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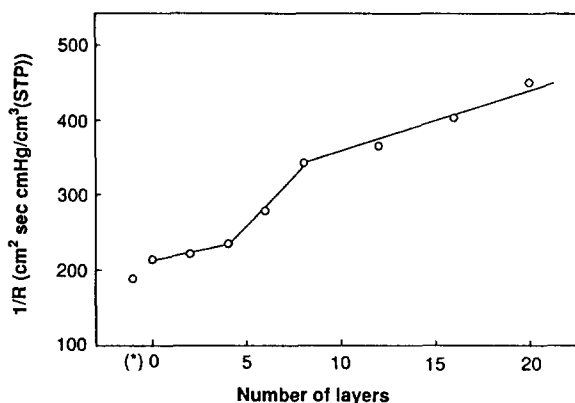
### An Evaluation of a Polymeric Langmuir-Blodgett Film on Porous Substrate by Gas Permeability and SEM Micrographs

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The Langmuir-Blodgett (LB) technique provides a unique approach to achieve supramolecular architectures of layered assemblies of suitably designed organic molecules. The LB films have been used as sophisticated molecular devices useful to test molecularly controlled processes of energy transfer, charge carrier motion, energy conversion, molecular recognition, and separation.<sup>1</sup> In particular, the fact that its structure is highly organized in three dimensions makes such material well-suited for adjustment and optimization of its transport properties. But, the LB films have problems to be solved for their practical applications, which are in part due to the inherent instability and the defects of the layered assemblies.<sup>2</sup> Specifically, when we consider its use for separations, the mechanical stability of the film should be importantly taken into account, because the separation must happen through the films that are built up on stable, porous supports. As a breakthrough to improve the mechanical sta-



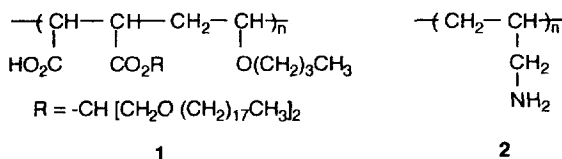
**Figure 1.** N<sub>2</sub> gas permeation rate (R) through LB films of **1** with **2** on a poly(propylene) membrane filter (METRICEL) measured by the pressure method. (\*); measured without poly(propylene) substrate.

bility, the use of preformed polymers has been investigated extensively in the recent years.<sup>3,4</sup> Among the reports on polymeric LB films, Kunitake *et al.* have demonstrated stabilization of the LB films by electrostatic interaction of ionic polymers with oppositely-charged amphiphiles<sup>5</sup> and by covalent cross-linking of ionically interacting polymers.<sup>6</sup>

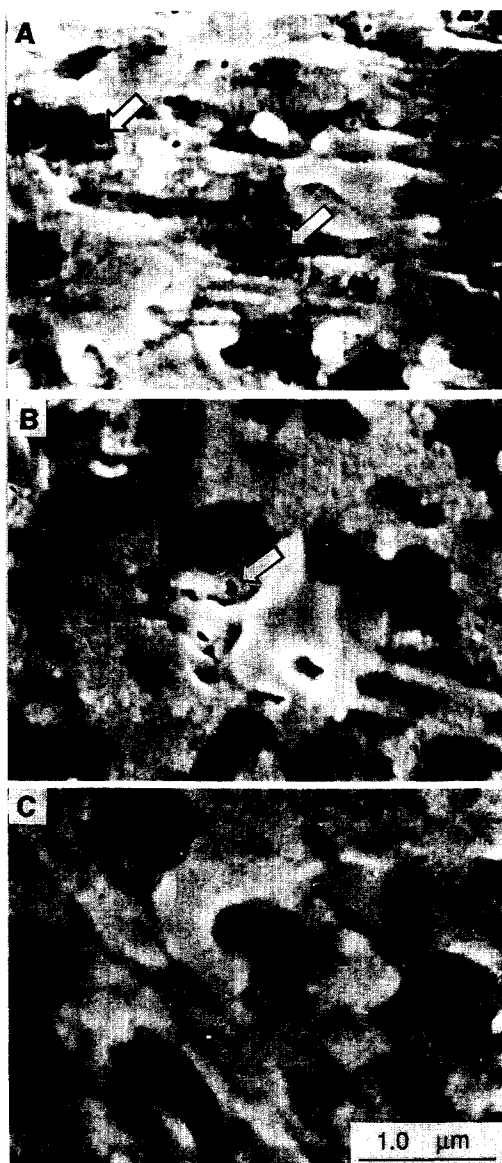
The gas transport through preformed polymeric LB films has been investigated by a few groups.<sup>7-12</sup> Stroeve *et al.* reported that the gas permeabilities of nitrogen, methane, and carbon dioxide in polypropylene-based asymmetric membranes were merely a function of the molecular weight of the gas.<sup>8</sup> Kunitake *et al.* determined the ratio  $\alpha$  of the oxygen and nitrogen permeation rates through a LB film of an amphiphilic polymer.<sup>9</sup> The  $\alpha$  value was found to be 3.2. Another study also showed that the composite films of a poly(*N*-dodecylacrylamide) revealed a higher permeation rate for oxygen.<sup>10</sup> In those studies of gas transport through the LB films, besides the structure of polymers employed, it is crucial for the utility of such a composite membrane that the pores of the support are homogeneously coated with the multilayer film. However, few systematic investigations on the relation between gas permeability and LB film quality have been reported.<sup>7</sup> Here we report a preliminary result as to the dependency of N<sub>2</sub> gas permeability on the macroscopic states of a polymer LB film observed by SEM.

### Results and Discussion

The properties of the monolayers at the air-water interface and the resulting LB films of **1** polyion-complexed with **2** were already described.<sup>6</sup> The polymer **1** was spread on aqueous polyallylamine **2**. The monolayer gives expanded



phase. The formation of a polyion complex at the interface and in the LB films could be confirmed by  $\pi$ -A isotherms,



**Figure 2.** SEM micrographs of LB films on a poly(propylene) membrane filter(METRICEL). A; 4 layers B; 6 layers C; 8 layers. Typical defects are indicated with arrows.

FT-IR spectroscopy, and XPS measurements. An elemental analysis of this film, which was performed by XPS measurement, showed that the content of the N atom from **2** incorporated from the subphase in the LB film is 2.4 per maleate unit and the content of ammonium N by salt formation between carboxyl and amino groups becomes 33% of the maleate unit.<sup>6</sup> For the permeability measurement the monolayers were transferred onto poly(propylene) membrane filters (pore diameter, 0.2  $\mu\text{m}$ ). The Y type deposition was carried out at a surface pressure of 15 mN/m and a transfer rate of 4 mm/min. The transfer ratio was 1.2 to 0.9 for 20 layer depositions.

Figure 1 shows permeability of  $\text{N}_2$  gas through the LB films measured by the pressure method. The curve reveals three distinct slopes with the increasing number of deposited layers. Although the LB films don't play a role as permeation

barrier until 4 layers, the reduction of gas transport is clear from the 6 layers. And then, the reduction rate of gas transport is decreased from 8 layers. This reduction pattern of the transport rate is different from that observed from polymerized LB films of cadmium salts of hexacosyl-10,12-diyonic acid, where the LB films revealed half reduction of transport rate by two layers and no more significant reduction of transport rate more than 12 layers.<sup>7</sup> In the latter case, however, there was no mention of the correlation between the permeability and the film state under 12 deposited layers, and SEM figures of the composite films coated with less than 12 layers had not been presented. SEM observation of present LB films on poly(propylene) membrane filters gives an explanation on the correlation between gas permeability and macroscopic structure of the films. As shown in Figure 2, the macroscopic hole-defects of the LB films are gradually reduced with the increasing number of deposited layers. We can observe the defects until 6 layers, but the defects are not seen from 8 layers. Although the gas transport through the microdefects, which were not detected by SEM, can not be totally excluded, the reduction pattern of the gas transfer rate with the deposited layers is supposed to be accountable along with the decrease of the macroscopic defects.

## Experimental

**Materials.** The preparation of copolymer **1** ( $M_w=5.9 \times 10^4$ ,  $M_w/M_n=4.5$ ) was described previously.<sup>6</sup> Poly(allylamine) hydrochloride ( $M_w=1.0 \times 10^4$ ) was purchased from Nitto Boseki Co. and treated with a strong anion exchange resin (Amberlite IRA-402) to obtain free poly(allylamine). The concentration of the amino group in aqueous solution was determined by colloid titration with standard poly(vinyl sulfate) solution using Toluidine Blue O as indicator. All the solvents were commercial products of spectroscopy grade, and nitrogen gas was of five nine grade.

**Fabrication of LB Films on Porous Substrate.** The formation and characterization of the monolayer was already described.<sup>6</sup> The deposition of the monolayer was performed in the vertical mode by using a computer-controlled film balance(FSD-50) and lifter(FSD-51) system(San-esu Keisoku). The transfer onto porous solid substrate was carried out at a surface pressure of  $15.0 \pm 0.2$  mN/m and a deposition rate of 4 mm/min. The temperature of the subphase was kept at  $30 \pm 0.1^\circ\text{C}$ . The employed substrate was a poly(propylene) membrane filter (METRICEL, pore diameter; 0.2  $\mu\text{m}$ ).

**Measurements.** Gas permeabilities were obtained at  $25^\circ\text{C}$  in the Yanaco(GTR-10VS) permeation apparatus. The maximum initial pressure in the upstream chamber was 10 Torr and the initial pressure in the downstream chamber was less than 0.1 Torr. The pressure change in the downstream chamber was recorded with a differential pressure transducer(MKS Baratron). Scanning electron microscopy(SEM; Hitachi S-900) was used to observe the surface morphology of a poly(propylene) membrane filter (METRICEL). An acceleration voltage of 2 kV was employed. The sample was sputtered with Pt-Pd before observation.

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