Assessing the Influence of Temperature-Memory Creation on the Degradation of Copolyesterurethanes in Ultrathin Films

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Copolyesterurethanes (PDLCs) based on oligo(ε-caprolactone) (OCL) and oligo(ω-pentadecalactone) (OPDL) segments are biodegradable thermoplastic temperature-memory polymers. The temperature-memory capability in these polymers with crystallizable control units is implemented by a thermomechanical programming process causing alterations in the crystallite arrangement and chain organization. These morphological changes can potentially affect degradation. Initial observations on the macroscopic level inspire the hypothesis that switching of the controlling units causes an accelerated degradation of the material, resulting in programmable degradation by sequential coupling of functions. Hence, detailed degradation studies on Langmuir films of a PDLC with 40 wt% OPDL content are carried out under enzymatic catalysis. The temperature-memory creation procedure is mimicked by compression at different temperatures. The evolution of the chain organization and mechanical properties during the degradation process is investigated by means of polarization-modulated infrared reflection absorption spectroscopy, interfacial rheology and to some extend by X-ray reflectivity. The experiments on PDLC Langmuir films imply that degradability is not enhanced by thermal switching, as the former depends on the temperature during cold programming. Nevertheless, the thin film experiments show that the leaching of OCL segments does not induce further crystallization of the OPDL segments, which is beneficial for a controlled and predictable degradation.

1. Introduction

The endeavor to imitate and surpass nature has led to the advent of stimuli sensitive and responsive materials.[1] One example are temperature-memory polymers (TMP), which are able to execute a predetermined shape change when heated and exceeding a switching temperature \( T_{sw} \). \( T_{sw} \) is determined by the temperature \( T_{def} \) applied during a preceding deformation step.[2] On the molecular level, the temperature-memory effect is implemented by two structural features. Switching domains are fixing the temporary shape and driving the recovery by entropy elasticity. Crosslinks define the permanent shape in its original and recovered state. They transmit macroscopic deformations to the molecular level. For the latter, physical crosslinks based on high melting crystallites are of particular interest, because the resulting material is reprocessable. For application of TMP as implant material, \( T_{sw} \) should be adjustable in a range tolerable for the human body. Degradability is required as an additional function in case of temporary implants. Such multifunctional materials have been realized with multiblock copolymers based on crystallizable oligo(ε-caprolactone) (OCL) controlling units which are coupled with hydrophobic and high melting[3] oligo(ω-pentadecalactone) (OPDL) segments by urethane junction units.[2] These materials can degrade via ester hydrolysis, whereby crystalline units are expected to degrade slower than amorphous ones.[4,5] Therefore, it can be speculated that the melting of OCL crystallites to execute the shape switching could enhance degradability. As consequence, the temperature-memory and degradation function would be sequentially coupled, with the programmable switching temperature \( T_{sw} \). Based on these considerations, a qualitative assessment of the degradability of macroscopic copolyesterurethanes (PDLC) test specimen under accelerated conditions (Figure S8, Supporting Information) was carried out. The degradability is indeed varying strongly in dependence on \( T_{def} \) and degradation temperature. Yet, under the highly acidic conditions used, the catalytic activity of protons is probably similar on all ester bonds, and therefore, less harsh conditions are required to understand the function interrelations.

Based on the hydrolysis rates of OPDL segments[6] and poly(ε-caprolactone) (PCL),[7] it can be expected that the mode of degradation of PDLCs in vivo is a gradual leaching of OCL blocks from the material. This effect can be simulated in Langmuir monolayer degradation experiments, where, in the presence of lipase enzymes, only the OCL segments are leached.
Whether or not enzymatic catalysis also plays a role in the degradation of PCL based implants is not yet clear. A moderate acceleration of the mass loss rate of PCL in vivo in comparison to in vitro conditions may point in that direction.[7]

Here, we hypothesize that the melting of the controlling units, which enables the shape shifting in PDLCLs, also accelerates their enzymatic degradation, in a way that can be considered as sequential coupling of material functions, resulting in a programmable material degradation.

To facilitate a rapid assessment of the degradation behavior of PDLCLs supported by in situ techniques, the degradation is carried out in ultrathin films at the air-water interface.[9] To demonstrate the impact of the temperature-memory creation and shape shifting on the degradability of PDLCLs, four scenarios are compared:

First, a material that has not undergone temperature-memory creation, where the OCL segments are completely amorphous (Figure I). Second, a material that has undergone temperature-memory creation at high $T_{\text{deform}}$ and is degraded at the same temperature (Figure III). Third, a material compressed at low $T_{\text{deform}}$. The material was then switched by heating to a high $T_{\text{sw}}$ where it was also degraded (Figure III) and fourth, a material which has been compressed at low $T_{\text{deform}}$ and was degraded at the same temperature, without execution of the thermal switching. (Figure IV).

The experiments were carried out on the surfaces of Langmuir troughs, which were coupled to three different interfacial in situ characterization tools: First, a polarization modulation infrared reflection absorption spectrometer (PM-IRRAS), which is sensitive to changes in conformation and orientation of the polymer chains. Second, an interfacial shear rheometer, measuring the torque on a biconical disc which is oscillated at constant frequency with its edge positioned within the layer. Third, an X-ray reflectivity (XRR) setup (LISA diffractometer) at the German electron synchrotron (DESY). The general procedure for the degradation experiments, which is described in detail in the

![Figure 1](image-url)
Experimental Section, was to prepare the layer in one of the four different ways explained above, and then induce degradation by injection of the lipase enzymes from *Pseudomonas cepacia* under the layer. The areal concentration of repeat units, identified by the surface pressure, was kept constant by compressing the layer to compensate for the dissolution of water soluble fragments. The chosen material is a PDLCL with 40 wt% OPDL content (PDLCL40), which was found to be the limiting concentration (PDLCL40), which was found to be the limiting concentration where both segments were still well mixed. To aid with the interpretation of PM-IRRAS spectra, experiments with OPDL and OCL ultrathin films were carried out.

2. Results and Discussion

From the literature, it is known that at surface pressures below \( \pi = 10 \text{ mN m}^{-1} \), PDLCLs form amorphous monolayers with no phase separation\(^{[11]}\), which agrees with the compression isotherm of PDLCL40 (Figure S9A, Supporting Information). The degradation of PDLCLs in the amorphous state at \( \pi = 8 \text{ mN m}^{-1} \) (Figure S9B, Supporting Information) was also described and quantitatively analyzed before\(^{[12]}\), and the degradation curve of PDLCL40 in the amorphous state (Figure S9B, Supporting Information) is exactly as expected from these previous experiments. The sigmoid shaped degradation curve levels off at \( \approx 40\% \) remaining area, corresponding to the OPDL content by weight. This confirms that first, only the OCL segments are dissolved and second, OPDL is amorphous at the beginning as well as at the end of degradation. If OPDL were crystallizing upon degradation, one would observe a step in the degradation curve due to sudden formation of 3D structures, as was, for example, observed for poly(β-hydroxybutyrate)\(^{[13]}\).

This result is rather remarkable, because PPDL has been described as polyethylene like\(^{[13,14]}\), meaning that it is highly crystalline and hydrophobic. Such a polymer is not expected to form amorphous layers at the air-water interface. The high tendency of OPDL to form crystalline 3D structures is confirmed both by PM-IRRAS (Figure 2) and by XRR (Figure S5, Supporting Information). Upon spreading pure OPDL, it crystallizes immediately, as can be seen by the very strong ester carbonyl (\( \nu = 1730 \text{ cm}^{-1} \)) and methylene (\( \nu = 2853 + 2917 \text{ cm}^{-1} \)) vibration. PM-IRRAS only detects vibrations with a preferential orientation with respect to the air-water interface. For amorphous polymers, that means that only the vibrations in chain direction are detected. The vibrations perpendicular to the chain direction are randomly distributed due to the random walk of the chains. Both carbonyl and methylene vibrations are therefore of very low intensity in PM-IRRAS spectra of amorphous polyesters at the air-water interface. The sharp peaks observed for OPDL even at \( \pi = 1 \text{ mN m}^{-1} \) suggest a high degree of ordering and therefore crystallization. The XRR measurements return a thickness between 1.5 and 3 nm. The absence of asymmetric C=O=C stretching vibrations along the chain direction (\( \nu = 1240 \text{ cm}^{-1} \))\(^{[15]}\) further indicates the crystal long axis is direction of the surface normal with a certain tilt angle. The largely featureless PM-IRRAS spectrum of amorphous PDLCL40 does not change upon complete leaching of OCL segments (Figure S10A, Supporting Information), showing very clearly that the OPDL segments are not crystallizing during degradation. The fits for the XRR curves before and during degradation (Figure S4, Supporting Information) suggest that the layer thickness increases very moderately from \( \approx 0.8 \text{ to } 1.1 \text{ nm} \), while the roughness remains very close to the value of the bare air water interface (\( \sigma = 0.3 \text{ nm} \)). One notable difference between the layers prepared by leaching and the layers prepared by spreading is the presence of urethane junction units. The number average molecular weight (\( M_n \)) of the OPDL diols used to synthesize PDLCL40 was greater than the one of the OPDLs that were spread directly. Both chain-ends and junction units are defects that are excluded from OPDL crystals, but the defect content for the spread layers was higher. Still, these layers crystallized immediately, while the layers prepared by leaching did not. It is unlikely that the junction units impeded the crystallization since in bulk, the OPDL blocks containing junction units are able to crystallize. There is also evidence that hexamethylene diurethane junction units can enhance the crystallization rate in polyesters\(^{[16]}\). The other fundamental difference between the layers prepared by spreading and the layers prepared by leaching is the solvent. It seems that the transition of the molecules from chloroform to water is either energy intensive or slow compared to crystallization. Yet, for molecules that are already swollen by water, spontaneous crystallization does not occur. The ability of polyethylene-like polymers with phosphoester groups equally spaced between 20 methylene units to form both amorphous and crystalline structures at the air-water interface\(^{[17]}\) gives another indication that water can be a solvent.

![Figure 2](image-url) PM-IRRAS spectra of A) time dependent OCL crystallization at room temperature and \( \pi = 10.5 \text{ mN m}^{-1} \). B) Crystallization of OPDL upon spreading and during compression. C) Surface pressure dependent crystallization of PDLCL40.
for rather hydrophobic polymers. Then, hydration will lower the thermal transitions, which is highly relevant for polymers in biomaterial applications, especially in formulations allowing for fast hydration such as nanoparticles or hydrogels.[7] While there are no systematic investigations on the melting point depression of polymers by water, studies with other polymers having hydrophilic groups have shown melting point depressions of up to 120 °C[8] and even water solubility at elevated pressure.[9] A more detailed study on the melting and crystallization of polymers in the presence of water is ongoing.

Altogether, when starting from amorphous material, the transition from a mixed block-copolymers layer to a pure OPDL layer proceeds smoothly without phase transformations or separation. In that, the degradation of PDLCL40 was similar to the degradation of pure OCL, which was also observed by PM-Irrras (Figure S10B, Supporting Information) and XRR, which returned a layer thickness of ≈0.5 nm for both OCL (Figure S2, Supporting Information) and PDLCL40 (Figure S4, Supporting Information), and an increasing diffuseness of the polymer-water interface during degradation (Figures S3 and S4, Supporting Information).

In order to mimic the phase transitions during temperature-memory creation and switching of PDLCL40, crystallization was induced by compression. The broad plateau of the surface pressure versus area isotherm indicates that a phase transition takes place between $\pi = 10$ mN m$^{-1}$ and $\pi = 12.5$ mN m$^{-1}$.[11] The PM-Irrras spectra recorded upon compression clearly show that the ester bonds become crystalline at $\approx$11 mN m$^{-1}$, and at 12 mN m$^{-1}$, also strong signals from methylene units and from C–O–C vibrations are observed. The spectra of PDLCL40 are compared to both pure OCL and OPDL (Figure 2). The appearance of signals between $\nu = 1520$–1570 cm$^{-1}$ during crystallization might be attributed to amide II vibrations arising from an organization of the urethane junction units. Interestingly, the PM-Irrras spectrum of crystalline OCL shows as prominent signal only the carbonyl vibration, almost no methylene or C–O–C vibrations. A recent detailed analysis of the crystallization behavior of PCL Langmuir films arrives at the conclusion that the chain axis of the crystals is in direction of the surface normal, albeit with considerable tilt,[17] which might suppress the methylene signals in PM-Irrras. In contrast to the spectra of OCL, the OPDL spectrum has strong methylene and C–O–C vibrations. Altogether, the spectrum of crystalline PDLCL40 is a combination of crystalline OCL and OPDL, which is expected as OPDL crystals in PDLCLs nucleate the growth of OCL crystals.[20]

Accordingly, a layer representing a TMP with a $T_{\text{sw}}$ at room temperature containing both OCL and OPDL crystals can be prepared by compressing PDLCL40 to 11.5 mNm$^{-1}$. When doing so in an interfacial shear rheometer, we observe a two-stage mechanical response, where the interfacial viscosity ($\eta$) varies differently with compression. Up to a film area (A) of $A \approx A_0$, where $A_0$ is the area where the surface pressure $\pi = 11.5$ mN m$^{-1}$, the viscosity increases weakly. Upon further compression, a strong increase of the viscosity is observed (Figure 3B). The viscosity scales with the film area according to $\eta \propto A^{-1.4}$. The chosen condition of $\pi = 11.5$ mN m$^{-1}$ is already very well within that second regime. The injection of the lipase enzymes leads to further compression of the layer and at first, also an increase of the dynamic shear moduli (Figure 3A). It seems reasonable that the material becomes more elastic upon leaching of amorphous OCL, as the areal density of OCL/OPDL crystallites as well as amorphous OPDL increases. However, the moduli start to slowly decrease at $\approx$35% area reduction. Yet, the maximum area reduction is only 40%. This implies that the area is covered to 40% by amorphous OCL, and the rest is either crystalline OCL or OPDL. This observation is in line with the behavior of the material in bulk, where the overall crystallinity is between 40% and 50% after deformation.[2] We note that the loss modulus is below the storage modulus at all times, however, both moduli converge as the material becomes more and more viscous during degradation.

The next sample represents a TMP, which was deformed at a high $T_{\text{deform}}$ of 40 °C and was degraded at the same temperature. That means that the OCL segments achieve a lower crystallinity. The area reduction of almost 60% after injection of lipase (Figure 4A) implies that most OCL was amorphous. Initially, the overall complex interfacial viscosity of the layer scales with the same exponent (Figure 4C) as observed for the sample compressed and degraded at room temperature. However, at roughly 30% area reduction, the exponent decreases by more than three times. The break in slope in Figure 4C coincides roughly with the point in Figure 4A where storage modulus and loss modulus start to separate (green arrow in Figure 4A,C). It
is surprising to see that the layer becomes more viscous upon leaching of the OCL segments. At this high surface pressure, where both polymers are able to crystallize, one would expect to end up with a highly crystalline OPDL layer upon leaching of OCL. While the crystallization temperatures of OPDL in bulk are at ≈70 °C, and the temperature of 40 °C should be more than sufficient for OPDL crystallization, we cooled the layer to 15 °C to check for solidification. Yet, while both moduli increased, the shear modulus remained above the loss modulus (Figure 4B). This behavior is different from other semicrystalline polyesters such as PHB, which shows pronounced crystallization upon degradation in thin films. [13] Again, we observe a suppression of the crystallization of OPDL, either due to the 2D confinement or due to the presence of water.

The last sample was subjected to a temperature program that reflects a material with a T_{deform} at room temperature, which was then heated to T_{sw} of 40 °C where it was also degraded. This program is close to the conditions that would be expected for a medical application. Crystallization was initiated by compressing the layer to π = 11.5 mN m\(^{-1}\) with T_{deform} at room temperature. After the area had stabilized, it was heated to T_{sw} of 40 °C, resulting in an increase of the surface pressure of ≈1 mN m\(^{-1}\). The area was then allowed to relax at that surface pressure. Then, the lipase enzymes were injected and the layer was degraded at 40 °C (Figure 5A). This layer did not reach the same degree of degradation as the layer with a T_{deform} of 40 °C, although the final temperature was identical. The final degree of degradation of ≈30% was close to the experiment with T_{deform} and degradation both at room temperature. This leads to the conclusion that the degradability of PDLCLs under ambient conditions or close to body temperature is determined by their cold programming history and that the degradability is not enhanced by switching of the controlling segments. Thus, our experiments suggest that there is no sequential coupling between temperature-memory and degradability. The lack in enhancement of the degradability upon melting of PCL may in some part be explained by the activity of the lipase toward crystalline PCL. [21]

Again, the layer did not crystallize or solidify under degradation, as the loss modulus and storage modulus remained similar. Here, we focus on the storage modulus (G′) rather than the viscosity, because the former undergoes the most pronounced changes. During stabilization after heating, we observed that G′ ∼ A\(^{-2}\), whereas during degradation, G′ ∼ A\(^{-3.5}\) (Figure 5B). The scaling exponents observed during degradation-induced compression can be correlated with the solvent state of the OPDL segments. If the assumption holds that degradation is caused by dissolution of OCL segments while OPDL segments remain at the interface, the surface concentration of OPDL

![Figure 4](image1)
![Figure 5](image2)
(Γ_{OPDL}) is given by Γ_{OPDL} = \frac{Γ}{A}. From published theoretical and experimental studies on the scaling behavior of polymers in 2D,[22] it is known that \( \Gamma' \sim \Gamma \), whereas \( \eta \sim \Gamma^3 \), where \( y \) is the scaling exponent related to solvent quality. From our experiments, we find that the exponent \( y \) for OPDL is \( \approx 3 \), which is the value expected for a good solvent. It is highly surprising that the air-water interface is a good solvent for OPDL, both at 40 °C and at room temperature. We further note that it is well known that in the semi-dilute regime, the surface pressure of polymer Langmuir films scales according to \( \pi \sim \Gamma^y \).[23] In our experiments, we find for PDLCL40 a value of \( y \approx 2.7 \). Thus, the solvent quality of the interface does not change upon leaching of OCL from PDLCL40, which explains the absence of degradation induced crystallization. Different scaling exponents than \( y \approx 3 \) were observed for PDLCL40 at high degrees of degradation (Figure 4C) and prior to degradation (Figure 5B). The high exponent prior to degradation might be related to the residual crystallinity after heating. The low exponent found at the end of degradation could, for example, indicate the OPDL was below the entanglement molecular weight, but this would require a certain degree of OPDL hydrolysis.

In terms of degradation kinetics, the materials with programmed temperature-memory also behave very different from other materials. For polymers like PCL[22] or poly(ε-caprolactone-co-glycolide) (PLGA),[24] exclusively random chain scission mechanisms were observed under enzymatic catalysis. This mechanism is characterized by a sigmoidal degradation curve. Dissolution is initially very slow, because the molecular weight of the chains is high, but as the molecular weight decreases by random chain cuts, the dissolution rate increases. While this was clearly the case for amorphous PDLCL40 (Figure S9B, Supporting Information), the kinetics after crystallization are different. After an initial expansion caused by disturbance of the layer by inserting the lipase enzymes, the dissolution kinetics correspond to an exponential decay (Figures 4A and 5A), where the highest degradation rate is observed at the beginning. This excludes a random scission mechanism, and we suggest that the polymer undergoes surface erosion. In a Langmuir monolayer, the theoretical treatment of surface erosion is very straightforward, since the dissolution rate is simply proportional to the remaining surface. This directly leads to a first order exponential decay of the surface area according to \( \frac{A}{A_0} = 1 - \Delta A_{\text{max}} \cdot \exp(-kt) \). Here, the parameter \( \Delta A_{\text{max}} \) corresponds to the maximum degree of dissolution. For PDLCL40, this would be 0.6 according to the OCL content, provided that the layer is completely amorphous and \( k \) is the first order erosion rate constant, which differs from a molecular reaction rate constant. It describes the average time it takes a whole molecule to dissolve, and would for instance be slightly molecular weight dependent. As can be seen, the fit curves according to the first order exponential decay match the degradation curves in Figures 4A and 5A very well. The assertion of a surface erosion process is further substantiated by the increasing viscosity during degradation (Figures 3B, C, and 5B). This means that during degradation, the layer remains mechanically intact. Especially at room temperature, we see no alteration of the scaling behavior of the viscosity of the layer before and during degradation (Figure 3B). This is very different from amorphous polymers like PLGA undergoing bulk degradation, where the elastic moduli drop to near zero before any dissolution is observed.[26] Of course, it is not surprising that the materials undergo surface erosion under enzymatic catalysis. From XRR, the layer has a thickness of \( \approx 1 \) nm at \( \pi = 8 \) mN m\(^{-1} \) (Figure S4, Supporting Information). The thickness of the layer at \( \pi = 11.5 \) mN m\(^{-1} \) is at least 8 nm. Clearly, the lipase enzymes cannot penetrate that deep into the physically crosslinked material.

3. Conclusion

The impact of temperature-memory creation and switching on the degradation behavior of thermoplastic TMPs were explored using the Langmuir technique. This was facilitated by manipulating the semicrystalline morphology of a Langmuir film to represent a bulk polymer material with a thermomechanical history. Including a variable semicrystalline morphology into the thin film is a very important step toward bridging the gap between real world material and the 2D model system. For PDLCL containing 60 wt% degradable OCL controlling segments and 40 wt% OPDL segments, we found that the degradability increases with \( T_{\text{form}} \), while no substantial enhancement of the degradation occurred upon switching of the OCL controlling domains. We conclude that there is no direct coupling between the shape shifting and degradation function, at least for degradation under enzymatic catalysis. Despite the fact that OPDL segments crystallize immediately upon spreading from a volatile solvent, OPDL actually forms a stable monolayer when prepared by leeching of OCL segments from a PDLCL film. We showed that the rheological properties of the block copolymer during degradation are in large parts described by scaling laws, whereby the OPDL segments behave as in a good solvent at the air water interface, and no degradation induced embrittlement or crystallization was observed. This finding implies an important role of water in degrading polyesters, not only as reactant but also as a solvent.

4. Experimental Section

Materials: The OCL (Capa 2304, Solvay, Warrington (UK)) had a \( M_n \approx 2800–2900 \) g mol\(^{-1} \) as determined by NMR. The characterization by NMR was described in a previous article.[27] The number average molecular weight was also determined by GPC to be \( M_n \approx 2800 \) g mol\(^{-1} \). The characterization by GPC is described in a previous article.[27] The linear OPDL was synthesized via ring opening polymerization and had a molecular weight of \( \approx 3000 \) g mol\(^{-1} \) and a dispersity of 2.1 as determined by GPC. PDLCL40 had a number average molecular weight (\( M_n \)) of 31 kg mol\(^{-1} \) as determined by GPC (universal calibration) and a dispersity of 2. The \( M_n \) of the starting materials for the synthesis of PDLCL were 4300 g mol\(^{-1} \) for the OPDL diol, and 2800 g mol\(^{-1} \) for the OCL diol. The blocks were joined with hexamethylene diurethane junction units, and the polymer contained 40 wt% OPDL (NMR analysis in Figure S6, Supporting Information, structural formula in Figure S7, Supporting Information). The lipase from Pseudomonas cepacia was obtained from Sigma Aldrich and used without further purification.

PM-IRRAS: The vibrational bands of a film assembled at the air-water interface are recorded by a PM-IRRAS system from Biolin Scientific. An IR beam was reflected from the air-water interface at a grazing angle. The polarization of the incoming beam was modulated with high
frequency (2700 kHz) between s- and p-polarization, and a normalized differential intensity is calculated via $I_{\text{diff}} = \frac{I_s - I_p}{I_s + I_p}$. For a conducting surface, $I_s$ is zero, and only the component of the dipole moment that is parallel to the plane of incidence contributes to the absorption band. This simple selection rule does not apply to water, which is a dielectric. Instead, it was calculated that for an organic monolayer at the air-water interface, the best signal to noise ratio is observed at a grazing angle of $\sim 72^\circ$.\cite{25} Then, dipole moments oriented parallel to the air-water interface lead to a negative $\Delta$ while dipole moments oriented parallel to the air-water interface lead to a positive $\Delta$. If the signal intensities for both orientations were equal, complete cancellation would be observed for dipoles with an orientation of $45^\circ$ with respect to the air-water interface. That is, $I_{\text{diff}}$ would be zero for randomly oriented dipoles like water or CO$_2$. However, since signal intensity of the parallel component was higher than the signal intensity of the perpendicular component, the vanishing angle is shifted toward a higher angle of $39^\circ$ with respect to the surface normal.\cite{25} Therefore, the water absorption band was reduced but not removed from PM-IRRAS measurements at the air-water interface. Furthermore, the transmittance of the photoelastic modular is highly wavelength dependent, as is the reflectivity of water. The intensity modulation introduced by vibrational absorption bands of the organic layer was tiny compared to these effects. Therefore, the signal of the layer was compared to the bare subphase to remove these contributions: $S = \frac{I_{\text{sample}}}{I_{\text{bare}}} - 1$. This normalization worked well for fast experiments, but not for degradation experiments lasting several hours. Due to water evaporation and changes in humidity, the optical response of the subphase changes, and the normalization of spectra recorded during heating, resulting in an increase of the surface pressure. After the surface pressure had stabilized at $T_{\text{deform}}$, the new surface pressure was kept constant and the surface area was allowed to vary. Experiments involving degradation by lipase enzymes were carried out on a phosphate buffered saline subphase. The lipase enzymes were injected under the layers once these had become stable at the selected degradation surface pressure and temperatures. The final enzyme concentration depended on the experiment. For XRR measurements, $c = 1 \mu g \text{ mL}^{-1}$ because of the long integration time for each measurement. For PM-IRRAS, $c = 2 \mu g \text{ mL}^{-1}$ and for rheology, $c = 4.5 \mu g \text{ mL}^{-1}$ due to relatively fast data acquisition.

**Data Evaluation:** Degradation, PM IRRAS, and rheology data were processed with Origin 2018. Data fitting was carried out with a Levenberg-Marquardt algorithm and a fit function tolerance of $10^{-2}$. The raw rheology data were converted to interfacial values with the algorithm included in the Rheocompass software. All experiments shown here were carried out once. Each experiment started with a compression isotherm, which was very repeatable for OCL and PDCL, that is, a deviation of less than $1 \AA^2$ at $\pi = 8 \text{ mN m}^{-1}$. In isobaric experiments, errors arising from pressure fluctuations and uncertainty of trough area were below 1%, see ref. [24] for a deviation. The sensitivity limit of the rheometer in the applied geometry was $\sim 15 \times 10^{-4} \text{ Pa s m}$, which represents the error of each datapoint. PM-IRRAS experiments were strongly dependent on a background subtraction procedure and were affected by signal drift. Therefore, only strong peaks were used for qualitative evaluation. The error bars for XRR measurements (see Supporting Information) were the standard deviation of all acquisitions used to generate a single datapoint.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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