Polymer Networks with Lamellar Structure

Wolfgang Meier

Institut für Physikalische Chemie, Departement Chemie, Universität Basel,
Klingelbergstrasse 80, CH-4056 Basel, Switzerland

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ABSTRACT: The lamellar liquid crystalline phase of a pentaethylene glycol monododecyl ether ($C_{12}E_5$)/decane/water system is used as a matrix to create amphiphilic polymer network structures from α,ω-hydrophobically modified poly(oxyethylenes) bearing polymerizable end groups and hydrophobic comonomers. The polymer networks preserve the characteristic layer structure and the orientation of the liquid crystalline phase even after extraction of the templating matrix. This allows the preparation of highly anisotropic polymer gels from magnetic field aligned liquid crystalline phases. The changes of the macroscopic dimensions and the layer spacings of the polymer network structure upon swelling these systems in a selective solvent, like water, are strongly
of the bridging poly(oxyethylene) chains on the equil

Introduction

One characteristic feature of microemulsions and lyotropic liquid crystalline phases is their compartmentalized structure of nanometer-sized hydrophilic and hydrophobic domains. From a polymer chemist's point of view it is tempting to imprint their characteristic structural features on polymeric materials.[1−4] This has been used to synthesize ultrafine hydrophilic and hydrophobic polymer lattices[5−11] or mesoporous solids[12−15] from the droplet phase or bicontinuous structures of microemulsions, respectively. Recently, it has been demonstrated that microemulsions and liquid crystalline phases can also be used as a matrix for the production of amphiphilic polymer networks.[16−18]

Amphiphilic elastomers can be prepared by cross-linking end-group functionalized triblock copolymers in the respective phase structure of the underlying complex solvent.[16−18] It has been shown that the individual parts of polymers consisting of water- and oil-soluble segments can be selectively dissolved in the corresponding domains of the microemulsion or liquid crystalline phase.[19] The polymers may bridge different domains of the same type, thus leading to transient polymer network structures.[20−28] The formation of chemical bonds between reactive chain ends of different triblock copolymer molecules can be achieved because of their rather high local concentration within the interior of the domains.[16−18]

For example, in ternary mixtures of pentaethylene glycol monododecyl ether ($C_{12}E_5$)/decane/water, which form a low-temperature L_1-droplet phase and at higher temperatures a lamellar L_α-phase,[29] an α,ω-hydrophobically end-capped poly(oxyethylene) carrying additional polymerizable methacrylate groups at each chain end has been used as a bridging polymer.[17] The decane of the oil domains can be successively replaced by lipophilic comonomers for the reactive chain ends. Then, subsequent free radical polymerization may lead to hydrophobic nanogels in the interior of the hydrophobic domains which serve as cross-links for the system spanning the polymer network (see Figure 1). The network structure and the phase behavior of the underlying complex solvent, however, mutually influence each other.[17]

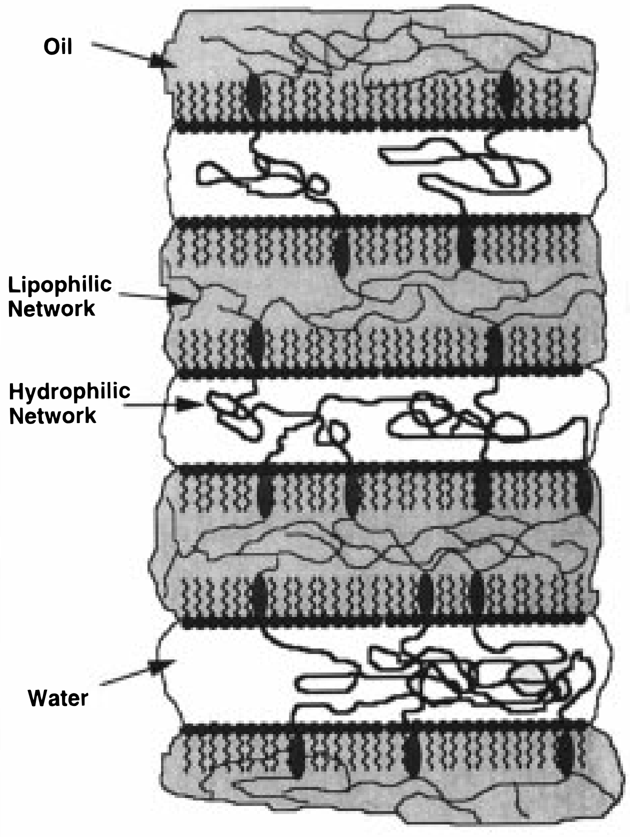

Figure 1. Schematic representation of an amphiphilic polymer network (formed by an α,ω-hydrophobically modified poly(oxyethylene) bearing polymerizable end groups and hydrophobic comonomers) cross-linked in the L_α-phase.

Depending on the phase structure of the matrix (L_1- or L_α-phase), the resulting polymer networks consist of spherical hydrophobic domains in a hydrophilic matrix or alternating hydrophilic and hydrophobic layers which stabilize the corresponding phase structure of their matrix. Interestingly, the phase behavior of a gel cross-linked in the lamellar phase has been shown to be completely different from that of gels cross-linked in the L_1-droplet phase, although both may have the same composition. Gels cross-linked in the lamellar phase exhibit only a lamellar liquid crystalline phase over a

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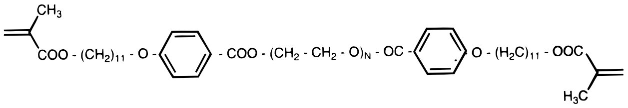
Chart 1. Structure of the End-Group Functionalized Polymer 1 ($N = 230, 270, 400, 450, 800$, Respectively)



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broad temperature region. It is obvious that the lamellar structure of such polymer networks does not fit any more into the nanodroplet structure of a L_1-phase and consequently prevents the formation of this phase.[17]

Due to the covalently cross-linked network structure the elastomers preserve the characteristic features of the underlying matrix even after extraction of the components not covalently attached to the polymer network (e.g. water, oil, surfactant, etc.). That means, an elastomer cross-linked in the lamellar phase still consists of alternating hydrophilic and hydrophobic layers. If the liquid crystalline phase is macroscopically uniform ordered (e.g. by applying strong magnetic fields or mechanical shear), the resulting polymer network exhibits anisotropic physical properties.[30]

In this paper we describe the preparation of uniformly aligned lamellar elastomers. The physical anisotropy of these systems is proved by swelling experiments in a selective solvent (i.e. water), swelling only the hydrophilic layers of the system. Using small-angle X-ray scattering (SAXS), the changes in the microscopic layer spacings upon swelling can be compared with those obtained from macroscopic sample dimensions. The influence of the molecular weight of the bridging polymer chains, i.e. the functionalized α,ω-hydrophobically end-capped poly(oxyethylene), on the swelling behavior of the resulting lamellar gels is investigated.

Experimental Section

Materials. Pentaethylene glycol monododecyl ether ($C_{12}E_5$) and decane were obtained from Fluka (purity $\geq$ 99%) and used without further purification. Water was doubly distilled.

The functionalized α,ω-hydrophobically modified poly(oxyethylenes) (**1**; see Chart 1) were prepared from poly(oxyethylene) with molecular weights ranging from 10 000 to 35 000 (always $M_w/M_n \leq 1.1$, using GPC) and 4-(11-methacryloylundecyl)oxybenzoyl chloride following the procedure of ref 16. The degree of conversion was always found to be larger than 98% by ^{1}H NMR, so that the fraction of polymer molecules bearing only one hydrophobic end group can be neglected in our considerations. The acid chloride was prepared starting from 11-bromoundecanol and 4-(hydroxymethyl)benzoate[31] and subsequent azeotropic esterification of the resulting 4-(11-hydroxyundecyl)oxybenzoic acid with methacrylic acid.[32] Reaction with $SOCl_2$ led then to the corresponding acid chloride.

The *lyotropic liquid crytalline matrix* was prepared by mixing weighed amounts of the individual components. The weight fraction of surfactant and oil is given by $c_o = (m_s + m_o)/(m_s + m_o + m_w)$, with m_i the mass fraction of surfactant ($i = s$), water ($i = w$), and oil ($i = o$), and was held constant at $c_o = 0.2$ throughout the experiments. Replacing the decane of the droplets by the mixture of the hydrophobic monomers (see below) did not alter structural parameters or the phase behavior of the system.

The weight fraction of the functionalized α,ω-hydrophobically modified poly(oxyethylenes) used in these experiments was $c_p = 0.038$ and has been the same for all samples. If not stated otherwise, the samples were prepared with the polymer with the molecular weight of 35 000 of the poly(oxyethylene) block.

Lamellar Elastomers. The preparation followed the procedure described in refs 16 and 17. For the creation of a hydrophobic subnetwork in the interior of the oil layers, the decane of the oil phase was partly replaced by a monomer mixture consisting of 5 wt % octanyl dimethacrylate and 95 wt % dodecyl methacrylate, keeping the total amount of the oil components constant. For the systems under investigation, always 20 wt % of the decane was replaced by the hydrophobic comonomers.

Measurements. Determination of the phase diagrams required thermostating of the samples in a water bath to within 0.02 K. Phase boundary temperatures were determined by visual inspection in transmitted light, in scattered light, and between crossed polarizers. The kinetics of phase separation and the reverse process, solubilization, was very slow (on the order of several days) in the covalently cross-linked samples.

Swelling experiments were performed with cylindrical samples of about 10 mm height and 2 mm diameter. The samples were allowed to swell in excess water until the swelling equilibrium was reached.

Freeze-Fracture Replication Transmission Electron Microscopy. A small piece ($\approx$10 μL) of the sample was brought onto a gold platelet at room temperature and was quenched by hand plunging into a mixture of 15% 2-methylbutane and 85% propane at 83 K. After quenching the sample was transferred into liquid nitrogen and clamped on a brass block (Balzer). It was mounted on a Balzer freeze etch device (BAF300), and subsequently the pressure was reduced to 5×10^{-7} mbar. After evacuation the sample was fractured with a liquid nitrogen cooled microtome. To enhance the contrast of the surface structure, the sample was warmed to 153 K and etched for 10 min. Thereafter the sample was cooled again with liquid nitrogen and shadowed with W/Ta under an angle of 30°. After the samples were warmed to room temperature and brought to atmospheric pressure, the replica was washed with chloroform, put on a 400 mesh copper TEM grid, and examined with a Hitachi H-8000 electron microscope operating at 100kV.

Small-Angle X-ray Scattering (SAXS). Small pieces of the dry or swollen samples were examined in a Kratky compact small-angle system which was equipped with a position sensitive detector. Ni-filtered Cu Kα radiation of a wavelength of 0.154 nm was used. The distance between the sample and the detector was 260 mm.

Results and Discussion

Free radical polymerization of the end-group functionalized polymers **1** in the comonomers containing the lamellar liquid crystalline phase of a $C_{12}E_5$/decane/water mixture leads to the formation of covalently cross-linked transparent polymer gels.[17] Figure 2 shows a freeze fracture electron micrograph of a covalently cross-linked lamellar gel. The figure demonstrates that the structure of the lyotropic liquid crystalline phase is preserved despite the cross-linking reaction. The interlayer distance can be directly measured from the micrograph, yielding values ranging from 15 to 33 nm. This is in good agreement with small-angle X-ray scattering measurements which find 24 nm (see below). The rather large fluctuations in the interlayer spacings and the thickness of the respective layers probably reflect the undulations of the flexible, oil-swollen surfactant bilayers.[33]

Without external fields the lamellar phase adopts a polydomain structure, consisting of small uniformly oriented lamellar domains randomly distributed in space, similar to a polycrystalline material. Consequently, the system is macroscopically isotropic. Due to the fluid character of the system the lamellar liquid crystalline phase can, however, be macroscopically uniform ordered prior to polymerization, leading to a structure comparable to a single crystal. This can be achieved by applying strong magnetic fields, by electric

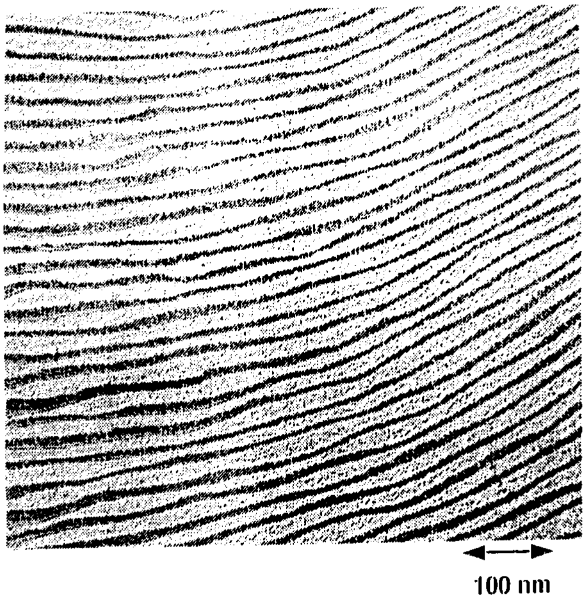

Figure 2. Micrograph of a freeze-fracture replica of an covalently cross-linked amphiphilic polymer network in the L_α-phase.

fields, or by mechanically shearing the samples.[34] In our system the oriented samples were obtained by slowly heating (at a heat rate of 0.1 K/min) from the L_1-droplet phase into the lamellar L_α-phase in a strong magnetic field (of 2 T) before initiating the polymerization.

Preliminary investigations on these systems determined that also highly uniform orientations could be obtained upon mechanically shearing the fluid samples. Due to difficulties in controlling the shear rate in our experimental setup, however, only data concerning magnetic field aligned samples are reported in this paper.

Information about the degree of orientation in the covalently cross-linked samples can be obtained using small-angle X-ray diffraction. With the X-ray beam parallel to the original direction of the aligning magnetic field, characteristic diffraction patterns were found. A typical example is shown in Figure 3. The pattern contains only two equatorial reflections reflecting the one-dimensional order in a macroscopically uniform aligned lamellar structure. The Bragg maxima on the equator represent an interlayer spacing of 24 nm. No discrete reflections were obtained when the beam was perpendicular to the original aligning field. This is consistent with an orientation of the layer normals perpendicular to the magnetic field. Additionally, the absence of arcing in the reflections reveals a nearly perfect macroscopic alignment of the lamellae.

Subsequent extraction of the polymer gels with methanol and dichloromethane allows the soluble components, i.e. surfactant, water, oil, and unreacted monomers and polymers, to be removed. The weight of the dried residue was always in good agreement with a complete conversion during polymerization, i.e. was always above 95 wt % of the weighed-in amounts of polymers and monomers. Due to the covalently cross-linked structure of these elastomers the characteristic features, like the layer structure and the orientation, of the underlying matrix should be preserved.

Reswelling the polymer networks with a selective solvent like water (being a good solvent for the poly(oxyethylene) chains and a nonsolvent for the poly(alkyl methacrylate) layers) leads to anisotropic polymer gels with interesting physical properties.[35,36] For such systems there has, for example, been shown to exist an asymmetric elastic response to compression and stretching parallel to the layer normal. While compression in these gels is mainly determined by the osmotic pressure, the restoring force associated with stretching is dominated by the elasticity of the polymer chains.[35,36]

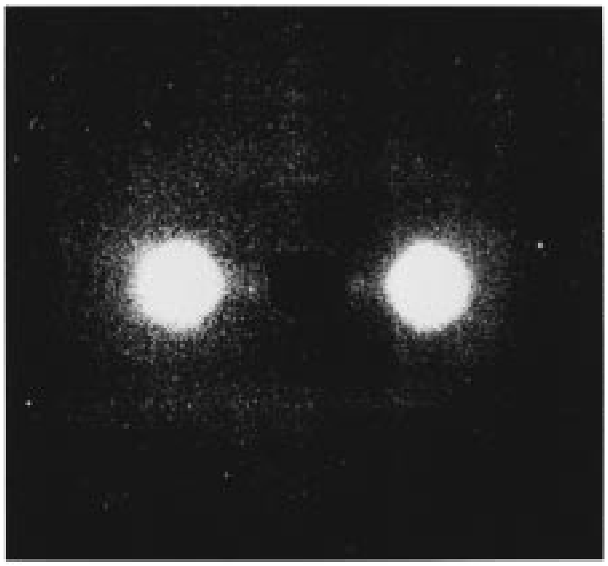

Figure 3. X-ray diffraction pattern of a magnetically aligned amphiphilic polymer network in the L_α-phase (equator vertical).

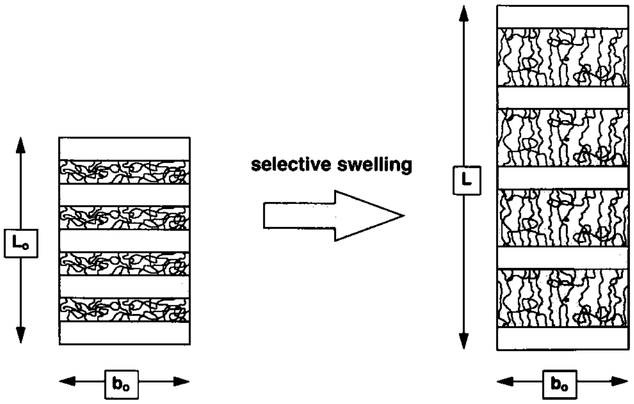

Figure 4. Schematic representation of the one-dimensional swelling of an aligned lamellar polymer network in a selective solvent.

Since the hydrophobic layers are not miscible with water, they retain their initial dimensions during the swelling. As a consequence the sample dimensions parallel to the layer planes are determined by the hydrophobic domains, i.e. do not change during swelling. A macroscopically uniform aligned lamellar elastomer is, therefore, expected to swell uniaxially in water, only in the direction of the layer normals[35,36] (see Figure 4 for a schematic representation).

The experimental results of the swelling experiments are shown in Figure 5. The figure shows the dimensional changes as a function of time for typical samples swollen with water. For comparison the data of a nonaligned polydomain sample are displayed together with that of a macroscopically uniform oriented “single crystal”. For both systems the sample dimensions

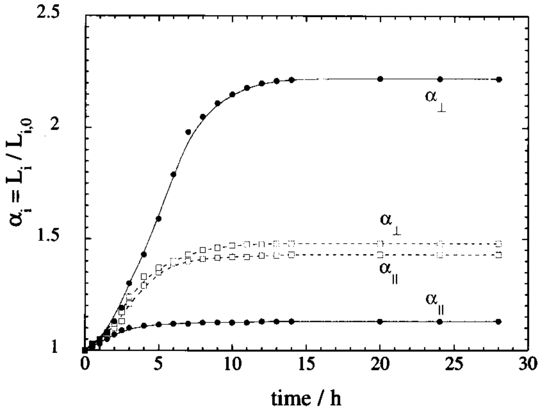

Figure 5. Degree of swelling $\alpha_i = L_i/L_{i,0}$ of lamellar polymer networks as a function of time. L_i and $L_{i,0}$ are the sample dimensions of the swollen and the dry samples in the i-direction (i = ∥ or ⊥, i.e. parallel or normal to the layer structure): ●, magnetic field aligned sample; □, polydomain sample.

increase continuously until after about 12 h a constant value is reached, reflecting the swelling equilibrium. It was found that the swelling behavior of the samples was reversible at all stages, namely, after removing the samples from water and drying they completely recovered their original dimensions.

The data clearly display that the polydomain sample swells isotropically within experimental accuracy. The aligned system, however, swells strongly anisotropically. The dimensions perpendicular to the layer planes increase to more than 200% of the original values, while parallel to the layer structure the sample diameter increases only about 10%. Similar results have been observed upon selective swelling of the middle block of uniformly oriented lamellar polystyrene-polybutadiene-polystyrene triblock copolymers with alkanes. In this case the glassy polystyrene domains act as cross-links. Since these systems were not covalently cross-linked, the swelling behavior was irreversible beyond a certain degree of swelling.[37]

It has to be emphasized that in our systems the overall volume increase during swelling was identical for the polydomain and the monodomain samples within experimental error. This reflects that the polymer network structure of the samples is identical except for the orientation of the individual layers.

Regarding the microscopic structure, the swelling process must correspond to a reversible increase of the thickness of the hydrophilic layers due to incorporation of water. All other dimensions remain constant. Figure 6 shows typical SAXS patterns as a function of the scattering vector **q** (for a lamellar structure the position of the first-order Bragg peak corresponds to $q = 2\pi/d$, with d being the interlamellar spacing) obtained at different stages of swelling.

To prepare the samples for these experiments, they were removed from the water at the corresponding stage of swelling. Prior to the SAXS investigations they were allowed to equilibrate for at least 24 h in a small closed chamber to prevent solvent evaporation. This ensures that the solvent is homogeneously distributed within the sample. The SAXS experiments always reveal reflections obeying the ratio 1:2:3, characteristic for lamellar structures. For the dry elastomer a second-order peak can be observed, and with increasing swelling of the sample develops an additional third-order peak. Obviously during the drying process the samples lose some of their orientation. This is eventually due to local internal stress gradients frozen in the sample during deswelling. These stress gradients may lead to local deformations of the layer structure which lowers the state of order in the sample. This could probably be avoided if the sample deswelling is provided to occur perfectly homogeneously or by annealing the dry samples at elevated temperature. This will be clarified in the future. Upon reswelling the system with water, the segmental mobility of the polymer chains increases and defects in the structure heal again.

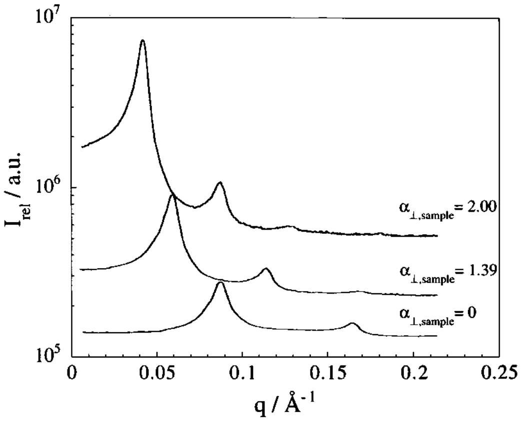

Figure 6. Scattering intensity versus scattering vector **q** for different degrees of swelling of a macroscopically uniform aligned lamellar polymer network.

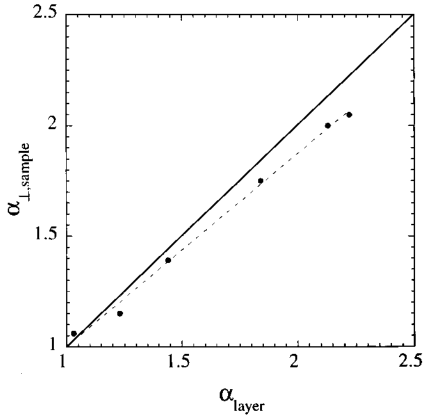

Figure 7. Degree of swelling of the layer structure $\alpha_{\mathrm{layer}} = d/d_0$ (d and d_0 being the layer thickness of the swollen and the dry sample versus the changes of the sample dimensions perpendicular to the layer structure $\alpha_{\perp,\mathrm{sample}} = L_\perp/L_{\perp,0}$. $L_\perp$ and $L_{\perp,0}$ are the sample dimensions of the swollen and the dry sample perpendicular to the layer structure. The solid line corresponds to an affine transformation of the changes in the layer spacings to the macroscopic sample dimensions valid for a perfectly aligned single crystal.

The position of the peak maxima is shifted toward smaller q values, reflecting an increase in the interlamellar spacing as was to be expected from the dimensional changes of the samples upon swelling.

The changes in the spacings obtained from these X-ray measurements can be compared with those of the macroscopic sample dimensions. This is shown in Figure 7, where the increase of the layer spacings is plotted against the degree of swelling, $\alpha_{\perp,\mathrm{sample}}$, perpendicular to the preferred direction of the layer planes. There is a good correspondence between the changes of the lattice spacings and the macroscopic dimensions. The increase of the sample dimensions perpendicular to the layer planes is, however, only about 90% of that of the layer spacings. This is consistent with the fact that some of the volume uptake occurs, as shown above, also parallel to the layer structure. The systems under investigation are obviously not perfectly oriented single crystals. Defects leading to such effects could be undulations in the layer structure, such as those shown in the electron micrograph of Figure 2, as well as a nonperfect alignment of the layers (leading, for example, to a certain angular distribution between the magnetic field direction and the local layer planes).

For the lamellar elastomers under investigation the molecular weight of the bridging poly(oxyethylene) chains can be expected to be of significant influence on the layer structure and the equilibrium degree of swelling. While, for example, in lamellar mesophases of block copolymer melts, the layer thickness d scales as $d \sim N^{2/3}$,[38] with N being the degree of polymerization, in lamellae swollen in a good solvent $d \sim N$ can be expected.[38]

To check these relations for the system under investigation, functionalized poly(oxyethylenes) with molecular weights ranging from 10 000 to 35 000 have been synthesized. The weight fraction of the polymer (i.e. $m_p = 0.038$) and the overall composition of the reaction mixture has been kept constant throughout all experiments. As a consequence, with increasing molecular weight the number of polymer chains in the system decreases. During the cross-linking reaction the overall interfacial area to which the polymers are attached via their hydrophobic end groups is determined by the lamellar liquid crystalline matrix. This area is determined by the composition of the liquid crystalline matrix and, therefore, always the same in the experiments.

The interfacial area σ at the surfactant/water interface, which is available to the individual polymer chains, increases with the molecular weight of the modified poly(oxyethylene) due to the decreasing numbers of polymer molecules which have to share the overall interface in the system. As a result σ must scale as $\sigma \sim N$. After extraction of the matrix and drying of the elastomers, the sample dimensions and, therefore, also the surface of the layers decrease. Since, however, the weight ratio of hydrophilic and hydrophobic domains is kept constant throughout the experiments, this shrinking process occurs always to the same degree and the relation between σ and N, i.e. $\sigma \sim N$, is still valid. Then the thickness d of the poly(oxyethylene) layers in the dry elastomer is determined by the incompressibility condition: $d\sigma = Na^3$.[38] With $\sigma \sim N$ this thickness depends only on a, the size of the monomeric units, i.e. becomes independent from the degree of polymerization N of the poly(oxyethylene) chains. The shorter polymer chains must, therefore, in order to fill up space in the layer, be stretched to a higher degree than the longer chains.

The results of the SAXS investigations, shown in Figure 8, are in good agreement with these considerations, yielding a periodicity of about 7.2 nm for the lamellar elastomers independent from the molecular weight of the bridging poly(oxyethylene) chains.

This correlation between σ and N, in these systems, must also be taken into account for the swelling experiments. It has been shown that in swelling equilibrium the thickness of a swollen layer d_e of a lamellar gel is given by $d_e \approx N(a^2/\sigma)^{1/3}a$,[35,36] corresponding to the c^* condition of densely grafted and aligned polymer brushes.[39] Considering again that $\sigma \sim N$ leads to $d_e \sim (N/\sigma^{1/3}) \sim N^{2/3}$.

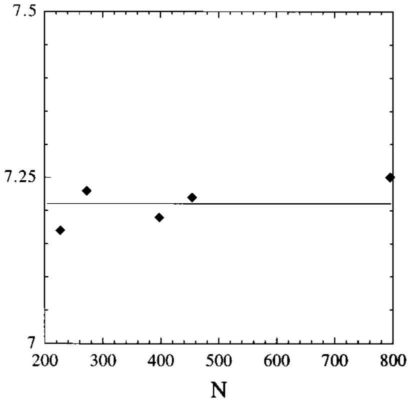

Figure 8. Layer spacings d for dry lamellar polymer networks as a function of the degree of polymerization N of the bridging polymer **1**.

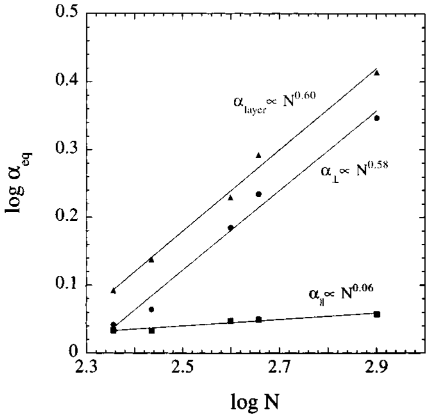

Figure 9. Degree of swelling in water α_{eq} (corresponding to swelling equilibrium) as a function of the degree of polymerization N of the bridging polymer **1**: ▲, increase of the layer spacings upon swelling $\alpha_{layer} = d_e/d_o$ (with d_o being the layer spacing of the dry sample and d_e being the layer spacing of the swollen sample (corresponding to swelling equilibrium)); ●, degree of swelling normal to the layer structure $\alpha_{\perp}$ (corresponding to swelling equilibrium); ■, degree of swelling parallel to the layer structure $\alpha_{\parallel}$ (corresponding to swelling equilibrium).

The results of the swelling experiments are shown in Figure 9 as a function of the degree of polymerization N of the bridging polymer chains. The sample dimensions and the layer spacings of the dry elastomers were always the same within experimental error. For convenience, therefore, Figure 9 shows the degree of swelling $\alpha_i = L_i/L_{i,0}$, with $L_{i,0}$ and L_i being the sample dimensions in the i-direction in dry and in swollen states and $\alpha_{layer} = d_e/d_o$ being the corresponding increase of the layer spacing upon swelling, as a function of N.

It can be easily seen that the increase of the sample dimensions parallel to the layer planes was in all cases rather low and nearly independent from the molecular weight of the poly(oxyethylene) chains. As was to be expected in the direction of the layer normals, however, a power law dependence of the equilibrium degree of swelling on the molecular weight can be observed. The data reveal an increase of the sample dimensions with $N^{0.58}$ and of the layer spacings with $N^{0.60}$ in good agreement with the considerations above, the more since obviously the layer structure of these systems is not perfectly aligned. This is reflected again in the fact that, in agreement with the observations above (see Figure

7), the increase of the sample dimensions was always below that of the layer spacings, namely, for all samples between 84 and 91% of α_{layer}.

Conclusion

The compartmentalized structure of a lamellar liquid crystalline phase can be used to create covalently cross-linked amphiphilic polymer network structures from α,ω-hydrophobically modified poly(oxyethylenes) bearing methacrylate groups at each end and hydrophobic alkyl methacrylates. Using magnetic fields, the liquid crystalline phase structure can be macroscopically uniformly aligned prior to polymerization. This leads to highly anisotropic polymer gels. The network structure preserves the characteristic structure and orientation of the liquid crystalline phase even after extraction of the matrix.

Reswelling these lamellar polymer networks in a selective solvent, like water, leads to a strongly anisotropic increase of the sample dimensions. The dimensional changes occur mainly perpendicularly to the preferred orientation of the layer planes. Parallel to the layer planes, however, the samples swell also to a certain degree. This reflects that the samples are not perfectly aligned "single crystals". One possibility of increasing the state of order in these systems is, probably, to use mechanical shear for aligning them. This method has also been shown to work successfully for block copolymer melts.[37]

The dimensional changes upon swelling can be traced to a corresponding microscopic increase of the layer spacings of the network structure. The molecular weight of the bridging poly(oxyethylene) has a significant influence on the equilibrium swelling characteristics of these systems and can be understood in the framework of the theoretical considerations of refs 35 and 36. An interesting feature of such lamellar gels is, according to these considerations, an asymmetric elastic response to compression and elongation. Additionally, the deformation of the polymer chains is expected to be nonaffine. Investigations on the mechanical properties of these lamellar polymer networks will be the subject of future studies.

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