Nanophase Separated Amphiphilic Conetwork Coatings and Membranes

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ABSTRACT: Covalently surface-attached coatings and free-standing membranes of some 20 μm in thickness were prepared by photocopolymerization of a bitelechelic methacrylate-terminated poly(dimethylsiloxane) (PDMS) and silyl-protected 2-hydroxyethyl acrylate. After cleaving the silyl groups, the resulting amphiphilic conetworks exhibit two nanoseparated phases in bulk as well as on their surface as shown by atomic force microscopy (AFM). Thereby, the surface structure is controlled by the chemical nature of the surface covering material. Comparing the swelling behavior of 1D swelling of the coatings with the 3D swelling of the membranes revealed perfect interconnectivity of the hydrophilic phase in all compositions prior to and after water treatment. The hydrophobic PDMS phase, on the other hand, is not interconnected in dry state at compositions with less than 80 wt % PDMS. Diffusion experiments indicate that the PDMS phase reorganizes upon swelling and becomes continuous at PDMS contents of about 50 wt % and more.

Introduction

Amphiphilic polymer conetworks[1,2] represent a relatively new class of promising materials for applications such as contact lenses,[3,4] pervaporation membranes,[5] drug delivery systems,[6−18] biomedical scaffolds for tissue engineering,[19−23] and catalysts support.[24−26] They consist of hydrophilic and hydrophobic chain segments covalently bonded to each other. Because of the incompatibility of their chain segments, these polymers phase separate. However, the covalent cross-linking of the polymer chains prevents a macroscopic demixing, resulting in a phase separated morphology with domains in the nanoscale.[27−29] One of the key features of amphiphilic conetworks is their capability to swell in both aqueous and organic media without losing their dimensional stability and without encountering macroscopic phase separation or polymer leaching.[6,7] Assumingly, the two phases can be swollen, each with the respective solvent. In both swelling cases, the huge interface between the polymers is preserved. Such networks might have a great potential for heterogeneous catalysis and phase transfer reactions.[26]

Numerous amphiphilic conetworks have been described in the past decade, but only in recent works the nanophase separated bulk structure of such conetworks could be proven by AFM, TEM, SAXS, and SANS measurements.[27−29] It was shown that, depending on the composition, the nanophase separated polymer domains are interconnected. To date, very little is known concerning the surface of such materials. Morphology development in bulk and at surfaces during film formation was not investigated. Prime requirement for applications of amphiphilic conetworks, requiring transport in the two polymer phases, is the presence of both of these phases on the very surface. Unfortunately, because of thermodynamic reasons such as minimizing surface energy, one component enriches on the surface during the synthesis of the network. This was shown by Kennedy and co-workers, who have performed XPS surface studies on amphiphilic poly(2-hydroxyethyl methacrylate)-*l*-polyisobutylene (PHEMA-*l*-PIB) and poly(*N*,*N*-dimethylacrylamide)-*l*-PIB networks and found a strong enrichment of PIB compared to the bulk.[30] There is no experimental evidence reported that clearly proves the presence of both polymer phases on the surface of amphiphilic conetworks.

Here we describe the synthesis of amphiphilic conetworks on the basis of bitelechelic poly(dimethylsiloxane) macromonomers (PDMS) and 2-hydroxyethyl acrylate (HEA) as thin coatings and free-standing membranes that exhibit a nanophase separated morphology in their bulk as well as on their surface.

Experimental Section

Materials. Silanol terminated poly(dimethylsiloxane) was provided by Wacker (Munich, Germany). The photoinitiator Irgacure 651 (2,2-dimethoxy-1,2-diphenylethane-1-one) was kindly provided by Ciba (Basel, Switzerland). Chloromethacryloxypropyldimethylsilane and 2-(trimethylsilyloxy)ethyl acrylate (TMSOEA) were synthesized as described previously.[31] Adhesive poly(propylene)-tape (PP; Tesafilm, Tesapack 4024) was purchased from Tesa AG (Hamburg, Germany).

Synthesis of α,ω-Methacryloxypropylpoly(dimethylsiloxane) (MA-PDMS-MA). Silanol terminated PDMS (150 g, 50 mmol) and triethylamine (21.6 mL, 16.2 g, 160 mmol) were dissolved in toluene (300 mL). The solution was stirred vigorously and cooled to 0 °C, and chloromethacryloxypropyldimethylsilane (26.4 g, 120 mmol) dissolved was added dropwise in such a way that the temperature did not exceed 5 °C. After complete addition the mixture was stirred for 4 h at 0 °C, washed with 200 mL of 1 N $NaHCO_3$, and subsequently washed twice with 200 mL of water. The phases were separated, and then methanol was added to the organic phase until the product dissipated. It was separated, diluted with 150 mL of toluene, and washed twice with 50 mL of water. After drying over $NaSO_4$, toluene was removed in a vacuum.

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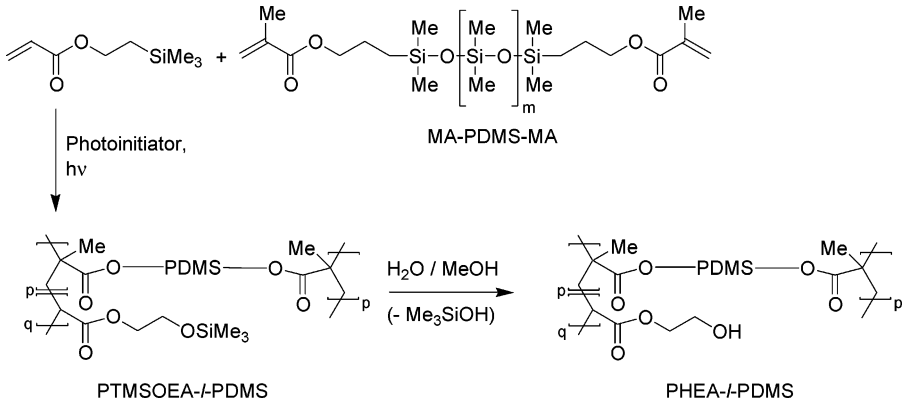
Table 1. Synthesis Parameters of the Preparation of PHEA-*l*-PDMS Amphiphilic Conetworks

PDMS content [wt %]	V_{TMSOEA} [μL]	m_{TMSOEA} [mg]	n_{TMSOEA} [μmol]	$m_{MA-PDMS-MA}$ [mg]	$n_{MA-PDMS-MA}$ [μmol]
90	8.4	7.7	41	43.0	8.26
80	16.1	14.8	79	36.6	7.03
70	23.2	21.3	113	30.7	5.90
60	29.7	27.3	145	25.3	4.86
50	35.7	32.8	174	20.2	3.89
40	41.3	38.0	202	15.6	3.00
23	49.9	45.9	244	8.4	1.62
10	55.8	51.3	273	3.5	0.68

Scheme 1. Synthesis of Amphiphilic PHEA-*l*-PDMS Conetworks via a Precursor Approach



^{1}H NMR (300 MHz, $CDCl_3$): $H_{a2}C{=}C(CH_{b3})COOCH_{c2}CH_{d2}$-$CH_{e2}Si(CH_{3f})_2OR$, δ [ppm] = 6.00 (s, $2H_a$ cis), 5.45 (s, $2H_a$ trans), 4.00 (t, $4H_c$), 1.85 (s, $6H_b$), 1.60 (dt, $4H_d$), 0.50 (m, $4H_e$), 0.00 (s, $n{\cdot}6H$). M_n = 5200 g/mol according to the integration of H_b and H_f.

^{29}Si NMR (59.6 MHz, $CDCl_3$): $-Si_aMe_2-O-Si_bMe_2-O-Si_c$-$Me_2-(CH_2)_3-$methacrylate 6.84 ($1Si_c$), −22.08 ($1Si_b$), −22.70 ($n{\cdot}Si_c$). The bifunctionality was determined to be 92%.

M_w/M_n = 1.3 as measured by gel permeation chromatography (GPC) in $CHCl_3$.

Conetwork Synthesis. Surface attached PHEA-*l*-PDMS films were synthesized according to the following procedure. Glass slides (7.6 × 1.5 cm^2) were immersed into Piranha solution (concentrated H_2SO_4/30% H_2O_2, 3:2, v:v) for 30 min, rinsed with water, air-dried, and given to a 20 vol % solution of 3-methacryloyltrimethoxysilane in toluene. After sonication at room temperature for 2 h, the slides were thoroughly rinsed with water and air-dried for at least 16 h.

A methacrylate-modified slide was covered with 60 μL of a monomer mixture containing TMSOEA, MA-PDMS-MA in variable ratios (cf. Table 1), and Irgacure 651 (0.3 mg, 1.2 μmol), and 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 720 s. After removing the top slide, 10 conetwork-coated slides were four times incubated in a methanol/water mixture (1:1 v/v, 90 mL) for up to 24 h in order to remove the protecting trimethylsilyl groups. Then these slides were rinsed with methanol and dried to constant weight under vacuum at 60 °C. Thicker films were prepared using PP-spacers of 50 μm thickness and 60 μL monomer mixture for each spacer.

PHEA-*l*-PDMS membranes were synthesized by placing 120 μL of the monomer mixture between an unmodified glass slide (2.6 × 7.6 cm^2) and an PP-tape-covered slide followed by subsequent polymerization (irradiation time: 720 s). After removing the PP-covered slide, the membrane was given in methanol/water (1:1 v/v, 3 × 24 h). Upon deprotection it floated on the liquid. The membranes were rinsed with methanol and transferred onto a filter paper. They were air-dried (3 h) and then dried in a vacuum (30 min, 60 °C, 10 mbar).

The sol fraction was determined by weighing a dried PHEA-*l*-PDMS (50 wt % PDMS) membrane before and after Soxhlet extraction with *n*-heptane (100 mL) for 16 h. The sol fraction was calculated as the ratio of the mass of the extracted polymer to the mass of the nonextracted sample.

The poly(2-hydroxyethyl methacrylate)-*l*-polyisobutylene (PHEMA-*l*-PIB) conetwork was synthesized by thermally initiated radical copolymerization of α,ω-dimethacrylate terminated polyisobutylene and trimethylsilyloxyethyl methacrylate followed by the removal of the protecting groups in the conetwork as described earlier.[7,27,29] The PIB content of the final conetwork was 69 wt %.

Methods. NMR spectra were obtained on a Bruker ARX 300 spectrometer. 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 with unpolarized light with a 4 cm^{-1} resolution and 20 scans. Bulk spectra were obtained from ground samples. The tapping-mode atomic force microscopy (AFM) was 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 the samples and on cryofractures of the films. Swelling experiments with PHEA-*l*-PDMS were performed on film surfaces and experiments with PHEMA-l-PIB on cryocut surfaces using a novel type of sample holder.[32] These tapping mode images were obtained in the MAC Mode using a pico SPM II (Molecular Imaging).

The swollen conetworks were examined while being immersed in water. Differential scanning calorimeter (DSC) thermographs of conetworks were recorded on a Perkin-Elmer DSC-7 from −150 to 150 °C under nitrogen at a heating rate of 20 °C/min in the second heating cycle. The mass of the samples was 4−16 mg.

Swelling Measurements. Swelling experiments were carried out by immersing a conetwork sample in large excess of distilled water or *n*-heptane at ambient temperature. One-dimensional swelling of films was determined by measuring the thickness of a film cross section with an Axioplan 2 imaging microscope (Zeiss, Jena, Germany) in dry and in swollen state until a constant thickness was achieved. The equilibrium volumetric degree of swelling S_{sa} equals the linear degree of swelling and was calculated from

$$S_{sa} = \frac{d_e}{d_0}$$

where d_e and d_0 are the sample thicknesses of the swollen and the dry films, respectively.

Three-dimensional, unconstrained swelling of membranes was determined by measuring the samples volume with a Binocular (Will Strüblin, Wetzlar, Germany). The equilibrium volumetric degree of swelling S_{uc} was calculated from

$$S_{uc} = \frac{V_e}{V_0}$$

V_e and V_0 are the volume of the swollen and the dry sample, respectively.

Diffusion Studies. Diffusion studies were carried out with Congo Red and picric acid in water and with Oil Red O in *n*-heptane at 25 °C. To this end a disk of 1.6 cm diameter was cut from a membrane. The disk was swollen in water and placed between two layers of solvent-resistant adhesive foil, leaving a round hole in the foil (diameter 1.1 cm) covered with the membrane. The foil sandwich was dried in a vacuum (60 °C, 10 mbar) and clamped between two compartments (each 200 mL in volume) of a thermostated glass transport cell. One compartment of the cell was filled with solvent and the other one with a solution of the dye (10 mmol/L). Each compartment was stirred continuously throughout the experiment. The acceptor compartment was sampled frequently and the concentration of the dye measured by UV/vis on a Lambda 11 spectrometer (Perkin-Elmer) (Congo Red: $\epsilon_{509\ nm} = 16\ 400\ M^{-1}\ cm^{-1}$; picric acid: $\epsilon_{358\ nm} = 14\ 500\ M^{-1}\ cm^{-1}$; Oil Red O: $\epsilon_{518\ nm} = 9770\ M^{-1}\ cm^{-1}$). The samples were placed back into the compartment afterward. The thickness of a membrane was measured with a light microscope. The permeability P was calculated from the linear slope of the concentration vs time plot using the following equation:

$$P = \frac{J}{A}\frac{d_m}{\Delta c_0}\ [cm^2/s]$$

where $J = \Delta c_{acceptor} V/\Delta t$ is the dye flux (mmol/cm^2 s), A is the membrane area (cm^2), d_m is the membrane thickness (cm), Δc_0 is the difference in dye concentration between the two compartments (mmol/L), V is the chamber volume (L), and $\Delta c_{acceptor}$ is the change in dye concentration in the acceptor compartment during a time period Δt (mmol/(L s)). Δc_0 was assumed to be constant throughout the experiment.

Results and Discussion

Synthesis and Characterization of Conetwork Coatings and Membranes. Amphiphilic poly(2-hydroxyethyl acrylate)-*l*-poly(dimethylsiloxane) (PHEA-*l*-PDMS) conetworks were prepared by a precursor approach[7,27,29] to circumvent monomer incompatibility, which would lead to macrophase separation of the monomers prior to polymerization. UV-initiated free radical copolymerization of the hydrophobic monomer α,ω-dimethacrylate-terminated poly(dimethylsiloxane) with the hydrophobic trimethylsilylated 2-hydroxyethyl acrylate yields a homogeneous hydrophobic precursor conetwork PTMSOEA-*l*-PDMS. This was subsequently rendered into an amphiphilic conetwork by removing the silyl groups, transforming the hydrophobic acrylate conetwork segments into the respective hydrophilic poly(2-hydroxyethyl acrylate) (PHEA) form (Scheme 1).

The PHEA-*l*-PDMS conetworks of compositions ranging between 10 and 90 wt % PDMS were synthesized as thin films, covalently attached to glass substrates with thicknesses between 15 and 35 μm as a function of the conetwork composition. (In general, a higher PDMS content leads to thicker films.) 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. Thicker films were obtained by introducing a spacer between the slides. After photoinduced polymerization, removal of the cover slide, and deprotection a transparent, thin coating with a smooth surface was obtained.

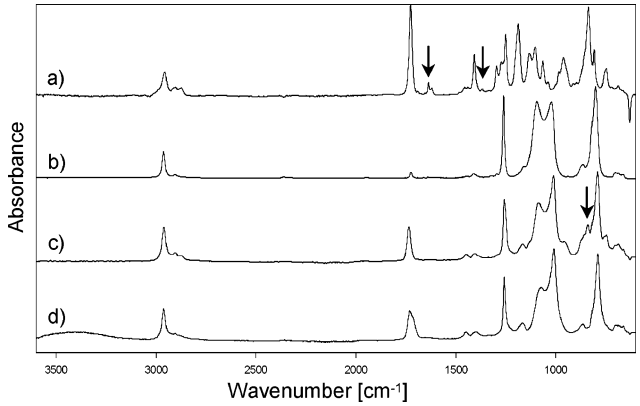


Figure 1. ATR−FTIR spectra: (a) TMSOEA, (b) MA-PDMS-MA, (c) precursor conetwork PTMSOEA-*l*-PDMS (50 wt % PDMS), (d) amphiphilic conetwork PHEA-*l*-PDMS (50 wt % PDMS). The arrows indicate selected peaks at 1637, 1368, and 837 cm^{-1}.

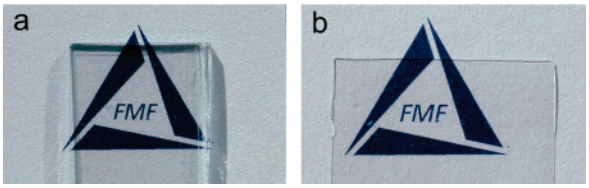


Figure 2. PHEA-*l*-PDMS conetwork: (a) surface-attached film on a glass slide, (b) membrane.

The conversion of the polymerization and the deprotection procedure were monitored by ATR-FTIR spectroscopy. A comparison of the ATR-FTIR spectra of the monomers, the precursor conetwork, and the corresponding PHEA-*l*-PDMS conetwork is displayed in Figure 1. These spectra indicate a complete monomer conversion during polymerization according to the disappearance of the typical double bond signals of TMSOEA at 1637 (C=C stretching), 1368, and 1336 cm^{-1} (Figure 1a). The spectra of TMSOEA and the precursor conetwork show a strong peak in the fingerprint region at 837 cm^{-1} which arises from the Si−C valence vibration of the TMS group (Figure 1a,c). This signal is not present in the PHEA-*l*-PDMS spectrum (Figure 1d) and thus can be taken as proof of a complete deprotection of the PTMSOEA segments. Similar results were obtained for all other synthesized amphiphilic conetworks (spectra not shown). The amount of the sol fraction extractable with *n*-heptane was determined to be 1.4 wt % for a conetwork consisting of 50 wt % PHEA. This low value indicates satisfactory monomer conversion and control over the conetwork structure during synthesis.

The conetworks show two distinct glass transition temperatures (e.g., for PHEA-*l*-PDMS (23 wt % PDMS): $T_g = -120$ °C and $T_g = -30$ °C) as revealed by DSC measurements. They can be related to the homopolymers [T_g(PDMS) = −127 °C,[33] T_g(PHEA) = −15 °C[34]]. This is typical for similar phase separated bicomponent polymeric systems.[6,7,29,35] However, the conetworks are optical transparent (Figure 2); thus, the domain size must be smaller than the wavelengths of light.

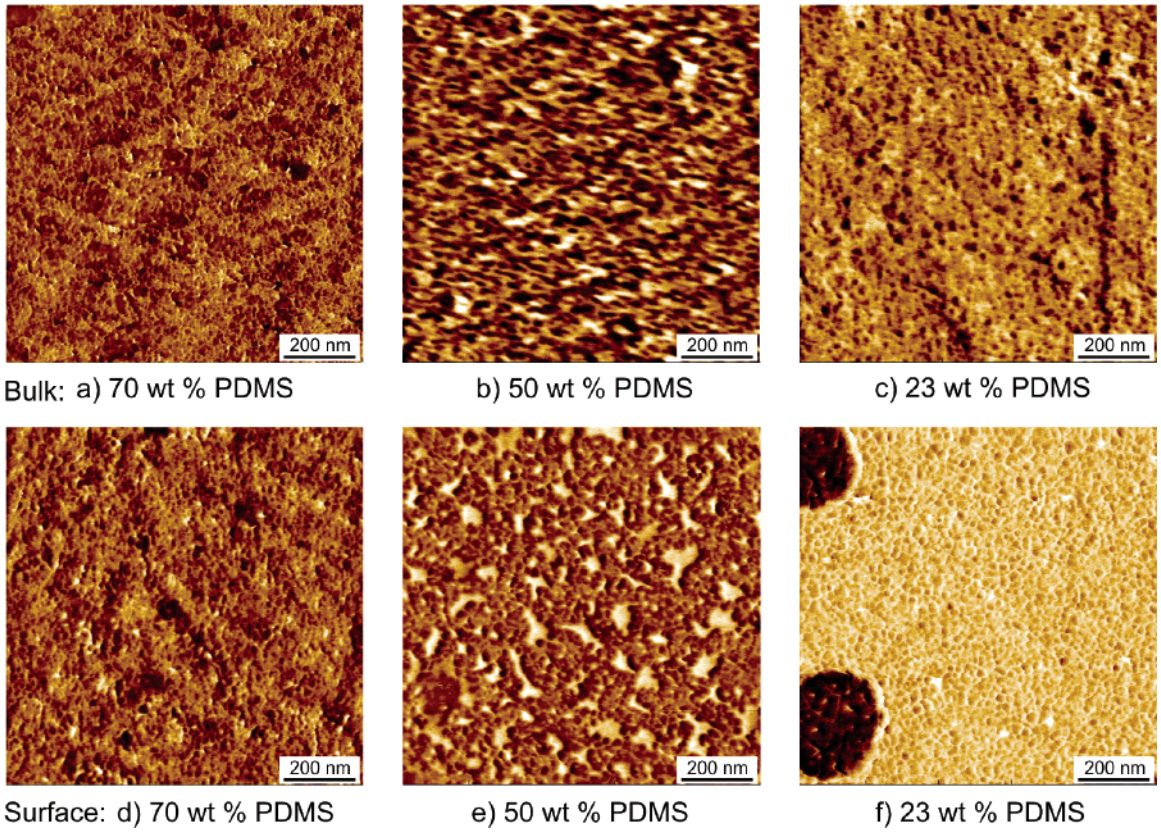


Figure 3. AFM phase mode images of PHEA-*l*-PDMS films with 70, 50, and 23 wt % PDMS content (contact surface during polymerization PP): (a, b, c) cross sections (= bulk morphology); (d, e, f) surfaces. PHEA shows light and PDMS dark.

The nanoscopic morphology was further investigated by phase mode AFM. As it was shown in previous work, the domain size data obtained by AFM is in accordance with data obtained by SAXS experiments.[27] In the images presented here, the hard PHEA phase appears brighter than the soft PDMS phase. The AFM measurements were performed on the surface of PHEA-*l*-PDMS films as well as on film cross sections created by fracturing of the films at −196 °C. Measurements from the cross sections were taken as representative information about the bulk morphology of the conetworks.

Figure 3 shows AFM images of PHEA-*l*-PDMS films containing 70, 50, and 23 wt % PDMS. All micrographs indicate nanophase separation of the two polymer components. In contrast to block copolymer morphologies, the phases show no long-range order; i.e., the domains are not arranged in a regular lattice. This is consistent with morphology data obtained for amphiphilic conetworks based on polyisobutylene.[27−29] The distorted structure results most likely from the random cross-linking in the conetworks. A tendency of the PDMS to form spherical domains is present in all compositions, whereas the PHEA forms interconnected, more oblong domains. The motive of all these morphologies can be depicted as a cocontinuous spongelike structure, where the PHEA forms the walls of the sponge, enclosing roundish PDMS domains.

As expected, the bulk of the conetworks shows a morphology typical for amphiphilic conetworks (Figure 3a−c). Regarding the sample containing 70 wt % PDMS, the poly(dimethylsiloxane) is a continuous matrix, nerved by thin, interconnected PHEA walls with a thickness between 2 and 4 nm. The PHEA domains become thicker with decreasing PDMS content, and the continuity of the PDMS phase gets disturbed. Samples with 50 wt % PDMS show a domain thickness of PHEA ranging between 10 and 25 nm. In the coatings with 23 wt % PDMS, the size of the hydrophilic phases is in the same range as the 50 wt % sample. The hydrophobic domains in 50 wt % PDMS conetworks are partially interconnected, whereas in samples with 23 wt % PDMS mostly isolated, spherical poly(dimethylsiloxane) domains exist next to interconnected ones. The average distance between the PHEA domains, i.e., the diameter of the PDMS domains, of all samples ranges from 6 to 25 nm.

For an application of the conetworks using the independent swelling of the polymer phases in suited solvents, it is crucial to have both phases present on the surface. This is a general problem in amphiphilic conetworks because usually one phase will be concentrated on the surface.[30] However, the AFM images of the surfaces of the photopolymerized PHEA-*l*-PDMS conetworks displayed in Figure 3d−f show both polymer phases, albeit the structure is not always the one of the respective bulk material. The surface morphology of the PHEA-*l*-PDMS conetwork with the highest PDMS content is the same as that of the bulk, but conetworks with lower PDMS content show distinct structural differences between surface and bulk.

The conetwork with 50 wt % PDMS contains regions on the surface that are similar to the features of a 70 wt % PDMS containing conetwork next to quite large domains of pure PHEA (20−80 nm). Conetworks with 23 wt % PDMS show mainly a spongelike surface morphology, rich in PHEA, with 2−7 nm thick PHEA walls and PDMS domains of 12−22 nm in diameter. Interestingly, large round PDMS-rich domains with a diameter of 200−350 nm are also present. These PDMS-rich regions, which are not present in the bulk, are

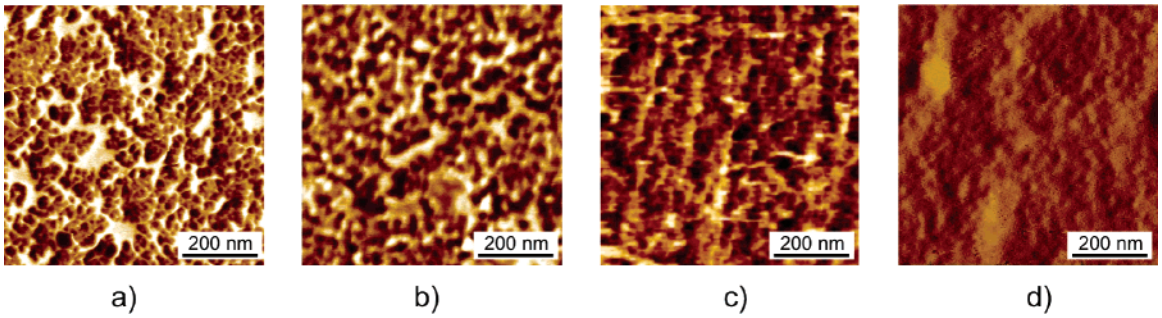


Figure 4. Influence of contact surface during polymerization on conetwork morphology: AFM-phase mode image of PHEA-*l*-PDMS conetwork surfaces (59 wt % PDMS) synthesized against (a) PP, (b) glass, (c) Teflon, and (d) argon atmosphere.

nerved by thin PHEA walls, similar to the morphology found for the conetworks containing 70 wt % PDMS. They might form because of the tendency of the most nonpolar monomer (MA-PDMS-MA) to accumulate at the surface in contact with the nonpolar PP-film during polymerization. Such a pronounced surface enrichment is not observed at higher overall PDMS content, possibly because the viscosity of the monomer mixture is higher with greater macromonomer content, leading to a faster gelation and less mobility of the PDMS chains.

It is well-known that polymer blends and mixtures selectively separate on surfaces depending on the chemical nature of the material in contact with that surface. To investigate this effect on the PHEA-*l*-PDMS conetworks, additionally to PP used so far, glass, PTFE, and an argon atmosphere were applied as cover materials. Figure 4 shows AFM images of the respective samples. The conetwork synthesized in contact with a (polar) glass surface instead of the typically used PP surface has a morphology similar to the one found for the PP cover, but the PHEA domains at the resulting surface are slightly thicker; i.e., the PHEA content is greater at the surface by applying a glass cover. Polymerization against a Teflon surface yields morphologies that are related to the ones obtained against PP. However, rough surfaces were obtained because of the Teflon's roughness, distorting the phase mode AFM images. Polymerization in argon without a counter surface lead to films with no nanophase separation on their surface. ATR-FTIR measurements of the latter sample revealed that the surface is covered mainly with PDMS.

The photoinitiated polymerization of the conetworks was chosen to avoid large scale phase separation of the forming chain segments by a fast cross-linking reaction. As shown above, this concept was successful for coatings with some 20 μm in thickness. However, thicker samples might tend to large scale phase separation on the surface because the polymerization rate will be slower there, leaving the PDMS more time to migrate to the surface. To investigate the surface morphology dependence on the coating thickness, PHEA-*l*-PDMS samples (50 wt % PDMS) of 52, 82, 190, and 660 μm were prepared, and their surface was investigated by AFM. Figure 5a shows the AFM image of a sample 52 μm in thickness. Surprisingly, it does not show large domains of PHEA as it is the case for the 20 μm thick coating (see Figure 3e) but exhibits similarity to the morphology found for 20 μm thick PHEA-*l*-PDMS films with 70 wt % PDMS, a conetwork with a higher PDMS content. Increasing the thickness up to 190 μm does not change the surface morphology (data not shown). Further enhancing of the thickness (660 μm thick sample)

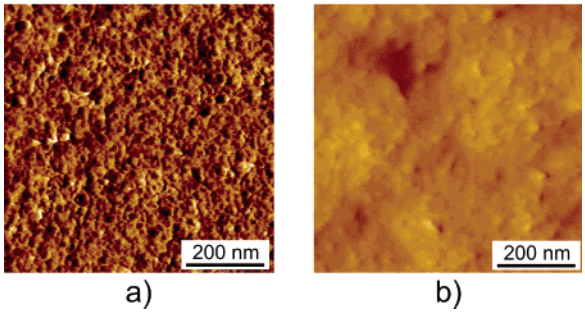


Figure 5. AFM phase mode images of PHEA-*l*-PDMS conetwork surfaces (50 wt % PDMS, contact surface during polymerization PP): (a) 52 μm thick, (b) 660 μm thick.

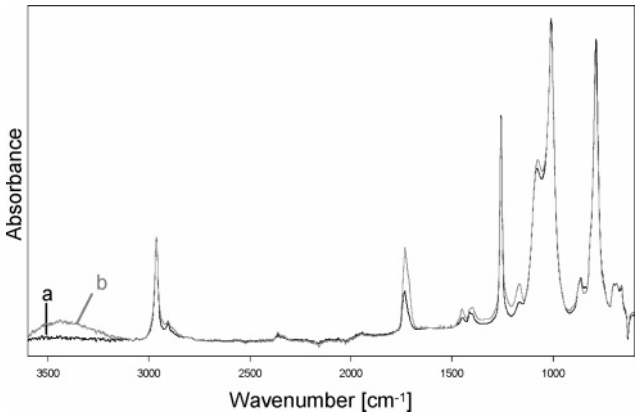


Figure 6. ATR-FTIR spectra of 660 μm thick PHEA-*l*-PDMS conetwork (50 wt % PDMS): (a) surface; (b) bulk. The spectra were normalized to the peak at 2960 cm^{-1}.

resulted in samples that show no nanophase morphology on the surface (Figure 5b). This indicates that a macroscopic phase separation has taken place, leading to an enrichment of one component at the surface of the conetworks. Without a phase contrast it is not possible to determine from the AFM image which of the two components is solely present. ATR-FTIR is a surface-sensitive method that measures the IR spectra of the first approximately 500 nm of a sample. The spectra of the surface of the 660 μm thick sample shows distinctive differences from the spectra of the same sample which has been previously ground (Figure 6). Most prominently, the OH valence band at 3600−3200 cm^{-1}, which is related to the alcohol groups of the PHEA segments, is not present in the spectra of the samples surface. The carboxyl peak at 1730 cm^{-1}, which arises mostly from the carboxyl bond of the PHEA segments, is weaker, whereas the signal arising from the PDMS segments at 790 cm^{-1} (Si−C valence) is more intense. Thus,

macroscopic phase separation has taken place at the surface, completely covering it with PDMS.

The phenomenon of surface demixing is widely known throughout the literature for all kinds of bicomponent polymeric systems and is generally suppressed if the polymer films are very thin, e.g., up to several hundreds of nanometers. However, in a somewhat intermediate thickness range of several micrometers this is not achieved easily. The results of surface characterization of poyisobutylene-based amphiphilic conetworks show a strong enrichment of the hydrophobic component at the surface of samples with a thickness of 2 mm.[30] However, these conetworks were synthesized by thermally initiated free radical polymerization, a rather slow reaction compared to the fast UV curing used to synthesize the PHEA-*l*-PDMS conetworks. The dependence of the surface morphologies on the sample thickness can most probably be accounted for by the rate of the polymerization, and therefore the time until gelation takes place. Assumingly, the homogeneous monomer solution is "frozen" in its liquid morphology at high polymerization rates, whereas thermodynamically favorable surface demixing, even for the two hydrophobic polymer segments of the nascent precursor conetwork, is favored by slower polymerization. In thinner samples the amount of energy per volume is higher than in thicker samples, leading to a faster polymerization and less polymer demixing during this process. This may explain the observed marginal PDMS enrichment for samples with thickness of 52−190 μm and the macroscopic enrichment for the thickest sample.

Free-standing membranes were obtained by replacing the methacrylate-modified slide during conetwork synthesis with an unmodified glass slide. The thickness of the membranes was 36−54 μm. AFM investigations on the two surfaces of PHEA-*l*-PDMS membranes (50 wt % PDMS) revealed the same morphologies and domain sizes found for the corresponding surface-attached films created against a PP and against a glass cover. It can be concluded that the surface morphology is independent of both the covalent attachment and of the swelling mode in the deprotection step, i.e., one-dimensional swelling for surface-attached films and three-dimensional for the free-standing membranes.

Swelling Behavior of PHEA-*l*-PDMS Conetwork Membranes and Coatings. The swelling properties of amphiphilic conetworks in different solvents are crucial characteristics of these materials. Chemically attaching a conetwork to a surface confines the volume change to one dimension, normal to the surface. Therefore, the swelling behavior will be altered.[36,37] The volumetric equilibrium degree of swelling was measured for surface attached PHEA-*l*-PDMS films and for free-standing membranes in water and *n*-heptane (Figure 7a). As expected, the swellability in heptane increases and the swellability in water decreases with greater PDMS content. The comparison of the volumetric degree of swelling of surface-attached conetworks and unconstrained conetworks shows that the nonattached conetworks swell to a much higher degree than the surface-bond ones. This observation is consistent with the common notion that a reduction of the degree of freedom for swelling decreases the overall volumetric change of a gel. From simple geometric considerations, it could be expected that the volumetric degree of swelling of a surface-attached conetwork will be the cube root of the unconstrained conetwork ($S_{sa} = S_{uc}^{1/3}$). However, the

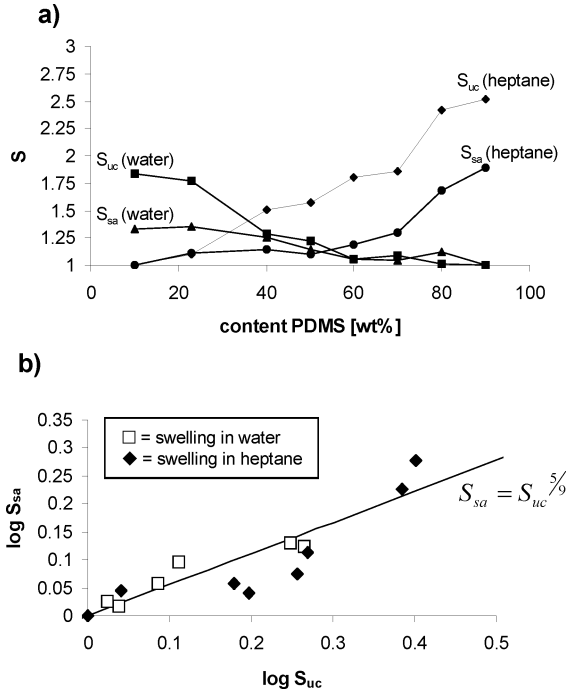


Figure 7. (a) Equilibrium volumetric degree of swelling of surface-attached films (S_{sa}) and of free-standing membranes (S_{uc}) vs PDMS content. (b) A log−log plot showing the relationship between the volumetric swelling degree S for surface-attached and free-standing conetworks.

observed swelling of the constrained conetworks is higher that predicted by this equation. Recently, it has been shown for thin homopolymer hydrogel films that the volumetric swelling degree of surface-attached films equals the volumetric swelling degree of the unconstrained polymer to the power of $^5/_9$, in compliance with the Flory−Rehner theory.[37]

Figure 7b displays the swelling of the attached coatings vs that of the free-standing membranes for conetworks of varying PDMS content. The swelling in water confirms the results of recently described homogeneous cross-linked networks that exhibited swelling according to the Flory−Rehner theory, indicating that the hydrophilic phase of the PHEA-*l*-PDMS conetworks acts like a homogeneous networks. In contrast, the PDMS phase swollen in *n*-heptane does not seem to follow the theory of a homogeneous network. It is clearly seen in Figure 7b that the swelling of the attached coatings in heptane dramatically increases with greater PDMS content compared to similarly composed free-standing membranes.

To explain the effect, two facts that distinguish the PDMS phase from a homogeneous network must be considered: First, the molecular weight between two cross-linking points is constant in all compositions and in the unusually swelling samples greater than that of PHEA; i.e., the swelling of PDMS will be restricted by the PHEA phase. (Note that M_c was calculated from the ratio monomer/cross-linking double bonds as suggested by Kennedy.[38]) Second, the phases are not completely interconnected. Isolated PDMS phases can hardly swell due to the great resistance of the surrounding nonswollen PHEA phase against dimension expansion. Taking these differences into account, the swelling in heptane of the free-standing membranes, particularly the one with isolated phases, i.e., with low PDMS content, will happen in two steps. The isolated PDMS phases swell

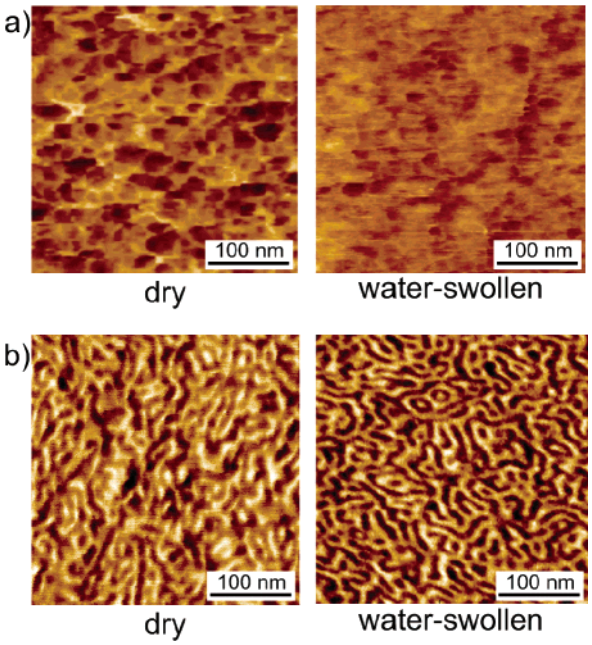


Figure 8. Phase mode AFM images: (a) PHEA-*l*-PDMS conetwork surface (50 wt % PDMS, M_n(PDMS) = 1100 g/mol) in dry state and swollen in water. (b) PHEMA-*l*-PIB bulk (69 wt % PIB) in dry state and swollen in water. PHEA and PHEMA show light and PDMS and PIB dark.

in heptane, stretching the surrounding nonswollen PHEA. The thinned phases result in a greater interconnectivity, which affords an overall increased swelling. A different situation is given for the surface-attached conetworks. Here, the swelling of the PDMS phases in the *Z*-direction leads to PHEA thinning perpendicular to the swelling. This results in greater interconnectivity only in the *X*,*Y*-direction. Since the conetworks cannot swell along these axes, the greater interconnectivity does not effect the overall swelling of the conetwork. This might explain the deviation of the swelling behavior of the conetworks with low PDMS content from the Flory−Rehner theory with regard to their 1D and unconstrained 3D swelling in heptane. With increasing PDMS content, the hydrophobic phase gets more interconnected and the plot S_{sa} vs S_{uc} follows more and more the theory.

The common notion that amphiphilic conetworks swell in both water and organic media raises the question, what kind of morphology changes are induced by the swelling? To investigate this, phase mode AFM of the swollen conetworks were carried out in water. A practical problem of this technique is the decrease in phase contrast upon swelling of the conetwork; i.e., the hard hydrophilic phase becomes softer in its water swollen sate. A surface-attached PHEA-*l*-PDMS conetwork was measured under water using phase contrast mode. Figure 8a shows the comparison of a dried and a swollen sample revealing that the overall structure of the conetwork in the *x* and *y* direction is not changed upon swelling.

Similar investigations were performed with a structurally similar conetwork composed of different polymers, a poly(2-hydroxyethyl methacrylate)-l-polyisobutylene (PHEMA-*l*-PIB) conetwork with 69 wt % PIB.[7,27,29,38,39] Figure 8b shows phase mode AFM images of the conetworks bulk before and after equilibrium swelling. The cocontinuous morphology is preserved during the swelling as it was the case for the PHEA-*l*-PDMS conetwork. Only the hydrophilic PHEMA domains swell by a factor of 1.5−2, whereas the dimensions of the PIB domains remain constant.

Table 2. Permeability of Amphiphilic PHEA-*l*-PDMS Membranes

PDMS content [wt %]	permeability [10^{-8} cm^2/s] Congo Red in water	picric acid in water	Oil Red O in *n*-heptane
70	<0.002	2.13 ± 0.11	80.6 ± 3.4
50	0.22 ± 0.02	7.8 ± 0.6	42.2 ± 1.3
23	4.4 ± 0.5	95 ± 5	<0.1

Permeability of PHEA-*l*-PDMS Conetwork Membranes. Free-standing polymer films can be considered as membranes if they are permeable to solutes. Because of their swelling properties, amphiphilic conetwork membranes should be permeable for nonpolar substances in organic media and polar molecules in water. Amphiphilic conetworks have been used as insulin delivering membranes[13,15−18,40] and pervaporation membranes.[5] However, these studies focused on transmembrane diffusion in water, and the permeabilities in organic solvents were not investigated. For catalyst carrier applications this property is as important as the permeability in water. PHEA-*l*-PDMS membranes with PDMS contents of 70, 50, and 23 wt % were subjected to permeability experiments with different dyes (Congo Red and picric acid in water and with Oil Red O in *n*-heptane). The flux *J* through a membrane is defined as

$$J = -P\left(\frac{dc}{dx}\right)$$

By measuring the initial linear increase in dye concentration in the accepting solution, permeability *P* was calculated as described in the experimental part. The permeabilities of the two water-soluble dyes show a dependency on the conetworks composition and on the type of the dye. They increase with increasing hydrophilic content of the conetwork. However, this is not a linear relationship, so that the ease of penetration is also most likely related to the morphology of the conetworks.

As seen in the AFM images (see Figure 3), the hydrophilic PHEA phase appears to be continuous in all cases. However, at a low PHEA content of 30 wt % it cannot be judged unambiguously from the AFM experiments if the PHEA domains are interconnected throughout the sample. The thickness of its domains increases rapidly with increasing PHEA content; i.e., wider channels for transmembrane diffusion are present.

Congo Red (M = 696.7 g/mol) does not permeate through the membrane with 30 wt % PHEA, indicating that the swollen hydrophilic phase does not provide channels big enough for the dye to pass through. Picric acid, however, diffuses through all of the membranes. The difference might be explained by the fact that picric acid is of smaller size (M = 229.1 g/mol). In addition, picric acid diffuses faster through the membranes than Congo Red, which also confirms that the size plays a role in the permeability.

In the case of heptane as solvent, the dye Oil Red O (M = 408.5 g/mol) diffuses readily through membranes with 50 and 70 wt % PDMS, indicating the presence of a continuous swollen PDMS phase. Membranes with a lower PDMS content of 23 wt % did not allow the diffusion through of Oil Red in heptane as far as

detectable with the experimental setup. This indicates that the spherical PDMS domains found with AFM (see Figure 3f) at this composition of the membrane might not be interconnected upon swelling but remain dispersed in the PHEA matrix or the interconnection points form too small channels for the dye to diffuse through.

Concluding, only PHEA-*l*-PDMS conetworks with a composition of 50 wt % PDMS are permeable to solutes in water and in organic solvent, indicating a true cocontinuous morphology in the swollen state.

Conclusions

It was demonstrated that the preparation of amphiphilic conetworks based on PHEA cross-linked with MA-PDMS-MA via photoinitiated polymerization results in nanophase separated coatings and membranes that show both polymer phases on their surface. Swelling experiments revealed that the PHEA phase features properties of a continuous network in all compositions. The PDMS phase swelling in *n*-heptane, on the other hand, deviates from the Flory−Rehner theory in compositions with less than 80 wt % in the whole conetwork. This is probably due to a lower degree of interconnectivity of the phase. AFM investigations of the surfaces of swollen amphiphilic conetworks indicate that swelling do not deteriorate the cocontinuous morphology. This finding is important for many application possibilities. It was found by permeability investigations that the free-standing membranes are permeable to solutes in both water and heptane. Altogether, because of the accessibility to solutes of both phases, the here presented PHEA-*l*-PDMS conetwork coatings and membranes are promising materials as matrix for a large variety of phase transfer reactions.

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