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Communications to the Editor

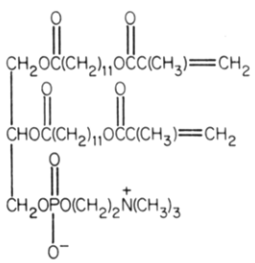
Polymer-Supported Membranes. A New Approach for Modifying Polymer Surfaces[1]

In this communication we describe a new and an extraordinarily simple technique for modifying surfaces of solid organic polymers.[2] Our method involves the polymerization of suitable lipid molecules adsorbed at aqueous–insoluble polymer phase boundaries. Resulting surfaces are termed *polymer-supported membranes*.

Surface structure and composition play a significant role in defining many of the physical properties and ultimate uses of polymers. In particular, features such as wetting,[3] weathering,[4] adhesion,[5] dye adsorption,[5] friction,[5] electrostatic charging,[6] permeation,[7] and biocompatibility,[8,9] which are important for engineering and biotechnological applications, are largely influenced by surface characteristics. Despite this fact, current methods available for modifying polymer surfaces in a well-defined manner remain limited.[2]

We have conceived of a new synthetic technique for altering polymer surfaces. Our general approach is outlined in Scheme I.[10] A lipid molecule composed of a hydrophilic head group, a hydrophobic segment, and one or more polymerizable groups is dispersed in an aqueous–hydrophobic, insoluble polymer two-phase mixture. In analogy to the behavior of lipids in oil/water mixtures,[11] a monolayer is expected to form at the phase boundary. Subsequent polymerization secures the membrane to the polymer surface (1) through extended hydrophobic interactions, (2) through covalent linking to alkyl radicals generated on the original surface, and/or (3) by virtue of the insolubility of the newly formed cross-linked network (when lipids with two or more polymerizable groups are employed).[12]

In order to test the feasibility of polymer-supported membranes, we attempted the synthesis of phosphatidylcholine-modified polyethylene film. Commercial low-density polyethylene film, 3-mil (Petrothene NA 344-55; 0.920 g/cm^3; 2.0 melt index),[13] was (1) cut into 2 × 10 cm pieces, (2) heated for 2 h in refluxing 1:1 $CHCl_3$–CH_3OH (3) extracted (Soxhlet) with $CHCl_3$ for 12 h, and (4) dried [6 h, 78 °C (0.1 mm)]. Resulting strips were each placed into 25-mL quartz test tubes, followed by addition of 20 mL of a vesicle dispersion of bis[12-(methacryloyloxy)dodecanoyl]-L-α-phosphatidylcholine (1).[14–16] Each tube was



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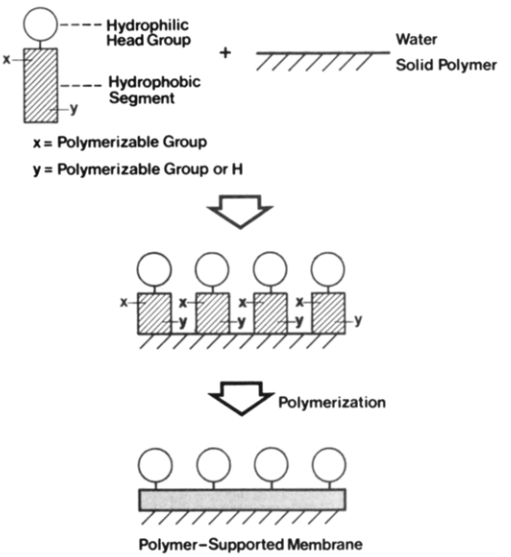
Scheme I



purged with nitrogen for 10 min, sealed with a No-Air stopper, placed in a Rayonet photochemical reactor, and irradiated for 1 h (2537 Å).[16] The films were then removed from the tubes, gently hand shaken in air for ca. 15 s, and washed by immersing them into distilled water (ca. 100 mL) and gently agitating them (each film was moved in and out of the wash six or seven times). The washing procedure was repeated four times, using, in each case, freshly distilled water. Finally, each strip was immersed in 1:1 $CHCl_3$–CH_3OH for 24 h at room temperature, transferred directly to a Pyrex tube, slowly pyrolyzed, and analyzed for phosphorus.[17]

Figure 1 shows the number of lipid molecules immobilized per cm^2 of geometrical area as a function of lipid concentration used in the aqueous dispersion. A maximum loading is reached at ca. 1.5×10^{14}/cm^2. Exposure of the modified film to 5.4 M HCl for 24 h led to the quantitative removal of phosphorus derived from 1.[19,20] If a "surface" group is defined as one that can interact with a reagent which would be expected to be insoluble in bulk polyethylene (i.e., HCl) and which is dissolved in a solvent that does not swell polyethylene (i.e., water), this result provides strong evidence that 1 is secured to the polymer surface (i.e., at the polyethylene–water interface) and not within the film.[2b] In contrast, 1 polymerized onto polyethylene was completely stable to water, 1% aqueous sodium dodecyl sulfate, THF, and 1:1 $CHCl_3$–CH_3OH at room temperature for 24 h. As expected, phosphatidylcholine-modified polyethylene is hydrophilic. The contact angle for water measured on this surface was 35°; unmodified polyethylene had a contact angle of 100°.[21] Control experiments performed with polyethylene plus dispersions of polymerized 1, or nonpolymerized 1 (in the absence of

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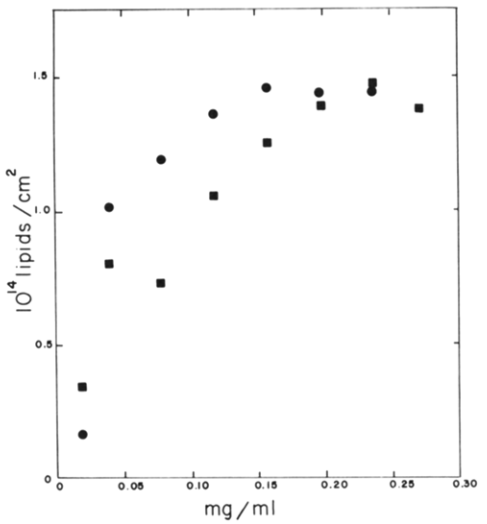
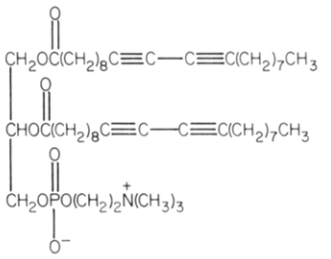


Figure 1. Plot of number of phospholipid units per cm^2 of geometrical film area as a function of aqueous lipid concentration: (●) 1; (■) 2. Samples of 2 were irradiated (2537 Å) for 15 min.

UV light), and polyethylene plus dipalmitoyl-L-α-phosphatidylcholine (with UV irradiation) showed negligible phospholipid incorporation and retention of the hydrophobic surface.

In an effort to obtain molecular-specific information at the film surface, the attenuated total reflectance IR (ATR IR) spectrum was taken.[22] In addition to the absorption bands due to polyethylene, a weak but distinct carbonyl band (1732 cm^{-1}) attributable to the ester moieties in 1 was clearly visible. Spectra of pure polyethylene or the germanium reflection element alone showed no observable carbonyl bands. Absorption bands for the phosphatidyl head group were too weak to be seen, even with a larger number of averaged scans.

Scheme I represents an idealized assembly of lipid monomers, tightly packed at the polymer–water phase boundary and properly oriented for efficient polymerization. Alternatively, a loosely packed monolayer or isolated and nonoriented monomers adsorbed at the surface could be envisaged. In order to probe for possible alignment of phosphatidylcholine molecules at the polymer surface, we attempted the analogous polymerization of 2 onto polyethylene.[23] The photopolymerization of conjugated diacetylenes is topotactic, and its efficiency depends on the proper orientation of monomer units.[24,25] Using procedures similar to those described for 1, we successfully immobilized lipid 2 onto low-density polyethylene. The profile of attached 2 vs. aqueous lipid concentration was very similar to that found for 1; both showed the same maximum loading (Figure 1). Control experiments performed with 2 plus polyethylene (in the absence of light) showed no incorporation of phospholipid.



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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. The major difficulty in characterizing these films is that there are no

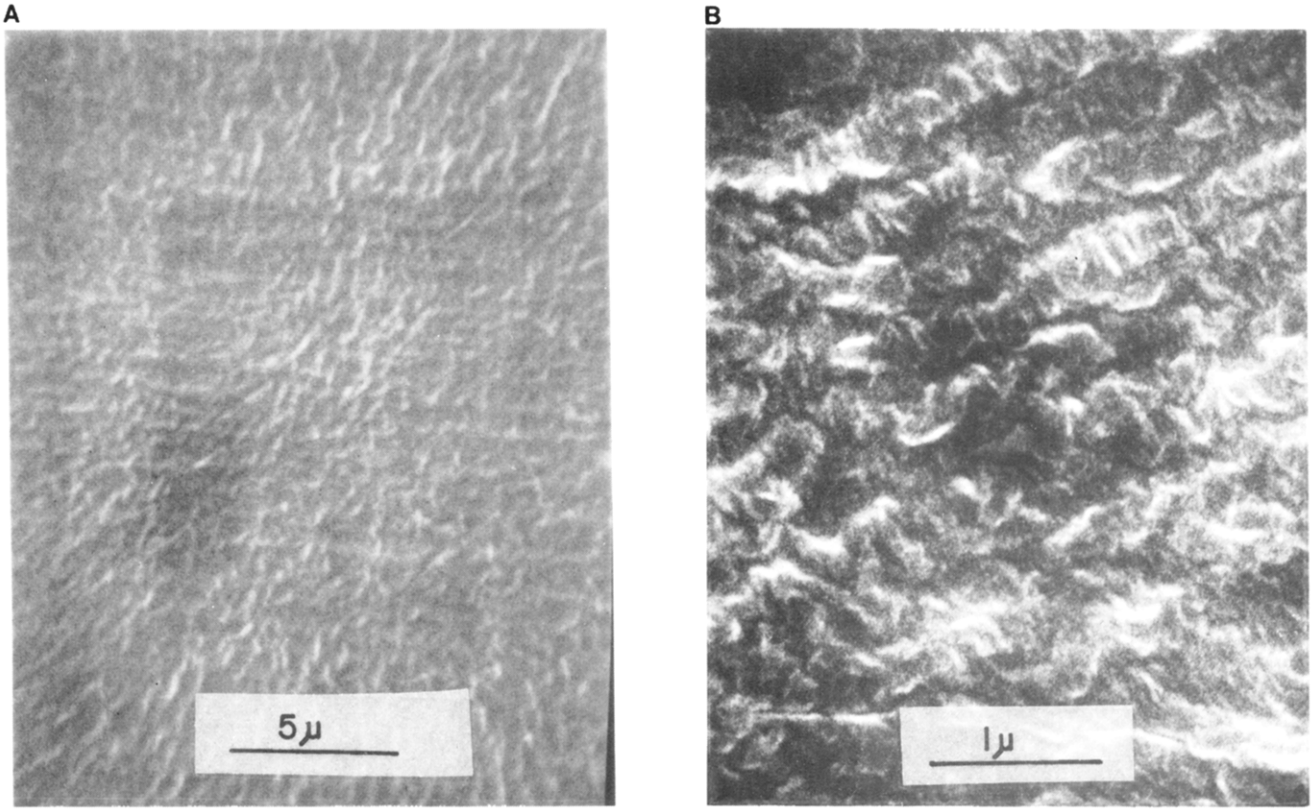

Figure 2. SEM photomicrographs of commercial polyethylene film extracted with $CHCl_3$: (A) 4500× magnification; (B) 22 500× magnification. The film was sputter coated with 60/40 Au/Pd. Photomicrographs were obtained with a Philips 400 STEM electron microscope operating at 20 kV using a SED detector.

existing methods for analyzing quantitatively the surface roughness (Figure 2) and *true* surface area of solid organic polymers.[2b] If we make the crude estimate that the geometrical surface and the true surface are identical (i.e., that the film is perfectly flat) and if we assume that the cross-sectional area of **1** and **2** is ca. 70 Å^2,[26] the maximum packing density of these lipids in a monolayer framework (1.4×10^{14}/cm^2) compares well with the maximum loading indicated in Figure 1. Since the geometrical area represents a lower limit of the true area, this maximum loading infers ≤expanded monolayer coverage. The fact that **1** and **2** exhibit the same maximum loading together with the fact that **2** requires alignment for efficient polymerization strongly suggests that all of the available surface has been covered and that most, if not all, of the phospholipid polymer is intimately associated with the polyethylene surface. Polymerization of **2** clearly cannot proceed as growing chains extending away from the film surface; prior ordering must exist, as would be expected for a tightly or loosely packed adsorbed monolayer. Moreover, if chains of **1** and **2** extended away from the surface, there would have to be (1) the same number of chains/cm^2 having the same average molecular weight or (2) a different density of chains with fortuitous molecular weight distributions such that the same apparent maximum loading would be observed. Both situations seem highly improbable.

Preliminary experiments carried out with a phosphatidylcholine monomer bearing a single polymerizable group (i.e., 1-palmitoyl-2-[12-(methacryloyloxy)dodecanoyl]-L-α-phosphatidylcholine)[16] indicate that similar photoinduced attachment to polyethylene film is not possible; no bound lipid could be detected by phosphorus analysis, and the surface remained hydrophobic. This result suggests that the binding of polymerized **1** and **2** to polyethylene is due primarily to the insolubility of the newly formed cross-linked network.

Studies now in progress are aimed at further characterizing polyethylene-supported phosphatidylcholine and related membranes and examining the full scope of this technique for the modification of organic polymers and other hydrophobic surfaces such as graphite and silylated silica gel.

Acknowledgment. We are grateful to Professor George Whitesides (Harvard University) for valuable discussions. We are also grateful to Marion Hatchell (Medical College of Wisconsin) for assistance with the electron microscopy and to Ray Wieboldt (Northwestern University) for obtaining the ATR IR spectra.

Registry No. **1**·$H_2C{=}CH_2$ copolymer, 84050-12-4; **2**·$H_2C{=}CH_2$ copolymer, 84050-14-6.

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(13) Provided by Luetzow Industries.
(14) Films were handled with stainless steel forceps to prevent contamination of the surface.
(15) A typical vesicle dispersion was prepared by first dissolving 15 mg of **1** in 10 drops of $CHCl_3$ in a round-bottomed flask and then coating the lipid onto the walls of the flask by evaporating off the solvent (a stream of nitrogen was used initially followed by drying under vacuum (12 h, room temperature, 0.1 mm). Distilled water (40 mL) was then added and the mixture was hand shaken for 5 min, degassed with nitrogen for 10 min, and sonicated (bath type) for 1 h at 55 °C.
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(17) Typically, the Pyrex tube was heated very slowly over a direct flame to remove solvent and to melt the film into a small liquid mass. The tube was then cooled to room temperature and 50 μL of an ethanolic solution of $Mg(NO_3)_2{\cdot}6H_2O$ (10% w/w) was added. The contents of the tube was then slowly pyrolyzed. When the pyrolysis appeared to be complete, the contents was heated for an additional 2 min under an oxygen atmosphere. After the contents cooled to room temperature, another 50 μL of 10% ethanolic $Mg(NO_3)_2{\cdot}6H_2O$ was added and the solvent evaporated by placing the tube in a drying oven. The tube was then heated (ca. 5 min) over a direct flame until the evolution of brown fumes ceased, cooled to room temperature, placed in a water bath (100 °C) for 15 min (after 0.5 mL of 0.1 M HCl had been added), and cooled to room temperature. A solution (1.7 mL) was prepared by mixing 10% ascorbic acid in water (w/w) with 0.5% $(NH_4)_6Mo_7O_{24}$ in 1.0 N H_2SO_4 (w/w), in a ratio of 1:6, and then added to the tube. After 20 min of heating at 45 °C, the contents was cooled to room temperature and the absorbance measured at 820 nm. An appropriate calibration for this analysis was made by using dipalmitoyl-L-α-phosphatidylcholine as a standard.[18] A residual amount of phosphorus remained after extractive cleaning of the commercial film (the average of six samples was $(6.75 \pm 0.25) \times 10^{-5}$ μmol/cm^2); this quantity was subtracted from the total phosphorus content to yield the corrected phospholipid incorporation. Control experiments performed with a reagent blank showed no detectable phosphorus.
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(19) In this experiment the phosphorus content in the original polyethylene, 1-modified polyethylene, and HCl-washed 1-modified polyethylene were compared. Residual phosphorus present in the original commercial film was not removed under these conditions.
(20) After exposure to HCl, the film surface remains hydrophilic. We presume that loss of phosphorus results from acid-catalyzed hydrolytic cleavage of the phosphatidyl head group and/or the ester moieties.
(21) Flat contact angles were measured with a specially assembled apparatus involving an optical projection technique to magnify a droplet of water placed on the film. The droplet was projected on a screen and the contact angle measured directly. Placement of the water droplet at different positions on the film indicated that the film was uniformly wetted.

(22) ATR IR spectra were obtained with a Nicolet 7199 instrument (100 scans) and an MIR stainless steel holder set at an angle of 45°. Films were cut to cover the entire germanium sample faces used. The thickness of the germanium plates was 3 mm.
(23) Compound 2 was prepared by procedures similar to those previously described for related phospholipids: O'Brien, D. F.; Whitesides, T. H.; Klingbiel, R. T. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 95. Johnston, D. S.; Sanghera, S.; Pons, M.; Chapman, D. *Biochim. Biophys. Acta* **1980**, *602*, 57.
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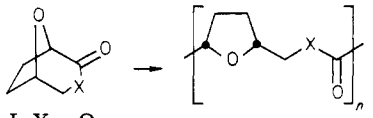
Ion-Binding Properties of Poly(iminomethylene(*cis*-tetrahydro-2,5-furandiyl)carbonyl) and Poly(oxymethylene(*cis*-tetrahydro-2,5-furandiyl)-carbonyl)

In previous publications,[1] we reported the syntheses and ring-opening polymerization of 3,8-dioxabicyclo[3.2.1]octan-2-one (I) and 3-aza-8-oxabicyclo[3.2.1]octan-2-one (II) to polyester III and polyamide IV, respectively. We now



I, X = O
II, X = NH

III, X = O
IV, X = NH

report preliminary data on the ion-binding properties of these materials.

The ion-binding properties of macrocyclic systems such as crown ethers,[2] cryptates,[3] and polymers containing these structures as pendent entities[4] are well-known. However, the ion-binding properties of linear polymers are less defined. Recently, Smith and co-workers[5] prepared *threo*- and *erythro*-poly(tetrahydro-2,5-furandiyl) and found that the threo polymer was an effective binder of lithium, potassium, and barium cations, while the erythro isomer was ineffective. The difference in binding properties was attributed to the ability of the threo isomer to exist in a helical conformation with the oxygen atoms pointed inward. Böhmer and co-workers[6,7] have recently prepared a series of linear, acyclic, ion-binding poly(ether amides) and have reported preliminary ion-binding data.

Picrate extractions[5-7] were used to assay the binding characteristics of polyester III and polyamide IV. The polymer to be tested was dissolved in chloroform at a repeat unit concentration of 10^{-2} M. The solution was allowed to reach thermal equilibrium in a water bath at 25 °C and an aliquot, typically 5 mL, was mixed with an equal volume of an aqueous solution of an alkali metal picrate (10^{-3}–10^{-4} M). The mixture was shaken intermittently, and after 1 h, the lower, organic layer was removed. An aliquot of the lower layer, typically 2 mL, was quantitatively diluted with ethanol to 5 mL, and the picrate concentration was determined spectrophotometrically (λ_{max} = 360 nm, log ϵ = 4.15 determined in chloroform–ethanol solution). The amount of alkali metal picrate extracted was expressed as a percent of the initial picrate concentration. Alkali metal picrate salts were prepared by the reaction of picric acid and alkali metal carbonates or hydroxides.[8] In the absence of polymer, no detectable amount of alkali metal picrate was extracted by chloroform alone.

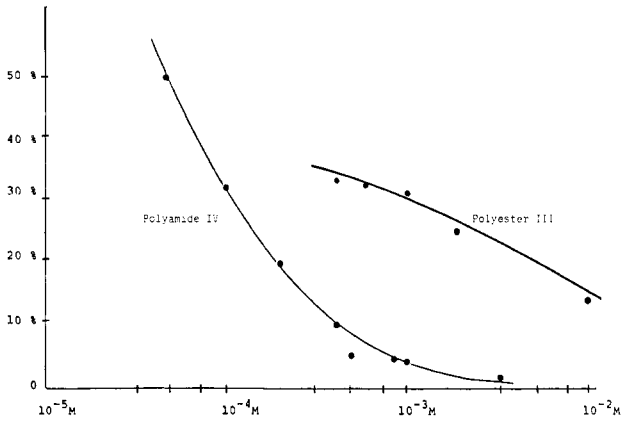


Figure 1. Percent solute extracted vs. log (total solute) for polyester III and polyamide IV. Solute: potassium picrate.

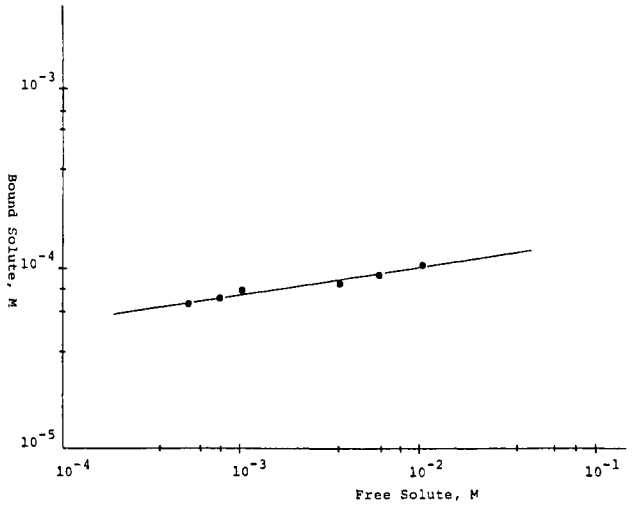


Figure 2. Log (bound solute) vs. log (free solute) for polyamide IV. Solute: potassium picrate.

The results of the ion-binding experiments for polyamide IV, polyester III, and polymers prepared by Böhmer and Smith are presented in Table I. The other data given in the table are for comparison. The amount of solute extracted varies as a function of the total solute concentration, as illustrated in Figure 1. It is apparent that measuring the extent of ion-binding at only one concentration may not be a good measure of the binding capacity of the material. To understand better the ion-binding behavior of polyamide IV and polyester III, plots of log (bound solute) vs. log (free solute) were prepared (Figures 2 and 3, respectively). Bound solute is the amount of picrate extracted into the organic phase, and free solute is that which remains in the aqueous phase. The figures show data for potassium picrate as solute but data for lithium, sodium, and cesium exhibit the same trends.

For polyamide IV (Figure 2), the concentration of bound solute is virtually constant over 3 orders of magnitude of free solute concentration. This observation is in direct contrast to that for polyester III (Figure 3), where changing free solute concentration has a much larger effect on the bound solute concentration. Based on the different

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