adjacent double bonds. This conformation, the lowest in energy, is in good agreement both with the conformation proposed by Brückner et al.[5] and with the spatial positioning of the chains in the unit cell proposed by Bassi et al.[2] The orientation of the polymer sample can produce at least a partial conformational change from the skew to the cis arrangement, higher in energy. This change can be explained by the relatively low energy barrier to rotation around bonds adjacent to double bonds. By analogy, in *cis*-1,4-polyisoprene, the structure of which can be interpreted on the basis of a statistical succession of two different conformations along the chain,[19] a change from one of the two conformations to the other (having slightly different energy) is influenced by external stress.[20] For ITPP the difference in energy between skew and cis arrangements is high and therefore the skew arrangement, the most probable in unoriented samples, should prevail also in oriented samples.

Acknowledgment. Financial support of the Ministero della Pubblica Istruzione, Italy, is gratefully acknowledged.

Registry No. ITPP, 29191-23-9.

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Charge-Mosaic Membrane from a Polymer Blend with a Modulated Structure

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ABSTRACT: A charge-mosaic membrane was prepared from the solution-cast film of the polymer blend of chloromethyl polystyrene (CMPS) with poly(acrylonitrile-*co*-styrene) (SAN). The membrane was prepared as follows: (1) each polymer was dithiocarbonated to introduce a photo-cross-linkable site (a few mole percent in the polymer); (2) the dithiocarbonated polymers were solution cast to thin films with regularly phase-separated co-continuous structure (modulated structure); (3) this precursor film was cross-linked by UV radiation; (4) the CMPS phase was quaternized with bis(dimethylamino)hexane; (5) the SAN phase was sulfonated with chlorosulfonic acid. The film thus modified exhibited negative osmosis and selective permeability, i.e., permeable to salt but not to nonelectrolyte, as expected for a charge-mosaic membrane. The high salt permeability seems to originate from the characteristic two-phase structure in the precursor film.

Introduction

A charge-mosaic membrane consists of a set of anion and cation exchange elements arranged in parallel, each element providing a continuous pathway from one bathing solution to the other. When a gradient of electrolyte concentration is established across the membrane, anions and cations can flow in parallel through their respective pathways without a violation of macroscopic electroneutrality, resulting in a circulation of current between the individual ion-exchange elements. As a result of current circulation, the charge-mosaic membrane shows negative osmosis and salt permeability much greater than its permeability to nonelectrolytes.[1]

Since Weinstein and Caplan[2] prepared a model membrane by embedding cation-exchange beads and anion-exchange beads in a silicone rubber matrix, many attempts have been performed to prepare the charge-mosaic membrane.[3] Some are by chemical modifications of two-phase polymer systems, i.e., polymer blends, graft copolymers, and block copolymers. Among them, the most effective membrane was made by Fujimoto et al.[4,5] As a precursor polymer, they prepared a specially designed pentablock copolymer, poly(isoprene-*block*-styrene-*block*-isoprene-*block*-(4-vinylbenzyl)dimethylamino-*block*-isoprene), and chemically modified the solution-cast film of the block copolymer. Our studies in this article are along the same line as theirs, but we have employed a different precursor which is more easily available and the morphology of which may be more desirable for the charge-mosaic membrane.

In our recent article,[6] we found the development of a regularly phase-separated structure in solution-cast films of polymer blends. Characteristic features of the structure are periodicity and dual connectivity of phases, as schematically shown in Figure 1. We call this a modulated structure. The blended film with modulated structure is

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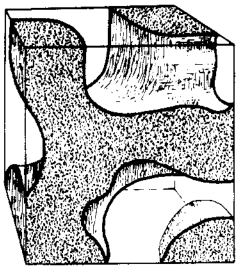


Figure 1. Schematic representation of the unit cell of modulated structure.

expected to be a desirable precursor for the charge-mosaic membrane because both phases are continuous and by chemical modifications could be converted to the co-continuous ionic pathways in the membrane.

In this paper, the precursor system is a polymer blend of chloromethyl polystyrene (CMPS) with poly(styrene-*co*-acrylonnitrile) (SAN). Prior to solution blending, each polymer is dithiocarbonated at a few mole percent level to generate photo-cross-linkable sites in the polymers. The modified polymers are solution-cast to form thin films with modulated structures. The cast film is subjected to a series of chemical reactions; both phases are cross-linked, the CMPS phase is quaternized, and the SAN phase is sulfonated. The performance of the modified film is evaluated in terms of reverse osmosis and selective permeability to electrolyte.

Experimental Section

Polymer Specimens. A SAN containing 27 wt % acrylonitrile (M_w = 140 000, M_n = 62 000) was supplied by Dr. Y. Aoki, Mitsubishi Monsanto Chemicals Co., Ltd. A CMPS with M_w = 192 000 and M_n = 75 000 was purchased from Aldrich. These molecular weights were estimated by gel permeation chromatography calibrated with polystyrene standard.

Dithiocarbonation. CMPS and SAN were dithiocarbonated by the modified procedure reported by Nakagawa et al.[7] to introduce a cross-link site, in advance to solution blending. The following dithiocaronation reactions and all handlings of the products were carried out in dark.

To the solution of 10 g of CMPS in 190 mL of dimethylformamide (DMF) was added 0.526 g of *O*-ethylxanthic acid potassium salt in 20 mL of DMF. After the mixture was stirred for 5 h at 25 °C, the solution was poured into 2 L of methanol. The polymer obtained was washed with distilled water and purified by reprecipitation in acetone–methanol.

SAN was brominated prior to dithiocarbonation. The solution of 10 g of SAN, 2.31 g of *N*-bromosuccinimide, and 0.2 g of benzoyl peroxide in 190 mL of benzene was refluxed for 8 h. The resulting solution was poured into 2 L of *n*-hexane, rinsed with hot water, and purified by reprecipitation in acetone–methanol. The brominated SAN thus obtained was dithiocarbonated in the same way as in the case of CMPS.

The degree of dithiocarbonation was estimated by elemental analysis. The obtained dithiocarbonated polymers are referred to X-CMPS and X-SAN, respectively.

Blend Preparation. Equal amounts of X-CMPS and X-SAN were dissolved to 5 wt % in dichloromethane. The solution was cast onto mercury. The rate of solvent evaporation was adjusted to prepare the cast film with modulated structure.[6] The cast film was further dried under vacuum of 10^{-4} mmHg for 10 h. The structure of the dried film was observed under a light microscope. The periodic distance in the modulated structure was estimated by light scattering.[6]

It was found that this neat polymer blend film resulted in a polymer film insufficiently cross-linked by UV radiation; i.e., when the irradiated film was immersed in dichloromethane, more than 50 wt % dissolved out and a highly swollen gel remained. We had tried to elevate the cross-link density in the irradiated film. After several trails, we found that photosensitizer and cross-linking coagent should be added to increase the cross-link density. The most favorable recipe of the casting solution was X-CMPS/X-SAN/diethylene glycol dimethacrylate/*p*,*p*′-bis(dimethylamino)benzophenone/dichloromethane methacrylate/*p*,*p*′-bis(dimethylamino)benzophenone/dichloromethane = 50/50/20/5/2000 (weight ratio). This solution was cast in the same way as the neat polymer blend. The presence of photosensitizer and cross-linking coagent did not disturb the formation of the modulated structure in cast film. The thickness of the cast film was 70 μm.

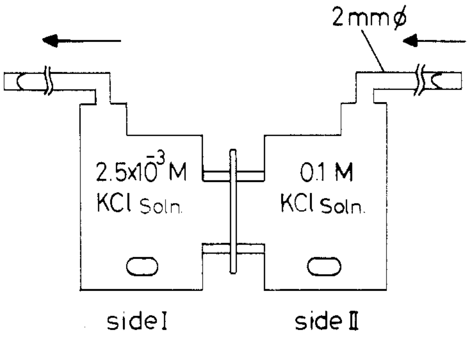


Figure 2. Schematic diagram of the cell for the measurement of volume flow (reverse osmosis).

Photo-Cross-Linking. The cast film was irradiated by a mercury lamp (100 W) for 1.5 h. The irradiated film was dipped in a large amount of dichloromethane for 50 h and its weight loss was measured.

Quaternization of the CMPS Phase. The photo-cross-linked film was dipped in bis(dimethylamino)hexane (TMDA)[8] at 120 °C for 40 h. The reacted film was rinsed with methanol, i.e., dipped in a methanol solution of hydrochloric acid (1 N) for 5 h to neutralize residual TMDA.

The infrared spectrum of the quaternized film was recorded by a FT-IR/3 spectrometer, Japan Spectroscopic Co., Ltd., with 2-cm^{-1} resolution. The cation-exchange number was measured after dipping the film in 0.5 N aqueous solution of KCl for 12 h.

Sulfonation of the SAN Phase. The cross-linked and quaternized film was swollen with dichloromethane. Chlorosulfonic acid, 0.3 mL, and 1 g of paraformaldehyde[9] were dissolved in 100 mL of dichloromethane. The reaction was carried out by dipping the swollen film into the chlorosulfonic acid solution for 10 min. The reacted film was rinsed with dichloromethane and then with acetone.

In addition, the film was dipped in a MWS solution (methanol/water/NaCl = 60 mL/100 mL/12 g) for 12 h and then in a 1:1 mixture of the MWS solution with a 0.1 N aqueous solution of NaOH for 24 h, rinsed with water, and dipped in a 0.5 N aqueous solution of KCl for 12 h. Hereafter we call the film a charge-mosaic membrane.

Cation-Transport Number. The cation-transport number t_+ was determined by measuring the concentration potential ϕ_m at 25 °C in an aqueous solution of KCl,

$$\phi_m = -(2t_+ - 1)\frac{RT}{F}\ln\frac{a_{II}}{a_I}$$

where a_I and a_{II} are activities in the solutions on either side of the membrane, 0.02 and 0.01 mol/L, respectively, F is the Faraday constant, R is the gas constant, and T is absolute temperature.

Reverse Osmosis. Volume flow through the charge-mosaic membrane was measured by using the cell shown in Figure 2. It consists of two compartments, I and II, separated by the membrane, and two horizontal capillaries. Compartments I and II were filled with a dilute (2.5 × 10^{-3} mol/L) and a concentrated (0.1 mol/L) aqueous solutions of KCl, respectively. The volume flow was measured by reading the meniscus position in each capillary at appropriate intervals.

Dialysis. The dialysis cell consisted of two compartments divided by the membrane. Compartment I was filled with an aqueous solution of NaCl and sucrose; the initial concentration of each solute was 0.1 mol/L. Compartment II was filled with a distilled water. The change in concentration of compartment II with dialysis time was measured: NaCl concentration by electroconductivity and sucrose concentration by absorptiometry

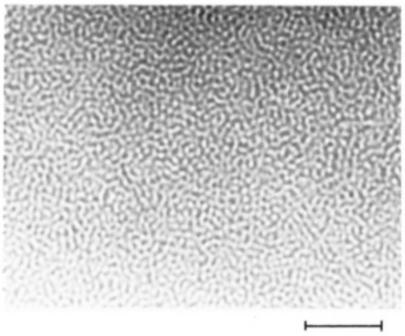
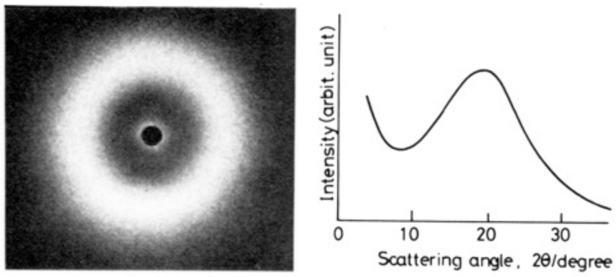


Figure 3. Light micrograph of solution-cast film. The scale bar is 20 μm.



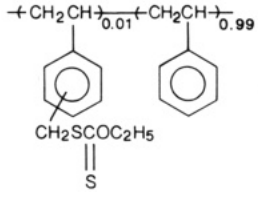
(a) (b)

Figure 4. (a) Light scattering pattern from the cast film in Figure 3 and (b) its goniometer trace. A He–Ne laser of 632.6-nm wavelength was radiated.

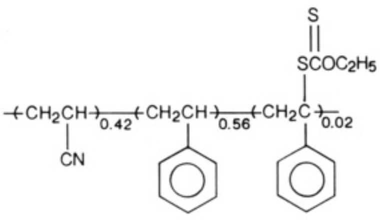
using the phenol–sulfonic acid coloring method.

Results and Discussion

According to the results of elemental analysis, the dithiocarbonated polymers are described by



X-CMPS



X-SAN

where the numbers on the formula represents mole fraction.

Figure 3 is a light micrograph of the cast film of the X-CMPS/X-SAN blend involving photosensitizer and cross-link coagent. A highly interconnected two-phase morphology with uniform domain size is seen in the micrograph. Figure 4 shows a light-scattering pattern and its profile from the cast film of Figure 1. The ring pattern indicates some degree of regularlity of the phase-separated structure in Figure 1. The Bragg spacing from the peak in the scattering profile (1.8 μm) corresponds to the periodic distance in Figure 1.

The insoluble (in dichloromethane) fraction of the UV-irradiated film was 90 wt %. The 10% soluble fraction may consist of photosensitizer residue and the unreacted cross-link coagent. Taking into account the figures of these low molecular weight additives in the recipe of the casting solution, it seems that the polymers are cross-linked at a very high level.

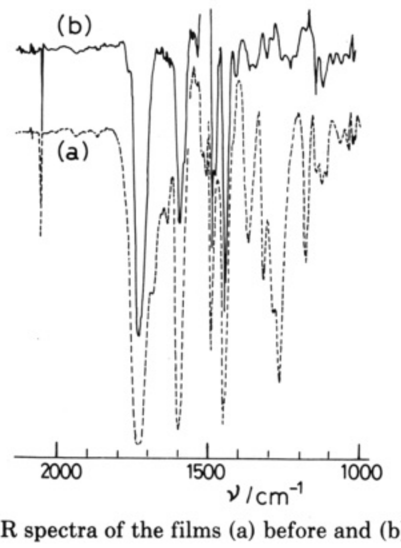


Figure 5. IR spectra of the films (a) before and (b) after quaternization.

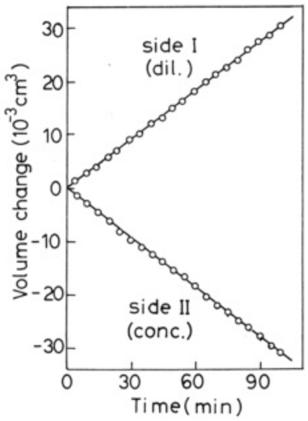


Figure 6. Volume change in each half-cell in Figure 2, indicating negative osmosis.

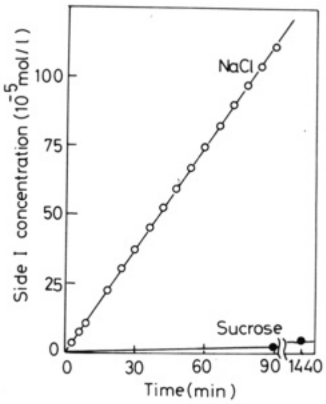


Figure 7. Solute permeability: (○) NaCl; (●) sucrose.

Figure 5 shows infrared spectra of the cross-linked films and the quaternized one. In the latter spectrum, the absorption bands characteristic to p-CH_2Cl and m-CH_2Cl groups at 1287 and 1267 cm^{-1}, respectively, are hardly seen. Taking the cyano absorption at 2238 cm^{-1} as a reference, the degree of quaternization is estimated to be 94.5%.

Figure 6 shows the results of volume flow. The volume change in each half-cell indicates a flow from side II to I, i.e., from the concentrated side to the dilute side, implying a negative osmosis characteristic of the charge-mosaic membrane. The flux, J_v, obtained from the slope in Figure 6 is 7.86×10^{-6} cm^3 cm^{-2} s^{-1}.

Figure 7 shows the results of dialysis. NaCl rapidly permeates the membrane, while sucrose hardly permeates. This behavior represents the selective permeability characteristic of a charge-mosaic membrane, permeable to electrolyte but not to nonelectrolyte. The solute flux, J_s, estimated from the slope in Figure 7 is J_s(NaCl) = 2.65

$\times 10^{-8}$ and J_s(sucrose) = 3.77×10^{-10} mol cm^{-2} s^{-1}. Note here that the value of J_s(NaCl) is several hundred times that of a conventional ion-exchange membrane. The ratio of J_s(NaCl) to J_s(sucrose) is 70.4.[10] This high value of solute flux ratio also cannot be attained by the conventional ion-exchange and semipermeable membranes.

Concluding Remarks

It has been shown that a charge-mosaic membrane can be prepared by introducing cationic and anionic groups in a cross-linked two-phase polymer system with a modulated structure. The high level of salt permeability J_s of the membrane is of interest. It is close to that of the membrane from a block copolymer.[4,5] According to theory,[1] the larger (periodic) distance between cationic and anionic elements induces a higher resistivity to current flow, resulting in a lower J_s. The periodic distance in our membrane from a polymer blend is 1.8 μm, while that in the membrane from a block copolymer is on the order of several hundred angstroms. Despite the large difference in the periodic distance, both membranes show comparable J_s values. We believe that the high J_s in our membrane originates from the co-continuous nature of the modulated structure: both elements penetrate from one surface to the other.

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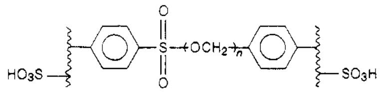
(8) TMDA is expected to elevate the cross-link density through interchain quaternization.
(9) Paraformaldehyde is added to elevate the cross-link density via the structure



(10) It has recently been found that a charge-mosaic membrane with J_s(NaCl)/J_s(sucrose) = 350 could be obtained by increasing the cross-link density.

Photophysics of Alternating Copolymers of Acenaphthylene and Methacrylic Acid and Maleic Acid

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ABSTRACT: Copolymers of acenaphthylene and methacrylic acid or maleic acid were prepared, along with methoxy or ethoxy esters. On the basis of the method of preparation, these polymers are believed to be substantially alternating. All these systems display stronger excimer fluorescence in organic solvents than the corresponding 2-vinylnaphthalene polymers. While the excimer fluorescence decay shows a distinct buildup at early times, the rate of this buildup tends to be faster than the decay of the monomer precursor state. This implies that a significant fraction of excimers are formed by a very rapid (static) process. For PAcN-*alt*-MA (methacrylic acid) ca. 1 mol % of anthracene was covalently attached to the polymer to act as a long-range energy trap (Förster $R_0 \simeq 24$ Å). Sensitization of the anthracene via naphthalene excitation was reasonably efficient (ca. 30%) as measured from steady-state spectra and the shortening of the naphthalene fluorescence lifetime in the anthracene doped polymer. Fluorescence quenching by CCl_4 in organic solvents implied that there is essentially no energy transfer down the chain. In aqueous solutions (pH ≥7) excimer fluorescence dominated the steady-state spectrum and all fluorescence lifetimes were shortened. Fluorescence quenching effected by Cu^{2+} was quite efficient and operates primarily as a static process (the fluorescence lifetimes are changed only slightly). It is proposed that this high quenching rate is the joint result of electrostatic attraction of Cu^{2+} for the polyanion and energy migration between naphthalene groups that have collapsed into a micellar type structure. This structure also enhances excimer trapping of the singlet state.

Introduction

The photophysics and photochemistry of polymers has been the subject of several recent books and/or symposia recently.[1] One interesting class of polymers that has been the subject of only a few publications are alternating polymers. Those containing alternating hydrophilic–hydrophobic groups are amphiphilic and have very different properties in aqueous solution than random copolymers with the same pendent groups. A structural model for these polymers in water has not yet been proposed to our knowledge.

This paper describes fluorescence experiments on two members of this class containing the acenaphthylene chromophore. The polymer based on methacrylic acid and maleic acid respectively are denoted PAcN-*alt*-MA and PAcN-*alt*-MAA. There exists earlier work published for

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