Communications to the Editor

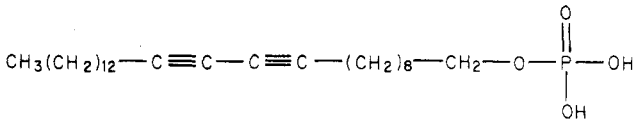
Polymer-Supported Membranes

S. L. Regen, P. Kirszenstejn, and A. Singh recently published a communication in *Macromolecules* with the title "Polymer Supported Membranes. A New Approach for Modifying Polymer Surfaces".[1] We read this paper with great interest, because it claims to present a very simple method to coat solid surfaces with ordered monolayers.

We ourselves have coated a variety of polymer materials with well-ordered polymerizable lipid systems and have investigated their properties for some years.[2-5] Our method of choice so far is the classical Langmuir–Blodgett (LB) technique.[6] Because the LB technique requires some effort, we tried to find other, less troublesome methods to achieve an ordered coating of solids by amphiphiles. This included the ultrasonication of support materials in a vesicle suspension: Up to now without success.

After having read the communication of Regen et al., which claims that the average thickness of the coating of one molecule, calculated with experimental data,[7] corresponds to a true overall monomolecular coating, we tried to verify their conclusions.

For our experiments we used the polymerizable diacetylene amphiphile:



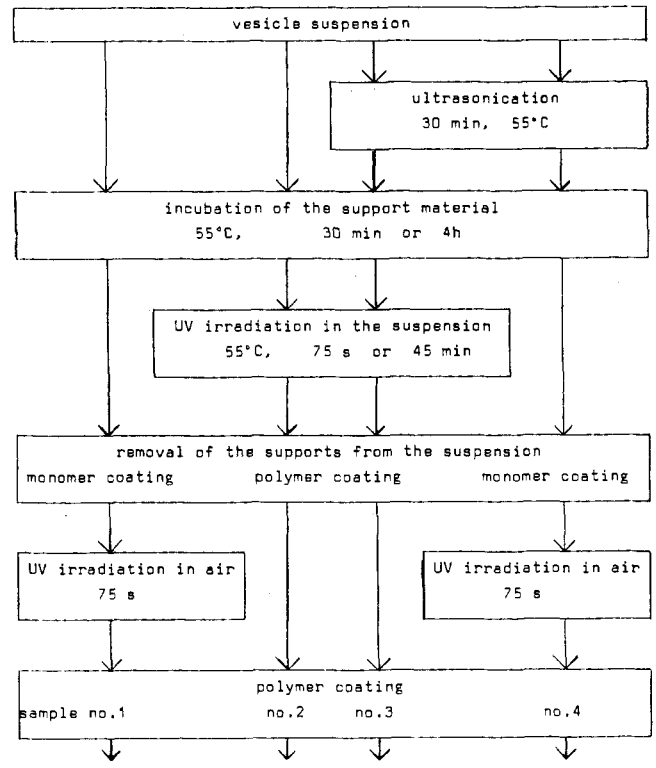
1

This monomer is known to form strongly colored polymers. It is possible to judge the macroscopical homogeneity of a single monolayer by its color.[3] Thus the quality control of the coating is simplified considerably. Furthermore, 1 was shown to build LB films on many support materials,[3,5] nearly free of defects.

To achieve an ordered coating of support materials, we investigated not only the effect of the irradiation of support materials in a vesicle suspension (applying the technique described by Regen et al.) but also the effect of the combination of irradiation and sonication.

As polymer support materials we used two different PTFE samples (a solid Teflon sheet, 1-mm thick, and a 0.1-mm Teflon foil) and a polypropylene foil (Celgard 2400). These materials can be easily coated by using the LB technique by a variety of lipids.[4,5] The polymerized LB layers on these materials exhibit homogeneous color, i.e., macroscopically homogeneous coating.[4,5]

Scheme I
Sequences of Treatment of the Support Foils in the Vesicle Suspension of 1



The support materials were thoroughly cleaned with pure analytical grade ether and rinsed several times with water (Millipore water purification system Milli-Q 4 bowl). This procedure was shown to be sufficient for LB deposition.[4,5] The flexible PP and PTFE materials were fixed on a 1-mm sheet of Teflon as a sample holder. The vesicle suspension used was prepared by sonication of 1 in a bath sonicator at 55–60 °C; the amphiphile concentration was 0.2 mg/mL. The vesicle suspension exhibits a very strong blue color after a few seconds of UV irradiation (pen ray UV lamp, Hamamatsu Corp., No. 937-002), which indicates the polymerization of the amphiphile.

The coated samples were treated in 4 different ways, as demonstrated in Scheme I. The UV irradiation of the samples is sufficient to polymerize LB monolayers and

Table I
Properties of Samples 1–4 Treated according to Scheme I[a]

	PTFE sheet, 1 mm				PTFE foil, 0.1 mm				PP foil			
	1 (75 s)[b]	2 (75 s)[b]	3 (75 s)[b]	4 (75 s)[b]	1 (75 s)[b]	2 (75 s or 45 min)[b]	3 (75 s or 45 min)[b]	4 (75 s)[b]	1 (75 s)[b]	2 (75 s or 45 min)[b]	3 (75 s or 45 min)[b]	4 (75 s)[b]
hydrophobic surface	+	+	+	+	+	+	+	+	+	+	+	+
hydrophilic surface	0	0	0	0	–	–	–	–	–	–	–	–
color intensity	+	+	+	+	+	+[c]	+[c]	+	+	+[c]	+[c]	+
color homogeneity	–	–	–	–	–	–	–	–	–	–	–	–

[a] +, yes; –, no; 0, a few spots in mechanically stressed areas.
[b] Irradiation times are given in parentheses after the sample number. Due to Scheme I, the irradiation of the sample sheets was performed either in the vesicle suspension (samples 2 and 3) or after removal from the suspension (samples 1 and 4). Extended UV irradiation of more than 45 min causes bleaching of the colored polymer.

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multilayers of 1.[3,5] Before examination, the foils were washed with water. The results are summarized in Table I.

Some of the samples showed a few blue spots and the Teflon foil even showed some larger blue areas. The blue areas were found only where the material had been stressed or where defects were visible. These colored spots retained droplets of water; i.e., they were hydrophilic. The bulk area of the surface was strongly hydrophobic. The visually observed color was very inhomogeneous and generally more intense than the color of polymerized LB monolayers or bilayers.[3,5]

Due to the topochemical control of the polymerization, the color indicates the existence of ordered domains, e.g., adsorbed crystallites. However, there exists definitely no overall order, let alone a monolayer coverage. Because the poor quality of the coating is visible to the naked eye, more detailed investigation by scanning electron microscopy was not performed.

Comparing our results with the conclusions drawn by Regen et al., we consider their postulated monolayer or monolayer-approaching coverage of the lecithins on polyethylene supports highly improbable: The effects reported by them should not be restricted exclusively to the combination of amphiphile and support used by Regen et al. We are positive that, unfortunately, the proposed method does not provide homogeneous, polymerized coatings as claimed. Whether a more sophisticated variation of the simple techniques described above will lead to ordered coatings of amphiphiles in the future cannot be decided yet. If possible, it would be an important step toward tailor-made surface properties, without geometrical limits, which are a major shortcoming of the LB technique.

Registry No. 1 (homopolymer), 78067-05-7.

References and Notes

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(7) The calculation of the thickness of the polymerized lecithin coatings is based on a quantitative analysis of the phosphorus bound and an assumed cross-section of 70 Å^2 per lecithin molecules. This value corresponds to the liquid analogous phase of the lecithins used.[8-10] In case of the diacetylene lipid used, the topochemically controlled polymerization is bound to the solid analogous phase;[10] i.e., the cross section per molecule has to be below 50 Å^2.[9,10] Therefore, Regen's data imply that either no polymerization or no complete coating is achieved.
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Further Evidence for Polymer-Supported Membranes and a Statement Concerning Synthetic Scope and Surface Structure[1]

We have recently reported a new technique for modifying the surface of low-density polyethylene film (PE) using phospholipids **1** and **2** (Chart I).[2] Experimentally, this method consists of immersing the film (Petrothene NA 344-55; 0.929 g/cm^2; 2.0 melt index; 3-mil thickness)[3] into an aqueous dispersion of either lipid, irradiating the resulting mixture with UV light (254 nm), and washing the recovered film with water and 1:1 $CHCl_3$–CH_3OH. On the basis of (a) the film's lipid content, hydrophilicity, and lability toward removal of phosphorus by HCl, (b) the similarity in loading behavior of **1** and **2**, and (c) the requirement that **2** be properly aligned for efficient topotactic polymerization,[4] we have proposed that polymerization proceeds as an adsorbed lipid monolayer. Since phospholipid **3**, bearing a single polymerizable moiety, failed to modify the PE surface under similar conditions, we further suggested that the binding of **1** and **2** to PE was due primarily to the insolubility of the newly formed cross-linked network.

In this communication we provide additional data which support our hypothesis that polymerized lipids *approaching monolayer coverage* are present at the surface of PE/**1** and PE/**2** and report our findings that other surfactants (e.g., lipids **4** and **5**) appear to modify PE in a similar manner.

By use of procedures similar to those previously described,[2] PE was irradiated in the presence of **4** and **5** to produce PE/**4** and PE/**5**; plateaus in the observed loading were reached by using surfactant concentrations of 0.1 mg of **4**/mL and 0.4 mg of **5**/mL and were 3.6×10^{14} lipids/cm^2 and 1.3×10^{14} lipids/cm^2, respectively.[5,6] The plateaus for **1** and **2** on PE corresponded to 2.4×10^{14} and 2.1×10^{14} lipids/cm^2, respectively.[6] Flat contact angles for water on the surface of PE/**1**, PE/**2**, PE/**4**, and PE/**5** were 35°, 46°, 60°, and 51°, indicating relatively hydrophilic surfaces; untreated PE showed a contact angle of 100°. Placement of water droplets at different locations on each film indicated that the surfaces were uniformly wetted. Similar to the behavior of **3**, lipid **6** (a monopolymerizable surfactant) failed to modify PE, as indicated by phosphorus analysis and by the retention of the hydrophobic surface. Modification of cleaned PE, obtained from a second commercial source (0.910–0.925 g/cm^3),[7] with **1** showed a loading and surface hydrophilicity which was identical with that supplied to us by Luetzow Industries.

Pressure–area isotherms of **1**–**4** were recorded with a computerized MGW Lauda film balance (22 °C). The surfactants were spread on the water surface from a 9:1 v/v hexane–ethanol solution containing approximately 1 mg of lipid/mL. The limiting area of each of these lipids is in the range of ca. 60–70 Å^2, at 33 dyn/cm; in the polymerized monolayer state, the limiting areas are presumed to be somewhat less than these values.[8] If we take the lower value (60 Å^2) as the maximum area occupied by lipids **1**–**4** in a tightly packed polymeric monolayer, the resulting membrane would be composed of a minimum of 1.7×10^{14} lipids/cm^2.

To a first approximation, lipids **1**, **2**, and **5** exhibit a loading on PE which is in the expected region of monolayer coverage; lipid **4** shows a somewhat higher loading. One major difficulty in characterizing such films at the molecular level is that there are no existing methods for an-

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