Supplemental information to the manuscript

'Thermo-Responsive PNiPAAm-*g*-PEG Films for Controlled Cell Detachment'

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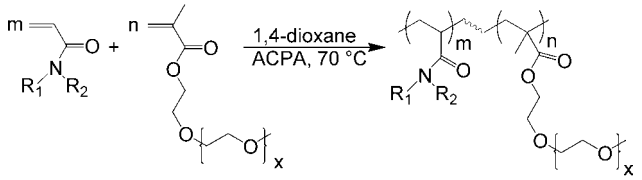
The supplemental information gives details to the synthesis of the polymers and the plasma immobilization procedure, which have been submitted for publication.

Standard Copolymerization Procedure



P1: R_1 = H, R_2 = iPr, m = 0.987, n = 0.013, x = 44
P2: R_1 = H, R_2 = iPr, m = 0.979, n = 0.021, x = 44
P3: R_1 = Et, R_2 = Et, m = 0.994, n = 0.006, x = 44
P4: R_1 = Et, R_2 = Et, m = 0.960, n = 0.040, x = 7

The two monomers were mixed with 0.3 mol-% 4,4'-azo-bis-(4-cyanopentanoic acid) (ACPA) and dissolved in dioxane giving a 10 wt.-% solution. The solution was degassed with three freeze and thaw cycles, then sealed and placed into a preheated bath at 70 °C. After 16 to 24 h reaction time the polymerization was stopped and the polymer was purified by repeated precipitation into cold di-ethylether or pentane. White solids or colorless waxes were isolated as products. The yields ranged from 62 to 85 %.

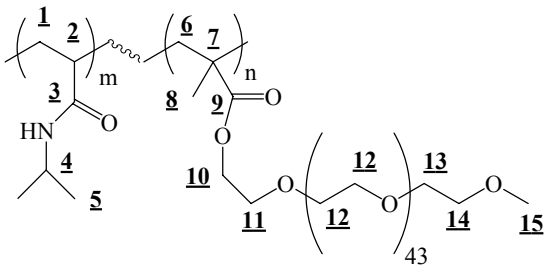
NMR and IR characterization of P1:

^{1}H NMR (DMSO-d_6, δ in ppm): 7.5 – 6.9 (NH); 4.03 (**10**); 3.83 (**4**); 3.61 (**11**); 3.51 (**12, 13**); 3.43 (**14**); 3.25 (**15**); 1.9 (**2**); 1.4 (**1**, **6**); 1.06 (**5**); 0.95 – 0.8 (**8**)

^{1}H NMR (D_2O, δ in ppm): 8.3 – 7.3 (NH); 4.2 (**10**); 3.87 (**4**); 3.77 (**11**); 3.67 (**12, 13**); 3.59 (**14**); 3.35 (**15**); 2.0 (**2**); 1.5 (**1**, **6**); 1.12 (**5**); 1.0 (**8**)

^{13}C NMR (DMSO-d_6, δ in ppm): 175.8 (**9**); 173.6 (**3**); 71.35 (**14**), 69.85 (**12**); 69.66 (**13**); 68.1 (**11**); 63.1 (**10**); 58.09 (**15**); 45.1 (**7**); 41.5 (**2**, **6**); 40.3 (**4**); 35.2 (**1**); 22.3 (**5**) 19.7 (**8**)

^{13}C NMR (D_2O, δ in ppm): 180.8 (**9**); 178.2 (**3**); 73.90 (**14**), 72.49 (**12**); 72.34 (**13**); 71.21 (**11**); 67.27 (**10**); 50.97 (**15**); 48.3 (**7**); 45.5 (**2**) 44.6 (**4**); 44 (**6**); 40 - 36 (**1**); 24.50 / 24.14 (**5**) 22.4 (**8**)



IR (KBr, cm^{-1}): 3450 (s), 3290 (s), 3075 (m), 2917 (s), 2122 (w), 1960 (w), 1652 (s), 1255 (m), 1104 (s), 950 (m), 842 (m), 578 (s)

Low Pressure Plasma Immobilization

Non-branched fluorocarbon films with a structure close to PTFE were prepared on silicon substrates with an oxide layer of 50 nm, which allows the ellipsometric investigation of the hydrogel preparation. The fluorocarbon films, kindly provided by the Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences (Chernogolovka, Russia), were deposited by plasma polymerization. Tetrafluoroethylene (C_2F_4) was introduced downstream into a low pressure argon discharge. Silicon wafers were placed further downstream of the discharge. The thickness of the obtained fluorocarbon films was about 50 nm.[1] The fluorocarbon surfaces were treated in argon plasma as described below for 120 s to obtain an appropriate wetting behavior for spin coating.

Thin films of the polymers P1 - P4 were prepared on the fluorocarbon surfaces by spin coating from a 0.5 % wt/wt solution in $CHCl_3$. A spin coater RC5 by Karl Suss, France, was operated at a velocity of 5000 rpm and an acceleration rate of 5000 rpm/s.

The films of P1-P4 were immobilized on the fluorocarbon surface using low pressure argon plasma. The plasma treatment was carried out in a computer controlled MicroSys apparatus by Roth&Rau, Germany. The cylindrical vacuum chamber, made of stainless steel, has a diameter of 350 mm and a height of 350 mm. The base pressure obtained with a turbomolecular pump is $<10^{-7}$ mbar. On the top of the chamber a 2.46 GHz electron cyclotron resonance (ECR) plasma source RR160 by Roth&Rau with a diameter of 160 mm and a maximum power of 800 W is mounted. Argon (99.999 %, Messer Griesheim) is introduced into the active volume of the plasma source via a gas flow control system. When the plasma source is on, the pressure is measured by a capacitive vacuum gauge. The samples are introduced by a load-lock-system and placed on a grounded aluminum holder near the center of the chamber. The distance between the sample and the excitation volume of the plasma source is about 200 mm. The following parameters were used for the experiments of this work: effective power 120 W, argon gas flow 38 standard cubic centimeter per minute, pressure $8 \cdot 10^{-3}$ mbar. The treatment time for

immobilization was 8 s. After the immobilization, the films were rinsed with $CHCl_3$ in order to remove all non-bonded polymer.

([1]) Vasilets, V. N.; Werner, C.; Hermel, G.; Pleul, D.; Nitschke, M.; Menning, A.; Janke, A.; Simon, F. *J. Adhesion Sci. Technol.* **2002**, *16*, 1855-1868.