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.

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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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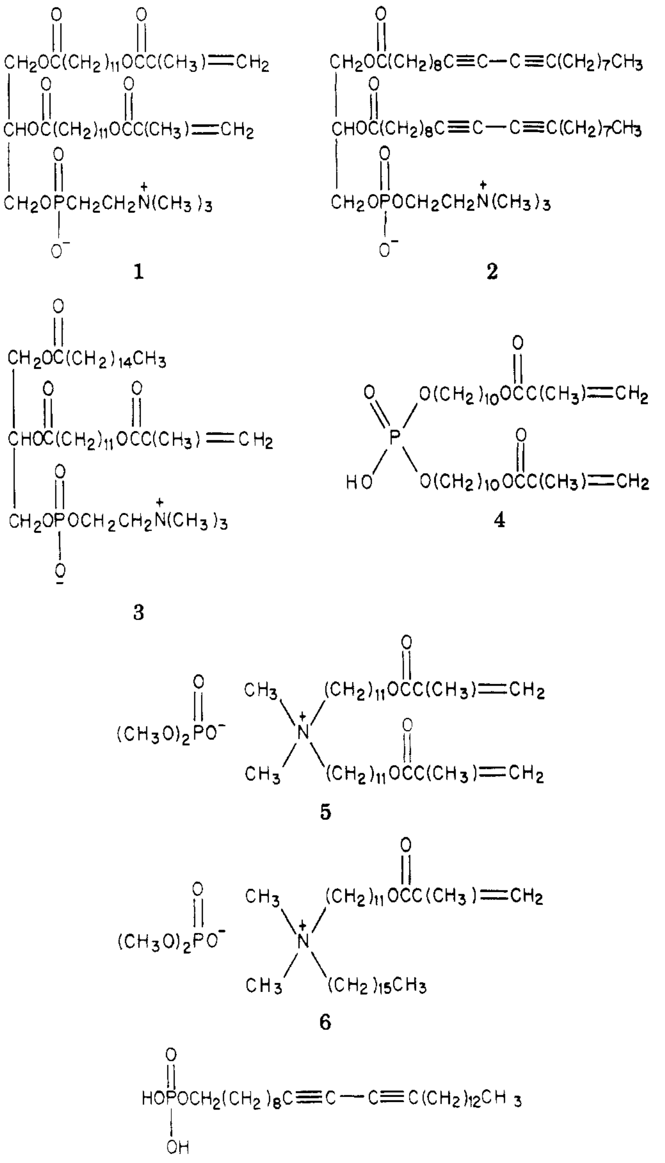
Chart I



alyzing, quantitatively, the surface roughness and true surface area of solid organic polymers.[9] A related problem is that it is not possible to discern whether the coatings extend over the "hills and valleys" of a polymer surface, or whether they traverse the "hills". In our earlier work, we did not not claim a method for coating solid surfaces with ordered polymerized monolayers.[2,10] We also made no claims regarding the generality or synthetic scope of this technique. We in fact stated: "The question of whether or not a polymerized phosphatidylcholine monolayer of **1** or **2** has been attached to polyethylene cannot be answered unambiguously at the present time. However, the above results, taken together, *strongly suggest that a polymeric structure at least approaching monolayer coverage is present*". In this prior publication we also demonstrated that our method is very sensitive to the precise structure of the surfactant and concentrations used. Recently, it has been reported that compound **7** failed to produce a uniformly hydrophilic surface on Teflon and on polypropylene by using procedures and conditions which were similar to those described above.[10] These negative results cannot be used, in any way, to draw inferences regarding either the surface structure that exists in PE/**1**, PE/**2**, PE/**4**, and PE/**5** or the generality of this technique. This compound is substantially different in structure from those surfactants which we have successfully employed. Moreover, these films differ significantly in surface structure and composition.

A broad study aimed at examining the synthetic scope of this technique as well as elucidating surface structure is now in progress. Complete experimental details including synthetic procedures used for the preparation of **1–6** will be reported shortly.

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Registry No. **1** (homopolymer), 90064-68-9; **2** (homopolymer), 90046-25-6; **4** (homopolymer), 90046-27-8; **5** (homopolymer), 90046-29-0; PE, 9002-88-4.

References and Notes

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Quasi-Elastic Light Scattering of Polyelectrolyte–Micelle Complexes

The association between surfactants and synthetic polymers has been the subject of increasing attention, partly because these interactions may resemble phenomena in biological assemblies,[1] but also because of their bearing on certain applications of water-soluble polymers, e.g., in enhanced oil recovery.[2] The most intense association occurs between strong polyelectrolytes and oppositely charged amphiphiles; however, studies with these compounds have been carried out only well below the cmc,[3–5] primarily because precipitation commonly occurs at higher surfactant concentrations. Nonionic polymers, which do not exhibit such phase separation, have been extensively examined,[6–9] but the nature of their interaction with surfactants is somewhat obscure and relatively weak.

We have recently observed that the phase separation of

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