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Preparation of a Multilayered Film of Ultrathin Poly(tetraallylammonium bromide) Network

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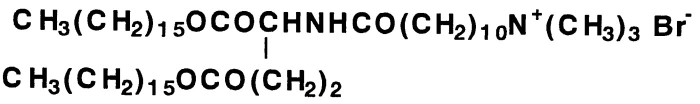
A multilayered film of two-dimensionally cross linked poly(tetraallylammonium bromide) was prepared using a cast film of bilayers of a double-chain ammonium amphiphile as template. This film displayed unique electrochemical properties.

We have reported that novel multilayered polymer films are obtainable via composite films of curable monomers or polymers and self-assembling amphiphiles. The composite films with layered structures are prepared by casting of aqueous dispersions. After the subsequent crosslinking, the amphiphile component is removed by extraction and a cured film remains in the multilayered form.[1,2] Extension of this technique to charged monomers will produce multilayered ion-exchange membranes with ultrathin unit layers that are appealing in both of fundamental and practical research. We described separately that casting of a polymerizable self-assembling salt of amphiphile was suitable for this purpose.[3] Tetraallylammonium halides are known to give crosslinked cyclopolymers by free radical polymerization.[4-7] The polymers display anion exchange capacity.[4] Therefore, tetraallylammonium bromide (TAABr) is promising as a starting material of charged two-dimensional (2-D) network. The monomer was prepared as described in literature.[6]



$$\begin{array}{l}\mathrm{CH_3(CH_2)_{15}OCOCHNHCO(CH_2)_{10}N^+(CH_3)_3\ Br^-}\\ \qquad\qquad\qquad\qquad\ \ |\\ \mathrm{CH_3(CH_2)_{15}OCO(CH_2)_2}\end{array}$$

1

$\mathrm{(CH_2{=}CH{-}CH_2)_4N^+Br^-}$ **TAABr**

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Amphiphile **1** [2] (30 mM) was dispersed by sonication (Ultrasonic Disruptor UD-201) in an aqueous monomer solution (60 mM). Photoinitiator (Darocur 2959 Merck, 2 mol% of the monomer) was added and the mixture was cast on a fluorocarbon polymer sheet for 2 days at 25 °C and 60% relative humidity. A transparent, flexible self-supporting film resulted.

X-Ray diffraction (Rigaku Denki, RAD-R-32, CuK$_\alpha$) of the composite cast film showed a regular multilayered pattern with long spacing of 58 Å. This spacing is close to that of the single component (amphiphile alone) cast film. Differential scanning calorimetry (DSC, Seiko Instr. SSC 5000) exhibited the gel-to-liquid crystal phase transition of the bilayer component at 59 °C ($\Delta H = 90$ kJ mol^{-1}), in close agreement with that without the monomer component.

The film was then subjected to photoirradiation with an ultrahigh-pressure Hg lamp (Ushio Denki, Model UI-501C) at a distance of 14 cm at room temperature for 3 min. The long spacing of the resulting polymerized film was 64 Å and a DSC peak was located at 61 °C ($\Delta H = 81$ kJ mol^{-1}). Thus, the photopolymerization did not extensively affect the film organization. The bilayer component was then extracted by immersing the cast film in ethanol for 48 h. The remaining film was self-supporting, colorless, and insoluble in all the solvents examined. IR spectroscopy showed disappearance of amide and ester peaks characteristic of amphiphile **1**, and the lessened intensity of $\nu_{C=CH}$ at 3080 cm^{-1} corresponded to 80% consumption of the allyl unit. Gel permeation chromatography of the ethanol extract indicated a broad peak of the sol fraction of the polymer, in addition to the amphiphile peak.

Scanning electron microscopy (SEM, Hitachi S 900) of the cross-section of the polymer film reveals an omnipresent multilayered structure running parallel to the film plane. An expanded view of the cross-section is shown in Fig. 1. The observed layer thickness, 50 - 250 nm, is much greater than is expected from the regular structure of the composite film, probably due to limited SEM resolution. A film of TAABr that was cast and polymerized without the bilayer template [three-dimensional (3-D) film] gave a smooth, non-structured cross section.

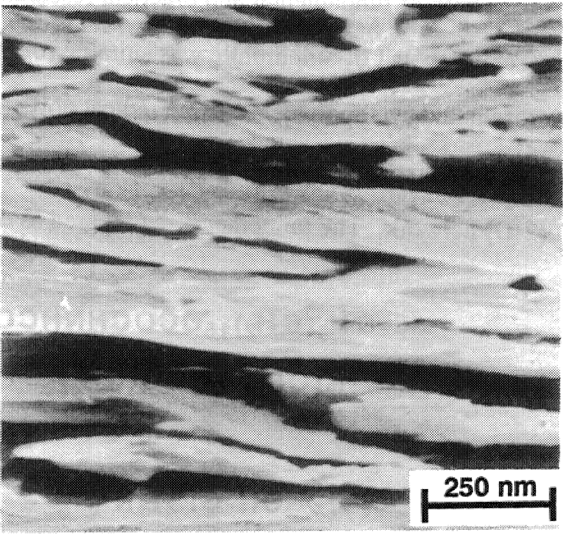

Fig.1. SEM micrograph of the cross-section of the multilayered polymer network. The sample was cleaved in liquid nitrogen and coated by Pt/Pd prior to the observation.

The unique nature of the multilayered 2-D film is expressed by anisotropic swelling and ion exchange properties as shown in Table 1. Its water content that was determined from weight difference before and after drying(8) was 1.5 times greater than that of the 3-D film. The corresponding swelling ratio was essentially identical in 2-D and 3-D films in the lateral direction, but was 2.2 times greater for the 2-D film in the perpendicular direction.(9)

Table 1. Swelling in water and ion-exchange properties of 2-D and 3-D films

	Water content	Swelling ratio (%)		Anion exchange (%)			
	(wt%)	Lateral	Perpendicular	$NaVO_3$	$Na_2NiEDTA$	$K_2Ni(CN)_4$	Na_3VO_4
2-D Film	53	21	55	93	59	84	76
3-D Film	35	25	25	81	25	45	20

Anion exchange experiments were conducted by immersing these films in 0.1 M aqueous solution of given salts at room temperature for 24 h and the following extensive washing. The extent of ion exchange was determined by XPS measurements(10) of residual bromine in well-ground samples. As is obvious from Table 1, the anion exchange is more efficient for the 2-D film than the 3-D film. The ion-exchange capacity of the 2-D film (Table 2) measured by the standard method(11) is also four times higher than that for 3-D due to facile transport of ions in the interlayer space.

Table 2. Membrane characteristics of 2-D and 3-D poly (TAABr) films of thickness 0.03 mm(a)

	Ion-exchange capacity	E_C	t_-	Areal resistance
	$mequiv \cdot g^{-1}$	mV		$\Omega\ cm^2$
2-D Film	2.1	40.3	0.98	0.41
3-D Film	0.5	31.1	0.87	0.52

a) Symbols are explained in the text. All experiments were carried out at 25 °C.

The capacity of the 2-D film corresponds to 54% of the theoretical value and is comparable to those of commercially available anion-exchange membranes.(12) The membrane concentration potential E_C was determined using Ag/AgCl electrodes between 0.5 M and 2.5 M NaCl solutions. The transport number of anion t_- calculated from E_C for the 2-D film indicated its higher permselectivity.(8) The difference in permselectivity must be derived from the film structure. The monomer molecules in the composite cast film are expected to be uniformly distributed with molecular thickness and crosslinking would proceed accordingly.(2) This produces ultrathin layers with uniformly distributed ammonium groups which act as efficient barrier against anion transport. In contrast, it is known that crosslinking in 3-D gels is non-uniform due to formation of microgels.[13,14] This leads to lesser permselectivity. The transport number of the 2-D film is larger than those of commercially available membranes.[12] The areal resistance of the 2-D film measured in 0.5 M NaCl using platinum black electrodes is slightly lower than that of the 3-D film.

In conclusion, we showed that the multibilayer template is effective for preparing a novel multilayered ion-exchange film. The use of this film for electrodialysis and diffusion dialysis would be interesting.

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