

## Langmuir Film Polymerization of 1,22-Bis(2-aminophenyl)docosane: A Two-Dimensional Cross-linked Polyalkylaniline

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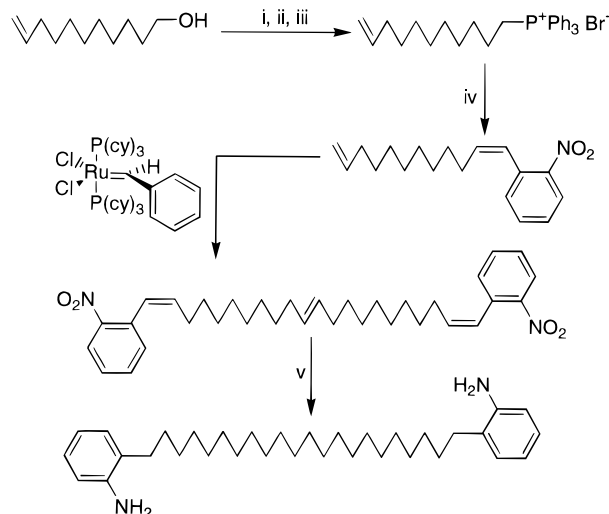
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Ultrathin films have been proposed for many applications such as in nonlinear optical<sup>1–5</sup> and electroluminescent devices<sup>6,7</sup> and sensors.<sup>8,9</sup> However, most applications require the films to be mechanically, thermally, and chemically stable under environmental conditions, which is often difficult to achieve. Polymeric systems are usually more stable than low molar mass analogues due to covalent bonding in the film plane and are often preferred.<sup>10</sup> Further, network polymers in 3-dimensions are generally more stable to thermal and physical stress than their non-cross-linked counterparts, and therefore, free-standing monolayers of this type should also have improved stability. Though the potential for these types of films is great, there are few published reports that deal with Langmuir films that form 2-dimensional network polymers.<sup>11–15</sup> Self-assembled organic monolayers on solid substrates show some of these characteristics, but require specific substrates and therefore cannot be a general method to produce stable, free-standing films.<sup>16–18</sup>

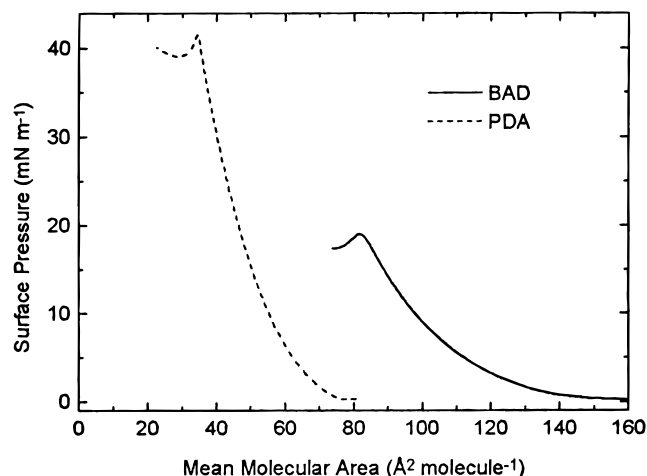
This communication presents the Langmuir film polymerization of a dipolar monomer, 1,22-bis(2-aminophenyl)docosane (BAD), which forms a 2-dimensional network polymer of polyalkylaniline. The surface behavior of BAD is presented and compared with that of the monopolar surfactant, 2-pentadecylaniline (PDA), which is routinely polymerized in Langmuir films.<sup>19–21</sup>

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### Scheme 1



(i) TsCl, pyridine, and  $\text{CHCl}_3$ ; (ii) LiBr, acetone, and heat; (iii)  $\text{PPh}_3$ ,  $\text{CH}_3\text{CN}$ , and heat; (iv) potassium *tert*-butoxide, 2-nitrobenzaldehyde, and THF; (v)  $\text{H}_2$ , 10% Pd on carbon, and 95% ethanol.

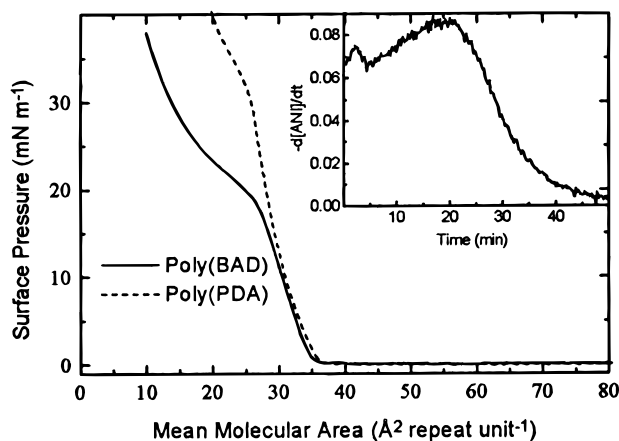


**Figure 1.** Surface pressure ( $\pi$ ) vs mean molecular area ( $A$ ) isotherms of BAD and PDA on 0.01 M  $\text{H}_2\text{SO}_4$  at 25 °C.

Scheme 1 shows the synthetic route by which BAD was prepared. In this route, two molecules of 1-(2-nitrophenyl)-1,11-dodecadiene were coupled at the terminal olefin by a metathesis reaction using a ruthenium alkylidene catalyst.<sup>22</sup>  $^1\text{H}$  NMR studies of this coupling reaction suggest that this self-metathesis reaction occurs selectively at the terminal olefin and not at the olefin next to the aromatic ring. PDA was synthesized by a route previously reported.<sup>19</sup>

The surface pressure ( $\pi$ ) vs mean molecular area ( $A$ ) isotherms of BAD and PDA on a 0.10 M  $\text{H}_2\text{SO}_4$  subphase had pressure onset areas at ca. 150 and 74  $\text{\AA}^2$  molecule<sup>-1</sup>, respectively (Figure 1). As expected, the pressure onset area of BAD was about twice that of the PDA, indicating that both of the anilinium groups were adsorbed to the interface with the long chain oriented away from the surface. Isobaric creep experiments of the monomers showed that the BAD film was more stable over time than PDA under similar conditions. For example, at a surface pressure of 15  $\text{mN m}^{-1}$ , the monolayer film of BAD crept ca. 0.048  $\text{\AA}^2$  anilinium

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**Figure 2.** Surface pressure ( $\pi$ ) vs mean molecular area ( $A$ ) isotherms of poly(BAD) and poly(PDA) on 0.01 M  $\text{H}_2\text{SO}_4$  and 0.03 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  at 25 °C.  $-\text{d}[\text{ANI}]/\text{dt}$  vs time for the polymerization of BAD at 10  $\text{mN m}^{-1}$  and 25 °C.

$\text{unit}^{-1} \text{min}^{-1}$ , while PDA had a film creep of  $0.30 \text{ \AA}^2 \text{ anilinium unit}^{-1} \text{min}^{-1}$ .<sup>23</sup>

The Langmuir polymerization of PDA and the experimental details have been reported.<sup>19</sup> The polymerizations of BAD and PDA were carried out on a 0.10 M sulfuric acid and 0.03 M ammonium peroxydisulfate subphase solution. The surface pressure was held constant while the film area was monitored over time. In the case of aniline-type monomers, the area that a polymer repeat unit occupies at the interface is less than that of the monomer,<sup>20</sup> making this a useful technique to monitor the reaction kinetics.

The polymerization rate can be calculated from the change in  $A$  of the surfactant at a constant applied surface pressure from the equation<sup>19</sup>

$$-\frac{[\text{ANI}]}{\text{dt}} = \left(\frac{2}{A}\right) \left(\frac{\text{d}[(A_0 - A)/(A_0 - A_\infty)]}{\text{dt}}\right)$$

where  $[\text{ANI}]$  is the concentration of anilinium groups at the interface and  $A_0$  and  $A_\infty$  are the surface areas of the monomer at the beginning and end of the reaction. Figure 2 shows the polymer formation rate with time. The plot indicates that the polymerization rate increased with time early in the reaction, suggesting that autoacceleration occurred. This effect has been observed in the solution polymerization of aniline<sup>24</sup> and in the Langmuir film polymerization of PDA.<sup>19,20</sup> The  $\pi$ - $A$  isotherm of poly(BAD) had a pressure onset area of ca.  $70 \text{ \AA}^2 \text{ molecule}^{-1}$  or  $35 \text{ \AA}^2 \text{ repeat unit}^{-1}$ , while the onset area of poly(PDA) was  $35 \text{ \AA}^2 \text{ repeat unit}^{-1}$  (Figure 2).

Once the polymerization was complete, the polymer could be expanded and compressed with little hysteresis. A dark blue material was collected from the interface by first compressing the polymer film to ca. 2 cm with the trough barriers, and then a glass frit connected to vacuum was used to pull the material from the surface (Figure 3). Unlike poly(PDA), this material was gel like and could be essentially collected in one piece. The material was insoluble in the solvents that usually dissolve polyaniline (NMP and sulfuric acid) and in the solvents typically used for poly(PDA) (chloroform and THF), making molecular weight analysis by GPC impossible.



**Figure 3.** Removal of poly(BAD) from the surface of the Langmuir trough. The polymer comes off the subphase in self-supporting, elastic sheets which easily draw down to fibers.

The infrared spectrum of the poly(BAD) polymerized on a 0.2 M HCl and 0.03 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  subphase reveals the characteristic C-C ring stretching of the polyaniline backbone at 1498 and  $1597 \text{ cm}^{-1}$ . The asymmetric and symmetric stretch and bending vibrations of the alkyl groups were recorded at 2924, 2852, and  $1461 \text{ cm}^{-1}$ , respectively.

The two polymerizable anilinium groups of BAD, allow for it to add to the polymer backbone in several ways. One possible ordering would involve incorporating the anilinium groups such that the linked groups are next to each other in a single polymer chain. This ordering would probably lead to a material with mechanical properties similar to those of poly(PDA). A second possible ordering would incorporate connected anilinium groups into the backbones of different polyaniline chains, which would lead to cross-linked polyaniline. The insolubility of the material and the fact that it could be lifted from the aqueous interface in one piece suggests that the second ordering is occurring to an appreciable extent and that a cross-linked polymer was formed. Such an architecture is an example of a 2-dimensional network polymer connected in two ways. A layer of rather stiff connections forms the polyaniline chains; these are sandwiched between an aqueous subphase and a layer of flexible alkyl chains that connect the backbones. Varying the length of the alkyl chain or copolymerizing it with PDA may provide an interesting means of controlling the ultimate porosity of the resulting network polymer.

Preliminary results show that BAD can be polymerized to form a novel insoluble organic material in a Langmuir film. The surface behavior of this dipolar molecule is much like that of PDA under similar conditions, while the polymer exhibits an increase in its mechanical strength compared to that of poly(PDA). This increase in mechanical strength could lead to a wider acceptance of highly ordered LB films in technical applications.

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**Supporting Information Available:** Synthetic details and characterization of each step in Scheme 1, including  $^1\text{H}$  and  $^{13}\text{C}$  NMR, MS, melting point, and CHN, and the FTIR and hysteresis of poly(BAD) (6 pages, print/PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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