A New Type of Spontaneous Vinyl Monomer Polymerization in Langmuir Films

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Received February 5, 2002
Revised Manuscript Received April 24, 2002

In today's science and technology of surfaces, it is often a challenge to get a very thin structured polymer layer. Of direct interest to that problem is the monolayers arranged on an aqueous subphase by the Langmuir method,[1,2] showing a surfactant/solution interface very much like in a micellar structure, although better organized. Different kinds of chemical reactions can take place at that interface: C═C bond oxidation, hydrolytic and photochemical processes, and particularly polymerizations. Extensive studies have been carried out on the polymerization of compounds with double bonds in their hydrophilic moiety[3−5] or in the hydrophobic part.[6−8] All these polymerizations were essentially initiated photochemically.

Moreover, organized monolayers may lead to some unexpected reactions that do not occur in the bulk, thanks to the specific combination of interfacial features. For example, different authors[9−11] have shown that octadecyltetracyanoquinodimethane was spontaneously reduced at the air−water interface, but only in the presence of a cationic amphiphilic molecule.

In that context, it appeared as particularly exciting to witness, simultaneously from surface pressure−area ($\pi-A$) isotherms and UV, IR, and NMR spectra, the occurrence of a spontaneous reaction in a compressed Langmuir film of dioctadecyldimethylammonium bromide (DODA) spread over an aqueous solution of sodium 4-styrenesulfonate (SSt)—a reaction which turned out to be a spontaneous polymerization as detailed in the present communication.

Experimental Section. Sodium 4-styrenesulfonate (SSt, 99% pure), poly(sodium 4-styrenesulfonate) (PSSt, 99% pure), and dimethyldioctadecylammonium bromide (DODA, 99% pure) were purchased from Aldrich and Sigma.

An appropriate amount of DODA solution in chloroform (1−2 mg mL^{-1}) was carefully spread onto aqueous ionic SSt or PSSt solutions at a chosen concentration. The Langmuir monolayers were compressed using a constant barrier speed of 4 Å^2 molecule^{-1} min^{-1} at 20 ± 1 °C. Built-up films on CaF$_2$, quartz, or glass substrates were obtained by the vertical lifting method at a target pressure of 30 mN m^{-1}, with a 10 mm min^{-1} dipping speed.

The LB experiments were carried out with a Nima trough (611D system). A Millipore purification system produced water with a resistivity higher than 18 MΩ cm.

Infrared (IR) spectra were recorded on a FTIR Equinox 55 Bruker spectrometer. UV−vis absorption spectra were recorded using a Uvikon 922 spectrophotometer and NMR spectra with a Bruker Advance DPX 250.

Results and Discussion. 1. Behavior of DODA Monolayers on a SSt Solution. The surface pressure/area ($\pi-A$) isotherms for DODA spread on SSt aqueous subphases are given in Figure 1 as a function of SSt concentration from 0 to 10^{-3} mol L^{-1}. Our DODA isotherm on pure water is in good agreement with reported ones,[12] as well as the 47 Å^2 molecular area which corresponds to a collapse pressure (π_c) of 50 mN m^{-1}. When SSt is added to the subphase, the $\pi-A$ curve is modified to an extent which depends on its concentration.

For SSt concentrations below 10^{-4} mol L^{-1} the collapse pressure decreases down to 45 mN m^{-1}, in agreement with former observations.[13] However, when the SSt concentration is increased above 10^{-4} mol L^{-1}, π_c abruptly increases to 60 mN m^{-1}. As indicated by the higher π_c, the stability of the monolayer is increased, a behavior which has only been observed when POLYelectrolytes—instead of small organic ions—are dissolved in the subphase.[14] Thus, these $\pi-A$ isotherms suggest an important interaction between the DODA monolayer and the SSt anions, if not the occurrence of some reaction.

2. Transfer onto Substrates. Well-organized LB films with more than one layer cannot be built up from a DODA monolayer spread on pure water and most salt-containing subphases.[15] The same behavior was observed here on a SSt solution, the concentration of which was lower than 5 × 10^{-4} mol L^{-1}. On the contrary, above that concentration, a multilayered structure could be deposited onto substrates with a transfer ratio close to unity. In this case LB film deposition was found to exhibit typical "Z-type" behavior (i.e., transfer occurring only during emersion).[2]

Similar transfer experiments were carried out with a DODA monolayer spread on PSSt solutions, with concentrations ranging from 5 × 10^{-5} to 10^{-3} mol L^{-1}. There again, multilayers could be deposited onto substrates as already reported.[16] The films transferred from SSt and PSSt subphases are noted as DODA/SSt and DODA/PSSt, respectively, the polymer content being given in monomer unit concentration.

3. UV Spectra. A SSt solution shows an absorption maximum at ca. 255 nm (Figure 2a). The UV spectrum of one monolayer of DODA/SSt transferred from a low SSt concentration subphase (10^{-4} mol L^{-1}) exhibits the same band; indeed, DODA is UV transparent, and no spectral shift seems to occur despite the condensed state of SSt in DODA in the LB film (Figure 2b). Much more striking is the fact that for high SSt concentration (10^{-3} mol L^{-1}) one observes a band at 225 nm for a 30-layer DODA/SSt LB film. Note that a PSSt solution absorbs at ca. 225 nm (Figure 3a).

On the other hand, the spectra of the subphase recorded before and after the film transfer—whatever the concentration—are typical of a SSt solution, indicating the absence of reaction in the subphase, contrary to what happens at the interface.

Also, the spectrum of DODA/PSSt film transferred from a 10^{-3} mol L^{-1} PSSt subphase is identical to the spectrum of a PSSt aqueous solution, indicating the occurrence of no spectral shift when PSSt is included in a DODA monolayer. Since these last two spectra are identical to the one described above for the DODA/SSt (10^{-3} mol L^{-1}) 30-layer film, we are thus led to the

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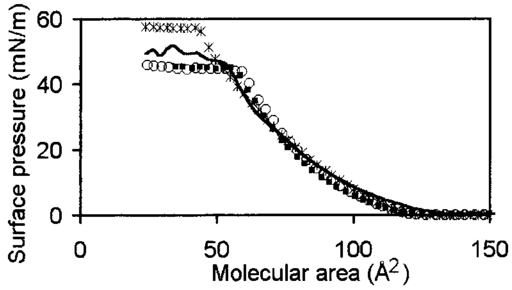

Figure 1. SSt concentration effect on DODA monolayer surface pressure vs area per molecule (π–A isotherm): [SSt] = 0 (–), 2 × 10^{-5} (■), 10^{-4} (○), and 10^{-3} mol L^{-1} (*). Compression speed: 4 Å^2 molecule^{-1} min^{-1}; T = 293 K.

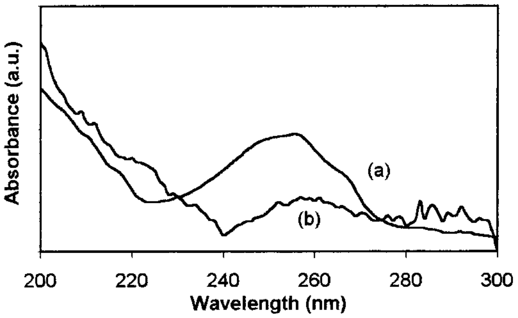

Figure 2. Absorbance spectra (arbitrary units) of (a) 10^{-5} mol L^{-1} SSt aqueous solution and (b) 1 monolayer of DODA/SSt (10^{-4} mol L^{-1}) LB film.

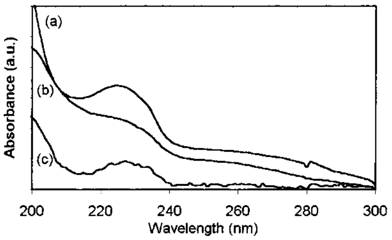

Figure 3. Absorbance spectra (arbitrary units) of (a) 10^{-5} mol L^{-1} PSSt aqueous solution, (b) 30-layer DODA/SSt (10^{-3} mol L^{-1}) film, and (c) 30-layer DODA/PSSt (10^{-3} mol L^{-1}) film.

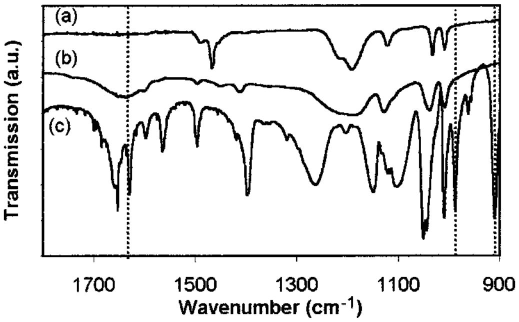

Figure 4. FTIR spectra of (a) 30-layer of DODA/SSt (10^{-3} mol L^{-1}) film on CaF_2, (b) PSSt, and (c) SSt (KBr pellets).

conclusion that the interfacial reaction is probably a polymerization of the SSt monomer.

4. IR Spectra. An FTIR study was then undertaken to corroborate that unexpected phenomenon, and the spectrum of a DODA/SSt (10^{-3} mol L^{-1}) LB film is shown in Figure 4a.

Bands at 2919 and 2850 cm^{-1} (stretching modes of CH_2) as well as the 1468 cm^{-1} band (scissoring mode of C_{18} chains) demonstrate the presence of DODA. On the other hand, bands characteristic of the sulfonate group are observed at 1120 and 1215–1180 cm^{-1} (S–O stretching)[17] and confirm the presence of SSt units in the film. The above data together with the UV spectra analysis obviously imply the occurrence of interactions between DODA and SSt ions.

To confirm the polymerization phenomenon, the spectrum of this DODA/SSt (10^{-3} mol L^{-1}) film was compared to PSSt and SSt KBr pellet spectra (Figure 4). It immediately appears that the three bands, diagnostic of the SSt vinyl group at 1628 cm^{-1} (C=C stretching), 987, and 910 cm^{-1} (out of plane vibrations), have disappeared in the LB film spectrum, which moreover is identical to that of a DODA/PSSt LB film.

A clear confirmation of the UV spectra, the FTIR analysis also indicates that polymerization of the SSt monomer associated with DODA takes place at the interface under certain experimental conditions.

5. NMR Spectra. The occurrence of the polymerization reaction was also qualitatively confirmed by the ^1H spectrum of a DODA/SSt (10^{-3} mol L^{-1}) 5000-layer LB film dissolved in d_6-DMSO. Indeed, the multiplets centered at 5.3, 5.8, and 6.9 ppm characteristic of the SSt vinyl group strongly decreased. Meanwhile, the two doublets from the phenyl ring centered at 7.1 and 7.5 ppm are replaced by two very broad resonances centered around 7.15 and 7.45 ppm, characteristic of commercial PSSt taken as standard.

6. Mechanism. Under the conditions described here a radical-initiated polymerization process would appear as the most probable one. Indeed, Ringsdorf et al.[18] already demonstrated that some photochemically induced vinyl monomer polymerizations impossible to perform in bulk can take place at the air–water interface. In the present case, however, no extraneous chemical or physical initiating agent was used. Experiments carried out under nitrogen atmosphere and/or in the dark showed no difference in the overall process or in the UV and IR spectra. Moreover, a rather conclusive indication was given by the fact that up to 10^{-3} mol L^{-1} added hydroquinone (though shown to interact with the monolayer) did not disturb the whole process. Thus, although some polymerization clearly occurs at the interface, it does not seem to be of a radical type and might intriguingly obey an ionic mechanism.

Conclusion. This study describes the adsorption of an ionic vinyl monomer along a positively charged Langmuir monolayer and its polymerization at the interface upon compression. This polymerization could be put in evidence by measurements of the π–A isotherms as well as the UV, IR, and NMR spectra. As far as we know, this is the first time where a monomer soluble in the subphase adsorbs on the monolayer and spontaneously polymerizes. That phenomenon opens the way to a new type of polymerization for chosen pairs of complementary monomers and monolayers.

Quite interestingly, above a critical monomer concentration of 10^{-4} mol L^{-1}, a number of successive polymer/DODA layers could be deposited onto a chosen substrate, in relation with the simultaneous polymerization which opens up the possibility to build multiionic films of controlled thickness.

Current studies are now progress to determine the scope of the reaction, the exact nature of the mechanism, the composition, and morphology of the resulting films and will be the topic of future publications.

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MA020190T