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Ultrathin Films of Amphiphilic Ionic Polyacetylenes

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ABSTRACT: Thin films of amphiphilic ionic polyacetylenes based on poly (*N*-octadecyl-2-ethynylpyridinium bromide) were formed using the Langmuir−Blodgett and layer-by-layer deposition techniques. The surface pressure−molecular area isotherms of the monolayers of these polymers at the air−water interface indicate that the alkyl (octadecyl) chains of the repeating units are oriented perpendicularly to the water surface while the rigid conjugated polymer backbones are located within the planar layer of the interface. The molecular organization of transferred polymer multilayers has been also studied by FT-IR, ATR, GAR, and ellipsometry. As a result of this study, a model of the molecular organization of ultrathin films is proposed, in which the conjugated backbone chains of the polymer molecules are oriented parallel to the substrate and are sandwiched between layers of interdigitated octadecyl groups. The electrical conductivity of the polymer films was found to increase substantially upon doping with iodine. Enhanced gas permeability and permselectivity of membranes from Nafion were achieved by deposition of ultrathin films of the above polyacetylene on these membranes.

Introduction

Polyacetylenes have been the focus of research in the field of molecular electronics as conducting wires. A large number of polyconjugated systems such as polyacetylenes and poly(diacetylene)s were also recently studied in the form of thin films.[1] We have recently reported on the synthesis and characterization of conjugated ionic poly(*N*-alkylethynylpyridinium bromides) with a long alkyl chain ($C_{18}H_{37}$) attached to the quaternized nitrogen. These polymers combine conjugation and amphiphilicity and are therefore prime candidates for the formation of two-dimensional conjugated systems.[2] The structure of these polymers is given in Figure 1. They were prepared by activation of the acetylenic bond through quaternization of the pyridine nitrogen, which resulted in a spontaneous polymerization of the triple bond.[3−4]

Control of the organization of a film on the molecular level is a very desirable feature for electronic applications. Techniques such as Langmuir−Blodgett film deposition and “layer-by-layer” self-assembly of polycation and polyanion are of interest. With both these approaches, thin films of ionic polyacetylenes with direct control over the degree and type of ordering and film thickness may be obtained. In this paper we report on the formation and characterization of thin films of a conjugated ionic polymer, poly(*N*-octadecyl-2-ethynylpyridinium bromide) [P2EPY/$C_{18}H_{37}$Br]. The uniform and facile formation of multilayers leads to layered systems which have potential in electro-optical, permeation, and permselectivity applications.

Experimental Section

1. Synthesis. P2EPY/$C_{18}H_{37}$Br was prepared using two different synthetic approaches. The first approach involved the direct reaction of 2-ethynylpyridine (2-EPY) with 1-bromooctadecane (1-BO). The second involved quaternization by 1-BO of uncharged poly(2-ethynylpyridine) (P2EPY) previously prepared by thermal polymerization.[5] A completely quaternized P2EPY/$C_{18}H_{37}$Br homopolymer was produced in the former reaction, while a random copolymer of 2-EPY and *N*-octadecyl-2-ethynylpyridinium bromide (P2EPY-q-octadecyl) was obtained in the latter due to partial quaternization (25−30 mol %) of P2EPY. We should note that assignment of complete quaternization is based on the absence of the peak at −74 ppm corresponding to the unquaternized nitrogen in the ^{14}N NMR spectrum, and the presence of residual unquaternized sites, at the level of sensitivity of NMR, may not be ruled out (see below). The details of synthesis and characterization of these polymers have been reported elsewhere.[2] The reaction schemes are shown in Figure 2.

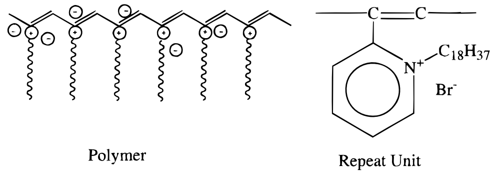

Figure 1. Schematic structure of P2EPY/$C_{18}H_{37}$Br.

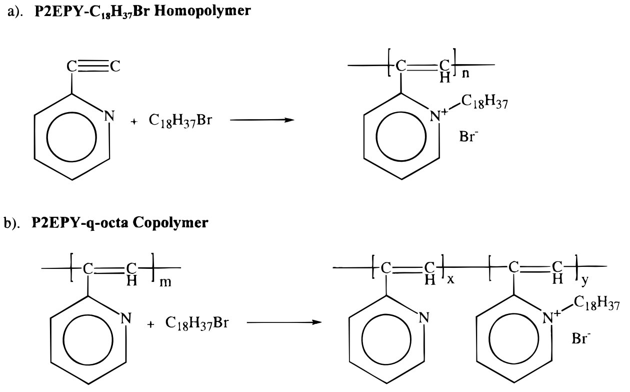

Figure 2. Reaction schemes of the homopolymer and copolymer formation.

2. General Procedures and Characterization. Compression Isotherms and L−B Multilayers. All pressure−area isotherm measurements and deposition of mono- and multilayers were carried out using a Lauda Langmuir Film-

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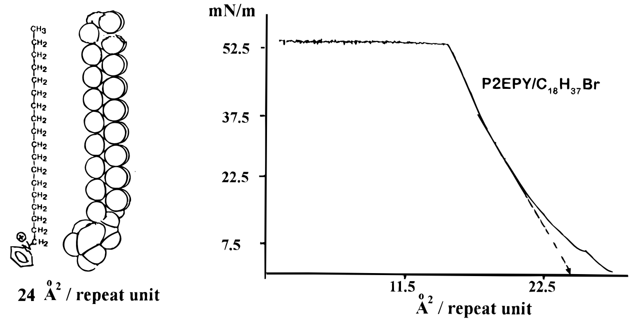

Figure 3. Surface pressure−molecular area isotherms of conjugated polyacetylenes at the air−water interface (subphase at pH = 7.0, 20 °C).

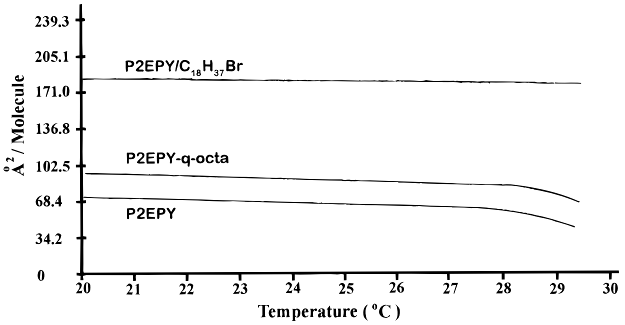

Figure 4. Stability of monolayers of polyacetylenes at the air−water interface as a function of subphase temperature. The surface pressure was maintained at 25 mN/m.

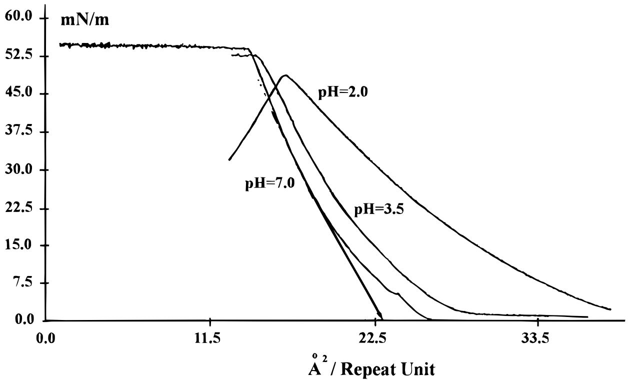

Figure 5. Influence of the pH of the subphase on the surface pressure−molecular area isotherm of P2EPY/$C_{18}H_{37}$Br at the air−water interface.

waage FW-2 trough. For compression isotherm studies about 100 μL of the polymer solution (10^{-4} M, in $CHCl_3$) was spread onto the water surface (ultrapure Milli-Q water, resistivity ≥18 MΩ cm) with the help of a syringe. After evaporation of the spreading solvent, the available surface area was gradually decreased with the help of a computer-controlled compression barrier, and the surface pressure was recorded against the surface area. The subphase temperature was maintained at 20 °C. During the transfer of the films onto solid substrates, the monolayer was held at a constant pressure of 25 mN/m. The downstroke and upstroke dipping speeds were 20 mm/min. The film was dried in air for 20 min before the next dipping stroke while a pause of 30 s was given at the end of each downstroke to ensure stabilization of the film. Transfer ratios were determined from the decrease in the surface area during each transit of the substrate and the surface area of the substrate. For the determination of the molecular area of the repeat unit we have used the value of the intersection of the tangent to the steepest portion of the compression isotherm.

Layer-by-Layer Alternating Deposition. Polymer thin films were also obtained using a layer-by layer method.[6,7] This is a 15 min process involving alternate dipping of a substrate into a dilute solution containing a polycation, washing with Mili-Q water, and drying under N_2, followed by dipping into a dilute solution containing a polyanion for 15 s and drying under N_2. Here sodium poly(styrenesulfonate) with a MW of 7 million (18 mg/120 mL of Milli-Q water, pH 5.5) was used as the polyanion and P2EPY/$C_{18}H_{37}$Br (10 mg/10 mL of MeOH) as the polycation.

FT-IR, UV−Visible, and Ellipsometry Measurements. FT-IR spectra of L−B mono- and multilayers of P2EPY/$C_{18}H_{37}$Br or P2EPY-q-octadecyl deposited on a ZnSe ATR prism (Harrick Scientific) were obtained using a Perkin-Elmer 1600 series FT-IR. A UV−vis spectrophotometer (GBC, UV/VIS 918) with temperature control and a computer-aided data analysis software program was used to measure the UV absorption of the conjugated multilayer films of P2EPY/$C_{18}H_{37}$Br and P2EPY-q-octadecyl deposited on quartz slides. L−B multilayers of the polymers deposited on a frosted glass were used for the measurement of thickness by ellipsometry (43603-200E, Rudolph Research, Flanders, NJ) at 632.8 nm.

Gas Permeation Measurements. A gas permeation cell (CSI Inc., Model CS-135) with a sample diameter of 3.0 cm was used. The thickness of Nafion membranes was 170 μm. All measurements were carried out at 30 °C, unless specified. A constant pressure differential of 14.7 psi was maintained across the membrane with downstream open to atmosphere. The data were recorded after the system attained a steady state. At least five measurements were taken for each sample. The standard deviation was within 5% of the reading.

Results and Discussion

Figure 3 illustrates a surface pressure−molecular area isotherm of P2EPY/$C_{18}H_{37}$Br at the air−water interface, which shows a well-defined isotherm with a collapse pressure in excess of 50 mN/m. The fully quaternized P2EPY/$C_{18}H_{37}$Br is considerably more expanded and more stable than the unquaternized and partially quaternized P2EPY. It can be seen from Figure 4 that the limiting molecular area increases with the extent of quaternization. The measured limiting area per repeat unit of the completely quaternized polymer is about 23−24 Å². This is not unreasonable for a cross-sectional area of an alkyl chain (20 Å²) which has a pyridinium ring head group.[8] We believe that the octadecyl chains are nearly perpendicular to the water surface with the conjugated polymer chain oriented in a plane parallel to the water surface.

The effect of temperature on the stability of the monolayers of P2EPY/$C_{18}H_{37}$Br, the unquaternized P2EPY, and the partially quaternized P2EPY was studied by varying the temperature of the monolayer held at a constant pressure. The initial pressure was achieved by compressing the monolayer at a speed of 6 Å² molecule^{-1} min^{-1} to a pressure of 25 mN/m and then allowing it to stabilize. The temperature of the subphase was varied with time and the molecular area was measured as a function of temperature. Figure 4 represents the variation of molecular area as a function of temperature for the three molecular systems. The monolayer of P2EPY/$C_{18}H_{37}$Br is very stable in the temperature range 20−30 °C, as compared to those of the unquaternized and partially quaternized P2EPY, which display a change of the molecular area with increasing temperature. Film stability increases with the degree of quaternization of the polymer, due to the increased amphiphilicity of the quaternized polymer.

The isotherms of P2EPY/$C_{18}H_{37}$Br recorded at low pH values of the subphase show a certain expansion of the monolayer with decreasing pH (Figure 5). This is possibly due to protonation of residual unquaternized sites that may be present in the "fully" quaternized polymer (see Experimental Section). These residual

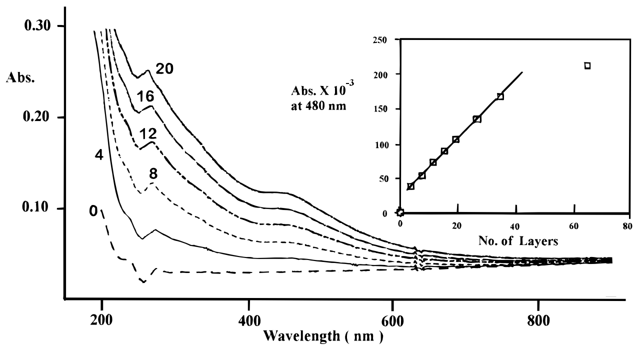

Figure 6. UV spectra of P2EPY/$C_{18}H_{37}Br$ L−B multilayers deposited on quartz. The number of layers deposited is indicated. The absorbance at 480 nm as a function of the number of layers is given in the inset.

sites may be accessible to protonation when the polymer is in its relatively extended conformation within the monolayer spread on the protonating substrate. The number of such sites, although small (less than 10%), can affect the conformation of the chain within the monolayer. A similar phenomenon has been observed for the partially quaternized P2EPY copolymer (25−30 mol % of unquaternized sites estimated from ^{14}N NMR spectra). The isotherm of unquaternized P2EPY showed, on neutral substrates, a more condensed molecular packing than the quaternized polymer. Monolayers could not be obtained at low pH values. This is due to the rapid dissolution of the polymer in the subphase upon protonation.

The UV−vis spectra of the fully quaternized P2EPY/$C_{18}H_{37}Br$ L−B multilayers are shown in Figure 6. For all transfer studies, the monolayers were compressed to an annealing surface pressure of 25 mN/m and then deposited vertically. The polymer was found to be very stable at the air−water interface and deposition proceeded as a Y-type film with approximately 95−100% transfer on the upstroke and 90−95% on the downstroke. The contact angle measurement of the outer surface of the L−B film was found to be 65−70° for water and less than 5° for heptane. This indicates that the outer surface of the film after the upstroke is hydrophobic. The linear increase in absorbance with the increase of the number of layers as is illustrated in Figure 6 confirms the reproducibility and uniformity of the transfer process.

Ultrathin films of polymers were also prepared using a simple and effective layer-by-layer deposition method. This process is based on the alternating deposition of polycationic and polyanionic systems assisted by the ionic interaction. In this method, one simply dips a substrate into a solution containing a positively charged polymer, rinses the substrate with water, dries it, and then dips it into a solution containing a negatively charged polymer. The uniformity of the ultrathin films obtained using this process is again determined by UV−vis spectroscopy (Figure 7). It can be seen from Figures 6 and 7 that, in the case of L−B layers, the deviation from linearity of spectral absorption with the number n of layers occurs at approximately $n = 60$, while for the self-assembled layers, this number is much lower, at approximately $n = 12$. One is led to conclude that the L−B technique results in more uniform and more condensed layers than the technique of layer-by-layer self-assembly. This is also indicated by a slightly higher value of the extinction coefficient for the L−B films as compared to self-assembled layers.

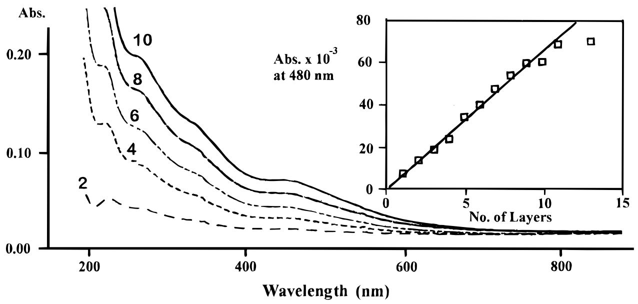

Figure 7. UV spectra of alternating multilayers of P2EPY/$C_{18}H_{37}Br$ deposited on quartz via the layer-by-layer technique. The number of treatments is indicated. The inset gives the plot of absorbace at 480 nm as a function of the number of layers.

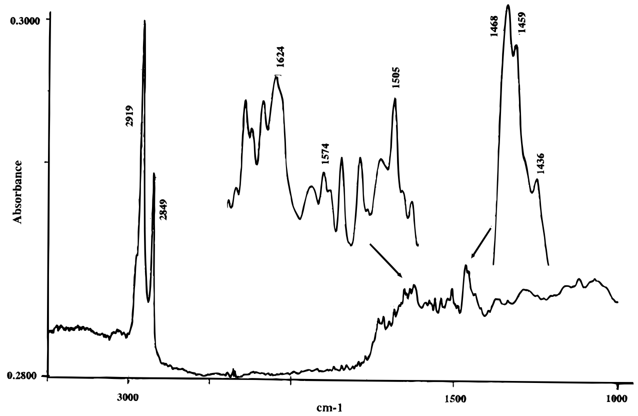

Figure 8. FT-IR spectrum of the L−B film (10 bilayers) deposited on the surface of a ZnSe prism.

The molecular orientation and structure of the P2EPY/$C_{18}H_{37}Br$ L−B films have been investigated by FT-IR, attenuated total reflection (ATR), and grazing angle reflection (GAR) spectroscopy. The strong absorbance bands arising from CH_2 asymmetric (2919 cm^{-1}) and symmetric (2849 cm^{-1}) stretching modes of the alkyl chains is indicative of highly ordered octadecyl chains within the layers (Figure 8).[9] Of particular interest in Figure 8 is the shape of the band near 1470 cm^{-1}, which is due to the CH_2 scissoring mode. The splitting of the CH_2 scissoring mode is indicative of an orthorhombic subcell packing of alkyl chains.[10] Another important feature of the FT-IR spectra of mono- or multilayers is the strong band at 1624 cm^{-1}, suggesting that −C═C− double bonds of the polymer are highly conjugated.[11] It is noted that all spectra of mono- and multilayers differ only by the intensities of the absorption peaks. These are proportional to the number of layers. This confirms the uniformity of deposition of multilayers onto solid surfaces.

GAR spectra of the L−B multilayers of P2EPY/$C_{18}H_{37}Br$ indicate that octadecyl alkyl chains are highly oriented within the layers. One can see that no absorption peaks were detected, at the level of sensitivity of these measurements, with the polarization vector vibrating perpendicularly to the substrate plane, i.e. angle of incidence of the beam at 0° (Figure 9a), while absorption peaks of the CH_2 and −C═C− double bonds were observed with the light vector vibrating parallel to the substrate plane, or the angle of incidence of about 90° (Figure 9b). The ATR spectrum shows strong multipeak absorptions between 2850−2960 and 1610 cm^{-1} (corresponding to absorption by oriented −CH_2− and −C═C− bonds of the films), which confirms the FT-IR and GAR measurements above.

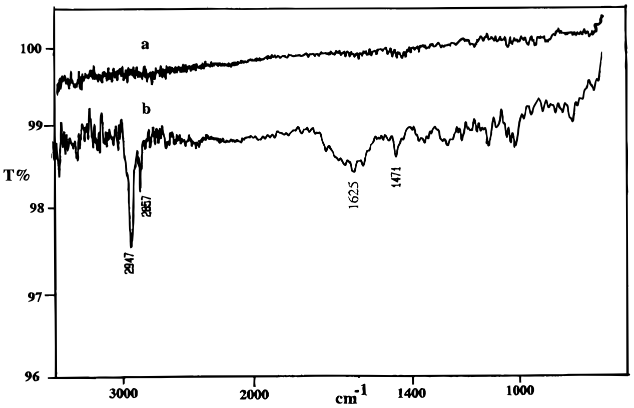

Figure 9. GAR spectra of P2EPY/$C_{18}H_{37}Br$ L−B film deposited on glass (10 bilayers); beam incidence at 0° (a) and at 90° (b).

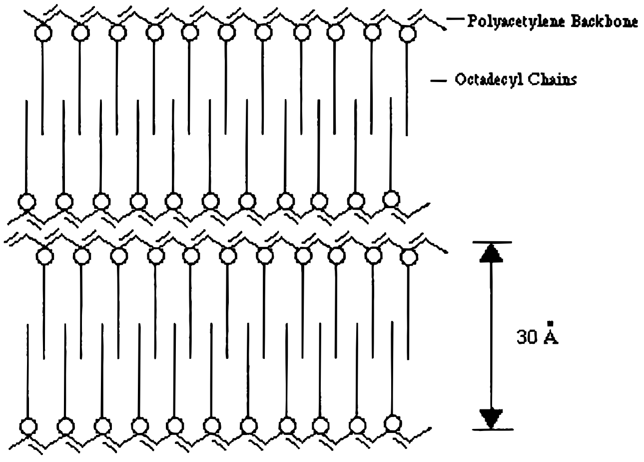

Figure 10. Schematic representation of the interdigitated molecular structure of L−B multilayers of P2EPY/$C_{18}H_{37}Br$.

Two L−B films, one containing 30 and the other 54 bilayers, gave, by ellipsometry, a thickness of 913 and 1576 Å, respectively. It follows that the thickness of one bilayer is approximately 30 Å, which is close to the values obtained from the literature for molecules of this type.[12] Based on the value of the molecular area of 24 Å and on the thickness of the bilayer, we believe that the molecular organization of the multilayers of P2EPY/$C_{18}H_{37}Br$ consists of the rigid conjugated backbone chains arranged parallel to the substrate and sandwiched between layers of flexible octadecyl groups. The latter may in principle be either interdigitated or tilted. We have ruled out the tilted model because such a tilt of side groups would be close to 40−45° with respect the layer normal and is contradicted by the strong dichroism of the GAR spectra. We believe that a model with interdigitated side groups (Figure 10) agrees better with our data. Such structures are not infrequent in the case of comblike smectogenic polymers which present cases of various types of interdigitation and which are structurally similar to the polymers studied in this work.[13] Interdigitated structures are also frequent in molecular complexes between polyelectrolytes and long amphiphilic chains.[14]

The UV−vis spectra of L−B multilayers of P2EPY/$C_{18}H_{37}Br$ display an absorption trailing to longer wavelengths, as compared to that of the corresponding polymer solution in methanol (Figure 11). This trailing may be indicative of increased conjugation induced by ordering of backbones within the L−B film, as compared to the polymer backbone in solution.

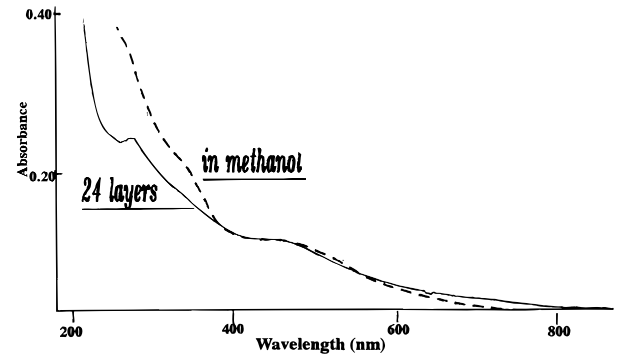

Figure 11. UV spectra of P2EPY/$C_{18}H_{37}Br$ multilayers (24 layers) deposited on quartz from a dilute solution of P2EPY/$C_{18}H_{37}Br$ in MeOH.

The electrical resistance of the L−B films of the undoped P2EPY/$C_{18}H_{37}Br$ (10 bilayers deposited on an interdigitated microelectrode) was high ($>2 \times 10^{11}$ Ω) and decreased to 2×10^{5} Ω upon doping with iodine. The high electrical resistance of the L−B films is attributed to the fact that the conjugated backbone is sandwiched between the insulating octadecyl chains.

We have previously reported on the gas permeation study of ionic polyacetylene/Nafion composite membranes in which 2-ethynylpyridine was thermally polymerized in situ within a commercial Nafion film 170 μm thick.[15] This composite membrane showed an interesting gas permeation behavior, namely high permselectivity and an excellent long-term stability. Low oxygen permeability, however, limited its application potential. Permeability (P) of a gas depends on the solubility (S) and the diffusion coefficient (D) of the gas in the membrane ($P = SD$).[16] It is known that substituted conjugated polyacetylenes are characterized by high oxygen solubility since conjugated −C=C− double bonds display a high affinity for oxygen.[17] This suggests that the oxygen permeability of Nafion films can be improved, while the nitrogen permeability is kept low, if a coating of conjugated ionic polyacetylene is applied in the form of a thin layer.

Several ionic polyacetylenes were prepared and deposited on Nafion films using the L−B technology and the layer-by-layer film deposition methods discussed above. Gas permeation properties of such membranes were evaluated and compared. The results are summarized in Table 1. Pure Nafion films show a low gas permeability and a low permselectivity. After a certain number of L−B multilayers of the ionic polyacetylene are deposited on Nafion, the composite membranes exhibit an increase in both oxygen permeability and permselectivity. For example, the Nafion membrane on which 5 L−B bilayers of the ionic polyacetylene P2EPY/$C_{18}H_{37}Br$ were deposited displays an increase of oxygen permeability $P(O_2)$ from 8.4 to 16.9 barrers and a concomitant permselectivity increase for oxygen $\alpha = P(O_2)/P(N_2)$ from 2.0 to 4.7. The conjugated system of double bonds in the ionic polyacetylene acts as a "molecular oxygen pump" increasing the gradient of oxygen across the membrane. As a result, there is an increase of the oxygen flux through the composite membrane as compared to a membrane based on the pure Nafion. Increasing the number of layers of P2EPY/$C_{18}H_{37}Br$ on Nafion decreases only slightly its permeability to oxygen. The simultaneous increase of permeability and permselectivity for oxygen is an unusual and very interesting phenomenon which may have poten-

Table 1. Permeation Behavior of Ionic Polyacetylene/Nafion and Ethyl Cellulose Membranes

sample	preparation	$P(O_2)$ (barrers)	$P(N_2)$ (barrers)	α
Nafion		8.4	4.1	2.0
2EPY/Nafion[14]	5% 2EPY polymerized in situ	3.1	0.7	4.4
P2EPY/$C_{18}H_{37}Br$/Nafion	10 L−B bilayers on Nafion	12.4	2.7	4.6
P2EPY/$C_{18}H_{37}Br$/Nafion	5 L−B bilayers on Nafion	16.9	3.6	4.7
P2EPY/$C_{18}H_{37}Br$/Nafion	10 alternating layers on Nafion	11.1	3.2	3.5
P2EPY/$C_{18}H_{37}Br$/Nafion	10 L−B bilayers on Nafion, aged for 10 months	17.0	3.8	4.5

tially important application in gas separation technology.

The membranes described above show excellent long-term stability. For example, the permeation of membranes based on P2EPY/$C_{18}H_{37}Br$ deposited on Nafion did not change significantly after 10 months of aging under ambient conditions. In contrast, the high oxygen permeability of nonionic polyacetylenes drastically decreases with age of the membrane.[17]

Conclusions

In summary, L−B films and alternating multilayers of an amphiphilic ionic polyacetylene, P2EPY/$C_{18}H_{37}Br$, have been obtained. The surface pressure−molecular area isotherms at the air−water interface suggest that the alkyl (octadecyl) chains of the repeating unit are perpendicular to the water surface while the rigid conjugated polymer chains are in the plane of the air−water interface. The IR studies indicate that the transferred polymer multilayers organize with the conjugated backbone chains oriented parallel to the substrate. The thickness measurements suggest that the polyacetylene backbones are sandwiched between layers of interdigitated octadecyl groups.

The electrical conductivity of the polymer films was found to increase substantially after doping with iodine. The study of oxygen and nitrogen permeation of membranes of P2EPY/$C_{18}H_{37}Br$ deposited on Nafion substrates shows that both permeation of oxygen and the permselectivity toward this gas increase simultaneously by incorporating ionic polyacetylene into the composite membrane. A very thin layer of ionic polyacetylene is needed to act as an oxygen pump. The membranes show an excellent long-term stability. A more detailed study of permeation by such composite systems will be published elsewhere.

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