Biomedical Materials

PAPER

Reversible 2D networks of oligo(ε-caprolactone) at the air–water interface

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Keywords: poly(ε-caprolactone), langmuir monolayer, two dimensional network, crystallization, cross-linking

Abstract

Hydroxyl terminated oligo(ε-caprolactone) (OCL) monolayers were reversibly cross-linked forming two dimensional networks (2D) at the air–water interface. The equilibrium reaction with glyoxal as the cross-linker is pH-sensitive. Pronounced contraction in the area of the prepared 2D OCL films in dependence of surface pressure and time revealed the process of the reaction. Cross-linking inhibited crystallization and retarded enzymatic degradation of the OCL film. Altering the subphase pH led to a cleavage of the covalent acetal cross-links. The reversibility of the covalent acetal cross-links was proved by observing an identical isotherm as non-cross-linked sample. Besides as model systems, these customizable reversible OCL 2D networks are intended for use as pH responsive drug delivery systems or functionalyzed cell culture substrates.

1. Introduction

Poly(ε-caprolactone) (PCL) plays a paramount role as degradable implant material or as matrix for controlled drug delivery systems. It can be processed to nanoparticles, micelles, microspheres, electro spun mats, scaffolds or films [1–4]. End-group functionalized poly- or oligo(ε-caprolactone)s as telechelics are starting materials for building complex architectures. In such polymer systems, thermal properties and degradation profiles are adjustable by controlling the number of arms and chain lengths of the telechelics. With capability of further polymerization, one dimensional telechelics give new opportunities for creating three dimensional dendrimers, bulk polymer networks and 2D nanostructures [5, 6]. Reversibly cross-linked polymer networks of PCL can be stimuli responsive. Temperature sensitive net-points can induce a shape memory response [7, 8] while reversible chemical bonds promote self-healing characteristics [9, 10]. Permanently cross-linked PCL networks are applied for tissue regeneration [11, 12] and in printing technologies [13, 14]. An important parameter in PCL networks modulated by cross-linking is ester bond cleavage by degradation [15–19]. The rate-determining step in PCL degradation by enzymatic hydrolysis generally slows down in the presence of netpoints formed by crystalline domains [20–22]. PCL based elastomers enzymatically hydrolyse completely over a wide range of temperatures at pH 7 when lacking crystalline domains. PCL elastomers combining controlled biodegradation and reasonable mechanical strength can be prepared by cross-linking a star-shaped hydroxyl-terminated poly(γ-methyl-ε-caprolactone) with bis(β-lactone) [15]. Implants prepared by cross-linking PCL during ring-opening polymerization of caprolactone with bis(trimethylene carbonate) exhibit reduced crystallinity and form-stability, but show suppressed enzymatic degradation [16]. Degradation kinetics are also influenced for benzoperoxide cross-linked PCL membranes in phosphate buffered saline [17]. Interestingly, PCL films prepared by photocross-linking with benzophenone or benzil exhibit faster hydrolysis due to enhancement in overall polarity of the film [18, 19]. These examples show that the physico-chemical properties, mechanical stability and degradation profiles of 3D networks can be tailored in a controlled fashion by cross-linking. On the other hand, 2D polymer systems with interconnected telechelics in lateral plane can also lead to
generation of new material features as seen for 2D materials such as graphene and its derivatives, which modulate responses with cells, tissues or other bio-interfaces [23, 24]. Although graphene materials have immense potential in healthcare such as for drug delivery, bio imaging, capturing pathogens and tissue engineering, several contradictory results are reported in literature due to graphene shape, size, concentration, carbon source, and cytotoxicity [25, 26]. Therefore, it is still a challenge to develop alternatives to conventional 2D materials for biological applications. We hypothesize that functionalized 2D polymer networks based on OCL telechics with different chemical functionalities can be used as building blocks for creating bioresponsive polymer 2D networks. Besides network stability, the degradability should be altered by an external stimulus such as by pH and has to be systematically investigated. Chemical functions sensitive to pH are of specific interest, since gradients of pH exist at different physiological levels and in nature. Sites of tumour and inflammatory tissues have a slightly acidic pH when compared to their surrounding healthy tissues. Moreover, the environment of endosomes and lysosomes that carry substances inside cells is acidic. Hence, systems with pH sensitive chemical cross-links have attracted a key focus in developing drug delivery systems and in tissue regeneration [16, 27–29]. There are several possibilities to have OCL cross-links sensitive to pH, such as by using ortho ester [30], cis-aconityl bond [31], Schiff base formed between hydrazine and ketone groups [32] and acetal cross-links [33].

The Langmuir technique is ideally suited for preparing 2D materials of non-water or partially water soluble precursors. It allows for positioning of reactive end groups of monomers at the air–water interface for linking by different reaction mechanisms such as by irradiation [34], enzyme [35], catalyst [36], metal ions [37, 38] and ‘click’ reactions [39]. Additionally, faster analysis of biodegradation processes are possible by this technique at molecular level [40]. While various ideally symmetric, small molecules are linked using Langmuir technique to form 2D materials [34, 37, 39, 41–44], only few studies described 2D cross-linking of oligomers or polymers using the Langmuir technique in recent years [5, 38, 45–49]. For example, a semi-interpenetrating oligomeric network is achievable by embedding cross-linked methacryloxypropyl-terminated polydimethylsiloxane in a cellulose acetate butyrate matrix [5]. In our concept for preparing biodegradable 2D polymer networks, we use OCL telechics end-capped with hydroxyl groups, because of their stability and well-studied behaviour at the air–water interface [50]. Acetal cross-links in hydroxyl terminated OCL monolayers are favoured since they are well described, can be used with different types of hydroxyl groups [51] and form under the conditions of the Langmuir technique experimental setup (aqueous subphase at room temperature). Acetal bonds form reversibly and provide the required pH sensitivity for a stimulus responsive material. This is a key advantage over traditional 2D materials forming irreversibly. The lateral size of 2D sheets is limited due to the nearly inevitable formation of grain boundaries when several sheets grow simultaneously next to each other. With reversible reactions, the grain boundaries can be cured and large lateral sizes can be achieved. The chemical equilibrium determines the number of unreacted chain ends that are available for further functionalization. As a proof of principle, the dialdehyde glyoxal is used, which imparts hemiacetal and acetal links in the hydroxyl terminated OCL polymer system and can react with four hydroxyl terminated chain ends of OCL. An idealised acetalization reaction scheme is shown in scheme 1.

The carbonyl group of glyoxal protonates under water, which is attacked by the nucleophilic hydroxyl group of an OCL molecule [52, 53]. After subsequent deprotonation of the intermediate species, hemiacetal bonds are formed. Hemiacetals are an unstable intermediate and can react with hydroxyl groups of an OCL chain present in the vicinity to form an acetal [51]. The acetal bonds are stable in alkaline pH while under acidic pH, cleavage of some acetals occurs to release free end groups. The density of OCL hydroxyl groups at the air–water interface can be influenced by modulating OCL molecule packing density. Here, we examine two approaches to form a covalent 2D network. With linear, hydroxyl terminated OCL diol, a network is formed because each glyoxal molecule can connect up to four linear molecules and act as a branching centre (scheme 1(a)). Here, a branching centre is a point in the network where more than two OCL chains are covalently connected. When eventually more chain-ends are connected in the branching centres, the branched macromolecular entities link and ultimately form a 2D network. When using star shaped OCL tetrals, a certain number of branching centres are already provided by the tetrals (scheme 1(b)). Hence, we expect a faster network formation for tetrals, compared to diols. The maximum cross-link density for both linear molecules and tetrals is determined by molecular weight or arm length, respectively. Here, we use tetrals with an arm length (3200 g mol⁻¹) that is similar to the molecular weight of the diol (2800 g mol⁻¹), and therefore, in the diol monolayer, the hydroxyl end-groups concentration per unit area is double compared to the tetral monolayer. It is known that PCL chain segments near covalent network points have limited mobility due to steric hindrance and hence their crystallization is hindered. We will use this effect to qualitatively evaluate the progress of the cross-linking reaction by studying the surface pressure induced crystallization of the layer. Furthermore, cross-links delay the biodegradation of OCL by reducing the number of free chain ends where small fragments can be generated relatively fast, so the
enzymatic degradation of OCL is studied to obtain further information on the degree of cross-linking.

To free OCL molecules from a cross-linked OCL 2D network, the formation of branching centres is reversed. This is achieved by breaking the acetal bonds. We expect that acetal bonds in the network can be cleaved to release free chain ends by reducing the pH. The reversion of the network formation after lowering of the pH is studied by π–A isotherms and pressure induced crystallization. The prepared pH triggered OCL 2D network aims in broadening applications of 2D crystallisable polymers, such as for forming pH triggered enteric drug delivery systems.

2. Experimental

2.1. Materials

Oligo(ε-caprolactone) diol (OCL diol, trade name CAPA 2304, Solvay Caprolactones, Warrington, UK) was used without any further purification. Star-shaped polymer based on ε-caprolactone with four-arms (4 arm OCL) was synthesized using the catalyst dibutyltin oxide and the initiator pentaerythritol [54]. Glyoxal (40% w/v, Sigma Aldrich, Germany) used as the cross-linker was dissolved in up to 5 ml water in required concentration before injecting into the sub-phase. The aqueous subphase and water for dissolution of glyoxal was obtained by a Milli-Q Gradient

Scheme 1. Reaction schemes of 2D network formation of (a) OCL diol and (b) OCL tetrol with glyoxal. Encircled area represents a branching centre. By progressive connection of the branched macromolecular entities, a 2D network is formed.
A-10 water purification system (Millipore, 18.2 MU cm, to < 4 ppb). For cleaning of trough, ethanol (HPLC grade; Bernd Kraft, Duisburg, Germany) and chloroform (HPLC grade, Roth) were used. For the used OCL diol and 4 arm OCL, the characterisation data were reported previously [35]. The average number molecular weight ($M_n$), determined by gel permeation chromatography (GPC) was 2800 g mol$^{-1}$ and 13 000 g mol$^{-1}$, respectively. The determined $M_n$ (GPC) per end group for OCL diol and 4 arm OCL was 1400 g mol$^{-1}$ and 3200 g mol$^{-1}$, respectively.

2.2. Langmuir monolayer technique

The surface pressure-area ($\pi$--A) isotherms were recorded with a Langmuir trough (KSV NIMA, Finland) placed on an active vibration isolation system (Halcyonics variobasic 40, Accurion, Germany) within a laser safety cabinet. The surface pressure ($\pi$) was measured by the Wilhelmy technique with a calibrated sensor located in the centre between the barriers. Water level compensation system was used to compensate the loss of water due to evaporation during the course of experiment to avoid false changes in the recorded surface pressure. The trough was cleaned thoroughly with ethanol followed by chloroform. Afterwards, the deionized water was filled and removed at least three times. By monitoring the surface pressure, the purity of the trough and the subphase was controlled. In the final aqueous subphase, while closing the barriers, the total change of the surface pressure was below 0.2 mN m$^{-1}$. For all OCL samples, the chloroform stock solutions had a concentration in the range of 0.2–0.4 mg ml$^{-1}$. The solution was applied drop-wise onto the air–water interface using a microsyringe (Hamilton Co., Reno, NV, USA). The chloroform was allowed to evaporate for ten minutes before the start of compression. The rate of compression and expansion of monolayer was 10 mm min$^{-1}$. The surface pressure was recorded as a function of the mean molecular area per repeating unit (MMA).

The elasticity modulus was determined using the formula, $\kappa = A^{-1}(\delta\pi/\delta A^{-1})$ where $A$ is the area per molecule and $\pi$ is the surface pressure. At the maximum of elasticity modulus, the corresponding surface pressure and mean molecular area is $\pi_i$ and MMA$_i$, respectively.

2.3. Cross-linking of OCL monolayer

For cross-linking by dialdehyde, OCL molecules were compressed and withheld at a constant surface pressure. Thereafter, glyoxal (Sigma Aldrich, Germany; vapour pressure of glyoxal 40% at 20 °C; 24 mbar) was injected into subphase (glyoxal/caprolactone molar ratio in the subphase = 20 000) and the monolayer was withheld at a specific constant surface pressure. Glyoxal is highly water soluble and its hydrate forms, which are considered non-volatile, contain reactive carbonyl groups [36]. After the fixed period of reaction time, the barriers were opened completely to initial position of the Langmuir trough and $\pi$--A isotherms of the cross-linked layers were recorded.

2.4. Degradation by lipase

For enzymatic degradation of OCL 2D networks, lipase (Sigma, Germany) from Pseudomonas cepacia (0.007 mg ml$^{-1}$) was injected into the subphase. For degradation of the control sample, glyoxal was also added just before the injection of the enzyme into the subphase. $A_i/A_0^{-1}$, as function of time was recorded where $A_0$ is the initial surface area occupied by Langmuir film at $t = 0$ and $A_i$ is the acquired surface area after a certain time interval, $t$. The degradation experiment of Langmuir film was performed at 7 mN m$^{-1}$; 22 ± 0.5 °C.

2.5. Brewster angle microscopy (BAM) studies

BAM images were recorded with ellipsometer nanofilm_ep3 (Accurion, Gottingen, Germany) equipped with a high performance CCD camera, a 10× magnification lens with a maximum lateral resolution of 2 μm, and a 658 nm class IIIB laser source.

2.6. Interfacial infrared spectroscopy

Polarization Modulation Infrared Reflection Adsorption Spectroscopy (PM-IRRAS; KSV NIMA) was used together with a Langmuir trough (KSV NIMA) with water level compensation to study the change in chemical composition of film under spectral range of 800–4000 cm$^{-1}$.

3. Results and discussion

3.1. Langmuir film isotherms

The $\pi$--A isotherm of a non-cross-linked OCL diol monolayer was recorded first to evaluate the suitable conditions for the acetalization reaction. It shows the typical Langmuir monolayer behaviour reported for PCL [57], and is marked by a sudden reduction of surface pressure (collapse pressure ~11.2 mN m$^{-1}$; figure 1). Based on the values of static elastic modulus of control (non-cross-linked) sample of OCL diol monolayer, acetalization reaction was performed at three different surface pressure values 2, 5 and 7 mN m$^{-1}$, corresponding to the increasing concentration of OCL end groups per area. To avoid hydrolysis of ester bonds, mild reaction conditions (pH 5.7; room temperature) were realized. After the reaction, the barriers were opened to initial position of the trough and $\pi$--A isotherms were recorded to compare reacted OCL 2D film with the control sample.

Apparently, compared to the control sample, lowering of mean molecular area, an increased $\pi_i$ (table 1) and an elevated collapse pressure was observable for all cases of OCL diol monolayer reaction. Rather, a clear
Table 1. Surface pressure and mean molecular area values at the highest point of static elasticity modulus.

| OCL monolayer reaction parameters | \( \pi \) (mN m\(^{-1}\)) | MMA\(_i\)(\(\AA^2\)) |
|----------------------------------|-----------------|-----------------|
| Bi functional, OCL diol         |                 |                 |
| Control                          | 6.9 ± 0.3       | 33 ± 1.0        |
| 5 h; 7 mN m\(^{-1}\)             | 7.1 ± 0.4       | 31 ± 1.5        |
| 18 h; 2 mN m\(^{-1}\)            | 7.4 ± 0.7       | 32 ± 2.0        |
| 18 h; 5 mN m\(^{-1}\)            | 8.2 ± 0.3       | 25 ± 1.0        |
| 18 h; 7 mN m\(^{-1}\)            | 8.1 ± 0.6       | 14 ± 1.0        |
| Tetra functional, 4 arm OCL     |                 |                 |
| Control                          | 6.0 ± 0.3       | 32 ± 1.0        |
| 7.5 h; 7 mN m\(^{-1}\)           | 7.5 ± 0.5       | 18 ± 1.0        |

effect on relative reduction of MMA\(_i\) was observed for all OCL 2D films prepared depending on end-groups concentration (figure 1). Such a contraction of a monolayer at the air—water interface by cross-linking was also reported for cross-linked PDMS 2D networks [5]. For OCL 2D films, a twofold decrease in MMA\(_i\) compared to the control sample was observed only after OCL diol monolayer was reacted at a high packing density of 7 mN m\(^{-1}\) for 18 h. The acetalization reaction at air—water interface is slow and depends on the OCL molecule end-group concentration. Thus, it is expected that increasing the end-group concentration promotes cross-linking via acetal formation [58]. After reaching the collapse surface pressure, OCL 2D networks formed during 18 h reaction at 5 mN m\(^{-1}\) and 5 h reaction at 7 mN m\(^{-1}\) showed no sudden decrease, rather a plateau region. Additionally, a collapse pressure in \(\pi\)—A isotherm was not observable until the end of compression for the OCL 2D film formed at the high packing density at 7 mN m\(^{-1}\) for 18 h reaction time. The shifting of collapse pressure of all OCL 2D films to a higher value compared to the control sample proves an increase in stability of the film due to acetalization reaction. To prove the acetalization reaction, Polarization Modulation-Infrared Reflection Absorption Spectroscopy (PM-IRRAS) spectra under different reaction times were recorded. The spectrum (figure 2(a)) before injection of glyoxal had no discernible peaks and was used as the reference spectrum, i.e. all spectra were normalized with respect to the spectrum at \(t = 0\). The PM-IRRAS signal of the OCL 2D network for visualizing acetal links was weak owing to molecular level ultrathin film. Nevertheless, the acetal doublet peaks (1060 and 1100 cm\(^{-1}\)) were clearly distinguishable. The peaks at 1100 and 1060 cm\(^{-1}\) were absent in the non-cross-linked OCL diol monolayer (figure 2(a)) and became visible in all spectra recorded after 21 h glyoxal reaction (figure 2(b)) with the monolayer. The bands are characteristic for acetals and attributed to symmetric COCOC (1100 cm\(^{-1}\)) and antisymmetric COCOC (1060 cm\(^{-1}\)) stretching.

Further evidence of occurrence of cross-linking was demonstrated by 4 arm OCL. Compared to 2D film of OCL diol, a ~2 fold decrease in MMA\(_i\) was reached in 2D film of 4 arm OCL in a relative less
duration of acetalization reaction (figure 3). This effect can be correlated to the structure and chemical composition of the molecules. In comparison to linear bifunctional OCL diol molecule, in tetrafunctional OCL, 4 arms of the OCL are connected to a central molecule which can be assumed as a branching centre. Hence, when the duration of the acetalization reaction for 4 arm OCL is decreased to 7.5 h (~60% time less compared to 18 h), a similar progression of isotherm as 18 h reacted bifunctional OCL diol monolayer at 7 mN m\(^{-1}\) is observed.

3.2. Crystallization behaviour of OCL 2D network

The crystallisation behaviour of OCL in restricted geometries is well studied and is affected by molar mass, film thickness, temperature, the field for chain diffusion and many other factors [50, 57, 59]. At the constant surface pressure of 10.5 mN m\(^{-1}\), which is between \(\pi_1\) (6.9 mN m\(^{-1}\)) and the collapse pressure (11.2 mN m\(^{-1}\)), the non-cross-linked OCL monolayer (control) shows an area reduction (figure 4(a)) due to formation of typical small sized 3D domains under BAM (figure 5(a)). These 3D domains of OCL seen as bright regions in the BAM image are the spherulites, which are surrounded by the amorphous layer (dark region). To study the crystallization behaviour of OCL 2D networks, we cross-linked OCL monolayers at 7 mN m\(^{-1}\) (in absence of spherulites) for different reaction times and then compressed the layers to the elevated surface pressure of 10.5 mN m\(^{-1}\).

Introduction of branching structure in PCL bulk systems lowers crystallization ability and \(T_m\) (melting temperature) while it increases the mechanical stability [60–62]. Since random cross-linking of OCL molecules in Langmuir monolayer presumably leads to branching of OCL chains to form a 2D network, we expect that a retardation of the crystallization process can provide an indirect proof of cross-linking of OCL monolayer.

For OCL 2D networks formed at 5 h reaction time at 7 mN m\(^{-1}\), the normalized area reduction at 10.5 mN m\(^{-1}\) was decreased compared to the control sample (figure 4(b)), with accompaniment of large sized spherulites observed in BAM (figure 5(b)). Such an increase in lateral dimensions can be asserted to an increased molar mass of the molecules after cross-linking and therefore such large spherulites, typically formed for intermediate molar mass (~8 kDa) of OCL molecules were observed [57].

On the contrary, the relative area reduction at 10.5 mN m\(^{-1}\) was minimal for the OCL 2D network formed at 18 h reaction time at 7 mN m\(^{-1}\) (figure 4(b)), with no visible crystals in BAM images (figure 5(c)). This strongly projects that cross-linking impedes the surface pressure induced lateral crystallization of OCL monolayer. By connection of OCL chains by acetal cross-links, molar mass in the monolayer increases while due to formation of cross-linking netpoints, the OCL chain mobility is decreased leading to a retarded crystallization. However, lateral surface pressure induced crystallization in ultrathin films is a dynamic process and cannot be directly interpreted

Figure 3. \(\pi\)–A isotherms of 4 arm OCL (tetrafunctional) with and without glyoxal reaction at 22 ± 0.5 °C on aqueous subphase (pH = 5.7). Vertical dotted lines represent MMA, and is calculated from the maximum of the elasticity modulus.

Figure 4. Area reduction of OCL 2D monolayer with respect to time at different isobaric surface pressures (a). Area reduction at 10.5 mN m\(^{-1}\) (b) for OCL 2D networks formed at different reaction durations at 7 mN m\(^{-1}\); 22 ± 0.5 °C on aqueous subphase (pH = 5.7). The relative surface area reduction of isobaric experiment, \(A_r[\%] = (A_s/A_0)^{-1}-100\).
and therefore can be seen only as an indirect proof of cross-linking.

A further insight into the crystallization behaviour is available by recording the expansion $\pi$–$A$ isotherms (figure 5). Expansion isotherms formed by opening the Langmuir trough barriers after the end of compression at a constant rate indicate the melting behaviour of surface pressure induced spherulites. The spherulites of the control sample dissolve during the expansion of the monolayer, where the polymer chains of the spherulites continuously unfold to render initial $'2D'$ monolayer state. This marks a faster initial decrease in surface pressure in the expansion isotherm followed by a plateau around 8.5 mN m$^{-1}$ (figure 5(a)). Such a similar progression of the expansion isotherm was also seen by OCL 2D networks formed after 5 h cross-linking at 7 mN m$^{-1}$ (figure 5(b)). However, for OCL 2D network formed after 18 h cross-linking at 7 mN m$^{-1}$, a plateau in the expansion isotherm was not observable, while the curve follows a similar trend as its compression cycle (figure 5(c)).

3.3. Degradation of OCL 2D networks

Figure 6 shows enzymatic degradation isotherms of OCL 2D networks formed under different cross-linking reaction durations at the surface pressure of 7 mN m$^{-1}$, in the absence of any 3D domains in the

![Figure 5. Compression-expansion $\pi$–$A$ isotherms and Brewster angle microscopy (BAM) images of (a) control sample and OCL 2D networks formed at (b) 5 h and (c) 18 h reaction times at 7 mN m$^{-1}$ (pH = 5.7; 22 ± 0.5°C). Dotted lines represent the expansion isotherms. BAM images are acquired at 30 ± 1.0 min at 10.5 mN m$^{-1}$ (scale = 100 $\mu$m).](image)

![Figure 6. Lipase (P. cepacia) enzymatic degradation of OCL 2D networks under isobaric conditions (7 mN m$^{-1}$) on aqueous subphase pH 5.7; 22 ± 0.5°C.](image)

![Figure 7. OCL diol monolayer at 7 mN m$^{-1}$; pH 2.5 in subphase with glyoxal (glyoxal/caprolactone molar ratio in the subphase = 20 000).](image)
layer. The catalytic triad of the enzyme lipase cleaves OCL chains into water-soluble fragments, causing monolayer area reduction. For control sample, after injection of lipase into the subphase (time = 0), a fast degradation was detected. It was previously shown that OCLs below molar masses of 10 000 g mol⁻¹ present identical degradation isotherms. On the contrary, the degradation isotherm for OCL 2D networks shifts substantially compared to the control sample. The slowest degradation rate was observed for OCL 2D networks formed after 18 h reaction time at 7 mN m⁻¹. Such a dense 2D network with modified and interconnected end groups of OCL molecules possibly hinders interaction of enzyme with OCL segments or has slow formation of water-soluble OCL fragments.

3.4. Reversibility of the cross-links

Figure 7 shows the behaviour of OCL diol monolayer at acidic pH of 2.5 with and without the presence of glyoxal in the subphase. A slower area reduction of OCL diol monolayer at pH 2.5 in presence of glyoxal suggests an interplay of acidic hydrolysis of ester bonds and the cross-linking reaction phenomenon. To prove that the acetal cross-links in the OCL 2D network are reversible, the reverse cross-linking reaction was promoted for retrieval of free OCL molecules by altering the pH and π–A isotherm (figure 8(a)) was recorded.

OCL 2D network was formed at 7 mN m⁻¹ after 18 h of glyoxal reaction of OCL diol monolayer in aqueous subphase of pH 5.7. To carry out the reverse acetalization reaction, the pH was shifted to 2.5 for the next 9 h. The barriers were opened to initial Langmuir trough position and compression-expansion isotherms were recorded (figure 8(a)). The π–A curve of OCL 2D network after alteration to acidic pH (figure 8(a)) deviates from the π–A curve of OCL 2D network formed at pH 5.7 (figure 5(c)). Indeed, it follows an identical slope with the control sample (figure 5(a)), with observance of collapse pressure at ~13.5 mN m⁻¹.

Change in crystallization behaviour further validates the reversibility of cross-links in the network. In contrast to the BAM image of OCL 2D network which shows no 3D domains at 10.5 mN m⁻¹ (figure 5(c)), the BAM image for OCL 2D network that underwent reverse acetalization reaction (figure 8(b)) shows occurrence of relatively larger spherulites comparable to the ones observed in non-cross-linked OCL layer at 10.5 mN m⁻¹ (figure 5(a)). This implies that alteration to acidic pH caused a decrease in the covalent acetal link density of the cross-linked OCL 2D network, allowing OCL chains to fold and participate again in the lateral crystallization process.

The similar compression-expansion π–A isotherm behaviour as the control sample and occurrence of spherulites implies an increase in the conformational freedom in OCL chain segments and enhanced crystallization degree in the film by the decrease of acetal cross-link density. Therefore, acetal links orchestrated the forming of a reversible OCL 2D network that is reversible by means of pH.

4. Conclusion

The 2D cross-linking of hydroxyl end-capped OCL monolayer by glyoxal at the air–water interface was demonstrated by changes in π–A isotherms, film crystallization behaviour and film degradation rate. Additionally, interfacial infrared spectroscopy demonstrated the acetal bond formation in the OCL 2D film. After cross-linking, π–A isotherm displayed a higher reduction in the mean molecular area for OCL 2D networks formed under high OCL molecular packing density and longer reaction time. Moreover, π–A isotherms demonstrated that reduction in mean molecular area is achieved faster for the 2D network based on tetrafunctional OCL tetrol compared with
bifunctional OCL diol. Reversibility of acetal cross-links in the OCL 2D network is demonstrated by altering the subphase pH to promote the reverse reaction. Such a film exhibited comparative crystallization and π–π isotherm of non-cross-linked OCL monolayer.

Such 2D networks of polymers can give fundamental insights on physical chemistry and rational design of bulk polymer networks. Further work on covalent functionalization of unreacted end-groups will explore how such a stimuli responsive 2D polymer network can be used for delivery of bioactive substances, as coating for medical devices and as functionalized substrates for studying cell behaviour.

Acknowledgments

This work was financially supported by the Helmholtz Graduate School for Macromolecular Bioscience and the Helmholtz Association through programme-oriented funding.

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