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Artificial Membranes from Multiblock Copolymers. 3. Preparation and Characterization of Charge-Mosaic Membranes

Yoshiyuki Miyaki, Hiroshi Nagamatsu, Minoru Iwata, Koji Ohkoshi, Kazunori Se, and Teruo Fujimoto*

Department of Materials Science and Technology, Technological University of Nagaoka, Kamitomioka-cho, Nagaoka 949-54, Japan. Received January 12, 1984

ABSTRACT: Films prepared from poly(isoprene-*b*-styrene-*b*-isoprene-*b*-(4-vinylbenzyl)dimethylamine-*b*-isoprene) (ISIAI) pentablock copolymers were subjected to chemical modification: the A block was quaternized, the I block cross-linked, and the S block sulfonated, in that order. The three-layer lamellar structures of the original films were retained through these processes. The resulting membranes had substantial cation- and anion-exchange capacities and cation transport numbers near 0.50 for KCl. They exhibited a piezodialytic effect and negative osmosis as predicted for a "charge-mosaic" membrane.

Introduction

It is known that charge-mosaic membranes, which consist of parallel arrays of anion-exchange and cation-exchange elements, are very permeable to salts but not to low-molecular-weight nonelectrolytes.[1-5] These properties are desired for desalination of water or purification of biochemical materials or food additives. There are several reports of attempts to prepare such membranes.[6-20] The method of Weinstein and Caplan,[11] in which anion-exchange beads and cation-exchange beads were embedded in a silicone rubber matrix, and that of Leitz et al.[6,7,18] described as "latex-polyelectrolyte fabrication", provided membranes that had high salt permeabilities. However, practical applications of charge-mosaic membranes require membranes of greater physical strength than those reported in the literature. On the other hand, attempts to prepare charge-mosaic membranes from polymer blends or conventional block copolymers have failed to provide effective membranes.[13] It seems likely that, in the latter membranes, pinholes, cracks, or improper morphology changes occurred during the chemical modifications used to introduce anion- and cation-exchange groups into them.

In previous work[21-24] we described novel three-component block copolymers designated SIA and ISIAI, which consist of polystyrene (S), polyisoprene (I), and poly[(4-vinylbenzyl)dimethylamine] [poly(4-VBDMA)] (A) blocks linearly linked. We found that films of ISIAI pentablock copolymers with a proper molecular architecture provide tougher three-layer lamellar structures than those of SIA copolymers after chemical modification. We here report on the preparation of charge-mosaic membranes from ISIAI pentablock copolymers by quaternization of the A block, cross-linking of the I block, and sulfonation of the S block. We have found chemical reactions that effect the desired modifications of the three blocks in high conversions without disrupting the microphase structure of the original copolymer and have shown that the modified copolymer films function as charge-mosaic membranes.

Experimental Section

Polymer Samples and Films. The ISIAI pentablock copolymers used in this work were prepared by a sequential living anionic polymerization as reported in the preceding paper.[21] Average molecular weights of the component blocks constructing the pentablock copolymers, which were calculated from the amounts of monomers and initiator, are listed in Table I. ^{1}H NMR spectra indicated that the I blocks of these samples contain approximately 20% trans-3,4 units in addition to about 80% cis- and trans-1,4 units.

The polyisoprene sample used for the investigation of cross-linking of the I block was commercial Cariflex IR 305 (Shell). It contained 91.9% cis-1,4, 5.0% trans-1,4, and 3.1% trans-3,4 structural units, determined by ^{13}C NMR in CDCl$_3$. A triblock ISI copolymer used for investigation of the sulfonation of the S block was prepared by a sequential living anionic polymerization. Its molecular characteristics are shown in Table I.

Table I
Average Molecular Weights M_k of the Component Blocks of the Copolymers[c]

	$M_k/10^4$					
sample code	I	S	I	A	I	total
TUN 1004[a]	2.1	4.2	2.1	7.3	2.0	17.7
TUN 1008[a]	6.0	8.9	6.0	12.9	5.7	39.5
TSK 101[b]	3.9	8.4	3.8			16.1

[a] ISIAI pentablock copolymer. [b] ISI triblock copolymer. [c] I, polyisoprene block; S, polystyrene block; A, poly(4-VBDMA) block.

Films of the pentablock copolymers were cast on mercury, using benzene, dioxane, or cyclohexane as the solvent (films designated BZ, DO, and CH, respectively) as described in preceding papers.[21-24] Electron micrographs[21-24] show that films cast from benzene and dioxane solutions have a three-layer lamellar structure with a repeating unit –I–S–I–A–, while those cast from cyclohexane solutions have a sea-and-islands structure in which spherical S domains are dispersed in a matrix of A and I domains. Films of the ISI triblock copolymer prepared in the same way using benzene as the solvent have a lamellar structure of alternating I and S domains. The polyisoprene films were cast on glass plates from benzene solutions. All of the films used had a thickness of about 50 μm.

Chemical Modification Reactions. In order to prepare charge-mosaic membranes from the films cast from the pentablock copolymers, quaternization of the nitrogen atoms of the A block, cross-linking of the I block, and sulfonation of the S block were carried out sequentially. The quaternization must be done before cross-linking of the I block, since poly(4-VBDMA) reacts with the sulfur monochloride used for the cross-linking reaction. Furthermore, the I block must be cross-linked before the S block is sulfonated in order to maintain the microphase structure of the film during the violent sulfonation reaction and to suppress reaction of the I block with the sulfonation reagent. We first studied each of these modification reactions independently.

The A block was quaternized by treating the film with methyl iodide vapor. To establish the most favorable conditions for the reaction, the absorption of methyl iodide by films cast from benzene and cyclohexane solutions of sample TUN 1008 was investigated, and the quaternized films were examined by electron microscopy. A schematic diagram of the apparatus used is shown in Figure 1. The film was attached to the end of a quartz spring in a closed reactor that was connected with a reservoir of methyl iodide through a breakable seal. The reactor was evacuated and thermostated at 25 °C, and the reservoir of methyl iodide was maintained at 0 or 25 °C. The reaction was started by breaking the seal, exposing the film to methyl iodide vapor. The amount of methyl iodide absorbed by the film was estimated from elongation of the spring, read by a cathetometer. After 20-h exposure, the reservoir of methyl iodide was cooled to −196 °C. The spring length was again followed until it became constant.

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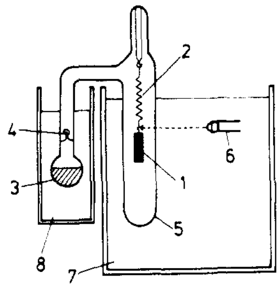

Figure 1. Schematic diagram of the apparatus used for investigating the absorption of methyl iodide by films of the pentablock copolymer TUN 1008: (1) film of TUN 1008; (2) quartz spring; (3) reservoir of methyl iodide; (4) breakable seal; (5) reactor; (6) cathetometer; (7, 8) thermostated baths.

A nitromethane solution of sulfur monochloride (S_2Cl_2) was chosen as the cross-linking reagent for the I block because its reaction with double bonds proceeds rapidly at room temperature.[13,25,26] We first investigated the cross-linking reaction with films of polyisoprene. The films were dipped into 20%, 5%, or 1% solutions of S_2Cl_2 in nitromethane and then allowed to stand in a dark and dry place for 3 h (20% solution) or 24 h (5% and 1% solutions). The cross-linked films were thoroughly rinsed with *n*-heptane containing 10% carbon disulfide to extract excess S_2Cl_2 and dried in vacuo at room temperature. They were examined by infrared spectroscopy and elemental analysis.

We gave up trying to sulfonate the S block of the copolymer films with concentrated sulfuric acid because the reaction was so violent that the films did not retain their shape during the reaction. We chose a 2% solution of chlorosulfonic acid in chloroform as the sulfonating reagent. The reaction was carried out at room temperature for 15 min by dipping the films into the solution. A preliminary experiment with films of the ISI triblock copolymer that had been cross-linked by treatment with a 20% of S_2Cl_2 in nitromethane revealed that 80–100% of the styrene units in the polymer were sulfonated.

Electron Microscopy. Quaternized films of the pentablock copolymer were exposed to a 1% aqueous solution of osmium tetraoxide (OsO_4), which stains the I block more heavily than the quaternized A block but does not stain the S block at all. The quaternized and cross-linked films were also exposed to the same solution. The quaternized, cross-linked, and sulfonated films were immersed in a saturated aqueous solution of tin(II) chloride, which stains the sulfonated S block selectively. The stained films were cut into ultrathin sections with an ultramicrotome and examined with a Model H-600 (Hitachi Seisakusho) transmission electron microscope.

Measurements of Ion-Exchange Capacities. The amounts of sulfonic acid and quaternary ammonium groups in the membranes were determined by titrimetric methods. For the sulfonic acid group, the membrane rinsed with water was immersed in a mixture of 1 N hydrochloric acid and methanol (2:1 (v/v)) for about 20 h at room temperature. It was then thoroughly rinsed with methanol and placed in a 0.01 N aqueous solution of sodium hydroxide containing sodium chloride (1 M) for 2 days at room temperature. The solution was titrated with 0.1 N sulfuric acid (x mL) with phenolphthalein indicator. The blank value (x_0 mL) was obtained with the same volume of the 0.01 N NaOH–1 M NaCl solution. The sulfonic acid group content (a^- mequiv) was calculated as

$$a^- = 0.1(x_0 - x) \tag{1}$$

To determine the quaternary ammonium group, the membrane rinsed with water was immersed in a 1 M aqueous solution of potassium chloride for 24 h at room temperature. It was then thoroughly rinsed with water and placed in a 1 M aqueous solution of sodium nitrate for 2 days at room temperature. After the membrane was removed, the Cl^- in the solution was determined by Volhard titration with 0.1 N solutions, titrating the excess Ag^+ ion with y mL of the 0.1 N NH_4SCN. The quaternary ammonium group content of the membrane (a^+ mequiv) was calculated from y and the blank value y_0 as

$$a^+ = 0.1(y_0 - y) \tag{2}$$

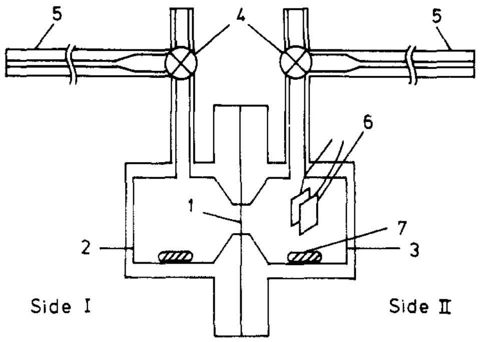

Figure 2. Schematic diagram of the cell used for the measurements of volume and salt flows through charge-mosaic membranes: (1) membrane; (2) compartment I; (3) compartment II; (4) three-way stopcocks; (5) capillaries; (6) Pt-black electrodes; (7) stirrer tip.

Cation Transport Number. Cation transport numbers (t_+) of the membranes were determined by measuring the concentration–membrane potentials $\Delta\psi$ at 25 °C with aqueous solutions of KCl, using the equation

$$\Delta\psi = -(2t_+ - 1)\frac{RT}{F}\ln\frac{c_{II}}{c_I} \tag{3}$$

Here, c_I and c_{II} represent the concentrations of the solutions on either side of the membrane (0.02 and 0.01 M, respectively), F is the Faraday constant, R is the gas constant, and T is the absolute temperature.

Piezodialysis. Piezodialysis experiments were carried out with aqueous solutions of NaCl, using a batch-type cell in which one membrane surface was in contact with a stirred solution under 30-atm nitrogen pressure and the other surface was in contact with a permeant solution at atmospheric pressure. The volume of the high-pressure solution was about 300 mL, the NaCl concentration was 10^{-6}–10^{-4} mol/cm^3, and the effective membrane area was 12.6 cm^2. The concentration of Na^+ was determined by a Shimadzu AA-646 flame analyzer.

Measurements of Volume and Salt Flows. Transport of water and KCl through the charge-mosaic membranes was investigated by use of the cell shown in Figure 2. It consists of two 20-mL compartments I and II separated by the membrane, two horizontal capillaries with inner diameter 0.60 mm and length 1 m, and Pt-black electrodes in compartment II. The capillaries are connected to the respective compartments through three-way stopcocks. The effective membrane area was 0.79 cm^2. Both compartments were immersed in a water bath thermostated at 25 ± 0.02 °C.

Compartments I and II were fitted with aqueous solutions of KCl of concentrations 5×10^{-5} and 2.5×10^{-5} mol/cm^3, respectively. The volume flow was measured by reading the meniscus positions in the capillaries at appropriate intervals. The conductance of the solution in compartment II was measured at the same time with an LCR meter ZM-341 (NF Circuit Design Block Co., Ltd.) connected to the Pt-black electrodes. The salt flux was calculated from the change of conductance. The solutions in both compartments were stirred by a magnetic stirrer and remained within 5% of their respective initial concentrations of KCl throughout the measurements.

Results and Discussion

Quaternization. Figure 3 shows the experimental data for absorption and desorption of methyl iodide by films of TUN 1008 that had been quaternized with the methyl iodide reservoir temperature at 25 and 0 °C. The plots show the quantities of methyl iodide absorbed by 1 g of film as a function of time. The absorption of film prepared with a reservoir temperature of 25 °C did not reach equilibrium but increased monotonically with time. The desorption curve for this film approached an equilibrium value of 0.28 ± 0.005, which is very close to the calculated value of 0.287 for the completely quaternized film of TUN

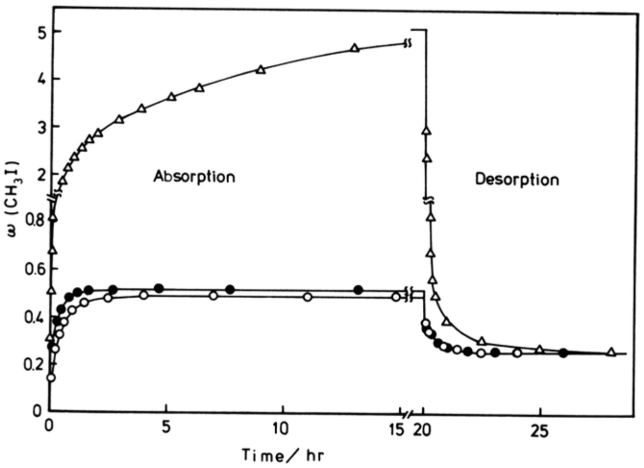

Figure 3. Absorption and desorption of methyl iodide by films of TUN 1008. ω is the amount of methyl iodide absorbed by 1 g of the film. (○) Benzene-cast film at reservoir temperature 0 °C; (●) cyclohexane-cast film at reservoir temperature 0 °C; (△) benzene-cast film at reservoir temperature 25 °C.

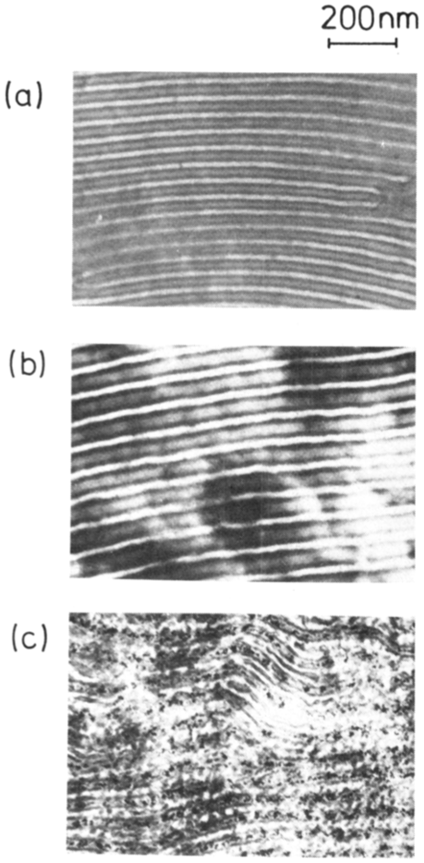

Figure 4. Electron micrographs of the benzene-cast films of TUN 1008: (a) as-cast film; (b) quaternized at reservoir temperature 0 °C; (c) quaternized at reservoir temperature 25 °C. The light, gray, and dark regions are polystyrene, quaternized or nonquaternized poly(4-VBDMA), and polyisoprene domains, respectively.

1008. On the other hand, in each of the absorption curves for films prepared with a reservoir temperature of 0 °C, equilibrium was reached in about 6 h, and the desorption curves approached the same equilibrium value, 0.28 ± 0.005. Moreover, the anion-exchange capacities of the films quaternized under the conditions shown in Figure 3 were in agreement with the calculated values for the completely quaternized films within experimental error. These facts indicate that the films can be completely quaternized within 6 h by methyl iodide under a pressure about one-third the saturation pressure.

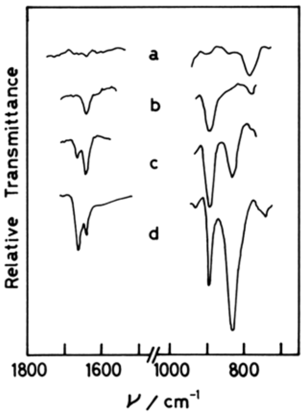

Figure 5. Infrared spectra of polyisoprene films cross-linked with S_2Cl_2 solutions: (a) 20 vol %; (b) 5 vol %; (c) 1 vol %; (d) un-cross-linked.

Table II
Elemental Analysis of Polyisoprene Films Cross-Linked with S_2Cl_2 in Nitromethane at 25 °C

sample code	S_2Cl_2 concn/ (vol %)	reacn time/h	content/(wt %) C	S	Cl
PIP-1	1.0	24	72.4	14.9	9.7
PIP-5	5.0	24	51.4	31.9	15.9
PIP-20	20	3	38.4	32.5	22.1

Figure 4 shows the electron micrographs of the films of TUN 1008, cast from benzene solutions and quaternized under the conditions described above. In the film quaternized at a reservoir temperature of 0 °C, a regular array of three-layer lamellae of the repeating unit –I–S–I–A^+– is observed, very similar to that in the as-cast film. On the other hand, in the film quaternized at a reservoir temperature of 25 °C, the structure is appreciably disordered. This is considered to be caused by molecular rearrangement in the film that absorbs a large excess of methyl iodide during quaternization. Thus, the quaternization by methyl iodide vapor must be done under a pressure lower than the saturation pressure in order to retain the initial morphology during the reaction.

Cross-Linking. Figure 5 shows infrared spectra of polyisoprene films treated with nitromethane solutions of S_2Cl_2 at the indicated concentrations. For comparison, it includes the spectrum of an unmodified polyisoprene film, in which the bands at 840 and 1665 cm^{-1} are due to vibrations of a double bond in the trans and cis $-C(CH_3)=CH-$ groups and the bands at 890 and 1645 cm^{-1} are due to those in the isopropenyl group $CH_2=C(CH_3)-$.[27] In the spectrum of the film treated with a 20% solution of S_2Cl_2, all of the bands of the double bonds of polyisoprene disappear. In that of the film treated with a 5% solution of S_2Cl_2, the bands assigned to the $-C(CH_3)=CH-$ groups still appear and, in that of the film treated with a 1% solution of S_2Cl_2, the bands assigned not only to the $-C(CH_3)=CH-$ groups but also to the $CH_2=C(CH_3)-$ group appear.

The results of the elemental analyses of these cross-linked polyisoprene films are shown in Table II, indicating that the numbers of chlorine and sulfur atoms in the film treated with the 20 vol % solution are 0.97 and 1.5, respectively, per monomer unit, while the numbers of chlorine atoms in the films treated with the 5 and 1 vol % solutions are considerably less than 1.0 per monomer unit.

Thus, if a nitromethane solution of 20 vol % S_2Cl_2 is used, the double bonds of a polyisoprene film react completely with S_2Cl_2 at room temperature, while, if the solution of 5 or 1 vol % is used, an appreciable fraction of

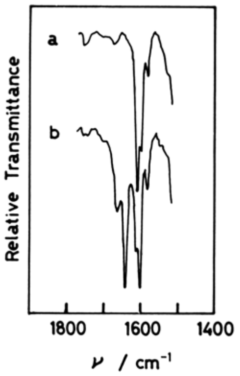

Figure 6. Infrared spectra of the benzene-cast films of TUN 1008: (a) quaternized and cross-linked film; (b) as-cast film.

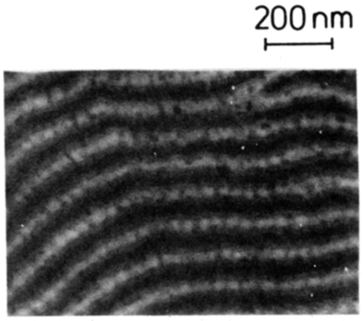

Figure 7. Electron micrograph of the film cast from the benzene solution of TUN 1008, quaternized and cross-linked.

double bonds remain unreacted. In the fabrication of a charge-mosaic membrane from the pentablock copolymer, the polyisoprene blocks should form neutral domains having no ion-exchange group. If significant numbers of double bonds remain unreacted in the I domains after cross-linking, cation-exchange groups can be introduced into the I domains during sulfonation of the S domains with chlorosulfonic acid.[28] It is, therefore, necessary that the 20 vol % solution be used as the cross-linking reagent for the preparation of a charge-mosaic membrane.

In Figure 6 are shown the infrared spectra of films cast from a benzene solution of sample TUN 1008 and of the film cross-linked with the 20% nitromethane solution of S_2Cl_2 after quaternization. The bands at 1665 and 1645 cm^{-1} do not appear in the spectrum of the cross-linked film, indicating complete reaction of the I block with S_2Cl_2.

Figure 7 shows an electron micrograph of the same cross-linked film of TUN 1008. The dark parts are the quaternized A domains (A^+), the light parts the S domains (S), and the intermediate gray parts the cross-linked I domains (I). It is seen that the film has a three-layer lamellar structure of the repeating unit $-I$–S–I–A^+–.

Characteristics of Charge-Mosaic Membranes. Figure 8a shows an electron micrograph of the charge-mosaic membrane CMM 1008/BZ, prepared by casting sample TUN 1008 from benzene solution and quaternizing, cross-linking, and sulfonating. The dark parts are the cation-exchange domains (S^-) of sulfonated polystyrene, the light parts the anion-exchange domains (A^+) of quaternized poly(4-VBDMA), and the intermediate parts the dielectric domains (I) of cross-linked polyisoprene. The membrane has a three-layer lamellar structure of the repeating unit $-I$–S^-–I–A^+–. Thus the initial microstructure was not disrupted during the chemical reactions. Figure 8b shows an electron micrograph of the membrane CMM 1008/CH cast from a cyclohexane solution of TUN 1008 and chemically modified in the same way. The spherical S^- domains are dispersed in a matrix of A^+ and I domains, although the A^+ and I domains are indistinguishable. This morphology is similar to that of the starting film, shown in the preceding paper.[24]

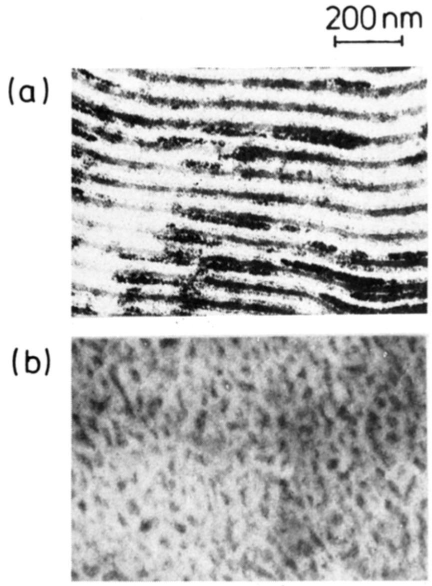

Figure 8. Electron micrographs of the quaternized, cross-linked, and sulfonated films of TUN 1008: (a) benzene-cast film (CMM 1008/BZ); (b) cyclohexane-cast film (CMM 1008/CH).

Table III
Ion-Exchange Capacities, A_m^+ and A_m^-, and Cation Transport Number, t_+, of the Membranes Prepared from Block Copolymers

membranes	A_m^{+a}	A_m^{-a}	t_+
CMM 1008/BZ	1.2_0	0.9_1	0.57
CMM 1008/DO	1.1_2	0.9_3	0.52
CMM 1008/CH	0.8_0	0.3_4	0.37
CMM 1004/BZ	0.9_2	0.5_3	0.77
TUN 1008/BZ-Q[b]	0	1.7_4	0.0033
TSK 101/BZ-CS[c]	2.3_0	0	0.97

[a] In mequiv/g of dry membrane. [b] Cast from the benzene solution of TUN 1008 and only quaternized. [c] Cast from the benzene solution of TSK 101, cross-linked, and sulfonated.

Cation- and anion-exchange capacities (A_m^+ and A_m^-, respectively) and cation transport numbers (t_+) of the charge-mosaic membranes prepared from the pentablock copolymers with various casting solvents are listed in Table III. Membrane CMM 1008/DO was prepared from the dioxane-cast film of TUN 1008, and membrane CMM 1004/BZ from the benzene-cast film of TUN 1004. This table includes data for the quaternized-only film of TUN 1008 and for a cross-linked and sulfonated film of TSK 101 for comparison. For each of the membranes CMM 1008/BZ and CMM 1004/DO, the value of A_m^+ is about 80% of the calculated value and nearly equal to A_m^-. The value of t_+ is close to 0.05, the ideal value for a charge-mosaic membrane. For membranes CMM 1008/CH and CMM 1004/BZ, A_m^+ is appreciably larger than A_m^-, and lower than the corresponding values of membranes CMM 1008/BZ or CMM 1008/DO. The differences in ion-exchange capacities among the membranes in Table III may reflect differences in morphology or in molecular weight of the starting pentablock copolymer. A polyion complex can easily form in a membrane prepared from a low-molecular-weight copolymer, as well as in one with a sea-and-islands microstructure.

The t_+ of CMM 1004/BZ is appreciably greater than 0.50, which may reflect the predominance of the cation-exchange region over the anion-exchange region in the membrane. In CMM 1008/CH, however, despite the

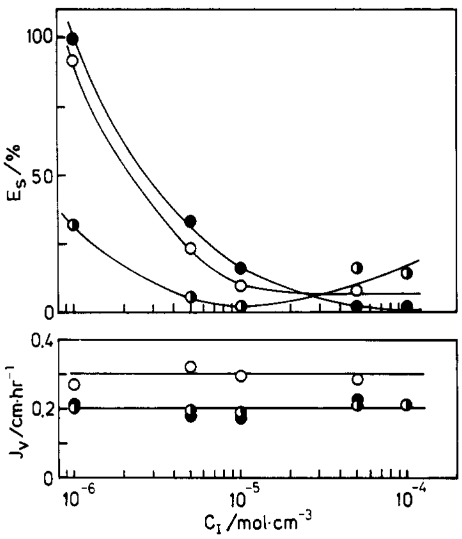

Figure 9. Salt enrichment E_s and volume flux J_v vs. concentration of high-pressure solution c_I for charge-mosaic membranes: (○) CMM 1008/BZ; (●) CMM 1008/DO; (◑) CMM 1008/CH.

predominance of the cation-exchange region, t_+ is less than 0.50. This is attributed to the morphology of the membrane, in which the anion-exchange part exists as a continuous matrix and the cation-exchange part as islands.

It is clear from the data in Table III that CMM 1008/BZ and CMM 1008/DO have better properties as charge-mosaic membranes than the others.

Transport Properties. The results of piezodialysis experiments with membranes CMM 1008/BZ, CMM 1008/DO, and CMM 1008/CH are shown in Figure 9. Percent salt enrichment E_s was calculated as

$$E_s\ (\%) = 100(c_{II}/c_I - 1) \tag{4}$$

with c_I the concentration of high-pressure solution and c_{II} the concentration of the permeant solution. The values of E_s and the volume flux J_v for each membrane are plotted against log c_I. For CMM 1008/BZ and CMM 1008/DO, the values of E_s increase rapidly with decreasing log c_I. This behavior of E_s is that theoretically expected for a membrane with a mosaic of discrete areas of anion- and cation-exchange resins passing from one face of the membrane to the other.[29] The curve for CMM 1008/CH shows a relatively low E_s value even in the very low concentration region and has a broad minimum near 10^{-5} mol/cm^3. Although we cannot account clearly for this anomalous behavior, it may be attributable to the undesirable morphology of the membrane. It is noted that J_v is almost constant within the c_I range studied for every membrane and that it does not differ significantly among the membranes.

The results of measurements of water and salt flows with membrane CMM 1008/BZ are shown in Figure 10, plotting the volume changes of both solutions at sides I and II and the conductance of the solution at side II against time. The volume of the solution at side I decreases and that at side II increases linearly with time at almost the same rate, and the concentration of the solution at side II also increases linearly. Thus, a volume flow across the membrane from the solution of higher to that of lower KCl concentration, i.e., negative osmosis, occurs along with the salt flow in the same direction. The salt and volume fluxes determined from the slopes of the data in Figure 10 were $1.0_9 \times 10^{-8}$ mol/(cm^2 s) and $2.8_8 \times 10^{-6}$ cm/s, respectively. Negative osmosis is a typical transport phenomenon of a charge-mosaic membrane, as first predicted by Kedem and Katchalsky[5] and demonstrated by Carr and Sollner[30] and by Weinstein et al.[11,31] with model membranes.

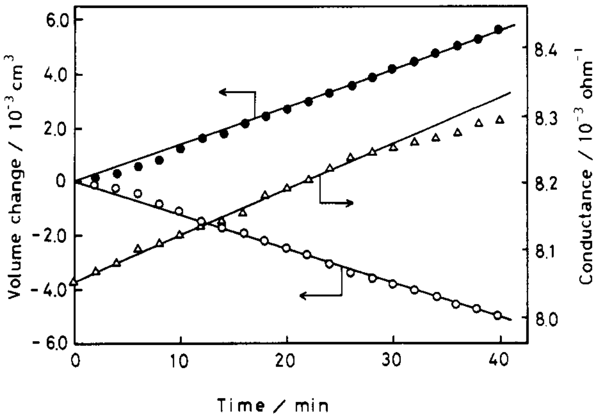

Figure 10. Volume and salt flow at zero hydrostatic pressure difference on membrane CMM 1008/BZ: (●) volume change at compartment II (low concentration); (○) volume change at compartment I (high concentration); (△) conductance at compartment II.

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Registry No. S_2Cl_2, 10025-67-9; ISI (copolymer), 25038-32-8; ISIAI (copolymer), 74418-57-8; ISIAI (copolymer) methyl iodide salt, 91899-28-4; polyisoprene (homopolymer), 9003-31-0.

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Zwitterion Polymerization of 2-Methyl-2-oxazoline and Acrylic Acid: Characterization of Ether-Soluble Products

Pathiraja A. Gunatillake and George Odian*

The City University of New York, College of Staten Island, Staten Island, New York 10301.

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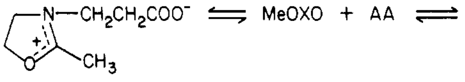
ABSTRACT: 2-Methyl-2-oxazoline (MeOXO) and acrylic acid (AA) were previously found to undergo reaction to form a copolymer, $[\mathrm{CH_2CH_2{-}N(COCH_3)CH_2CH_2COO}]_n$, which is precipitated from the reaction mixture by adding diethyl ether. A considerable amount (30%) of low molecular weight products remains soluble in the ether solution. The ether-soluble products were fractionated by analytical and preparative HPLC, and the isolated fractions were identified by ^{1}H and ^{13}C NMR. The formation of the various ether-soluble products is discussed in terms of the overall mechanism of zwitterion polymerization.

Introduction

Zwitterion polymerization of 2-methyl-2-oxazoline (MeOXO) and acrylic acid (AA) was reported by Saegusa and Tomalia and their co-workers.[1,2] Our study of MeOXO–AA provided strong evidence for the copolymer structure, $[\mathrm{CH_2CH_2{-}N(COCH_3)CH_2CH_2COO}]_n$, and the polymerization mechanism.[3] The initial reactions between MeOXO and AA involve the formation of the genetic zwitterion I and the protonated MeOXO species II. The former is responsible for initiation and propagation while the latter participates (along with AA) in termination. The genetic zwitterion reacts with itself to form a dimer zwitterion III. Growth continues in a smilar manner by the genetic zwitterion reacting with larger-sized zwitterions (macrozwitterions) (IV) and by the reaction of macrozwitterions with each other. Termination occurs by reaction of macrozwitterions with acrylic acid and with II to produce polymer structures Va and Vb containing olefinic, acetamido, and carboxylic end groups.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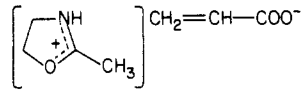
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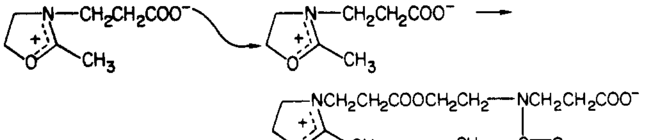
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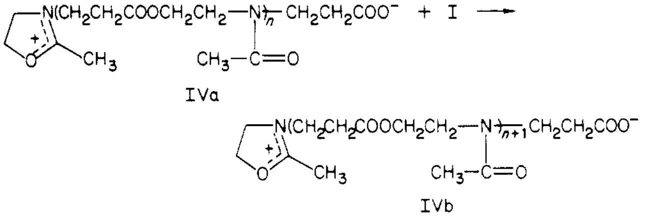
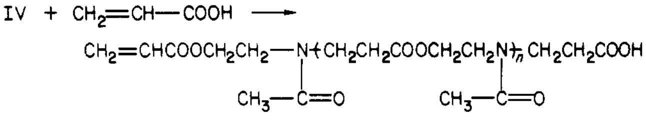
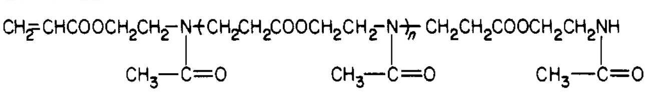

IVa

IVb



$$\mathrm{IV + CH_2{=}CH{-}COOH \longrightarrow CH_2{=}CHCOOCH_2CH_2{-}\underset{\substack{|\\ CH_3-C=O}}{N}{+}CH_2CH_2COOCH_2CH_2\underset{\substack{|\\ CH_3-C=O}}{N}{+}_n CH_2CH_2COOH}$$

Va



$$\mathrm{IV + II \longrightarrow CH_2{=}CHCOOCH_2CH_2{-}\underset{\substack{|\\ CH_3-C=O}}{N}{+}CH_2CH_2COOCH_2CH_2{-}\underset{\substack{|\\ CH_3-C=O}}{N}{+}_n CH_2CH_2COOCH_2CH_2\underset{\substack{|\\ CH_3-C=O}}{NH}}$$

Vb

Our previous work was limited to the characterization of the polymer obtained by precipitation of the reaction mixture in diethyl ether. A considerable amount (30%) of products is found in the ether solution. The ether-soluble products have not previously been studied. The characterization of these products is important to fully establish and understand the reactions which lead to low molecular weight products during zwitterion polymerization. In this paper we report on the fractionation and characterization of various products found in the ether solution.

Experimental Section

Materials. Acetonitrile, 2-methyl-2-oxazoline (MeOXO), and acrylic acid (AA, Aldrich) were dried and purified as previously reported.[3] Methanol (HPLC, Fisher) and anhydrous diethyl ether (Fisher) were used as received.

Polymerization and Isolation of Ether-Soluble Products. MeOXO (150 mmol), AA (150 mmol), *p*-methoxyphenol (0.8 mmol), and acetonitrile (15 mL) were mixed inside a drybox, placed in a sample tube, cooled with liquid nitrogen, sealed under vacuum, and heated at 70 °C for 48 h. The reaction mixture was dissolved in 25 mL of methanol and precipitated into 800 mL of anhydrous diethyl ether. The ether solution was decanted from the precipitated product and evaporated under vacuum to give a gummy product, which was then dried in a vacuum oven at 35

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