and semiconcentrated regimes to study the behavior of D_c. This represents the second aspect of our studies, i.e., to use the polymerization data to investigate some aspects of the scaling theory. Further experiments are in progress.

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Registry No. PMMA (homopolymer), 9011-14-7.

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Polymerizable Built Up Multilayers on Polymer Supports

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ABSTRACT: Polymeric Langmuir–Blodgett (LB) multilayers[1] of the cadmium salt of hexacosa-10,12-diynoic acid were investigated on gas-permeable polypropylene supports. Although the multilayer films are macroscopically homogeneous, scanning electron microscopy revealed the influence of the support surface structure on the microscopic perfectness of the deposited layers. The polymerization conditions and the surface pressure during the monolayer deposition were varied and did not show any effect on the surface structure of the multilayers. Such polymeric LB composite membranes reduce the gas flow of CH_4 markedly. Thus, such membranes may be well suited for gas separation.

Introduction

Recent work on the application of monolayers and multilayer systems[2,3] has included the use for separation processes.[4-6] Analogous to the biological cell membrane, LB multilayers and liposomes—as comparable, support-free systems—should be well suited for separation purposes, because of their extreme thinness and their overall microscopically defined structure.

To overcome the lack of mechanical and chemical stability, reactive amphiphiles had been polymerized in multilayers[7,8] and in liposomes[9] several years ago. It was shown that LB multilayers and polymerized liposomes show retention of ions and large molecules in aqueous systems.[10,11] In this paper we discuss the potential application of LB multilayers for gas separation. In the initial state of our work, we used amphiphilic diacetylenes. It is well-known that diacetylenes only polymerize under topochemical control to yield deeply colored polymers.[12,13] The color gives an indication of the homogeneity of the supported multilayer, the presence of macroscopic defects in the layers, and the progress of the polyreaction. On the basis of investigations of various amphiphilic diacetylenes on various support materials,[14,15] we carried out detailed studies with the cadmium salt of hexacosa-10,12-diynoic acid (1) on three different polypropylene supports. The surface structure of the LB films and the gas retention of such LB composite membranes were investigated.

$$CH_3(CH_2)_{12}\text{–}C{\equiv}C\text{–}C{\equiv}C\text{–}(CH_2)_8COOH$$

1

Experimental Section

Materials. The synthesis of hexacosa-10,12-diynoic acid is described elsewhere.[16] The cadmium chloride was pure grade (Merck). The water was distilled and purified by a Millipore water purification system (Milli Q, Millipore Corp.). The polypropylene

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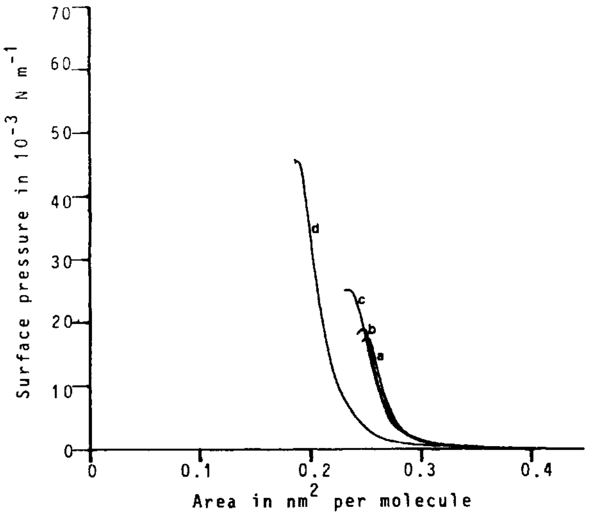

Figure 1. Surface pressure vs. area diagrams of 1 (20 °C, pH 5.5) as a function of the concentration of $CdCl_2 \cdot H_2O$ in the subphase in grams per liter: (a) 0; (b) 0.010; (c) 0.100; (d) 1.00.

supports used were a special fabrication, Celgard 2400 (Cellanese), and Trespaphan PED 6 (Kalle), hereafter, referred to as PP1, PP2, and PP3, respectively.

Methods. Monolayers were spread on $CdCl_2$-containing subphases from hexane solutions of 1 of about 0.5 mg/mL. The surface pressure–area diagrams were recorded by a computer-controlled film balance.[17] For monolayer deposition, a commercial Lauda film balance was used.

To achieve a coating exclusively on one side of the support and to reinforce the flexible support, it was attached to a Teflon disk of 50-mm diameter. A Teflon ring of 45-mm i.d. was used to fasten the polypropylene support to the disk. Thus, central areas of 45-mm diameter of the supports are coated.

In the cleaning procedure, PP1 and PP2 were washed twice with p.a. grade ether; PP3 was washed twice with p.a. grade acetone. The Teflon holder was cleaned in the same way as the support. The assembled holder and support were rinsed several times with water.

Monolayers were deposited at 20, 25, and 30 mN/m surface pressure, with a dipping speed of 5 cm/min downward and 2 cm/min upward, at 20.2 ± 0.2 °C. The layers were polymerized in air by a pen ray UV lamp (Hamamatsu Corp. Model No. 937-002) with an intensity of 500 $\mu W \cdot cm^{-2}$.

UV spectra were recorded on a Beckman Model 25 spectrometer.

Scanning electron micrographs were taken with a Cambridge Mark II A electron microscope. The samples were sputtered with gold.

The equipment for the gas permeation measurements is of a standard type and is described elsewhere.[18] The flow rates were determined barometrically at a pressure differential of 1.5 bar, using the central area of 30-mm diameter only of the coated and uncoated polypropylene supports.

Results

Spreading Behavior of the Monomer. The surface pressure–area isotherms depend strongly on the ion concentration in the subphase. As shown in Figure 1 for various concentrations of $CdCl_2 \cdot H_2O$, high concentrations of the salt increase the collapse pressure of the monolayers and reduce the collapse area; i.e., the monolayers are more stable and more densely packed. Therefore we used a subphase containing 1 g of $CdCl_2 \cdot H_2O$/L at pH 5.5. Furthermore, monolayers spread on subphases with low concentrations of $CdCl_2$ are sensitive to small amounts of polymer formed during the storage of the acid. That polymer decreases the long-time stability of the films at constant surface pressure. Subphases containing other bivalent cations such as Ba^{2+}, Ca^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+} proved to be even more sensitive to small amounts of the polymer and were not used for deposition experiments.

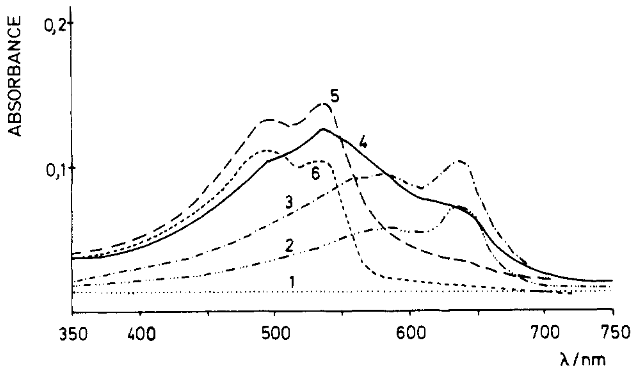

Figure 2. UV spectra of 30 layers of the cadmium salt of 1 deposited on PP3 as a function of the irradiation time (500 $\mu W \cdot cm^{-2}$, 20 °C, in air): (1) 0, (2) 0.5, (3) 3, (4) 12, (5) 21, and (6) 45 min.

Monolayer Deposition. The surfaces of the cleaned supports are strongly hydrophobic. Under the conditions chosen, a monolayer, deposition takes place at each downward and upward trip (*Y* deposition). A total of 250 monolayers could be deposited without significant decrease of the transfer ratio, as followed by the area decrease of the monolayer. The absolute value of the transfer ratio could not be determined, because the reinforcing Teflon disk is coated simultaneously. When up to 30 layers are deposited, the polymerized layers are always homogeneous in color.

Polymerization in the Multilayers. The topochemical polymerizations by UV light of diacetylenes in the solid state,[12] in monolayers, in multilayers, and in liposomes[11,19] are well-known. The polymer backbone consists of conjugated double and triple bonds, which absorb strongly in the visible region.[12] The polymerization of 1 in the multilayers was recorded by UV/vis spectroscopy as a function of irradiation time. Figure 2 shows the changes in the spectra of the multilayers with the time of irradiation on the clear PP3.

After a few seconds and up to 3 min of irradiation, an absorption peak at 640 nm is formed (blue form). Further irradiation produces a new absorption maximum at 540 nm and a second new peak at 495 nm (red form), and the 640-nm peak slowly disappears. Prolonged exposure to UV light decreases the overall absorption due to degradation processes.[20] UV/vis reflectance spectra of multilayers deposited on PP1 showed the same time dependence. Similar spectra of polymeric diacetylenes have been published and discussed in the past.[20-22] The shift in the absorption maximum is related to a conformational change of the polymer backbone.

Scanning Electron Microscopy (SEM). Except for the border region of the coated area, the color of the polymerized multilayers indicates macroscopically the homogeneity and the nearly defect-free coating of all three supports. However, SEM revealed important differences, based on the different surface structure, as shown in Figures 3–5.

The uncoated PP1 (Figure 3a) is characterized by a rough surface with two types of holes. Domains with holes of ca. 0.4-μm diameter are separated by zones of holes of ca. 1.5-μm diameter. In contrast, PP2 (Figure 4a) has a regular surface with uniform holes of ca. 0.2 × 0.05 μm, whereas PP3 (Figure 5a) is smooth and devoid of holes.

After deposition of 16 monolayers of the cadmium salt of 1, the modified surfaces of PP1, PP2, and PP3 still show significant differences. This is demonstrated by the comparison of the three sets of micrographs in Figures 3–5.

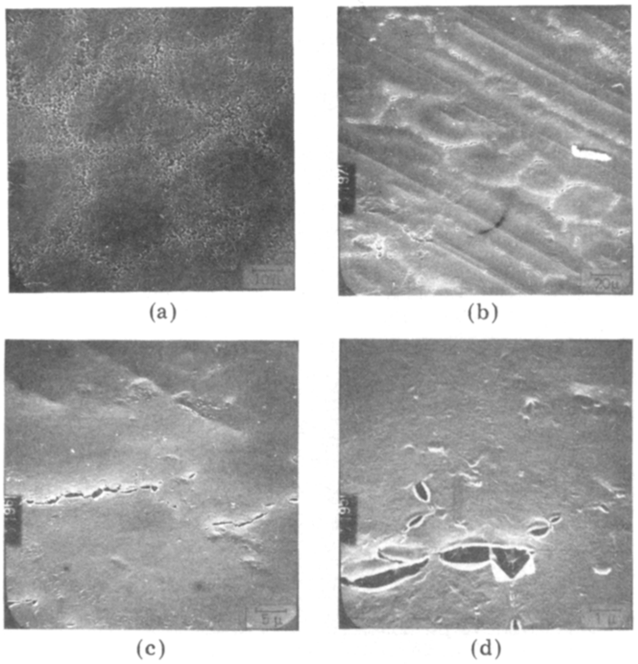

Figure 3. Scanning electron micrographs of coated and uncoated PP1: (a) uncoated, magnification 1000, 20 kV; (b) coated with 16 layers of the cadmium salt of 1, deposited at 20 mN/m, 20.2 °C, polymerized by UV irradiation for 20 min (see Figure 2), magnification 500, 20 kV; (c) detail of the center of (b), magnification 2000, 20 kV; (d) detail of the center of (c), magnification 10 000, 20 kV.

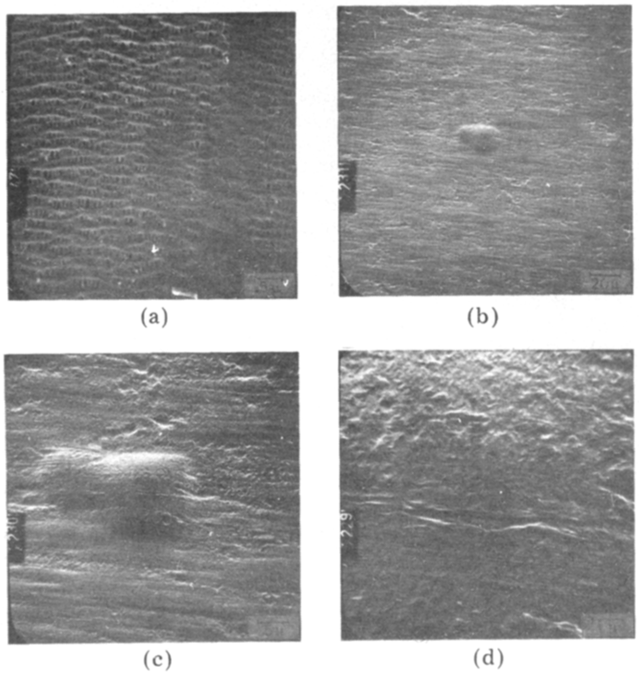

Figure 4. Scanning electron micrographs of coated and uncoated PP2: (a) uncoated, magnification 18 500, 20 kV; (b) coated with 16 layers of the cadmium salt of 1, deposited at 25 mN/m, 20.2 °C, polymerized by UV irradiation for 3 min (see Figure 2), magnification 500, 20 kV; (c) detail of the center of (b), magnification 2000, 20 kV; (d) detail of the center of (c), magnification 10 000, 20 kV.

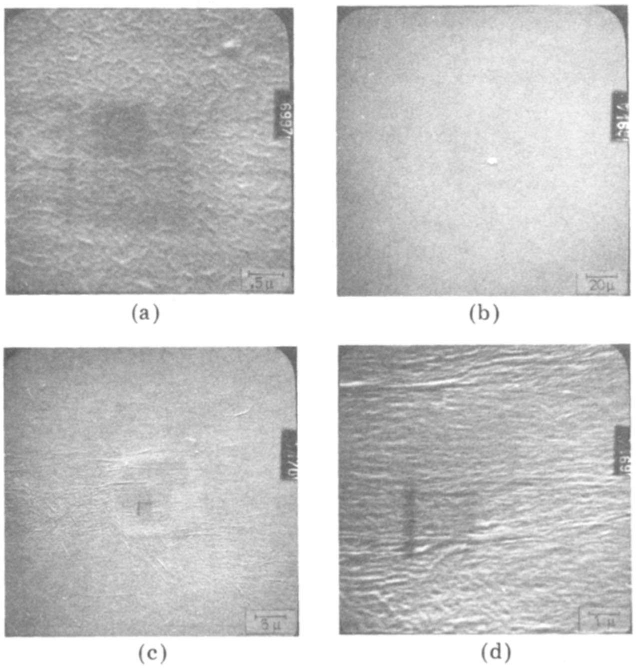

Figure 5. Scanning electron micrographs of coated and uncoated PP3: (a) uncoated, magnification 22 000, 20 kV; (b) coated with 16 layers of the cadmium salt of 1, deposited at 25 mN/m, 20.2 °C, polymerized by UV irradiation for 3 min (see Figure 2), magnification 500, 20 kV; (c) detail of the center of (b), magnification 2000, 20 kV; (d) detail of the center of (c), magnification 10 000, 20 kV.

The layers on PP2 (Figure 4) and PP3 (Figure 5) exhibit smooth and, up to a magnification of 20 000, defect-free surfaces, although there is a different surface texture due to the different supports. In the layers deposited on PP1 (Figure 3), however, rift systems can be observed as well as additional uncovered spots, both of which reach down to the surface of the support (Figure 3b–d). The comparison of these micrographs with the surface of PP1 (Figure 3a) strongly suggests that the cracks stretch above the zones of the big holes. At high magnification, the crack can be seen as a complete fracture of the built up multilayer (Figure 3c,d). The rough surface of the support material can be seen clearly in Figure 3d.

In contrast, micrographs b–d of Figure 4 of the coated PP2 show that the small holes can be bridged by the multilayer if the support surface is smooth enough. Further comparison with the micrographs of the coated PP3 (Figure 5b–d) suggests that the smoother and more regular the surface of the support material is (Figures 3a, 4a, and 5a), the more perfect is the modified surface after the multilayer deposition. Even the highest magnifications of the three coated polypropylenes (Figures 3d, 4d, and 5d) show that all the minor deformations in the surface of the supports are perfectly covered.

For all supports, the surface pressure of the deposition process was varied between 20 and 30 mN/m. No significant differences between the samples were observed. The influence of the polymerization was tested, too. Again, the samples of monomeric layers and polymerized layers in the blue form (3 min of irradiation; see Figure 2) and the red form (20 min of irradiation; see Figure 2) did not exhibit significant differences for all three supports.

Gas Permeation Measurements. Preliminary investigations of the permeation of CH_4 through the polymeric LB composite membranes on the porous supports PP1 and PP2 were made. Membranes built up on PP1 did not reduce the gas flow. However, membranes built up on PP2 reduced the gas flow depending on the number of layers deposited (Table I). This is in agreement with the SEM micrographs of the coated PP1 (Figure 3) and the coated PP2 (Figure 4). The cracks visible on PP1 (Figure 3b–d) apparently act as channels for unhindered gas flow.

Figure 6 shows that there is a rapid decrease in the permeability up to 12 layers deposited. This is probably

Table I
Gas Flow through LB Composite Membranes[a]

support	no. of layers	flow of CH_4, $m^3 \cdot s^{-1}$
PP1	uncoated	$>15 \times 10^{-6}$
PP1	6	$>15 \times 10^{-6}$
PP1	12	$>15 \times 10^{-6}$
PP1	18	$>15 \times 10^{-6}$
PP1	24	$>15 \times 10^{-6}$
PP1	30	$>15 \times 10^{-6}$
PP2	uncoated	15×10^{-6}
PP2	2	7×10^{-6}
PP2	6	4×10^{-6}
PP2	12	0.9×10^{-6}
PP2	18	0.5×10^{-6}

[a] The LB multilayers of the cadmium salt of 1 were polymerized for 2 min by UV irradiation (blue form) with 500 $\mu W \cdot cm^{-2}$ (see Figure 2). The uncoated PP1 and PP2 were washed and irradiated identically. The pressure differential was 1.5 bar at 20 °C. The gas flow through the coated PP2 is reduced at least 30-fold for 18 deposited layers of the cadmium salt of 1 as compared to the uncoated PP2.

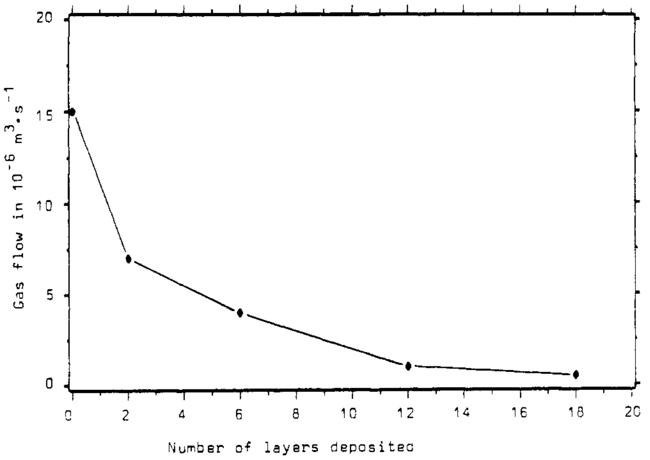

Figure 6. Flow of CH_4 through PP2 coated with the cadmium salt of 1, deposited at 25 mN/m, 20.2 ± 0.2 °C, polymerized for 2 min (blue form; see Figure 2).

due to improved coverage of the support. For coating with greater numbers of monolayers, there is only slight improvement against CH_4 flow. The coating may be perfect and the permeation is multilayer thickness dependent, or, alternatively, the coating may still have minor defects, which are eliminated by deposition of further monolayers. The latter explanation is more likely. This has to be checked by experiments using gases of different polarity, which should show different flow rates in the case of a perfect multilayer.

Discussion

Polymeric diacetylene multilayers on permeable supports have been shown to reduce permeation of certain gases and thus may be suited for gas separation. The necessary high quality of extended coated areas may be achieved with the LB technique.

Similar systems prepared by deposition of poly(vinyl stearate) on porous polypropylene were reported to reduce the flow of N_2.[24] Recent reports of Regen et al. claimed an alternative method to produce well-ordered support coatings by irradiation of polyethylene in a suspension of vesicles of polymerizable lipids.[23] However, these coatings have not yet been sufficiently characterized, and there is no evidence that an ordered coating was obtained.

The advantage of diacetylenes is that from the color of the polymer one can judge the homogeneity or inhomogeneity of the deposited layers and the extent of polymerization. However, they have a rigid, inflexible backbone, due to the polymerization in the hydrophobic part of the amphiphiles, and still possess reactive groups. These properties limit the application for separation processes. Amphiphiles with a polymerizable moiety in the hydrophilic part of the molecule (e.g., acrylic, methacrylic, and vinyl[11,24]) may result in materials having better properties.

Registry No. 1 homopolymer, cadmium salt, 82606-32-4; polypropylene, 9003-07-0.

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