2-Dimensional Network Formation from a Graft Copolymer at the Air-Water Interface

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Summary: The UV induced cross-linking of a well defined graft copolymer polynorbornene-*g*-poly(ethylene oxide) at the air-water interface has been investigated. Network formation has been monitored qualitatively by observing changes in surface pressure with UV exposure time working under constant area conditions. Surface film concentration has been used as the design parameter to manipulate initial film organization, and consequently position of the functional groups. Exposure of the copolymer film to UV light at different surface concentrations in the liquid condensed region shows the closer the molecules pack together the faster the cross-linking reaction, while no cross-linking occurs when the molecules are far apart in the liquid expanded state.

Keywords: air-water interface; crosslinking; monolayers; photopolymerization

Introduction

A great deal of interest has been directed towards self-assembled surfactant and polymer films at the model hydrophilic-hydrophobic, air-water interface as they form ordered structures by film compression.[1,2] The study of Langmuir monolayers is multidisciplinary and transcends disciplines with applications in many important areas such as chemo- and biosensor[3,4] developments, building blocks for nanomoterials,[5] models for membrane biophysics and for studies of chemical and biological reactions in two dimensions.[6] Monolayers can be physically adsorbed onto a solid substrate surface using the Langmuir Blodgett or reverse Schaefer methods, thus also providing a route for the fabrication of films at the air-solid interface. Monomolecular films are consequently well studied at the air-liquid interface, however their lack of stability (poor long term stability, low mechanical and thermal stability) is a limiting factor in their development. For example monolayers have to be mechanically stable so they stay intact during and after transfer to a solid surface, or films need to be resistant to external stimuli such as wind for reservoir water evaporation applications.[7] Cross-linking of the film via *in situ* polymerization could provide an attractive solution[8,9] to overcome the limitation of the low stability of Langmuir films toward mechanical, thermal, and environmental attack.[10,11]

Monomeric Langmuir films can be polymerized by irradiation, most commonly with ultraviolet light, although higher energy radiation has also been used.[12] When polymerization is initiated at the air-water interface, it can be followed in situ by measuring the changes in mean molecular area and barrier speed[13,14] using the Langmuir balance. Polymerization typically contracts the film area, changing the molecular arrangement of the film and varying macroscopic parameters such as surface potential and viscosity.[15,16] Polymerization studies in lipopolymer monolayers have revealed that film shrinkage due to polymerization could be reduced by starting with a polymer monolayer instead of a bifunctional amphiphile,[17] thus allowing the study of polymerization processes at

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constant area without having to be concerned about film cracking. Two dimensional network formation based on polymerization of surfactants functionalized with reactive groups, such as styrene,[18] have been carried out successfully showing an increase in apparent surface viscosity of the film during polymerization.

In this work we have taken advantage of the propensity of a functionalised amphiphilic macromolecule to self-assemble at the air-water interface, and have explored its spontaneous transition from a molecular monolayer to a two-dimensional cross-linked network via light stimulated polymerization. More specifically a graft copolymer, polynorbornene-*g*-poly(ethylene oxide) (PNB-*g*-PEO) (Figure 1), has been spread at the air-water interface where the exposed double bonds in the hydrophobic backbone can undergo polymerization via light activation. Here we discuss how the reaction is influenced by the initial monolayer organisation and the intensity of the UV light.

Materials and Methods

Materials

A well defined graft copolymer polynorbornene-*g*-poly(ethylene oxide), (PNB-*g*-PEO), has been synthesized using a combination of anionic and ring opening metathesis polymerisation methods. The molecular structure of the monomeric unit of the copolymer is given in Figure 1. Details of the synthesis procedure and material characterisation are presented elsewhere.[19,20] Suffice to say here that the PEO grafts and backbone have a degree of polymerization of 25 and 50 respectively and the copolymer has a polydispersity of 1.26 and a molecular weight of 74000 g mol^{-1}. Spectroscopic-grade chloroform (Sigma-Aldrich) was used as the spreading solvent and the subphase for all the experiments was doubly distilled and deionised water (18 Ω cm^{-1}).

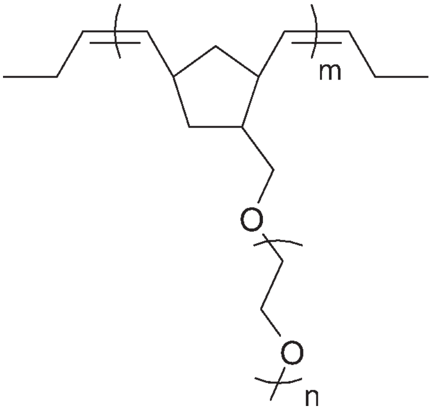

Figure 1.
Chemical structure of polynorbonene-*g*-poly(ethylene oxide) graft copolymer where m = 50 and n = 25.

Surface Pressure-Surface Concentration Isotherms

Surface film characterization was carried out using a NIMA 301 Langmuir trough (Coventry, UK) equipped with two moving barriers and a Wilhelmy plate (NIMA chromatography paper) for measuring surface pressure. The trough was placed on an in-house built vibration free table and dust free case to minimize the risk of film disruption or contamination. 1 mg ml^{-1} solutions were prepared by using chloroform HPLC grade (Sigma-Aldrich) as solvent and typically 10–30 μl of the solution were deposited evenly across the water surface using a 50 μl Hamilton syringe (Sigma-Aldrich). Chloroform was allowed to evaporate for 20 minutes to ensure no residual solvent remained. The subphase temperature was controlled at $25 \pm 0.1\,^{\circ}$C by circulating water under the trough. Surface pressure-surface concentration isotherms were collected by symmetrically compressing the film at a rate of 10 cm^2 min^{-1} and monitoring changes in surface pressure.

Polymerization Reaction

The polymerization of PNB-*g*-PEO was initiated by placing a UV lamp (254 nm) above the monolayer in the Langmuir trough ($\approx$15 cm) and recording changes in surface pressure under conditions of constant area. The procedure involves setting a surface pressure and holding the barriers at that corresponding molecular area (i.e. barrier speed 0 cm^2 min^{-1}). After 5 minutes equilibration time the UV lamp is switched on, and the Wilhelmy plate records the changes in surface pressure over time. The effect of initial film organisation was examined by selecting four starting surface pressures reflecting different areas of the isotherm. The effect of UV light intensity on the reaction kinetics has been studied by reducing UV intensity by covering the lamp with a layer of parafilm.

All isotherms and UV initiated experiments were repeated at least three times to ensure reproducibility. Between experiments the trough was cleaned with chloroform and rinsed several times with distilled and deionised water (18 Ω cm^{-1}).

Results and Discussion

Graft Copolymer Films

Initial work focused on characterising the behaviour of the graft copolymer at the air-water interface before activating the cross-linking reaction and a typical surface pressure-surface concentration isotherm is given in Figure 2. Due to limitations of trough area we could not monitor the graft copolymer isotherm in a single compression, consequently Figure 2 is comprised of 3 single compressions overlapped using surface concentration as design parameter. It is evident that the copolymer forms a stable film that self-assembles into two different organizational states during compression; liquid expanded (*LE*) and liquid condensed (*LC*). In the *LE* region a steep rise in the surface pressure is observed over a narrow concentration range (0.2–1.5 mg m^{-2}), thereafter the increase in surface pressure is reduced. The transition from *LE* to *LC* phase corresponds to a surface concentration of ~1.5 mg m^{-2} and a surface pressure of ~14 mN m^{-1}. Upon further compression the isotherm reaches a plateau value of circa 18 mN m^{-1}. This flat part of the curve has been traditionally considered as the collapse point of the monolayer,[21] where further compression forces the molecules out of the plane and into a 3-dimensional structure.[22] This has already been confirmed by neutron reflectometry studies.[19,20] Consequently we will consider that the collapse surface pressure for the copolymer is circa 18 mN m^{-1}. The

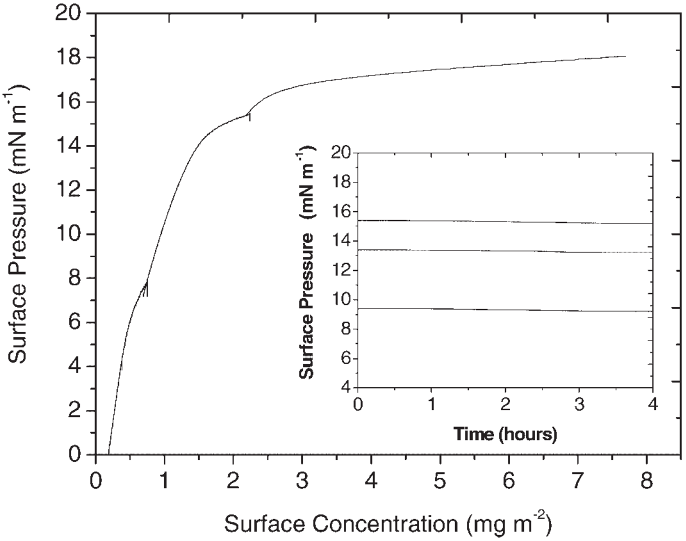

Figure 2.
Surface pressure-surface concentration isotherm of PNB-*g*-PEO graft copolymer at the air-water interface. The insert shows surface pressure as a function of time for three starting surface pressures 10, 13.5 and 15.5 mN m^{-1}.

stability and ageing of the film has been investigated for three different starting surface pressures (10, 13.5 and 15.5 mN m^{-1}) by monitoring surface pressure as a function of time. No significant change in surface pressure was observed for any of the three surface pressures (insert in Figure 2). This indicates the film is stable, at least overnight, at the air-water interface in both the *LE* and *LC* states. Compression-expansion experiments have also been undertaken to determine whether the film exhibits hysteresis. A range of target pressures were investigated that cover the full range of the isotherm ($\Pi = 0$–14 mN m^{-1}). For all target pressures, no hysteresis was observed i.e. the isotherms obtained during expansion and a further compression cycle were superimposable with the isotherm obtained during the first compression. This indicates that the surface film formation is macroscopically reversible.

Cross-Linking

Exposure of the copolymer films to UV light (254 nm) initiated a cross-linking reaction that has been monitored qualitatively by observing changes in surface pressure over time under conditions of constant area in a controlled nitrogen atmosphere (Figure 3). Due to the stability of the graft copolymer at the air-water interface, the observed decrease in surface pressure as a function of exposure time is not due to a loss of material at the surface, but instead is indicative of the copolymer film shrinking in two dimensions due to cross-links forming between the copolymer backbone units. The formation of these cross-links leads to the formation of a 2-dimensional network. Since no photoinitiator has been added we can consider that PNB-*g*-PEO undergoes a free radical polymerization mechanism.

Figure 3 compares the change in surface pressure over time for three different starting surface pressures; 16.6, 15.8, 14 mN m^{-1}. The slope of each data set gives an indication of the kinetics of the cross-linking reaction. It is evident that a sharper reduction, and hence faster kinetics, in surface pressure is observed for initial surface pressures of 15.8 and 16.6 mN m^{-1} than for 14 mN m^{-1}. Such differences can be correlated to the surface pressure isotherms where the transition from liquid expanded to liquid condensed is observed at ~14 mN m^{-1}. Consequently, the faster

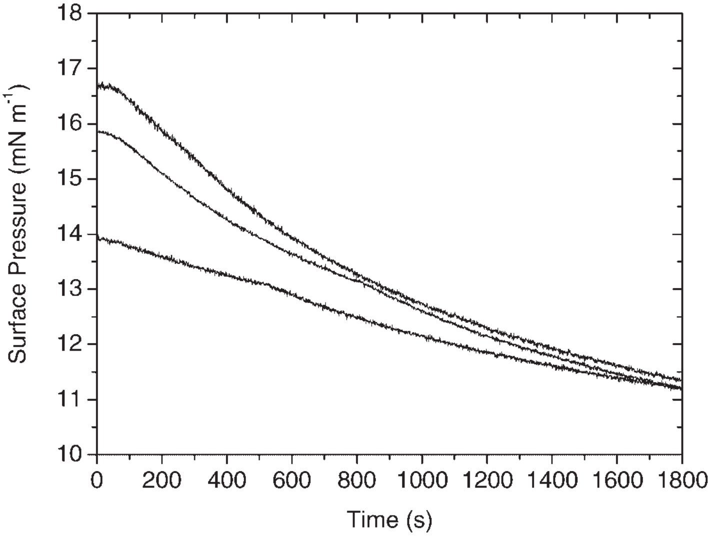

Figure 3.

Change in surface pressure as a function of time during UV initiated polymerization for three different starting surface pressures (16.6, 15.8, 14 mN m$^{-1)}$ of the graft copolymer in a N_2 atmosphere.

kinetics can be attributed to the closer packing of the PNB-*g*-PEO molecules in the condensed state, where functional groups are closer to each other, which facilitates the reaction between copolymers. The rate of the cross-linking reaction decreases over time for all initial surface pressures in the liquid condensed region. After a time of circa 1400 seconds all three values for surface pressure converge at a value of circa 12.5 mN m^{-1}. Subsequently only a slight decrease in surface pressure is observed. This leads us to believe that at this point, the reaction has reached equilibrium, and consequently we estimate that the reaction time is ~1400 s. When the initial starting pressure was in the *LE* region ($\pi < 13$ mN m^{-1}) no reduction in surface pressure was observed, indicating no covalent cross-links formed. This is likely to be due to the copolymer molecules, and hence their functional groups, being too far apart to react and/or the PEO grafts shielding the functional groups as they have space to radiate from the hydrophobic backbone.[19,20]

In order to eliminate the possibility that our observations are occurring due to any oxidation process, network formation has been monitored in both N_2 and O_2 atmospheres (Figure 4). It is clear there is no significant difference over time for each of the two different starting surface pressures (14 and 15.8 mN m^{-1}) for the different atmospheres; only a slight increase in the overall reaction rate under O_2 is observed in comparison to N_2. Consequently minimal oxidation of the copolymer is occurring. Moreover, Figure 4 indicates that O_2 does not act as radical polymerization inhibitor, as similar reductions in surface pressure are observed over time. However, after a reaction time of circa 1400 s, the curves reach different final surface pressures depending on the surrounding atmosphere; 12.5 and 11 mN m^{-1} for N_2 and O_2 atmospheres respectively. This suggests that the film shrinks further, hence has formed more cross-links, when the polymerisation occurs in the O_2 atmosphere.

Effect of Lamp Intensity

The effect of UV light intensity on the cross-linking reaction was examined by placing a single layer of parafilm over the light and monitoring changes in surface pressure over time. Results again showed a reduction in surface pressure as a function

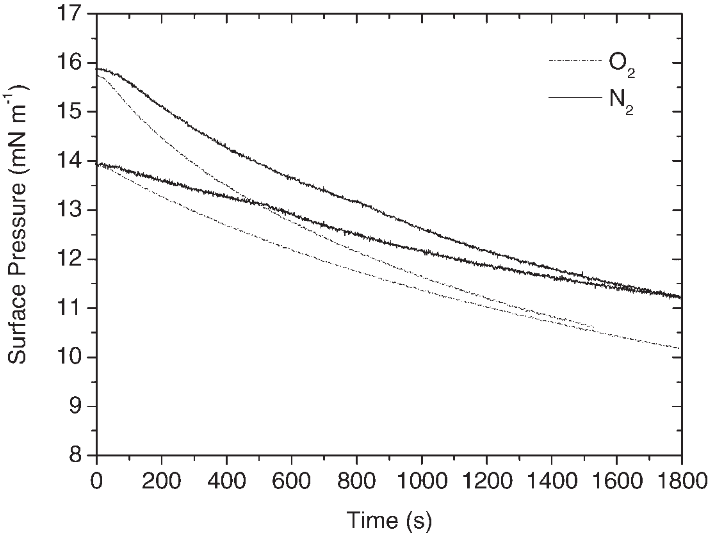

Figure 4.

Change in surface pressure as a function of time during UV initiated polymerization of the graft copolymer in O_2 (. . .) and N_2 (—) atmospheres for the initial surface pressures of 14 and 15.8 mN m^{-1}.

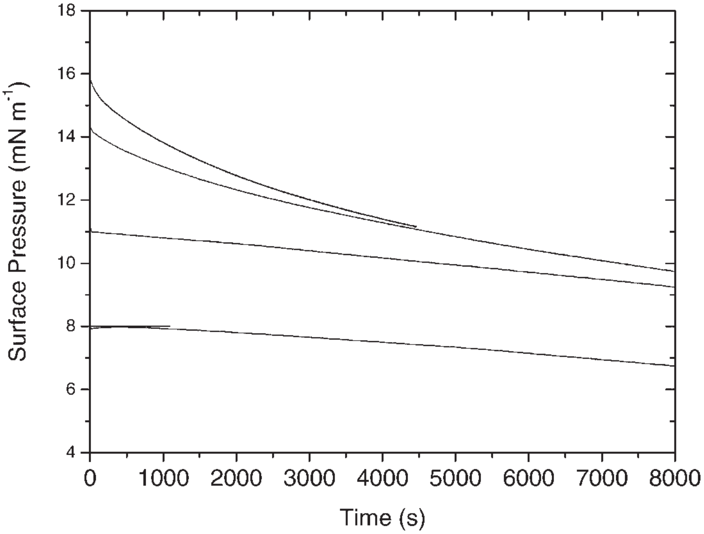

Figure 5.
Change in surface pressure as a function of time during reduced intensity UV initiated polymerization for four different starting surface concentrations (16.6, 15.8, 14 mN $m^{-1)}$ of the graft copolymer in a N_2 atmosphere.

of reaction time for surface pressures within the liquid condensed region of the monolayer (15.8 and 14.2 mN m^{-1}). However, it is clear that the cross-linking reaction occurs over significantly longer timescales and an equilibrium value of surface pressure is only approached at ~7000 seconds (in comparison to 1400 seconds for full UV intensity). For surface pressures in the *LE* regime (11 and 7.8 mN m^{-1}) an almost linear response is obtained over time, confirming no reaction takes place when working in the *LE* regime as discussed previously.

Since the reaction with reduced UV intensity takes significantly longer we were able to collect surface pressure-molecular area isotherms at different time intervals during photopolymerization. As the cross-linking reaction proceeds, the isotherm shifts to lower molecular areas. During the initial stages of reaction (i.e. t = 20 (1200 s) and 40 mins (2400 s)) the cross-linked monolayer still exhibits an *LE* to *LC* phase change with the transition shifting to lower molecular areas over reaction time; 23.5 to 18 and 16 Å^2 molecule^{-1} at 0, 20 and 40 mins. This indicates that the film shrinks and the molecules pack more closely during UV exposure. To gain further insight into film behaviour the compressibility of the monolayer was extracted from the surface pressure-molecular area isotherms using Equation (1),[23]

$$\chi = -\frac{1}{A} \times \left(\frac{\partial A}{\partial \pi}\right)_T \tag{1}$$

where A is the area per molecule and χ is the compressibility factor. Using Equation (1), χ can be calculated for a given molecular area, A, by extrapolating the slope of the isotherm at that particular point. Table 1 gives the isothermal compressibility at 25 °C of the graft copolymer monolayer in the *LC* state at A = 10 Å^2 molecule^{-1} as a function of UV exposure time. A clear decrease in monolayer compressibility is observed over exposure time as χ decreases from 0.94 to 0.07 m^2 mN^{-1} for the monolayer

Table 1.
Monolayer isothermal compressibility at T = 25 °C and A = 10 Å^2 molecule^{-1}.

UV exposure time (min)	$\left(\frac{\partial \pi}{\partial A}\right)_T$	$\left(\frac{\partial A}{\partial \pi}\right)_T$	χ (m^2 mN^{-1})
0	−0.11	−9.44	0.94
20	−0.21	−4.75	0.48
40	−0.36	−2.75	0.28
210	−1.48	−0.68	0.07

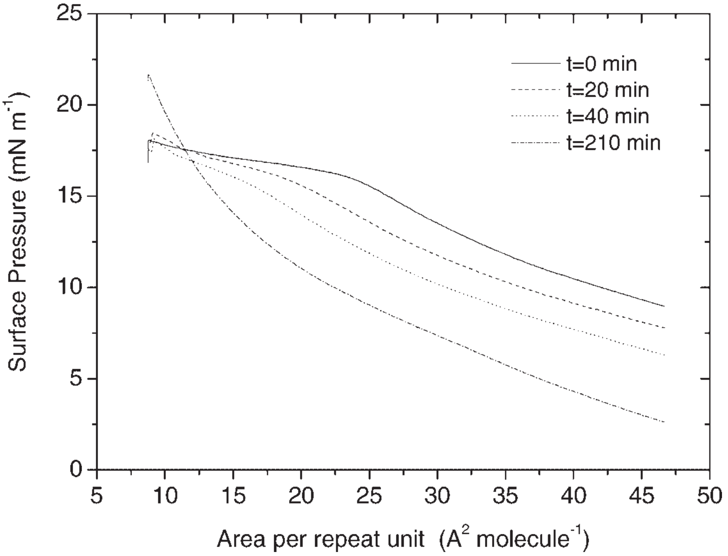

Figure 6.
Surface pressure-molecular area isotherms of the resulting graft copolymer network after different UV exposure times.

before and after network formation respectively. This confirms that the number of cross-links between different macromolecules increases over time, which gives rise to a network that is increasingly difficult to compress.

To highlight the sensitivity of the UV reaction, network formation was monitored under constant surface pressure conditions and results are presented in Figure 7. It is clear that at initial times a sharp decrease in molecular area is recorded as soon as the

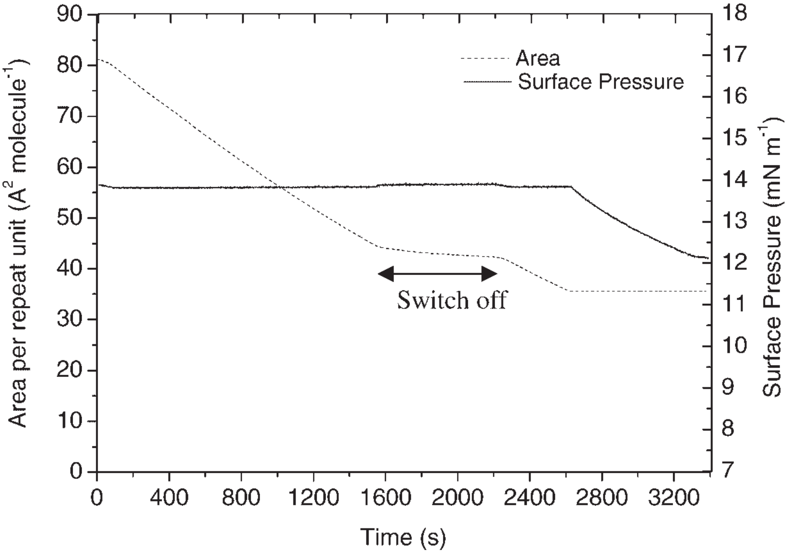

Figure 7.
Change in molecular area and surface pressure as a function of time during UV initiated polymerization of the graft copolymer under initial conditions of constant surface pressure.

lamp is switched on. However the reaction stops immediately when the UV lamp is switched off at 1600 seconds as the molecular area remains constant. A further decrease in molecular area is observed as soon as the UV lamp is switched back on. At ~2600 seconds the area cannot be reduced further hence a reduction in surface pressure is observed indicating the cross-linking reaction is ongoing. This responsive character, in combination with the lack of sensitivity of the reaction towards oxygen, is characteristic of radical polymerization.[24,25] Consequently we propose that the graft copolymer forms a 2-dimensional network via UV initiated radical polymerization.

Conclusions

PNB-*g*-PEO graft copolymer forms stable films at the air-water interface and molecules are either in a liquid expanded or liquid condensed phase. Cross-linking can be induced via UV-light initiation and the kinetics of network formation are dependent on both initial surface pressure, and hence molecular organisation, and intensity of the UV lamp. When in the liquid condensed state, increasing the initial surface pressure has been found to increase the overall reaction rate. As the UV induced reaction proceeds, the reaction kinetics decrease rapidly initially then more gradually before the reaction finally reaches an identical equilibrium state after a time dependent on UV intensity. No cross-linking reaction occurs when the molecules are in the liquid expanded state, presumably because the reactive groups are either too far apart or the PEO grafts are shielding them. The rate of the cross-linking reaction is dependent on the intensity of the UV intensity where a faster rate is obtained at higher UV intensities. Also no discernable effect was observed when the network was formed in O_2 or N_2 atmospheres.

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