Alk andhydride

Synthesis of TEG-alkyne

TEG (19.4 g, 0.10 mol), NaOH (4.0 g, 0.10 mol), TBAB (100 mg, catalytic amount) and water (1 ml) were introduced in a three-necked round bottom flask equipped with a septum, a condenser and a dropping funnel. The system was heated to 45 °C and propargyl bromide (15 g, 0.10 mol) was slowly added over a period of 20 min. Once the addition was completed, the temperature was raised to 60 °C and the solution was stirred for 6 h. Dichloromethane (25 ml) was added to the solution and the organic phase was extracted once with water, dried on $MgSO_4$ and the solvent was evaporated. The product was purified by column chromatography in a gradient of heptane/EtOAc from 70/30 to 0/100. The product was collected as orange oil. Yield: 3.53 g, 14 %. ^{1}H NMR (400 MHz, $CHCl_3$)δ (ppm): 2.43 (1 H, t, J = 2.4 Hz, -C≡C**H**), 2.64 (1 H, t, J = 6.0 Hz, -CH_2-O**H**), 3.58 (2H, m, -**CH_2**-OH), 3.65 (14 H, m, -O-C**H_2**-C**H_2**-O-), 4.19 (2 H, d, J = 2.4 Hz, -O-C**H_2**-C≡CH). ^{13}C NMR (100 MHz, $CHCl_3$) δ (ppm): 58.57, 61.92, 62.27, 70.51, 70.57, 70.71, 70.74, 70.79, 72.68, 74.73, 79.79.

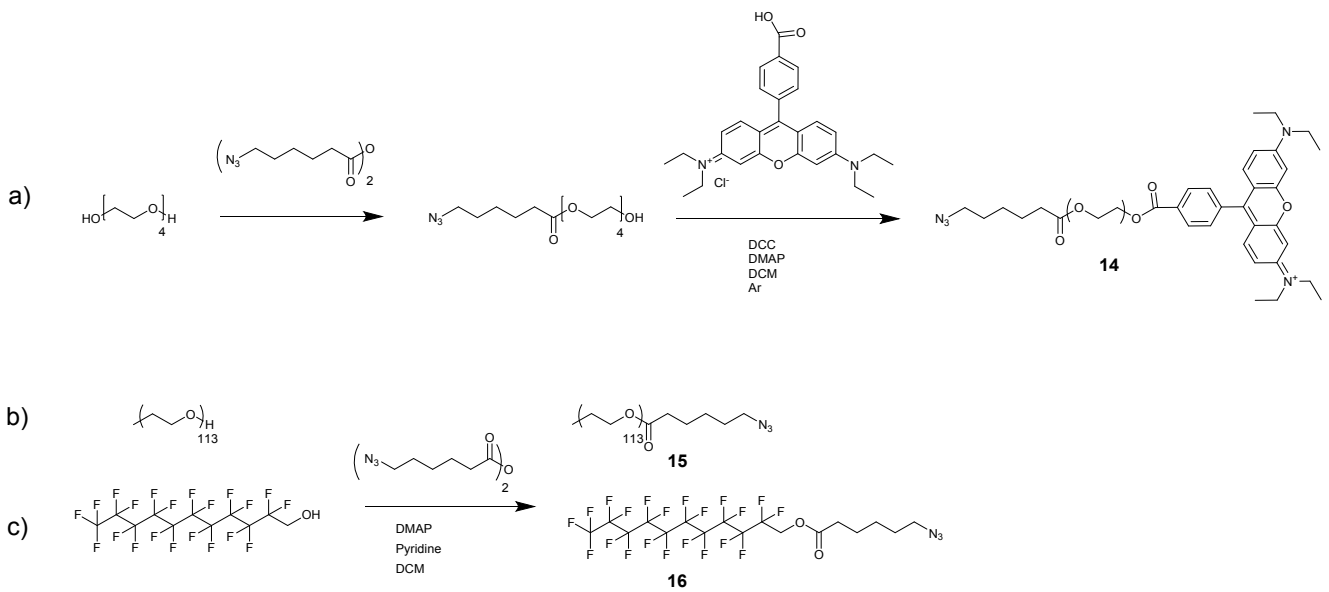
Synthesis of alkyne-TEG-acid

TEG-alkyne (3.53 g, 15.2 mmol), DMAP (371 mg, 3.0 mmol), pyridine (3.6 g, 45.6 mmol) and DCM (5 ml) were added to a round bottom flask. The solution was cooled on an ice bath and succinic anhydride (1.82 g, 18.2 mmol) dissolved in DCM (5 ml) was slowly added to the system. The solution

was stirred overnight. The excess anhydride was quenched with water and the organic phase was diluted with DCM (10 ml), extracted 5 times with $NaHSO_4$ (10% aq.) and dried on $MgSO_4$. The solvent was evaporated and the pure product was collected as orange oil. Yield: 4.85 g, 96 %. ^{1}H NMR (400 MHz, $CHCl_3$) δ (ppm): 2.43 (1 H, t, J = 2.4 Hz, -C≡C**H**), 2.63 (4 H, m, -O-C(=O)-C**H$_2$**-C**H$_2$**-C(=O)-OH), 3.66 (14 H, m, -O-C**H$_2$**-C**H$_2$**-O-), 4.19 (2H, d, J = 2.4 Hz, -O-C**H$_2$**-C≡CH), 4.26 (2 H, m, -C**H$_2$**-O-C(=O)-). ^{13}C NMR (100 MHz, $CHCl_3$) δ (ppm): 29.28, 29.55, 58.58, 64.07, 66.16, 66.24, 70.52, 70.61, 70.67, 70.70, 70.90, 74.79, 79.76, 172.20, 175.98.

Synthesis of alkyne-TEG anhydride (10)

Alkyne-TEG-acid (4.85 g, 14.6 mmol) and DCM (10 ml) were added to a round bottom flask. The solution was cooled to 0°C and DCC (1.5 g, 7.3 mmol) dissolved in DCM (1 ml) was slowly added. The solution was stirred overnight, filtered and the solvent was evaporated. The product was collected as orange oil. Yield: 4.2 g, 91 %. ^{1}H NMR (400 MHz, $CHCl_3$) δ (ppm): 2.43 (1 H, t, J = 2.4 Hz, -C≡C**H**), 2.69 (2 H, m, -O-C(=O)-C**H$_2$**-CH$_2$-C(=O)-O), 2.79 (2 H, m, -O-C(=O)-CH$_2$-C**H$_2$**-C(=O)-O), 3.66 (14 H, m, -O-C**H$_2$**-C**H$_2$**-O-), 4.19 (2H, d, J = 2.4 Hz, -O-C**H$_2$**-C≡CH), 4.25 (2 H, m, -C**H$_2$**-O-C(=O)-. ^{13}C NMR (100 MHz, $CHCl_3$) δ (ppm): 28.61, 30.37, 58.59, 64.30, 69.17, 69.29, 70.60, 70.77, 70.79, 74.75, 79.84, 168.06, 171.85.



Scheme S3 Synthesis route of postfunctionalized molecules a) rodamine-TEG-N_3, b) henicosafluoroundecyl 6-azidohexanoate and c) azide functionalized polyethylengycol

Synthesis of rhodamine-TEG-N_3 (14)

Synthesis of OH-TEG-N3

TEG (5g, 25.7 mmol), DMAP (628 mg, 5.14 mmol), pyridine (6.2 ml, 77.1 mmol) and DCM (10 ml) were added to a round bottom flask and the flask was cooled down to 0 °C. Azide anhydride (7.6 g, 25.7 mmol) was dissolved in DCM (10 ml) and the solution was slowly added to the round bottom flask. The reaction was stirred overnight. The organic phase was extracted 5 times with $NaHSO_4$ 10%

aq, 2 times with Na_2CO_3 10 % aq, dried on $MgSO_4$ and the solvent was evaporated. The product was purified by column chromatography in a gradient of EtOAc/Heptane. The product was collected as viscous oil. Yield: 2.96 g, 24 %. ^{1}H NMR (400 MHz, $CHCl_3$) δ (ppm): 1.35-1.41 (2H, m, -**CH_2**-CH_2-CH_2-N_3), 1.55-1.64 (4H, m, -**CH_2**-CH_2- **CH_2**-CH_2-N_3), 2.33 (2H, t, J = 7.4 Hz, -O-C(=O)-**CH_2**- CH_2-), 2.59 (1H, s, -CH_2-**OH**), 3.25 (2H, t, J = 6.9 Hz, **-CH_2**-N_3), 3.58-3.66 (14H, m, **-CH_2**- TEG), 4.21 (2H, t, J = 4.8 Hz, **-CH_2**-OH). ^{13}C NMR (100 MHz, $CHCl_3$) δ (ppm): 24.53, 26.36, 28.69, 34.08, 51.37, 61.89, 63.60, 69.34, 70.50, 70.68, 70.71, 70.80, 72.66, 173.60.

Synthesis of rhodamine-TEG-N3 (14)

Rhodamine B (500 mg, 1.05 mmol), DMAP (13 mg, 0.105 mmol), OH-TEG-N_3 (1g, 3.13 mmol) and anhydrous DCM (10 ml) were added to a round bottom flask. The flask was cooled to 0°C and DCC (260 mg, 1.3 mmol) was added. The solution was stirred overnight and filtrated. The organic phase was extracted 2 times with Na_2CO_3 10% aq, once with $NaHSO_4$ 10% aq and once with water, dried on $MgSO_4$ and the solvent was evaporated. The product was purified by column chromatography in a gradient of DCM/MeOH. Yield: 256 mg, 31 %. ^{1}H NMR (400 MHz, $CHCl_3$) δ (ppm): 1.30 (12H, t, J = 7.1 Hz, -N-(CH_2-**CH_3**)$_2$), 1.35-1.41 (2H, m, -**CH_2**-CH_2-CH_2-N_3), 1.54-1.60 (4H, m, -**CH_2**-CH_2- **CH_2**-CH_2-N_3), 2.30 (2H, t, J = 7.4 Hz, -O-C(=O)-**CH_2**- CH_2-), 3.24 (2H, t, J = 6.8 Hz, **-CH_2**-N_3), 3.54-3.64 (20H, m, -N-(**CH_2**-CH_3)$_2$ and-**CH_2**- TEG), 4.17 (4H, m, -C(=O)-O-**CH_2**- TEG), 6.77 (2H, s, -N-C=C**H**-C-), 6.88-6.91 (2H, m, -N-CH=**CH**-C-), 7.04 (2H, d, J = 9.5 Hz, -N-**CH**=CH-C-), 7.28 (1H, s, -C=**CH**-HC=CH-HC=C-C(=O)-), 7.72 (1H, m, -C=CH-HC=**CH**-HC=C-C(=O)-), 7.80 (1H, m, -C=CH-**HC**=CH-HC=C-C(=O)-), 8.30 (1H, m, -C=CH-HC=CH-**HC**=C-C(=O)-). ^{13}C NMR (100 MHz, $CHCl_3$) δ (ppm):12.84, 24.51, 26.34, 28.68, 34.07, 46.32, 63.55, 64.80, 68.85, 69.27, 70.61, 70.65, 70.67, 70.70, 96.41, 113.69, 114.42, 129.77, 130.36, 130.52, 131.49, 131.67, 133.36, 133.88, 155.67, 157.89, 159.02, 165.02, 173.54.

Synthesis of azide functionalized polyethylengycol (15)

Polyethylene glycol momomethyl ether (20 g, 0.01mol) was dissolved in CH_2Cl_2 together with DMAP (0.244g, 2.00 mmol) and 10ml of pyridine. And excess of allyl anhydride (7.72g, 0.02mol) was added in portions to the solution and the reaction was allowed to proceed overnight. The reaction was followed by 13C NMR. The solvent was evaporated and then the mixture was precipitated into 2L of diethyl ether followed by filtration. The product was obtained as a white powder after solvent evaporation (21g, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ_{ppm} 5.82-5.87 (m, 1H, CH_2=CH-), 5.27-5.15 (m, 2H, CH_2=CH-), 4.22-4.19 (m, 4H, -OCH_2CH_2O-), 3.99-3.97 (m, 2H, CH_2=$CHCH_2O$-), 3.76-3.41 (m, PEG backbone), 3.33 (s, 3H, -OCH_3), 2.62 (s, 4H, -$COCH_2CH_2CO$-)

Synthesis of henicosafluoroundecyl 6-azidohexanoate (16)

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heneicosafluoro-1-undecanol (1 g, 1.8 mmol) was dissolved in THF together with DMAP (44 mg, 0.36 mmol) and 440 µl of pyridine. And excess of 6-azidohexanoic anhydride (970 mg, 3.3 mmol) was added in portions to the solution and the reaction was allowed to proceed overnight. The reaction was followed by 13C NMR. After completion, the residual anhydride was quenched with water. The solution was then extracted 5 times with a 10 %

$NaHSO_4$ solution and 2 times with a 10 % Na_2CO_3 solution. The organic phase was dried on $MgSO_4$ and evaporated. The product was collected as a white powder. Yield: 1.237 g, 99 %. **^{1}H NMR** (400 MHz, $CDCl_3$): δ_{ppm} 4.63-4.57 (t, 2H, O=CC**H_2**CH_2-), 3.30-3.26 (t, 2H, O=CCH_2C**H_2**CH_2-), 2.46-2.42 (t, 2H, CH_2C**H_2**N=N=N), 1.74-1.39 (m, 4H, -CH_2C**H_2**C**H_2**N=N=N).

NMR spectra

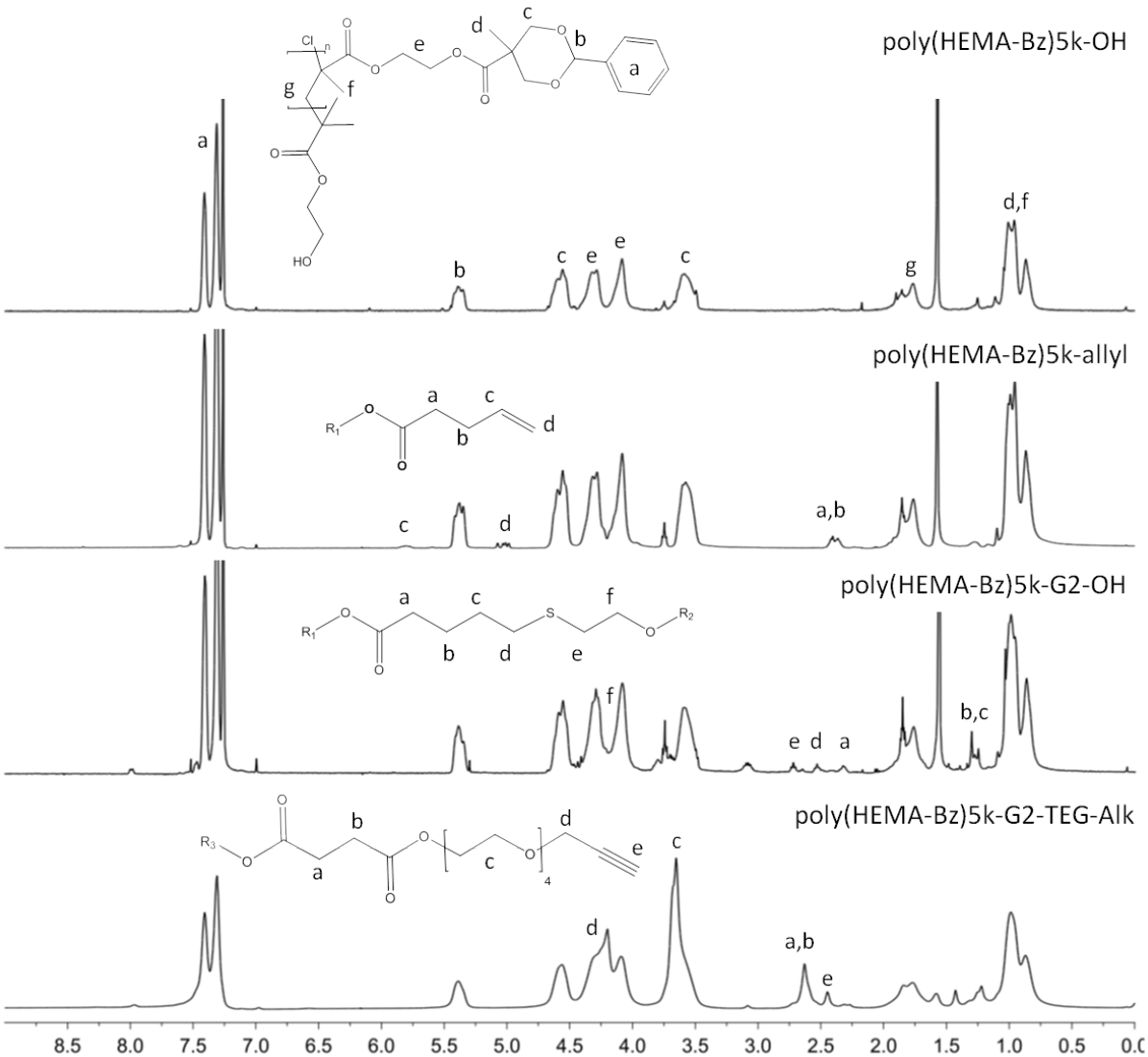


Figure S1 ^{1}HNMR spectra acquired in $CDCl_3$ for 5k system poly(HEMA-B_z)5k-OH **(5a)**, poly(HEMA-B_z)5k-ally **(7a)**, poly(HEMA-B_z)-G2-OH **(9a2)** and poly(HEMA-B_z)-G2-TEG-Alk **(11a2)**

Figure S1 showed the signal at 5.0 ppm and 5.8 ppm corresponding to the double bond completely disappeared while the signal at 2.5 ppm and 2.7 ppm appear corresponding to the proton next to sulfur atom after the thiol-ene coupling. For the modification with TEG anhydride, the signal at 2.4 ppm represents the proton in the acetylene group. All the assigned peaks can be seen corresponded to the structure on the left.

SEC spectra

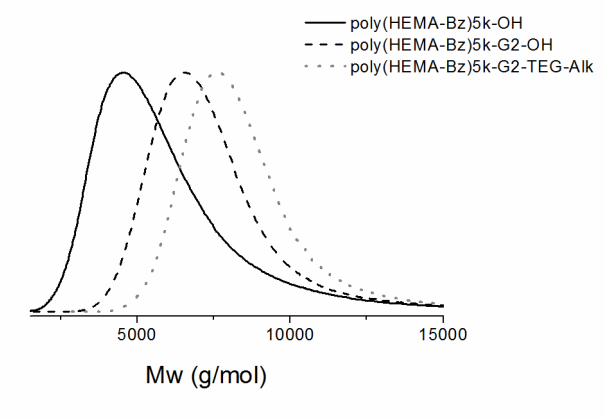


Figure S2. DMF SEC traces of poly(HEMA-Bz)5k-OH (P5), poly(HEMA-Bz)5k-G2-OH (P5-2) and poly(HEMA-Bz)5k-G2-TEG-Ac (P5-5)

Porous film formation

The standard casting conditions of linear dendritic hybrid polymers:

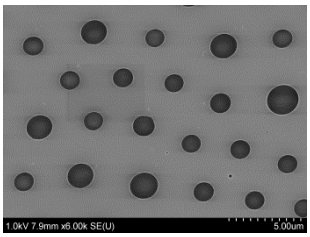
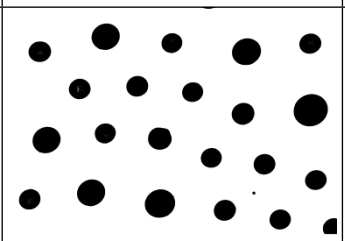
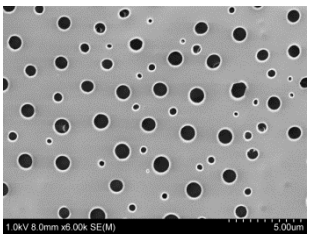
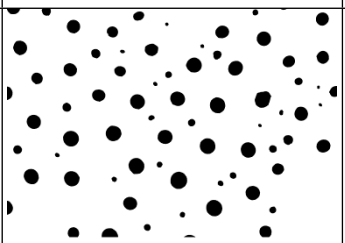
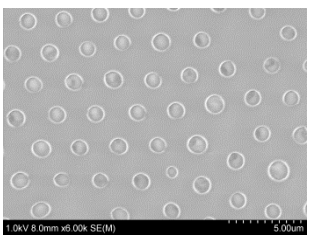
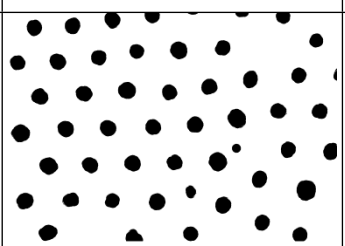
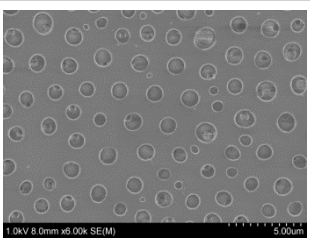
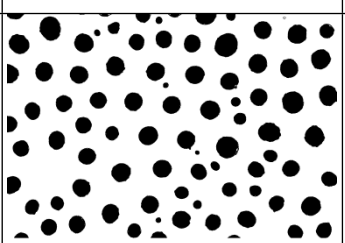
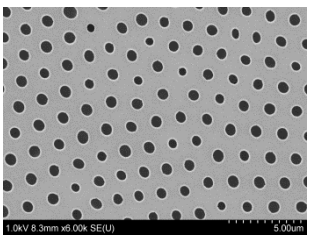
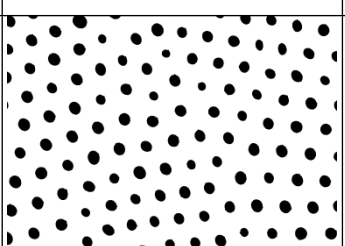
The polymers were dissolved in chloroform with the concentration of 20 $g.l^{-1}$. 40 µl of the solution was drop casted on glass substrate under the controlled humidity chamber with approximately 90% relative humidity at room temperature (~25 °C). Flat films were obtained by casting the polymers at the same concentration in chloroform on glass substrate in ambient conditions (22 °C and ≈ 23 % RH).

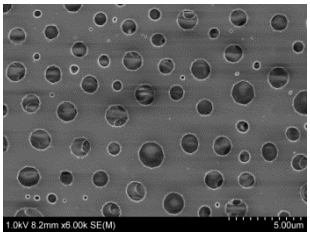
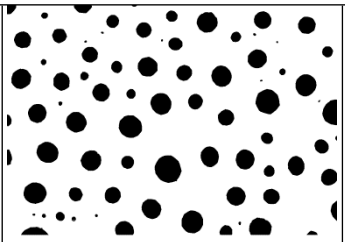
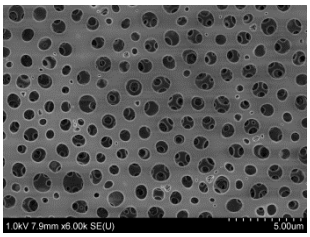
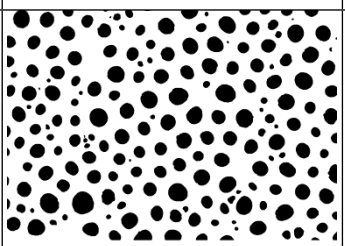
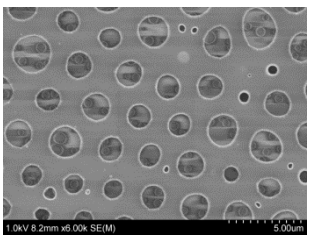
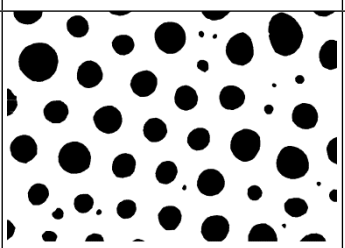
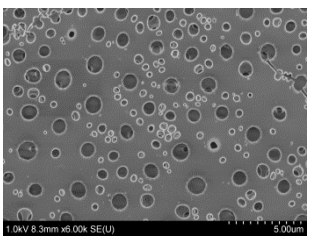
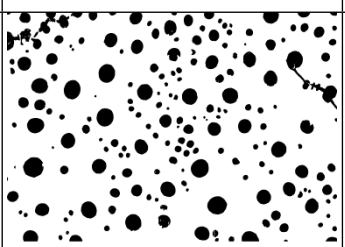
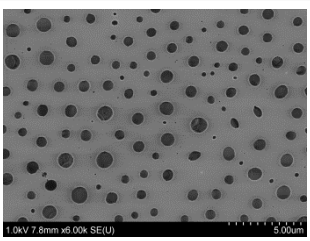
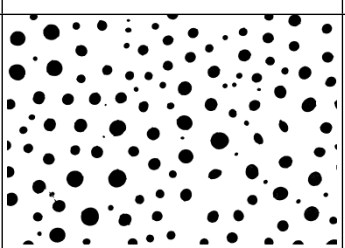
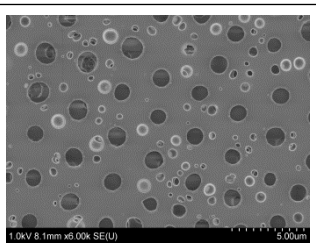
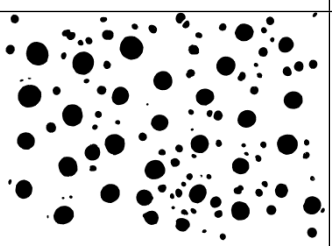
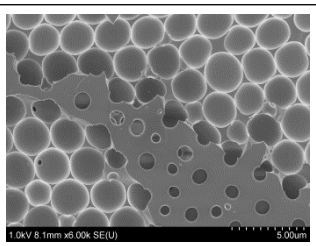
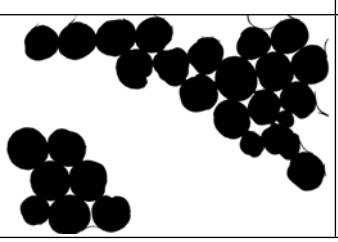
For open pored structure film formation from P22-5:

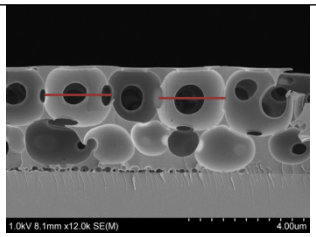
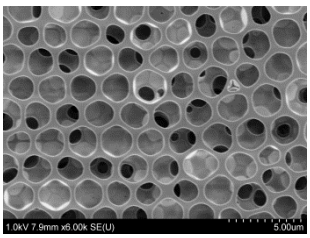
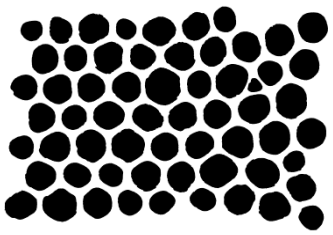
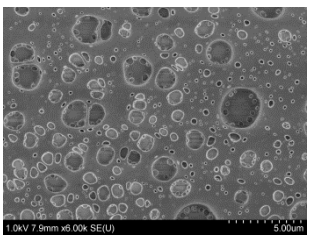
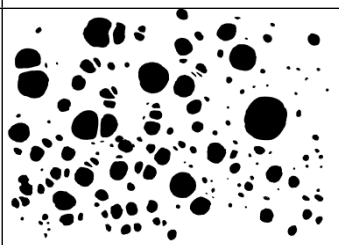
The polymers were dissolved in chloroform with the concentration of 2.5 $g.l^{-1}$. 40 µl of the solution was drop casted on glass substrate under the controlled humidity chamber with approximately 90% relative humidity at the cooled down temperature (~0 °C).

SEM micro graph and pore size estimation

Table S1 SEM micrograph of porous films obtained from linear dendritic hybrid polymers

Polymer code	Linear dendric hybrid	Illustration	SEM micrograph		Micro meter square	SD
P5	5k-OH				1.609	0.781
P5-0	5k-G0-OH				0.399	0.272
P5-1	5k-G1-OH				0.760	0.231
P5-2	5k-G2-OH				0.805	0.409
P5-3	5k-G0-TEG-Alk		No porous film was obtained			
P5-4	5k-G2-TEG-Alk		No porous film was obtained			
P5-5	5k-G2-TEG-Alk		No porous film was obtained			
P22	22k-OH				0.368	0.111

P22-0	22k-G0-OH				0.698	0.551
P22-1	22k-G1-OH				0.451	0.311
P22-2	22k-G2-OH				1.459	1.196
P22-3	22k-G0-TEG-Alk				0.267	0.309
P22-4	22k-G1-TEG-Alk				0.347	0.240
P22-5	22k-G2-TEG-Alk	 20 g.l^{-1}, RT			0.432	0.471
		 20 g.l^{-1}, RT Peeled off top layer			4.420	0.977
				Average pore diameter = 2.36 µm		

		 20 g.l^{-1}, RT Cross section		Average pore diameter = 2.29 µm		
		 2.5 g.l^{-1}, 0 °C			2.600	0.640
P22-6	22k-G2-Rh				0.402	0.701

Surface area calculation

The surface area was estimated based on the top view and cross section images of P22-5 porous film obtained from SEM utilizing imageJ software for calculation. The apparent surface area refers to the flat area on top of the film and the curvature surface generated from the porous structure. The calculation is based on spherical cap with the average radius obtained from the cross section. The porous curvature was calculated based on 2 average radii where the cut off limit is at 0.4 μm^2. The smaller radius represents the small pores (circled with red dot line) while the bigger radius represents the bigger pores (circle with blue dot line).

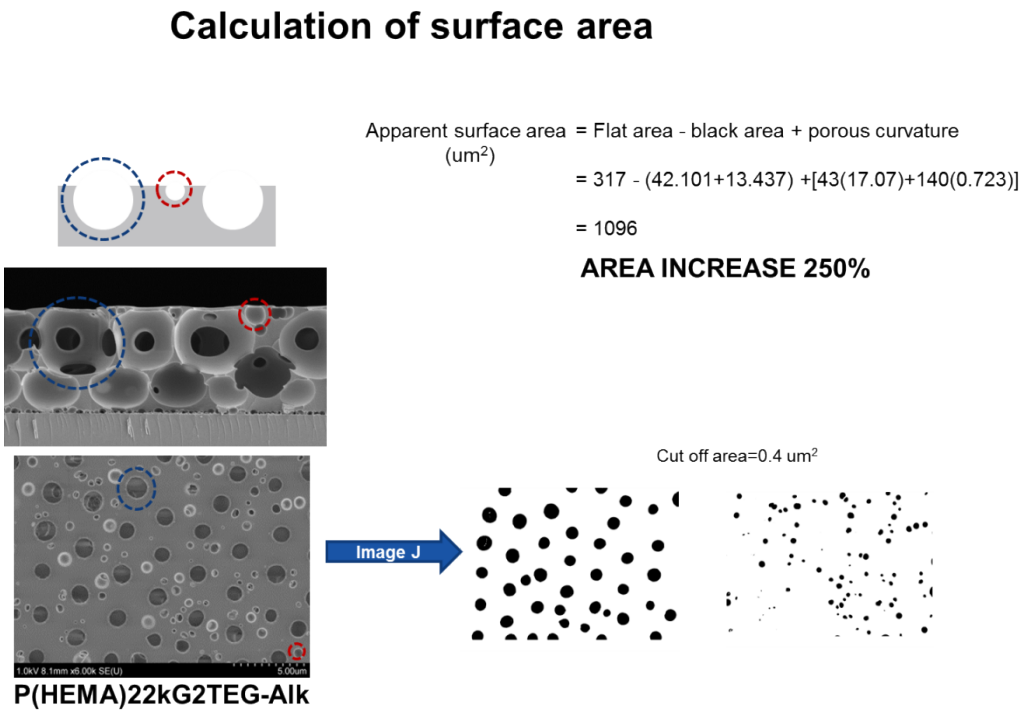
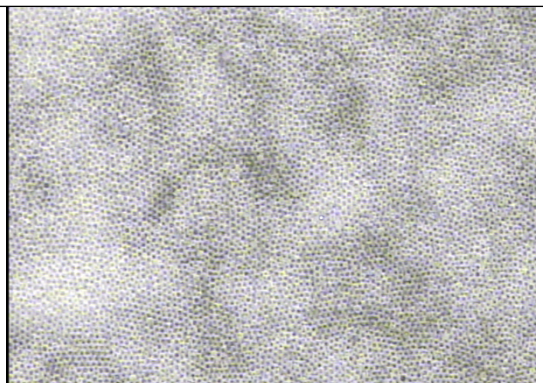
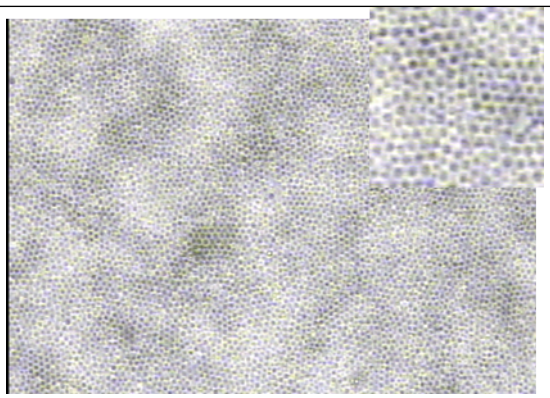
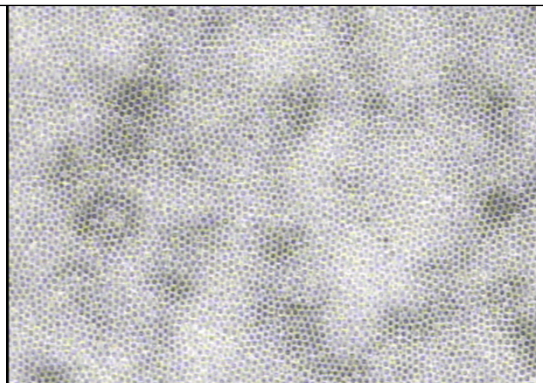
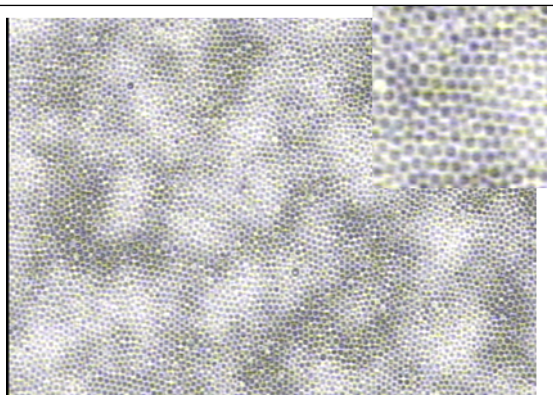
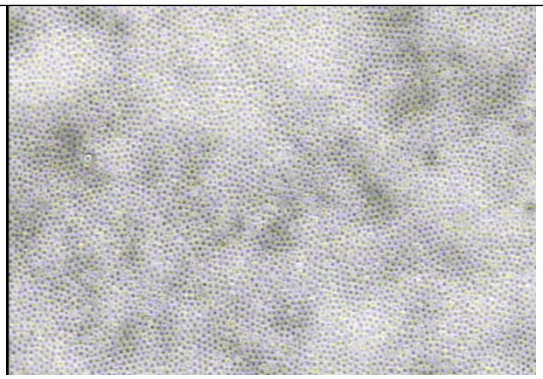
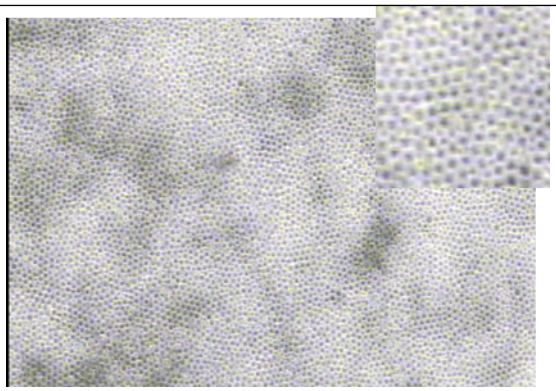


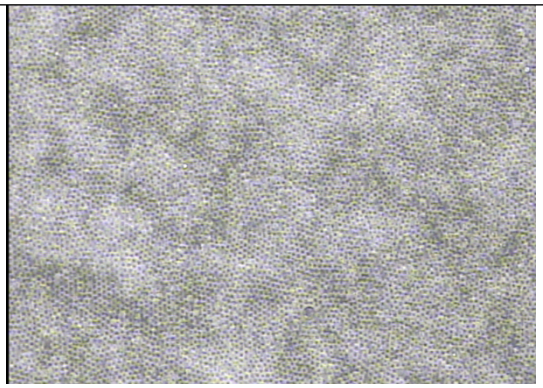
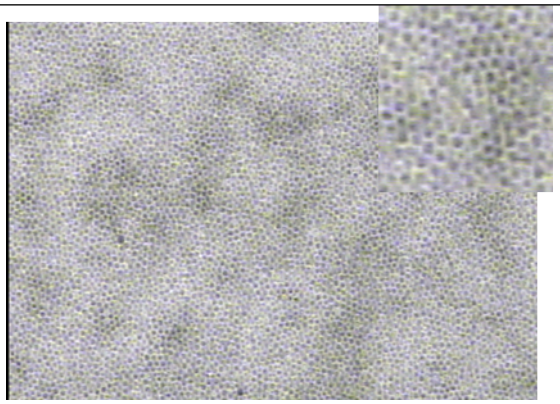
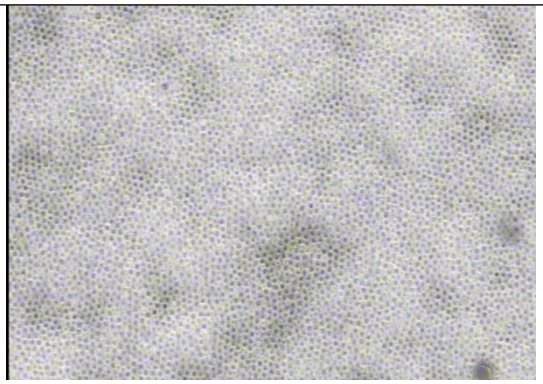
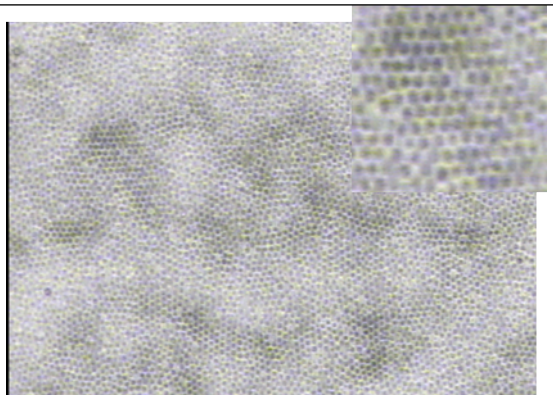
Figure S3 Estimation of surface area for P22-5.

Stabilization study

Evaluation of different pH

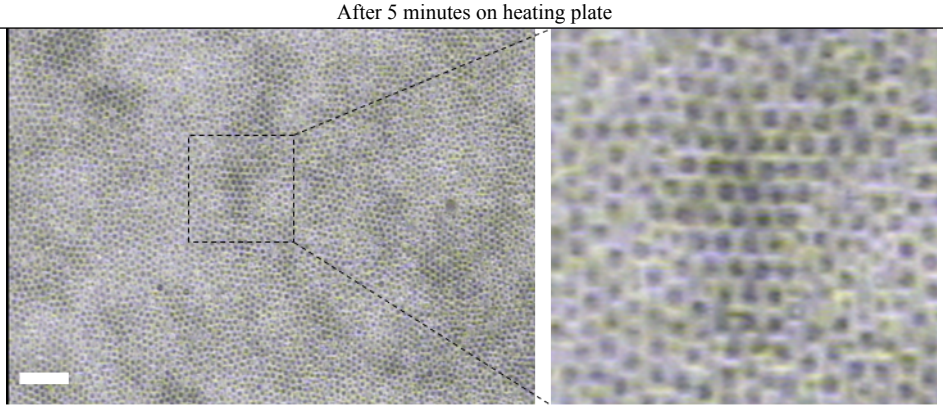
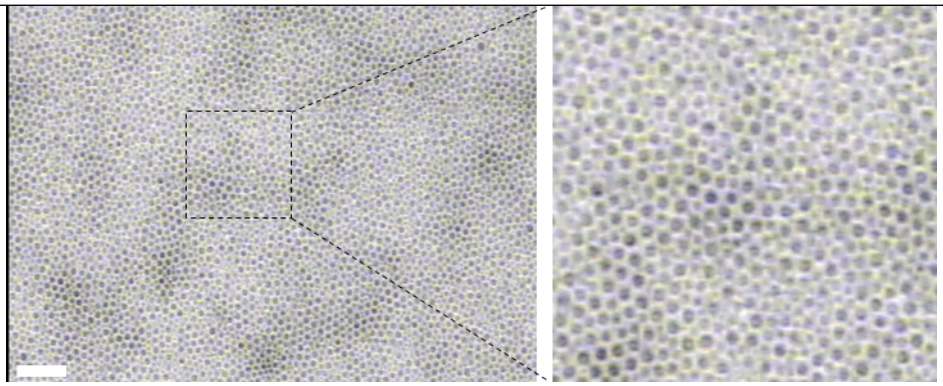
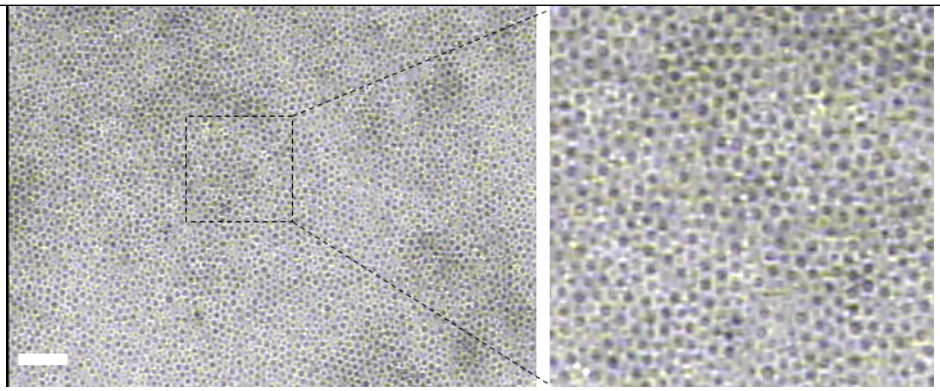
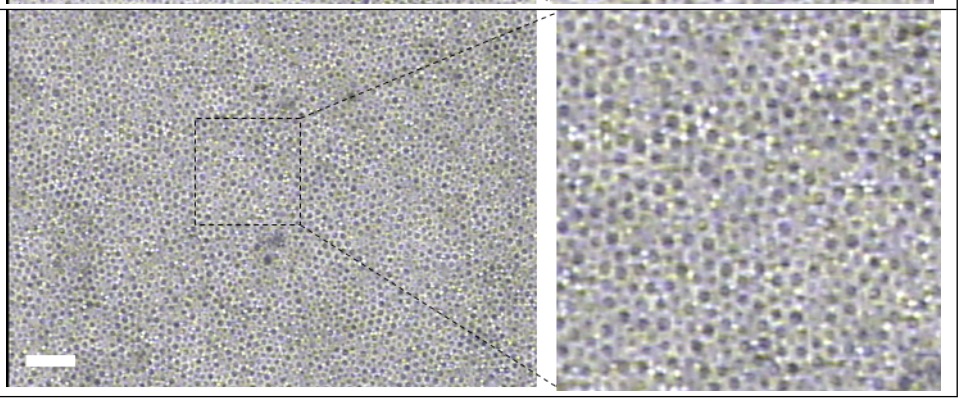
Table S2 Optical microscope images of porous films P22-5 before and after 30 minutes immersion in different pH buffer solution (Scale bar represent 20 μm).

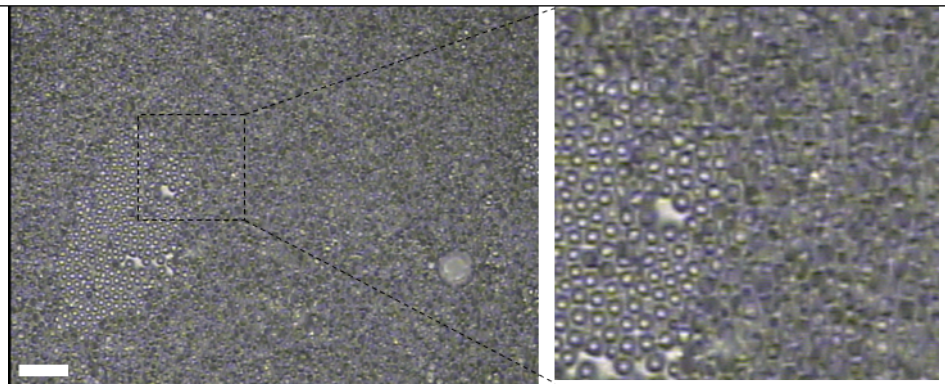
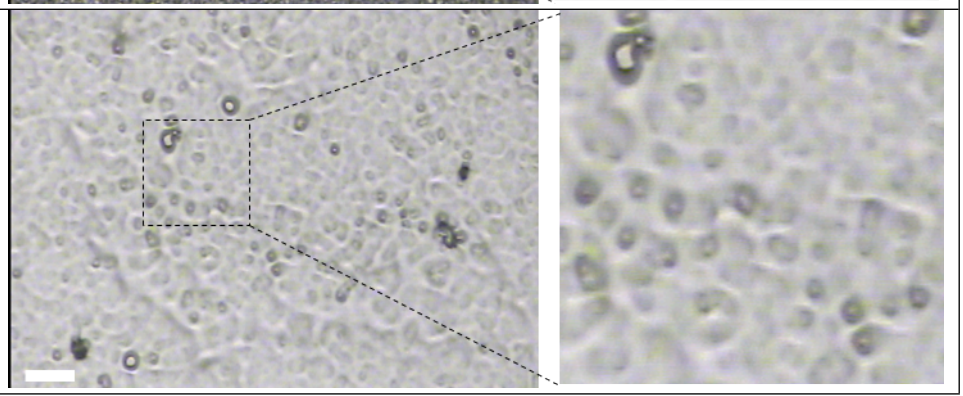
Buffer pH	Before	After 30 minutes immersion
4		
5		
6		

7		
8		

Toward temperature

Table S3 Optical microscope images of porous films P22-5 undergoing different temperature

Temperature (°C)	After 5 minutes on heating plate
Room Temperature (25)	
35	
40	
45	

50	
60	

Surface postfunctionalization

All the postfunctionaization was performed on porous film from P22-5 casted from 40 µl solution of polymer in chloroform with the concentration of 20 $g.l^{-1}$.

Surface post functionalization of rhodamine-TEG-N_3 (14) on P22-5

Rhodamine-TEG-N_3 **(14)** (4 µg, 4.9 µmol) and sodium ascorbate (0.2 µg, 0.9 µmol) were dissolve in 1 ml deionized water. The solution was poured over P22-5 porous film on a petri dish and lastly Cu(II)SO_4 (0.14 µg, 1.8 µmol) was added and the reaction was let on the shaking device (200rpm) for 30 minutes. Finally the porous film was washed with deionized water for several times.

Surface post functionalization of azide functionalized polyethylene glycol (15) on P22-5

Azide polyethylene glycol **(15)** (7 mg, 1.4 µmol) and sodium ascorbate (55 µg, 0.28 µmol) were dissolve in 1 ml deionized water. The solution was poured over P22-5 porous film on a petri dish and lastly Cu(II)SO_4 (34 µg. 0.14 µmol) was added and the reaction was let on the shaking device (200rpm) for 30 minutes. Finally the porous film was washed with deionized water for several times.

Surface post functionalization of henicosafluoroundecyl 6-azidohexanoate (16) on P22-5

Henicosafluoroundecyl 6-azidohexanoate **(16)** (0.95 mg, 1.4 µmol) and sodium ascorbate (55 µg, 0.28 µmol) were dissolve in 1 ml mixture of deionized water:methanol (6:1). The solution was poured over P22-5 porous film on a petri dish and lastly Cu(II)SO_4 (34 µg. 0.14 µmol) was added and the reaction was let on the shaking device (200rpm) for 30 minutes. Finally the porous film was washed with the mixture of deionized water and methanol for several times.

Cytotoxicity test

The films of polymer, P22-5, was tested for cytotoxicity through elution tests according to ISO10993-5 procedures[1]. Human dermal fibroblasts (hDF), and osteoblast-like human cell line, MG63, were cultured in complete growth medium, CGM, containing Dulbecco's modified eagle medium, DME/F12, with 10% fetal bovine serum (FBS), penicillin (100 U/ml) and streptomycin (100 µg/ml) in an incubator at 37 °C and 5% CO_2 in a humidified atmosphere. The cells were harvested with trypsin-EDTA and cell density was determined with hemocytometer. All reagents for cell culturing are purchased from Thermo ScientificTM HyCloneTM. Each coverslip with P22-5 film was extracted in 0.2 ml CGM in a 24-well tissue culture plate for 24 hours at 37 °C and 5% CO_2. The CGM extract were then used to culture hDF and MG63 in a density of 105 cell/ml in 96 well tissue culture plate for 24 hours at 37 °C and 5% CO_2. The CGM extract of the coverslip without films were used as negative control and cell culture with addition of 0.1% Triton X100 in CGM were used as positive control. Samples were run in triplicate. AlamarBlue Assay® (Life Technology) was performed to evaluate the metabolic activity of hDF and MG63. The fluorescent intensity, indicating the cell viability was measured with a plate reader (Tecan Infinite® M200 Pro) with excitation at 560nm and emission at 590nm.

In cell adhesion tests, the hDF cells were seeded directly on the coverslips coated with P22-5 films and cultured for 24 hours in an incubator at 37 °C and 5% CO_2 in a humidified atmosphere. The films were then fixed in 2.5% (v/v) glutaraldehyde in PBS and dehydrated in a series of ethanol solutions (30%, 50%, 70%, 85%, 90%, 95% and twice in 100%). The cell attachment and morphology was recorded with an inverted optical microscopy.

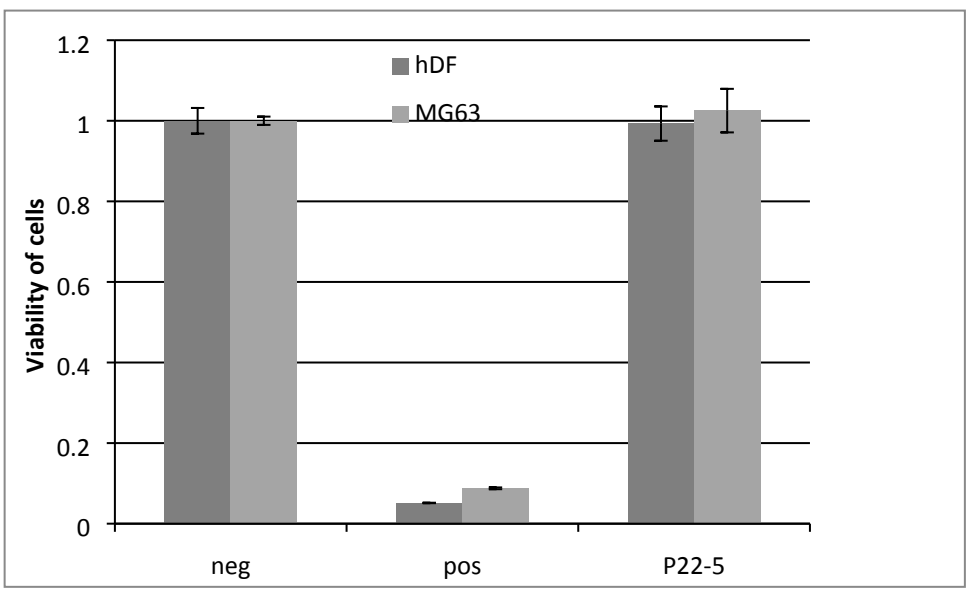


Figure S 4. Cell viability of hDF and MG63 after elution tests of the polymer P22-5. No cytotoxicity was observed by comparison of negative control (neg) and P22-5 samples. Cell culture with addition of Triton X100 served as positive control (pos)

References

[1] *ISO 10993-5, Biological evaluation of medical devices - Part 5: Tests for in vitro cytotoxicity* 2009.