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Nanophasic Amphiphilic Conetworks with a Fluorophilic Phase

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ABSTRACT: Amphiphilic conetworks, generally considered as hydrophilic/hydrophobic materials, are recently gaining great interest due to their wide range of possible applications in catalysis, sensors, and biomedical applications. However, little is known about conetworks with highly fluorinated phases. Here, we describe two readily available methods that allow the synthesis of nanophase separated hydrophobic/fluorophilic and hydrophilic/fluorophilic conetworks. The first kind was achieved by the novel "hot plate technique", which allows to homogenize a mixture of the perfluoro-tagged 1*H*,1*H*,2*H*,2*H*-hexadecylfluorodecyl acrylate and a dimethacrylate terminated poly(dimethylsiloxane). Upon photopolymerization, nanophase separated conetworks in all compositions were obtained. Further, hydrophilic/fluorophilic conetworks could be accessed by applying the precursor approach for the synthesis of amphiphilic conetworks. To this end, 2-hydroxyethyl acrylate was modified with a perfluoro-tagged silane, mixed with dimethacrylate-terminated perfluoropolyether, photopolymerized, and subsequently deprotected. The amphiphilic behavior as well as the nanophase morphology of all conetworks was proven with swelling experiments, AFM, TEM, and DSC measurements. Preliminary results show the great affinity of the hydrophilic/fluorophilic conetworks to the catalytically important enzyme lipase, indicating their potential as phase transfer matrix for biotransformations in perfluorinated solvents and supercritical fluids.

Introduction

In liquid phase organic chemistry, there are three immiscible solvent types: water, organic solvents, and perfluorinated solvents. In materials science, these three phases are represented by hydrophilic polymers, e.g., PEG, by hydrophobic polymers, e.g., PMMA, and by highly fluorinated, i.e., fluorophilic materials such as PTFE. A class of material that combines two of the phases in one material are amphiphilic conetworks. However, only amphiphilic conetworks comprising a hydrophilic and a hydrophobic phase have been studied in great detail.[1−7] They have been used for applications such as contact lenses,[8,9] drug delivery systems,[6,7,10−17] biomedical scaffolds for tissue engineering,[18−22] and catalysts support.[23,24] Conetworks that consist of hydrophilic or hydrophobic and fluorophilic chain segments are a lot more difficult to synthesize, because of the severe immiscibility of the monomers. Thus, only a few examples of macroscopically homogeneous conetworks are known. Mostly, the perfluorinated compound is added in very small amounts to modify the surface of hydrophobic materials without changing their bulk properties, due to the tendency of perfluorinated compounds to enrich on the surface.[25,26]

Recently, such amphiphilic conetworks were achieved by cross-linking of PEG or poly(dimethylsiloxane) (PDMS) with hyperbranched perfuorobenzyl ethers.[27] Although these materials show interesting properties regarding antifouling, they have the drawback of phase-separated morphologies in micrometer dimensions. Another example are networks on the basis of ABA blockcopolymers with cross-linkable end groups where either the A or the B block is perfluorinated [e.g. B = perfluoropolyether (PFPE)].[28] Besides the elaborate synthesis of well-defined blockcopolymers, this approach has the drawback that the content of the perfluorinated compound in the final network is dictated by the blocklengths and cannot be varied without the need to synthesize new macromonomers. PFPE based polyurethanes can be considered as amphiphilic conetworks, too.[29,30] However, due to the variety of side reactions of polyurethane chemistry, these networks are of rather undefined topologies. Finally, conetworks of α,ω-methacrylate functionalized PFPE macromonomers with small amounts of acrylates have been studied in detail.[25,31] The composition of such conetworks could not be varied over a broad composition range without obtaining opaque, i.e., microphase separated materials, and in most cases, the PFPE content is well below 2%.[25]

Although, the described amphiphilic conetworks with a fluorophilic phase have shown potential as antifouling coatings,[32] contact lens materials,[8] and low wettability surfaces,[33] they cannot be used for applications such as catalysis and sensor designs, which require a large interphase and a cocontinuous morphology.

Here we describe approaches to novel amphiphilic conetworks comprising a highly fluorinated phase, which enable the preparation of nanophasic hydrophobic/fluorophilic as well as hydrophilic/fluorophilic conetworks in every composition. Such conetworks should be ideal candidates to broaden the application of conetworks as catalysts support to media such as perfluorinated solvents and supercritical fluids.

Experimental Section

Materials. α,ω-Methacryloxypropylpoly(dimethylsiloxane) [MA-PDMS$_{1.1}$-MA; $M_n = 1150$ g/mol (^{1}H NMR), $M_n = 1060$ g/mol (^{29}Si NMR), degree of bifunctionality = 99% (^{29}Si NMR), $M_w/M_n = 1.1$ (GPC in $CHCl_3$)] was synthesized as described previously[2] by reaction of α,ω-silanol terminated poly(dimethylsiloxane) (DSM09, 1000 g/mol, kindly provided by Wacker, Germany) with methacryloxypropyl dimethylchlorosilane. The α,ω-perfluoropolyether diols (trade name Fomblin ZDOL, kindly provided by Solvay Solexis, Italy) are represented by the following structure:

$$HOCH_2{-}CF_2{-}O{-}(CF_2CF_2O)_m{-}(CF_2O)_n\text{-}CF_2{-}CH_2OH$$

with a random distribution of $-CF_2CF_2O-$ and $-CF_2O-$ and $m \approx n$. Samples of ZDOL 2000 and ZDOL 4000 were used [$m/n =$

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Table 1. Synthesis Parameters of the Preparation of PHDFDA-*l*-PDMS$_{1.1}$ Amphiphilic Conetworks

PDMS content in the final conetwork [wt %]	V_{HDFDA} [μL]	m_{HDFDA} [mg]	n_{HDFDA} [μmol]	$m_{\mathrm{MA-PDMS1.1-MA}}$ [mg]	$n_{\mathrm{MA-PDMS1.1-MA}}$ [μmol]
10	50.5	82.7	160	9.5	8
30	34.8	57.0	110	24.4	21
50	22.3	36.6	71	36.6	32
70	12.2	19.9	38	46.5	40
90	3.7	6.1	12	54.7	48

0.9 (NMR), degree of bifunctionality = 96% (^{19}F NMR), M_n(ZDOL 2000) = 2138 g/mol (^{19}F NMR), M_w/M_n(ZDOL 2000) = 1.5 (GPC), M_n(ZDOL 4000) = 4179 g/mol (^{19}F NMR), M_w/M_n (ZDOL 4000) = 1.15 (GPC)]. 2-(Trimethylsilyloxy)ethyl acrylate (TMSOEA) was synthesized as described previously.[34] The photoinitiator Lucirin TPO (2,4,6-trimethylbenzoyldiphenylphosphine oxide) was a gift from BASF AG (Germany). 1*H*,1*H*,2*H*,2*H*-Hexadecylfluorodecyl acrylate (HDFDA) and isocyanoethyl methacrylate, both supplied by Aldrich, were freshly distilled prior to use. 2-Hydroxyethyl acrylate (HEA) and triethylamine (NEt$_3$) were dried over CaH$_2$ and freshly distilled under argon prior to use.

1*H*,1*H*,2*H*,2*H*-Perfluorooctyldimethylchlorosilane (97%) and 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane (97%), supplied by ABCR, perfuorohexane and perfluorodecaline, both supplied by Fluorochem, and anhydrous CH$_2$Cl$_2$ (99.8%), ethyl acetate, and Sn dibutyl laurate, all obtained from Aldrich, were used without further purification. Lipase from *Candida antarctica* (2.7 U/mg) was purchased from Fluka. Methacrylate modified glass slides were prepared as previously reported.[2] Adhesive poly(propylene) tapes (Tesafilm and Tesapack 4024) were purchased from Tesa AG (Germany).

Synthesis of α,ω-Methacryloxyethylurethane Perfluoropolyether (MA-PFPE-MA). The synthesis of MA-PFPE$_{4.5}$-MA is reported here in detail.

Freshly distilled isocyanoethyl methacrylate (0.678 mL, 0.743 g, 4.79 mmol) was added dropwise under stirring to a solution of ZDOL 4000 (10.00 g, 2.393 mmol) and Sn dibutyl dilaurate (460 μL of a 1% solution in ethyl acetate) in 10 mL ethyl acetate at room temperature. The turbid solution was heated to 60 °C, where it became clear, and stirred at this temperature overnight. FTIR showed complete conversion by the disappearance of the typical isocyanate band at 2258 cm^{-1}. Ethyl acetate was removed in vacuo, the residue taken up in 10 mL of perfluorohexane, filtered through a PTFE membrane (0.2 μm) to remove ureas byproducts coming from the hydrolysis of isocynanoethyl methacrylate, and concentrated in vacuo to yield 9.88 g (92%) of MA-PFPE$_{4.5}$-MA as a colorless, viscous liquid.

^{1}H NMR (300 MHz, solvent free/D$_2$O-capillary): δ [ppm] = 1.87 (s, CH_3), 3.48 (m_c, NHCH_2CH$_2$O), 4.22 (m_c, NHCH$_2$CH_2O), 4.47 (m_c, CF$_2$CH_2O), 5.49 and 6.09 (2s, C=CH_2), 6.45 (bs, NH).

^{19}F NMR (300 MHz, solvent free/D$_2$O-capillary): δ [ppm] = −52.0 (OCF_2O), −53.6 (OCF_2O), −55.4 (OCF_2O), −56.3 (OCF_3), −58.0 (OCF_3), −78.0 (OCF_2CH$_2$O), −80.0 (OCF_2CH$_2$O), −83.6 and −83.8 (OCF_2CF$_2$O), −85.3 and −85.5 (OCF_2CF$_2$CF$_2$O), −89.0 (OCF_2CF$_2$O), −90.7 (OCF_2CF$_2$O), −125.9 (OCF$_2$CF_2CF$_2$CF$_2$O), −129.7 (OCF$_2$CF_2CF$_2$O). From these data, the methacrylic bifunctionallity was determined to be 98%.

ATR−FTIR: $\bar{\nu}$ = 3367, 2970, 1727, 1638, 1539, 1457, 1402, 1184, 1139, 1048, 907, 814, 768, 759, 684 cm^{-1}.

MA-PFPE$_{2.4}$-MA was prepared according to the same procedure.

^{1}H NMR (300 MHz, perfluorohexane): δ [ppm] = 2.00 (s, CH_3), 3.61 (m_c, NHCH_2CH$_2$O), 4.35 (m_c, NHCH$_2$CH_2O), 4.60 (m_c, CF$_2$CH_2O), 5.61 and 6.22 (2s, C=CH_2), 6.59 (bs, NH).

^{19}F NMR (300 MHz, perfluorohexane): δ [ppm] = −52.1 (OCF_2O), −53.7 (OCF_2O), −55.4 (OCF_2O), −56.0 (OCF_3), −58.1 (OCF_3), −77.9 (OCF_2CH$_2$O), −80.0 (OCF_2CH$_2$O), −83.7 and −83.8 (OCF_2CF$_2$O), −85.3 and −85.5 (OCF_2CF$_2$CF$_2$O), −89.0 (OCF_2CF$_2$O), −90.7 (OCF_2CF$_2$O), −125.9 (OCF$_2$CF_2CF$_2$CF$_2$O), −129.7 (OCF$_2$CF_2CF$_2$O). From these data, the methacrylic bifunctionallity was determined to be 100%.

ATR−FTIR: $\bar{\nu}$ = 3361, 2974, 1726, 1639, 1537, 1456, 1404, 1184, 1143, 1047, 907, 814, 768, 758, 685 cm^{-1}.

2-(1*H*,1*H*,2*H*,2*H*-Perfluorodecyldimethylsilyloxy)ethyl Acrylate (FDOEA) and 2-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyldimethylsilyloxy)ethyl Acrylate (FOOEA). A solution of 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane (5.043 g, 9.327 mmol) in 45 mL of anhydrous CH$_2$Cl$_2$ was carefully added within 2 h to a stirred solution of HEA (3.185 mL, 3.221 g, 27.74 mmol) and NEt$_3$ (1.871 g, 18.49 mmol) in 125 mL of anhydrous CH$_2$Cl$_2$ under argon at room temperature. The solution was stirred at room temperature for 3 h. Then 50 mL of saturated NaHCO$_3$ solution was added. The aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 25 mL) and the combined organic phases were dried over Na$_2$SO$_4$. The solvent was evaporated, and the residue was taken up in 8 mL of acetonitrile and extracted with perfluorohexane (30 mL + 4 × 10 mL). The perfluorinated phases were combined and concentrated in vacuo. Filtration over a short reversed phase silica column (acetonitrile) and column chromatography over silica (CH$_2$Cl$_2$) gave 4.482 g (77%) of FDOEA as a colorless liquid. The product contained 1.35 mol % of (C$_8$F$_{17}$C$_2$H$_4$)(CH$_3$)$_2$Si−O−Si(CH$_3$)$_2$(C$_2$H$_4$C$_8$F$_{17}$) as inert byproduct, as determined by ^{1}H NMR.

^{1}H NMR (300 MHz, CDCl$_3$): δ [ppm] = 0.17 [s, Si(CH_3)$_2$], 0.78−0.89 (m, SiCH_2), 1.97−2.16 (m, CH_2CF$_2$), 3.84 (m_c, CH_2-OSi), 4.24 (m_c, COOCH_2), 5.84 (dd, J_{gem} = 1.5, J_{cis} = 10.3, CH_2=C), 6.14 (dd, J_{cis} = 10.3, J_{trans} = 17.4, CH$_2$=CH), 6.43 (dd, J_{gem} = 1.5, J_{trans} = 17.2 CH$_2$=C).

ATR−FTIR: $\bar{\nu}$ = 2960, 1731, 1638, 1442, 1409, 1368, 1318, 1297, 1237, 1197, 1144, 1133, 1111, 1066, 967, 900, 841, 808, 791, 722, 704, 655, 558, 529 cm^{-1}.

FOOEA was synthesized according to the same procedure.

^{1}H NMR (300 MHz, CDCl$_3$): δ [ppm] = 0.17 [s, Si(CH_3)$_2$], 0.79−0.87 (m, SiCH_2), 1.97−2.17 (m, CH_2CF$_2$), 3.84 (m_c, CH_2-OSi), 4.24 (m_c, COOCH_2), 5.84 (dd, J_{gem} = 1.5, J_{cis} = 10.3, CH_2=C), 6.14 (dd, J_{cis} = 10.3, J_{trans} = 17.4, CH$_2$=CH), 6.43 (dd, J_{gem} = 1.5, J_{trans} = 17.4 CH$_2$=C).

Conetwork Synthesis. PHDFDA-*l*-PDMS$_{1.1}$. Surface-attached films were synthesized according to the following procedure. A mixture containing HDFDA, MA-PDMS$_{1.1}$-MA, and Lucirin TPO (0.5 wt %) (cf. Table 1) was heated to 110 °C, upon which it became monophasic, and vortexed until the initiator was dissolved. A preheated methacrylate-modified glass slide (7.6 × 1.5 cm^2) was placed on a hot plate (SD 160, Stuart, U.K.), which was set to 110 °C. 60 μL of the monomer solution were transferred with a hot pipet (110 °C) onto that slide and a glass slide, coated with an adhesive PP-tape and preheated to 110 °C was placed on top. The slide sandwich was irradiated on the hot plate with a halogen lamp (Argaphoto-BM, 500 W, Philips) at a distance of 15 cm for 2 min from each side and allowed to cool to room temperature. After the PP-coated slide was removed, 10 conetwork-coated slides were incubated in 90 mL of acetone for 14 h at room temperature under gentle shaking. The slides were rinsed with acetone and dried for 12 h in a vacuum at 60 °C.

Free-standing membranes were synthesized according to the same procedure by placing 120 μL of a monomer mixture between an unmodified glass slide (2.6 × 7.6 cm^2) and an PP-tape covered slide followed by polymerization on the hot plate.

ATR−FTIR: $\bar{\nu}$ = 2962, 2904, 1732, 1473, 1447, 1413, 1400, 1377, 1343, 1258, 1240, 1207, 1149, 1081, 1014, 863, 791, 703, 658 cm^{-1}.

PHEA-*l*-PFPE$_{2.4}$ from TMSOEA and MA-PFPE$_{2.4}$-MA. Surface attached PHEA-*l*-PFPE$_{2.4}$ films were synthesized by heating

Table 2. Synthesis Parameters of the Preparation of PHEA-*l*-PFPE$_{2.4}$ Amphiphilic Conetworks from TMSOEA and MA-PFPE$_{2.4}$-MA

PFPE content in the final conetwork [wt %][a]	V_{TMSOEA} [μL]	m_{TMSOEA} [mg]	n_{TMSOEA} [μmol]	$m_{\mathrm{MA-PFPE2.4-MA}}$ [mg]	$n_{\mathrm{MA-PFPE2.4-MA}}$ [μmol]
50	44.2	40.7	216	25.1	10.3
70	32.7	30.1	160	43.3	17.7
90	14.2	13.1	69.4	72.8	29.7

[a] Calculated for completely deprotected conetwork.

Table 3. Synthesis Parameters of the Preparation of PHEA-*l*-PFPE$_{4.5}$ Amphiphilic Conetworks from FDOEA and MA-PFPE$_{4.5}$-MA

PFPE content in the final conetwork [wt %][a]	m_{FDOEA} [mg]	n_{FDOEA} [μmol]	$m_{\mathrm{MA-PFPE4.5-MA}}$ [mg]	$n_{\mathrm{MA-PFPE4.5-MA}}$ [μmol]
10	81.3	131	1.7	0.38
30	77.4	125	6.2	1.38
50	71.3	115	13.3	2.96
70	60.2	97.0	26.3	5.86
85	43.3	69.8	45.9	10.2
90	33.8	54.5	57.0	12.7

[a] Calculated for completely deprotected conetwork.

a mixture of freshly distilled TMSOEA, MA-PFPE$_{2.4}$-MA and Lucirin TPO (0.05 mg/mL) (cf. Table 2) to 120 °C, upon which mixtures with c(MA-PFPE$_{2.4}$-MA) $\geq$ 50 wt % became monophasic.

This mixture was vortexed until the initiator was dissolved. Then 60 μL of the homogeneous mixtures were polymerized between a methacrylate-modified glass slide and an PP-covered glass slide on a hot plate at 120 °C as described for PHDFDA-*l*-PDMS$_{1.1}$. The slide sandwich was allowed to cool to room temperature and the PP-covered slide was removed. Then 10 conetwork-coated slides were twice incubated in 90 mL of a THF/water mixture (1:1) for 24 h in order to cleave the trimethylsilyl groups. Then they were incubated in acetone (90 mL) overnight, rinsed with acetone, air-dried (20 min), and then dried in a vacuum (30 min, 40 °C, 10 mbar).

ATR−FTIR: $\bar{\nu}$ = 3370, 2957, 1730, 1541, 1457, 1400, 1184, 1140, 1050, 979, 844, 756, 687 cm^{-1}.

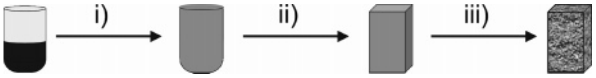
PHEA-*l*-PFPE$_{4.5}$ from FOOEA or FDOEA and MA-PFPE-MA$_{4.5}$. Surface attached PHEA-*l*-PFPE$_{4.5}$ films were synthesized according to the following procedure. A monomer mixture containing FOOEA or FDOEA, MA-PFPE$_{4.5}$-MA and Lucirin TPO (0.5 wt %) (cf. Table 3; for FOOEA analog) was heated to 100 °C for several minutes, sonificated in order to solve the initiator, and cooled to room temperature. Complete solvation of the initiator was only achieved with FOOEA, the mixtures containing FDOEA were used as saturated Lucirin solutions. Methacrylate-modified glass slides (7.6 × 1.5 cm^2) were covered with 60 μL of the monomer mixtures, a glass slide coated with an adhesive PP-tape was placed on top. The slide sandwich was irradiated in an UV reactor (type Heraflash, Heraeus Kulzer, Germany) for 900 s at ambient temperature. After removing the top slide, 10 conetwork-coated slides were twice incubated in 90 mL of a HCl (0.1 M)/THF mixture (1:1 v/v) for 24 h and in 90 mL of THF for 24 h, to remove the protecting perfluoro-tagged silyl groups. The slides were rinsed with THF, air-dried (1 h) and then dried 1 h in a vacuum (50 °C, 10 mbar).

Free-standing membranes were synthesized according to the same procedure by placing 240 μL (for PHEA-*l*-PFPE$_{4.5}$ with 10 or 30 wt % PFPE) or 120 μL of a monomer mixture between an unmodified glass slide (2.6 × 7.6 cm^2) and an PP-tape covered slide followed by polymerization and workup.

ATR−FTIR: $\bar{\nu}$ = 3370, 2953, 2884, 1728, 1541, 1450, 1399, 1186, 1158, 1063, 894, 844, 684 cm^{-1}.

Methods. NMR spectra were obtained on a Bruker ARX 300 spectrometer operating at 300 MHz. Attenuated total reflection Fourier transform infrared spectrometry (ATR−FTIR) was carried out on a Bruker Vektor 22 spectrometer, equipped with a Golden Gate accessory (Specac). Spectra were obtained from conetwork surfaces and ground samples with unpolarized light with a 4 cm^{-1} resolution and 20 scans. The tapping-mode atomic force microscopy (AFM) were carried out with a "nanoscope III" scanning probe microscope (Digital Instruments) at ambient conditions in phase mode using NCL-W (tapping mode) cantilevers (Nanosensors). The measurements were performed on the surface of surface-attached films and on cryofractures of the films. Transmission electron microscopic (TEM) measurements were carried out with a Zeiss (LEO) 912 Omega equipment using acceleration voltage of 120 kV. PHEA-*l*-PFPE conetworks were stained in an aqueous MnO$_4$ solution, dried and cut to 60−100 nm thick sections (Leica Ultra-Microtome) for obtaining TEM pictures. Differential scanning calorimetric measurements (DSC) have been carried out in a N$_2$ atmosphere by means of a Perkin-Elmer DSC-7. Samples were cooled from room temperature to −150 °C at a rate of 80 °C/min. Thermographs were recorded from −150 to +50 °C and from −50 to +150 °C at a heating rate of 20 °C/min in the second heating cycle. Additionally, PHDFDA-*l*-PDMS$_{1.1}$ samples were annealed at 120 °C for 20 min, quenched in liquid N$_2$ and mounted into the DSC apparatus at temperatures less than −150 °C. DSC traces of these samples were recorded from −150 to +50 °C at a heating rate of 10 °C/min. The mass of the samples was 4−16 mg. The glass transition temperature T_g was evaluated as transition midpoint of the trace. The solubility curve was determined by cooling mixtures of known composition from 120 °C to room temperature in a temperated oil bath until two phases appeared. The sol content was determined by Soxhlet extraction of conetwork membranes with acetone (100 mL) right after the polymerization step. Equilibrium volumetric degrees of swelling were measured as described previously.[2] A PHEA-*l*-PFPE$_{4.5}$ membrane (50 wt % PFPE) was loaded with lipase from *C. antarctica* according to a procedure reported earlier.[23]

Scheme 1. Synthetic Strategy toward Amphiphilic Conetworks: (i) Formation of a Homogeneous Monomer Mixture, (ii) Polymerization, and (iii) Phase Separation



Results and Discussion

Fluorophilic/Hydrophobic Conetworks: PHDFDA-*l*-PDMS$_{1.1}$. The preferred route to common hydrophilic/hydrophobic amphiphilic conetworks is based on the macromonomer approach, where networks are formed by copolymerizing monomers with a bifunctional macromonomer of opposite philicity. This results in conetworks with a segmented topology. These conetworks possess a large driving force for nanophase separation.[1] The various synthetic strategies toward these conetworks can be broken down into three steps (Scheme 1). First, a monophasic monomer mixture has to be prepared, overcoming the immiscibility of the monomers of different philicity, e.g., by a solvent,[7] by blockcopolymers, or by the precursor approach.[6] In the latter approach, a hydrophilic monomer is rendered hydrophobic by introducing a hydrophobic protecting group that can be cleaved after formation of the conetwork. In the second step, the monomers are polymerized, e.g., via radical initiation. Finally, the polymer segments of the resulting homogeneous conetworks are then forced to separate by removing the compatibilizing conditions such as solvent or

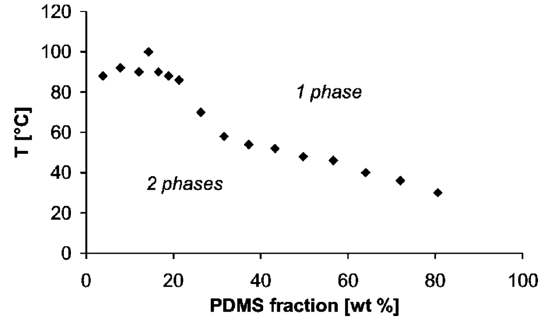
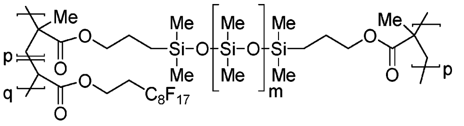


Figure 1. Cloud-point curve of the binary mixture of HDFDA and MA-PFPE$_{1.1}$-MA.

Scheme 2. Structure of PHDFDA-*l*-PDMS$_{1.1}$



protecting groups. However, due to the covalent bonds between the chain segments of different philicity, the demixing only occurs on the nanometer scale, leading to nanophase separated morphologies.

A rational approach to synthesize amphiphilic conetworks comprising a perfluorinated phase and a hydrophobic phase follows the same scheme. However, if the compatibilization of the monomeric mixture is not sufficient for the respective polymers, often phase separation occurs during polymerization. This results in micro or even macrophasic conetworks that usually appear cloudy, which was reported for fluoro-tagged acrylates copolymerized with a PDMS macromonomic cross-linker in the presence of a common solvent.[35] We followed a new and simple strategy for the first step, that arises from the temperature dependent mixing behavior of perfluorinated compounds and organic compounds, most prominently known from the fluorous biphasic catalysis: Organic and perfluorinated liquids do not mix, but above a certain temperature (cloud point), the mixture reversibly becomes homogeneous.[36−38] Figure 1 shows the cloud-point temperatures of mixtures of two liquid monomers:1*H*,1*H*,2*H*,2*H*-hexadecylfluorodecyl acrylate (HDFDA) and α,ω-methacryloyl terminated poly(dimethylsiloxane) (MA-PDMS$_{1.1}$-MA). The cloud point temperature increases from 30 to 90−100 °C with increasing fraction of the highly fluorinated monomer. At temperatures above 100 °C a homogeneous monomer mixture is obtained for every composition. Choosing of UV-initiated polymerization allows us to decouple the heating of the monomers from the polymerization step. In fact, monomer mixtures containing the photoinitiator could be handled at high temperatures for at least 30 min without gelling, i.e., unintentional polymerization. The monomers were placed between two glass slides, one which was surface-modified with methacrylate groups to yield a covalent attachment of the resulting cross-linked polymer to the glass. The untreated cover glass slide was coated with a PP-film to facilitate its removal after polymerization. The glass slides were heated prior to polymerization to 110 °C, and the polymerization was conducted on a hot plate, set to the same temperature. After UV-curing, the slides were allowed to cool to room temperature, allowing phase separation (Scheme 1, step 3). Poly(1*H*,1*H*,2*H*,2*H*-heptadecylfluorodecyl acrylate)-*l*-poly(dimethylsiloxane) (PHDFDA-*l*-PDMS$_{1.1}$) amphiphilic conetwork films with 10−90 wt % PDMS were synthesized. Free-standing membranes with the same compositions were obtained by using an unmodified glass slide instead of the one modified with methacrylate groups. The sol content was found to be in the range between 1.7 and 2.6 wt %, indicating a nearly quantitative conversion of the monomers and the macromonomers. Thus, the final conetwork composition can be approximated by the feed ratios of the monomers.

Table 4. Glass Transition Temperatures of PHDFDA-*l*-PDMS$_{1.1}$ Determined by DSC

PDMS content [wt %]	T_g [°C]	T_g [°C]
10	−119	n.d.[a]
30	−115	12
50	−103	19
70	−102	20
90	−98	19
100	−100	

[a] Not detected.

ATR−IR spectra of the conetworks show no signal at 1642 cm^{-1}, an absorption correlated to the C=C double bonds of the monomers. This indicates complete monomer consumption.

The polymer films are optically transparent, i.e., no macroscopic or microscopic phase separation has occurred. However they show two distinct glass transition temperatures, suggesting a nanophase separated morphology (Table 4). These glass transitions can be attributed to the homopolymers [T_g(MA-PDMS$_{1.1}$-MA) = −115 °C, T_g(PHDFDA) = 0 °C[39]], but they are shifted to higher temperatures, as it is expected for cross-linked polymers.[40] The conetworks also show a broad endothermic transition at 54−58 °C, which can possibly be explained as the phase transition between a biphasic and a monophasic morphology. To confirm this, conetworks were annealed at 120 °C and quenched thermally in liquid nitrogen. These networks just showed one single glass transition between −61 and −57 °C. Apparently, the two conetwork phases, which are separated at room temperature, mix at higher temperatures, and this homogeneous state can be frozen by rapid cooling. The mixed phase shows a T_g between the two of the phase separated conetwork.

Phase mode AFM measurements were carried out to investigate the phase morphology of the PHDFDA-*l*-PDMS$_{1.1}$ films. The measurements were performed on the surface of the films and on cross sections created by fracturing the films at −196 °C. The latter give an insight into the bulk morphology of the films. In these pictures the hard PHEA domains appear brighter than the soft PDMS$_{1.1}$ phase. The conetwork films show nanophase separated morphologies in bulk and on their surface, similar to conventional hydrophilic/hydrophobic amphiphilic conetworks reported in previous work [2,41,42]

Figure 2 shows AFM images of a PHDFDA-*l*-PDMS$_{1.1}$ film with a PDMS content of 70 wt %. A cocontinuous morphology with domain thicknesses between 10 and 25 nm for PHDFDA and 20 to 45 nm for PDMS is observed. The images prove that the morphology does not change from the interface to the glass slide (Figure 2a), throughout the bulk of the film to the edge between the conetwork and air (Figure 2b). The edge itself appears brighter than the film. Most likely this is an artifact and not a sign of surface enrichment of PHDFDA, because the films surface shows the same morphology as the one found in the bulk (Figure 2c).

The most characteristic property of amphiphilic conetworks is their ability to swell in orthogonal solvents, which is the basis for their application as catalysts support in phase transfer reactions.[23,24] Hydrophobic/fluorophilic conetworks should swell in apolar organic as well as in perfluorinated solvents. To explore this, the volumetric equilibrium swelling degree of free-standing PHDFDA-*l*-PDMS$_{1.1}$ membranes (S_{UC}) in *n*-heptane

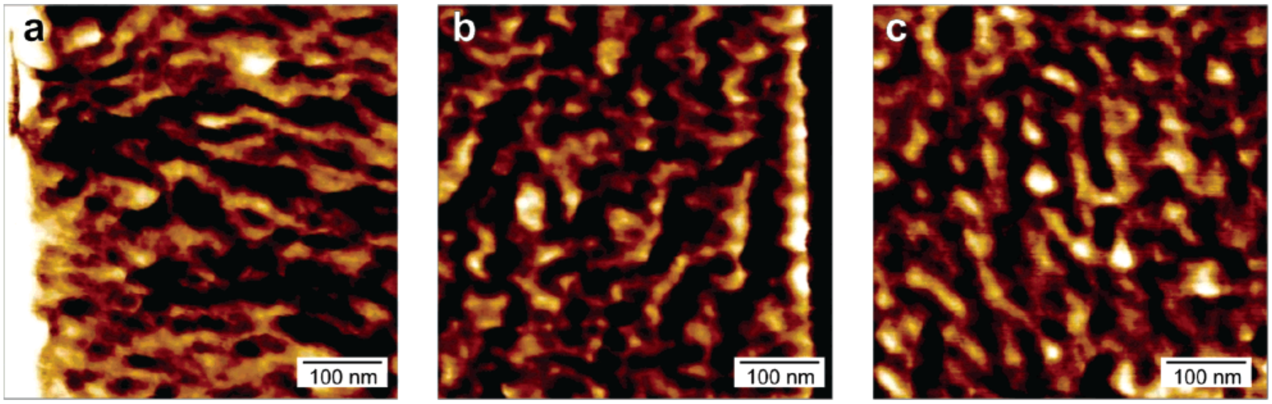


Figure 2. AFM phase mode images of an PHDFDA-*l*-PDMS$_{1.1}$ film with 70 wt % PDMS content: area of cross section at the interface to the glass substrate (a) and to air (b); (c) surface. PHDFDA shows light and PDMS dark.

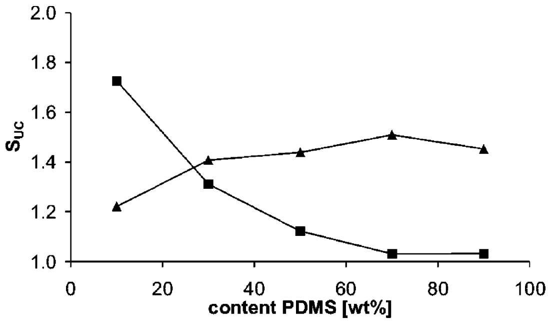


Figure 3. Equilibrium volumetric degree of swelling of PHDFDA-*l*-PDMS$_{1.1}$ conetworks vs PDMS content for a series of free-standing membranes in heptane (▲) and perfuorodecaline (■). The measurements were carried out in quadruplicate. The shown data are the mean values and have standard deviations in a range of 0.9 to 4.1%.

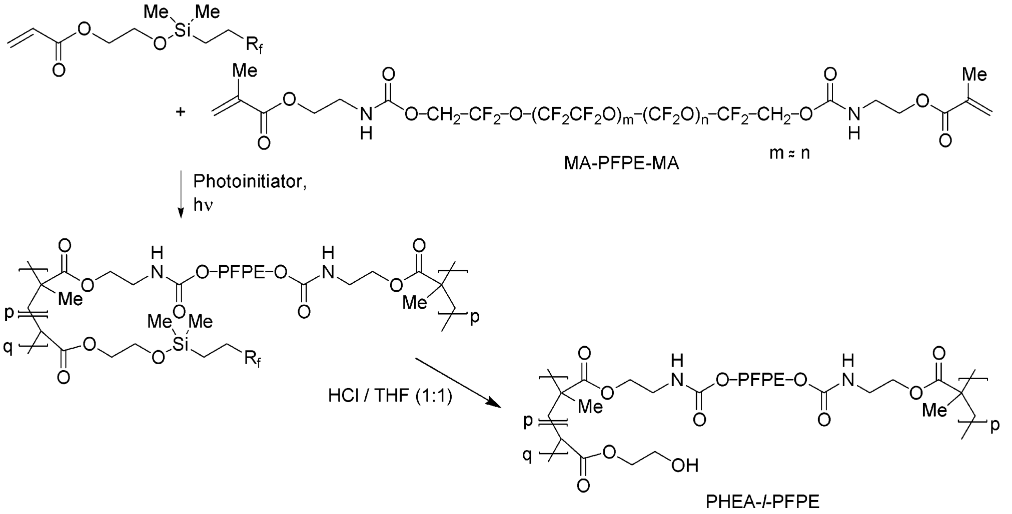
and in perfuorodecaline was measured in dependence of the conetworks composition (Figure 3).

The uptake of heptane is rather high for the lowest PDMS content measured ($S_{UC} = 1.22$). This indicates that not only the hydrophobic PDMS phase swells in that solvent, but that there is also a contribution from the perfluorinated polymer phase to the overall degree of swelling. Increasing the PDMS content in the conetwork up to 70 wt % leads to higher swelling degrees, however at higher PDMS content, the degree of swelling becomes smaller again. The maximum can be attributed to two effects that influence the swellability in different directions. On one hand side, the volume fraction of the better swellable PDMS phase increases, giving rise to a higher degree of swelling. On the other hand, as the cross-linker in the conetwork is the PDMS macromonomer, a higher PDMS content leads to a greater number of cross-links and a higher cross-linking density. This reduces the swelling.

As expected, the swelling in perfluorodecaline is negligible at 90 wt % PDMS content ($S_{UC} = 1.03$) and increases with decreasing PDMS up to $S_{UC} = 1.73$ at 10 wt % PDMS. Thus, it can be assumed that perfuolodecaline is a selective solvent that swells only the fluorophilic phase. The increase in volume fraction of the perfluorinated phase and the decrease of netpoint density both lead to an enhancement of swellability and thus a continuous increase in swellability is observed with decreasing PDMS content.

Hydrophilic/Fluorophilic Conetworks: PHEA-*l*-PFPE. Macroscopic homogeneous amphiphilic conetworks that comprise a hydrophilic as well as a fluorophilic phase are more difficult to synthesize than hydrophobic/fluorophilic conetworks, because of a greater immiscibility of the two components, albeit their expected properties should render them ideal as solid supports of water-soluble catalysts like enzymes in perfluorinated solvents and supercritical fluids. The general considerations on synthetic strategies toward amphiphilic conetworks let us to two different approaches to overcome the monomer immiscibility: the temperature dependent mixing behavior and a suitable precursor strategy. Hydrophilic and perfluorinated compounds do not mix even at high temperatures. If the hydrophilic monomer is rendered hydrophobic by a simple trimethylsilyl (TMS) protecting group, a mixing with perfluorinated compounds can be achieved at elevated temperatures. Readily available perfluorinated polyethers (PFPE) with reactive hydroxy end groups were chosen as fluorophilic compounds. They were converted to α,ω-methacrylate-terminated macromonomers (MA-PFPE-MA) by reaction with isocyanatoethyl methacrylate.[43] MA-PFPE$_{2.4}$-MA with $M_n = 2400$ g/mol mixes with TMS-protected 2-hydroxyethyl acrylate (TMSOEA) at 120 °C (the maximum processing temperature of the experimental setup) as long as the content of MA-PFPE$_{2.4}$-MA in the mixture is above 40 wt %. At lower PFPE content, the mixtures are still biphasic at 120 °C and were therefore not processed. Homogeneous monomer mixtures with MA-PFPE$_{2.4}$-MA contents of 50, 70, and 90 wt % were polymerized to thin films by UV irradiation on a hot plate at 120 °C. During the polymerization process, the 50 wt % sample became opaque and the 70 wt % sample turned slightly opaque, indicating a macroscopic phase separation with domain sizes at least as large as the wavelengths of light. ATR IR data shows that the TMS-protecting group is not affected under the polymerization conditions. After incubating the conetwork films in a 1:1 mixture of THF/H_2O to cleave the TMS groups, amphiphilic PHEA-*l*-PFPE$_{2.4}$ conetworks were obtained. Only the network with a content of 90 wt % PFPE was optically transparent. ATR IR spectroscopy proved a complete deprotection, but the spectra also show a depletion of PHEA in the networks with less than 90 wt % PFPE. Unfortunately, the spectra of the synthesized PHEA-l-PFPE$_{2.4}$ films are very similar, regardless the TMSOEA content of the starting monomer mixture indicating that all resulting conetworks have similar compositions. AFM investigations on the network with 50 wt % PFPE showed a porous structure with only minimal phase morphology. These findings suggest, that although the monomers readily mix at elevated temperatures, the two polymers PTMSOEA and PFPE are severely incompatible and the nascent chains phase-separate during polymerization before the gel point is reached. Upon deprotection in a polar solvent, the now hydrophilic PHEA-chains are extracted from the polymer. Only at sufficient high cross-linker concentration (90 wt % MA-PFPE$_{2.4}$-MA), the cross-linking process is fast enough to suppress the demixing.

Scheme 3. Synthesis of PHEA-*l*-PFPE Conetworks via a Precursor Approach ($R_f = C_6F_{13}$ or C_8F_{17})



These findings show that in principle this synthetic route toward hydrophilic/fluorophilic amphiphilic conetworks is feasible, however macroscopic homogeneous conetworks were only obtained with a high PFPE content of 90 wt %. The severe incompatibility between perfluorinated and hydrocarbon polymer chains is well-known in the literature and limits the amount of hydrocarbon monomers to a few percent when copolymerized with perfluorinated macromonomers.[25,31]

To obtain PHEA-*l*-PFPE conetworks with a broader range of compositions, we then focused on a precursor strategy (Scheme 3). The hydrophilic 2-hydroxyethyl acrylate was rendered fluorophilic by reacting it with 1*H*,1*H*,2*H*,2*H*-perfluorooctyldimethylchlorosilane and 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane, respectively. The resulting silyl ethers proved to be sufficiently robust to withstand the polymerization conditions. The masked monomers mix readily with MA-PFPE-MA at room temperature and the homogeneous monomer mixtures were UV-polymerized at ambient conditions to yield fluorophilic precursor-conetworks [poly(1*H*,1*H*,2*H*,2*H*-perfluoroctyldimethylsilyl hydroxyethyl acrylate-*l*-perfluoropolyether (PFOOEA-*l*-PFPE) and poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylsilyl hydroxyethyl acrylate-*l*-perfluoropolyether (PFDOEA-*l*-PFPE)]. MA-PFPE$_{4.5}$-MA with a molecular weight of $M_n = 4500$ g/mol was used to obtain networks with good swelling properties. Thin surface-attached films and free-standing membranes were synthesized and transformed into amphiphilic PHEA-*l*-PFPE$_{4.5}$ conetworks by cleavage of the silyl protecting groups, which was performed by incubating the precursor conetworks in an 1:1 mixture of HCl (0.1 M) and THF. The resulting conetworks were envisaged to have a PFPE content between 10 and 90 wt %. Transparent conetworks were obtained with the C_8F_{17} tag. The use of the C_6F_{13} tag gave optically clear conetworks for a PFPE content of 10, 30, and 90 wt % PFPE and slightly opaque polymers at mid range PFPE content of 50 and 70 wt %.

ATR−IR spectra of the films were recorded to determine the monomer conversion and to monitor the cleavage of the protecting groups. The spectra for a conetwork with a content of 50 wt % PFPE is presented in Figure 4 as an example. The spectra of the other conetworks show the same results. The absence of the signal due to the C=C stretching of the (meth)-acrylic double bonds at 1638 cm^{-1} in the spectra of the precursor conetwork indicates a complete monomer conversion (Figure 4, magnification). Complete cleavage of the silyl protecting groups was achieved within 1 day, as proven by the disappearance of the Si−C-valence band in the IR spectra at 841 cm^{-1}. ATR−FTIR-spectra of the conetworks surface and of ground samples were identical, indicating that no surface segregation has occurred and the chemical conversions, e.g., polymerization and deprotection, are homogeneous throughout the whole samples.

Table 5. Glass Transition Temperatures of PHEA-*l*-PFPE$_{4.5}$ Conetworks Obtained from FDOEA. Data Determined by DSC

PFPE content [wt %]	T_g [°C]	T_g [°C]
10	n.d.[a]	−24
30	−132	−13
50	−122	−11
70	−122	−20
90	−119	−13

[a] Not detected, but observed in an analogue conetwork obtained from FOOEA ($T_g = -121$ °C).

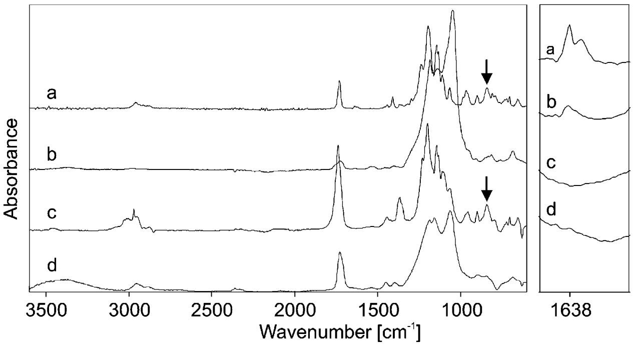


Figure 4. ATR−FTIR spectra: (a) FDOEA, (b) MA-PFPE$_{4.5}$-MA, (c) precursor conetwork PFDOEA-*l*-PFPE$_{4.5}$ (50 wt % PFPE), (d) amphiphilic conetwork PHEA-*l*-PFPE$_{4.5}$ (50 wt % PFPE). The box shows a magnification at 1638 cm^{-1}, the arrows indicate peaks at 841 cm^{-1}.

As it is the case for the conetworks described above, the optical transparency of the PHEA-*l*-PFPE$_{4.5}$ conetworks indicates the absence of phase separation in the macro or microscale. DSC experiments revealed two glass transitions at around −120 °C and −15 °C (Table 5). The two glass transition temperatures are close to those of the ones of the corresponding homopolymers (T_g(PFPE) = −111 °C,[43] T_g(PHEA) = −15 °C[44]). Thus, the conetworks are clearly biphasic with two strongly segregated, pure polymer phases with domain sizes in the nanometer scale.

To determine the phase morphology of the conetworks, phase mode AFM measurements were carried out. Figure 5 shows pictures obtained from cryofractured PHEA-*l*-PFPE$_{4.5}$ films

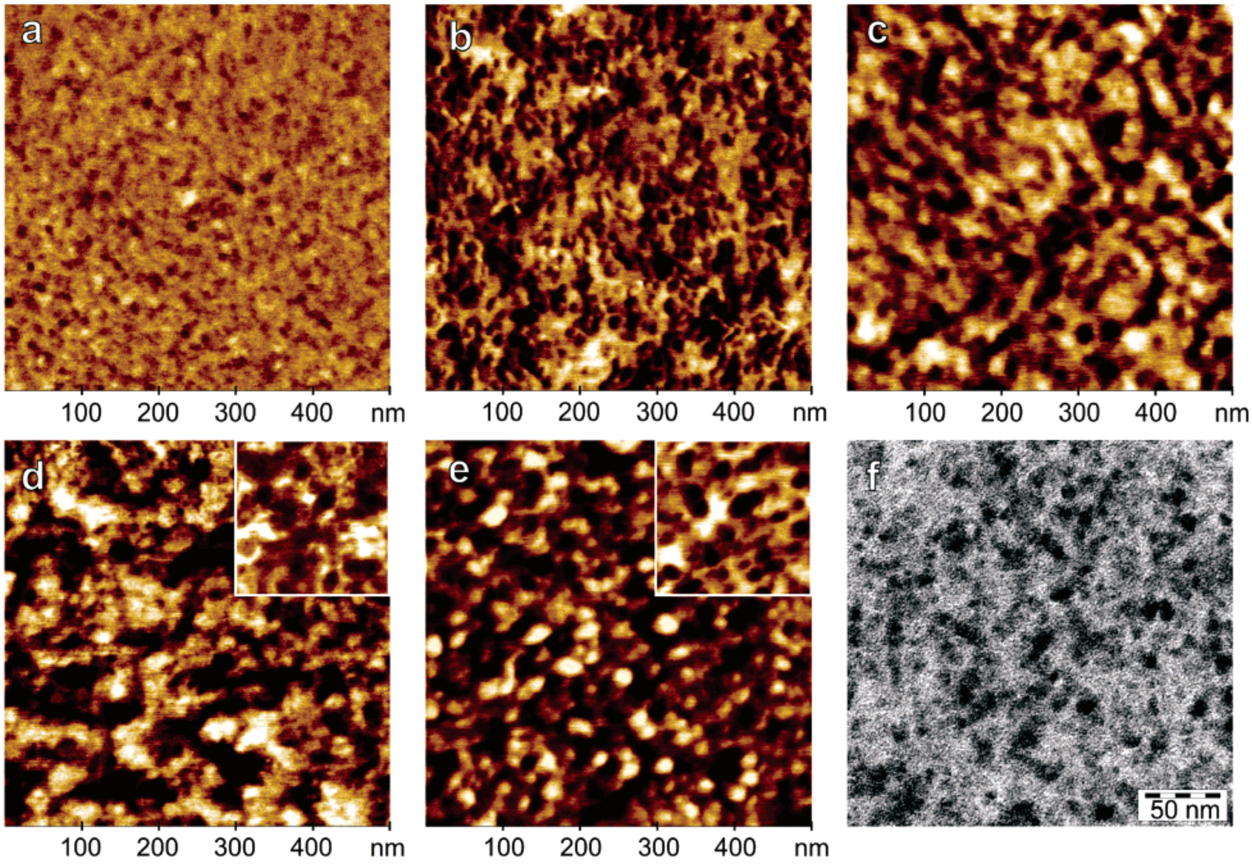


Figure 5. AFM phase mode images of cross sections of PHEA-*l*-PFPE$_{4.5}$ films with (a) 10, (b) 30, (c) 50, (d) 70, and (e) 90 wt % PFPE content. PHEA shows light and PFPE dark; the two inserts are color-inverted, so that there PFPE appears light. (f) TEM picture of PHEA-*l*-PFPE$_{4.5}$ conetwork with 70 wt % PFPE; the hydrophilic phase is stained with MnO_4 and appears dark.

obtained via the protecting group strategy with FDOEA. They give an insight into the bulk morphology development between 10 and 90 wt % PFPE content. In the images, the soft PFPE phases are dark gray or black, whereas the harder PHEA are lighter colored or bright. Domain sizes were determined by measuring the distance between points of intermediate color depth. For isolated and coalesced spherical domains, the size is given as the diameter of the spheres, whereas for spongelike domains, the size is referred to as the thickness of the walls formed by the phase. According to these images morphologies with distinct phase-separated domains in the nanometer regime are present at every composition and a macrophase separation is absent, which is in accordance with the transparency of the conetworks. Spherical PFPE phases with diameters between 10 and 15 nm are dispersed in the continuous PHEA matrix in the sample with the lowest PFPE content (Figure 5a). An increased PFPE content of 30 wt % results in some coalescence of the spherical PFPE domains, so that the PFPE phase becomes partly continuous. The PHEA matrix develops into distinct, interconnected PHEA domains (Figure 5b). These developments are more pronounced in the sample with 50 wt % PFPE (Figure 5c), where coalesced elongated PFPE domains with a “diameter” of 15 to 30 nm are embedded into a continuous PHEA “sponge” with domain thicknesses mainly between 30 and 70 nm. The AFM picture indicates that the PFPE domains have coalesced to such an extend, that the perfluorinated phase starts to become interconnected. At 70 wt % PFPE, a true cocontinuous morphology is observed, where roundish PFPE domains are interconnected by PFPE walls (Figure 5d). This phase interpenetrates the PHEA phase which is formed from spherical and oblong interconnected domains. Spherical areas of the PFPE phase are between 10 and 20 nm in diameter; however, the interconnectivity of the phase leads to larger overall domain sizes up to 170 nm. The diameter and thickness of PHEA domains dropped to values between 16 and 32 nm. At high PFPE content (90 wt %) isolated spherical PHEA phases exist next to elongated ones, which are still interconnected to some extent (Figure 5e). They are embedded into a continuous spongelike PFPE matrix with quite thick walls (12−65 nm). The diameter of the PHEA domains ranges between 7 and 20 nm with an average of 14 nm. The insets in Figure 5, parts d and e, are contrast inversion of an area of the respective AFM image. The one in Figure 5d resembles Figure 5d itself, which illustrates the cocontinuous morphology. The contrast inversion of Figure 5e shows that this morphology resembles an inverted morphology of the 30 wt % PFPE conetwork, insofar that the two phases are exchanged.

Transmission electron microscopy (TEM) measurements were performed on selected samples to obtain an alternative view of the conetwork’s bulk morphology. Figure 5f depicts the TEM image of a PHEA-*l*-PFPE$_{4.5}$ conetwork with 70 wt % PFPE, prepared with FDOEA as masked monomer. When treated with MnO_4, the polar PHEA phase was stained, while the PFPE domains remained unstained. This results in a good contrast of the two phases. A nanophase separated morphology can be seen with spherical, partly interconnected PHEA domains. It resembles the cocontinuous morphology observed with AFM; however the spherical PHEA domains appear to be significantly smaller. This is most likely due to the superimposing of several layers with unordered phase separation of small dimensions, which leads to smaller features in the TEM compared to the AFM.[41]

In conclusion, a composition dependent morphology development could be observed, with morphologies changing from

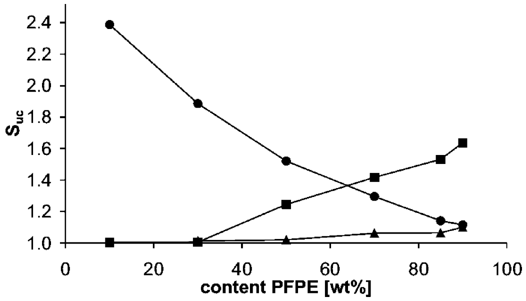


Figure 6. Equilibrium volumetric degree of swelling of PHEA-*l*-$PFPE_{4.5}$ conetworks vs PFPE content for a series of free-standing membranes in perfuorodecaline (■), in water (●), and in *n*-heptane (▲).The measurements were carried out in quadruplicate. The shown data are the mean values and have standard deviations in a range of 1.1 to 3.2%.

spherical to spherical/elongated to cocontinuous to elongated/spherical with increasing PFPE content. There are no sharp borderlines between the different morphologies and they are not symmetrically distributed over the composition range, which is the case for the morphologies of blockcopolymers.[45] An at least partial cocontinuity of the two phases is present for a wide composition range, which renders the materials ideal as phase transfer carriers for catalysts. Interestingly, the same compositionally asymmetrical morphology development has been reported for the well-known hydrophilic/hydrophobic poly(hydroxymethyl acrylate)-*l*-poly(isobutylene) conetworks.[41,46] This indicates that the morphologies found here represent intrinsic properties of amphiphilic conetworks based on a macromonomer cross-linker and an orthogonal monomer and are independent of the chemical nature of the monomers used, as it is the case for the well-established morphologies of blockcopolymers.

From an application point of view, it is desirable to have both polymer phases accessible, i.e., present at the surface of the conetworks. AFM investigations on the surface of the PHEA-*l*-$PFPE_{4.5}$ films revealed nanophase separated morphologies similar to those in the bulk of the conetworks.

The conetworks obtained from FDOEA were further characterized in respect to their swelling properties in perfluorodecaline, *n*-heptane, and water (Figure 6). At low PFPE contents up to 30 wt %, no swelling is observed for unconstrained free-standing membranes in the perfluorinated solvent. An increase in PFPE content results in an increase of the degree of swelling up to $S_{UC} = 1.61$ at 90 wt % PFPE. In water, much higher degrees of swelling are observed. They decrease with increasing PFPE content from $S_{UC} = 2.37$ at 10 wt % PFPE content to $S_{UC} = 1.10$ at 90 wt % PFPE. Only weak swelling in *n*-heptane is observed, and it increases slightly with increasing PFPE content.

The observed swelling behavior is prove of the hydrophilic−fluorophilic nature of the PHEA-*l*-$PFPE_{4.5}$ conetworks and shows that water and perfluorodecaline are selective solvents, which swell only the compatible phase. Higher degrees of swelling in water can be explained by the fact that, at great PHEA content, the volume fraction of swellable domains is high and that the cross-linking density is low. Another reason could be a difference in swelling power of the two solvents. The oelophobic property of the conetworks, i.e., the low swellability in heptane, indicates an only minimal presence of an unpolar hydrocarbon phase. One can assume that only the regions formed from the urethanmethacrylate end groups of the MA-PFPE-MA macromonomer swell in heptane. To sum up, the swelling data show that the synthesized PHEA-*l*-$PFPE_{4.5}$ conetworks can be considered as amphiphilic conetworks comprising a hydrophilic and a fluorophilic phase.

The question arises if these highly fluorinated materials can be loaded with enzymes, a crucial step for their application as phase transfer matrices for biocatalyis in unconventional media. To investigate this, a PHEA-*l*-$PFPE_{4.5}$ conetwork with a PFPE content of 50 wt % was immersed in 2 mL of a 0.825 g/mL solution of lipase from *C. antarctica* in acetate buffer (pH 4.0) overnight. The loading of lipase into the membrane was quantified by UV spectroscopy to be 299 mg/cm^3, i.e., this enzyme was concentrated in the conetwork by a factor of 360 compared to the loading solution. An explanation for this high loading might be that lipases are amphiphilic molecules that have high affinities toward hydrophilic/hydrophobic interfaces.[47] Apparently, the lipase has a similar affinity toward the interface between PHEA and PFPE domains.

Conclusions

In this work, we were able to synthesize macroscopically homogeneous amphiphilic conetworks that consist of a fluorophilic and an either hydrophobic or hydrophilic phase. Conetworks in a composition range between 10 and 90 wt % fluorophilic compound were easily accessible. Taking advantage of the temperature dependent mixing behavior of perfluorinated and aploar hydrocarbon liquids, fluorophilic/hydrophobic PHDFDA-*l*-$PDMS_{1.1}$ conetworks were obtained by heating of the monomer mixtures until they became homogeneous and subsequent polymerization at elevated temperatures. Hydrophilic/hydrophobic PHEA-*l*-PFPE conetworks were synthesized via fluorophilic precursor conetworks, where the hydrophilic PHEA chains were masked with an perfluoro tagged protecting group. Cleavage of the protecting groups rendered the networks amphiphilic. The conetworks have nanophase separated morphologies which depend on the networks composition, as revealed by AFM studies. They swell in orthogonal solvents, i.e., heptane and perfluorodecaline or water and perfluorodecaline, thus being true amphiphilic conetworks.

To our knowledge, this work is the first to describe simple, generally applicable synthesis routes toward amphiphilic conetworks comprising a fluorophilic phase. Especially highly fluorinated polymer conetworks that also swell in water have not been described previously. Preliminary results show that the PHEA-*l*-PFPE conetworks can easily be loaded with enzymes like lipase. The great affinity to enzymes makes the hydrophilic/fluorophilic conetworks interesting candidates as phase transfer matrices for biotransformations in nonaqueuos media, especially in perfluorinated solvents and supercritical fluids.

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