

A Study on the Preparation and Properties of the Heterogeneous Cation-Exchange Membranes of Sulfonated Polystyrene/Divinyl Benzene on an Acetal Base

SUEI Y. LAM-LEUNG* and HUAN R. LI†

Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon, Hong Kong

SYNOPSIS

The heterogeneous acetal-based membranes containing 50, 60, 70, 80, and 90% (w/w) of the sulfonated polystyrene crosslinked with 7% divinyl benzene were fabricated and studied. In addition, the heterogeneous acetal-based membranes of 85% (w/w) sulfonated polystyrene crosslinked with 1, 4, and 7% divinyl benzene were also prepared and studied. The gel water content, dimensional stability, ion-exchange capacity, area and specific ohmic resistance, permselectivity, and rate of ion exchange of the acetal-based membranes were determined. The sulfonated polystyrene crosslinked with 7% divinyl benzene resin was found to be the better material for preparing the acetal-based membrane with comparable good characteristics. A commercially available heterogeneous membrane (Shanghai Chemicals, 3361) of dry-molding sulfonated polystyrene-divinyl benzene resin was used as the reference membrane for the present investigation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The important applications of ion-exchange membranes in industrial separation processes has been greatly developed since 1970s. Starting from the desalination of saline solutions, electrodialysis and related processes have been introduced into many important solutions and into many important industrial applications, such as Brackish water desalination, food and pharmaceutical production, chlorine-alkaline electrolysis, and electrolytic regeneration of chromic acid etchants.¹⁻⁴ Unfortunately, a full description of how the degree of crosslinking in the resin is related to the physical and electrical characteristics of the fabricated ion-exchange membrane has been seldom reported in the literature. In this article, the characterization of heterogeneous ion exchange membranes fabricated by different degrees of crosslinking of sulfo-

nated polystyrene and divinyl benzene is described. The results of our investigation show that the heterogeneous acetal-based membranes of 50–90% (w/w) sulfonated polystyrene crosslinked with 7% divinyl benzene have the advantages of good elasticity, low electrical resistance, high permselectivity, and high membrane ion-exchange capacity.

EXPERIMENTAL

Apparatus

A conductance meter (Yellow Springs Instrument, Model 32) equipped with two $11 \times 10 \text{ mm}^2$ Pt electrodes was used for measuring the ohmic resistance of the fabricated membrane. A millivoltmeter (Orion, Model SA720) together with two standard calomel electrodes (Thomas, Model F15-4092) were used to measure the membrane potential. An anion-exchange column (Waters, IC-Pak A), equipped with a high-performance liquid-chromatography pump (Waters, Model 510), a sample injection system (Waters, Model U6K), and a conductivity de-

* To whom correspondence should be addressed.

† Visiting scholar from Zhongshan University, People's Republic of China.

tector (Waters, Model 430) and data logged to the Baseline 810 Chromatography Workstation, was used to determine the concentration of chloride or nitrate ions in the studied sample. An atomic absorption spectrophotometer (Varian, Model SpectrAA-10) was used for the determination of potassium.

Reagents

Chemicals used for membrane fabrication were of reagent grade. Chemicals used for the investigation of membrane properties were of analytical reagent grade. The dry-molding heterogeneous cation-exchange membrane (Shanghai Chemicals, 3361) was purchased from Shanghai Chemical Works.

Fabrication of the Heterogeneous Ion-exchange Membrane of Sulfonated Polystyrene-Divinyl Benzene Copolymer on an Acetal Base

The acetal-based membrane of sulfonated polystyrene-divinyl benzene was prepared first by dispersion of the fine powder of sulfonated polystyrene-divinyl benzene (SPSDVB) resin in an aqueous solution of poly(vinyl alcohol) and then by formation of a film of PSDVB resin paste, and, finally, by polycondensation of poly(vinyl alcohol) in the preformed film of PSDVB resin with methanal.⁵

Preparation of Fine-powdered Ion-exchange Resin of Sulfonated Polystyrene-Divinyl Benzene

A suitable amount (about 80 g) of the commercially granular resin of sulfonated polystyrene crosslinked with 1, 4, or 7% divinyl benzene was soaked in 100 mL of 2 mol L⁻¹ HCl solution for at least 12 h and then rinsed by D.I. water after filtration. The acid-form sulfonated polystyrene/divinyl benzene (H-SPSDVB) resin was then transferred to sodium form (Na-SPSDVB) by soaking in 100 mL of 2 mol L⁻¹ NaOH for 24 h. The clean and air-dried Na-SPSDVB resin was then ground to 200-mesh sieved powder by using a porcelain mortar. After drying in oven at 100°C for 0.5 h, at least 98% of the 200-mesh sieved resin was sifted through a 250-mesh sieve and readied for use in the casting membrane.

Preparation of the Na-sulfonated Polystyrene/Divinyl Benzene-Poly(vinyl alcohol) (Na-SPSDVB-PVA) Paste

The Na-SPSDVB-PVA resin paste was prepared by dispersing a suitable amount of 200-mesh Na-SPSDVB powder into 10 mL of poly(vinyl alcohol)

(PVA) solution. The amount of resin powder and also the concentration of the PVA solution used were dependent on the content of the ion-exchange resin in the fabricated membrane. About 1 mL of a 50% ethanol solution was added into the resin paste as an antifoaming agent if necessary.

Fabrication of Na-SPSDVB-PVA Sheet

For the preparation of a Na-SPSDVB-PVA sheet of about 100 cm² in area and 1.5 mm in thickness (wet), 2.5, 3.0, 3.5, 4.0, and 4.5 g of Na-SPSDVB 200-mesh powder were dispersed in 10 mL of 250, 200, 150, 100, and 50 g L⁻¹ PVA solution, respectively, to obtain the membrane containing 50, 60, 70, 80, and 90% (w/w) of 7% crosslinked Na-SPSDVB resin. Nearly one-third of the resin paste was poured along the short edge of a clean 16 × 24 cm glass plate, on which the resin paste was placed at least 4 cm apart from the top edge. Now, the Na-SPSDVB-PVA paste was spread on the glass plate using a clean glass rod to produce a 0.3 mm-thick layer of resin. A piece of 12 × 20 cm polyester net with 64 openings in 1 cm² was then pressed onto the resin layer by a glass rod and then fixed on the glass plate by several clips. The remainder of the resin paste was now evenly introduced on top of the previous layer and then spread into a smooth layer, about 7.5 × 13 cm in size, by moving to and fro a glass rod tied with a 1.5 mm-thick rubber band on each end to control the thickness of the fabricated Na-SPSDVB-PVA sheet.

Formation of H-form Sulfonated Polystyrene/Divinyl Benzene Acetal-based Membrane

After air-drying, the Na-SPSDVB-PVA sheet was immersed in solution A (containing 10% sulfuric acid, 20% sodium sulfate, 6% zinc sulfate, and 3.5% methanal) for 10 h at room temperature. After washing with D.I. water, the fabricated membrane was then soaked in solution B (containing 5% sulfuric acid, and methanal 16%) for 20 h. A smooth and soft H-SPSDVB-acetal-based membrane was then obtained. The adsorbed residue of methanal and sulfuric acid was removed from the fabricated membrane by washing with D.I. water.

Characterization of the Sulfonated Polystyrene/Divinyl Benzene Acetal-based Membrane⁶

Membrane Gel Water Content

The clean samples of the cation-exchange membranes in the hydrogen form were equilibrated in

Table I Characteristics of the Sodium Sulfonated Polystyrene/Divinyl Benzene Polymer Used for Membrane Fabrication

Types of Ion-exchange Resin	Ion-exchange Capacity (meq/g)	Degree of Crosslinked by Divinyl Benzene % (m/m)	Water Content % (m/m)	Color
IER1	4.5	1	85-90	Yellow
IER2	4.5	4	55-65	Pale brown
IER3	4.2	7	45-55	Dark brown

D.I. water for at least 2 days. The difference in mass of the membrane between the surface-dried membrane and the constant mass attained after being oven-dried at 100°C was determined. The gel water content was calculated from $100(W_{\text{surface-dried}} - W_{\text{oven-dried}})/W_{\text{oven-dried}}$, where $W_{\text{surface-dried}}$ denoted the mass of surface-dried membrane and $W_{\text{oven-dried}}$ denoted the mass of oven-dried membrane.

Membrane Dimensions

The thickness of each of the fabricated membranes and the dry-molding heterogeneous membrane of sulfonated polystyrene crosslinked by 7% divinyl benzene (Shanghai Chemicals, 3361) was obtained from the average of the triple-point measurements by using a micrometer. The swelling capacity of the membrane thickness was obtained from $100(\text{thickness in wet} - \text{thickness in dry})/\text{thickness in dry}$.

The width and length of the studied membranes were measured by using a caliper graduated 60 mm in 1 mm divisions. The longitudinal stretchability of the membrane was obtained from $100(\text{length of the membrane in wet} - \text{length of the membrane in dry})/\text{length of the membrane in dry}$.

Membrane Ion-exchange Capacities

Duplicate membrane samples of each of the fabricated membranes were equilibrated for 24 h in 2 mol

L^{-1} HCl and then rinsed free from chloride by soaking with 100 mL D.I. water for 4 h several times. The surface-dried membrane was then weighed and then equilibrated for 24 h in 50 mL of 1.00 mol L^{-1} KCl solution. The ion-exchange capacity of the sample was then determined by back-titration with a standardized 0.100 mol L^{-1} NaOH solution. The samples were then dried to constant weight in oven at 100°C. The ion-exchange capacity of the sample was calculated for the dry membrane.

Ohmic Resistance of the Ion-exchange Membrane

The ohmic resistance of each of the fabricated membranes was determined at $20 \pm 0.1^\circ\text{C}$. The conductivity of the cell filled with 0.100 mol L^{-1} KCl was measured with and without a membrane separating the two compartments of the cell. The two $11 \times 10 \text{ mm}^2$ Pt electrodes were placed in 15 mm apart. The effective area of the membrane used as the cell divider was identical to those of the Pt electrodes used. The positions of the electrodes and also the membrane were located side by side. The membrane area electrical resistance was then calculated from the conductivity data using the following equation:

$$R_A = A \left(\frac{1}{k_T} - \frac{1}{k'} \right)$$

Table II The Longitudinal Stretchability and the Swelling in Thickness of the Acetal-based and the Dry Molding Membranes of Sulfonated Polystyrene/Divinyl Benzene Resin

Types of Membrane	Swelling in Thickness	Longitudinal Stretchability
Acetal-based with 1% crosslinked	^a	^a
Acetal-based with 4% crosslinked	^a	27%
Acetal-based with 7% crosslinked	15.2%	16%
Shanghai 3361	17.7%	6%

^a Unsuccessful determination due to the poor mechanical strength of the dried membrane.

Table III Characteristics of the Acetal-based and the Dry-molding Membranes of Sulfonated Polystyrene/Divinyl Benzene

Crosslinked with DVB % (m/m)	Na-SPSDVB Content in Membrane % (m/m)	Membrane Thickness (wet) (mm)	Gel Water Content in Membrane % (m/m)	Membrane Area		Specific Membrane Resistance (ohm cm)	Ion- exchange Capacity (meq/g)	Membrane Potential in 0.1/0.2 KCl at 20°C (mV)	Apparent Permeability ^a in 0.1/0.2 Mol L ⁻¹ KCl, (α_2^*) (%)	Permeability ^a (ρ) (%)
				Ohmic Resistance (ohm cm ²)	Membrane Resistance (ohm cm)					
1	85	1.00	77	3.6	36	1.9	—	—	—	—
4	85	0.65	55	3.6	55	1.8	14.4	91.1	91.3	91.3
7	50	0.56	40	14.6	261	1.5	13.4	84.8	85.1	85.1
7	60	0.57	39	9.2	161	1.8	13.9	88.0	88.2	88.2
7	70	0.56	40	5.7	104	2.2	14.7	93.0	93.2	93.2
7	80	0.55	39	4.7	85	2.3	14.9	94.3	94.4	94.4
7	85	0.38	40	2.5	66	2.5	15.0	94.9	95.0	95.0
7	85	0.55	40	4.2	76	2.6	14.9	94.3	94.4	94.4
7	85	0.76	41	4.5	59	2.5	15.1	95.6	95.7	95.7
7	90	0.67	40	3.6	54	2.7	15.0	94.9	95.0	95.0
Shanghai 3361		0.53	36	6.4	121	2.2	14.9	94.3	94.4	94.4

^a The calculated potential difference between 0.1 and 0.2 mol L⁻¹ KCl solution was 15.8 mV at 20°C.

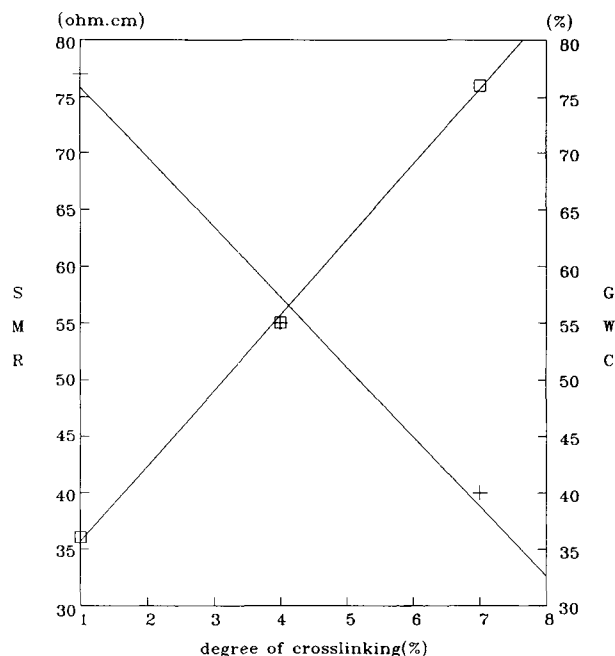


Figure 1 The relationship between the degree of crosslinking and the specific membrane resistance and the gel water content.

where R_A = the area electrical resistance of the membrane, ohm cm^2 ; k_T = the conductivity of the cell solution, $\text{ohm}^{-1} \text{cm}^{-1}$; and k' = the conductivity of the cell solution and membrane, $\text{ohm}^{-1} \text{cm}^{-1}$. The specific membrane resistance was then obtained from R_A divided by the thickness of the membrane used. Three fabricated membranes containing 85% of the resin of 1, 4, and 7% crosslinked Na-SPSDVB were selected for the study of their ohmic resistances at 20, 30, 40, and 50°C.

Permselectivity of the Prepared Membrane

The permselectivity of each of the fabricated membranes was determined from a potential measurement by the static method. The test system was built by two $69 \times 69 \times 41 \text{ mm}^3$ cells separated by a membrane sample with an effective area of $29 \times 43 \text{ mm}^2$. In the system, about 160 mL of 0.100 and 0.200 mol L^{-1} KCl solution were filled in the anodic and cathodic compartments, respectively. The solution in each compartment was well stirred using a mechanical stirrer. All measurements of the Donnan potential of the membrane samples were taken at $20 \pm 0.1^\circ\text{C}$. The apparent permselectivity α_{\pm}^a of the membrane was obtained from the ratio of the measured to the theoretically calculated potential dif-

ference between the two electrolyte solutions using a set of calomel electrodes. The asymmetry of the two calomel electrodes measured in well-stirred 0.2 mol L^{-1} KCl solution was less than 0.2 MV at 20°C .

Rate of Ion Exchange

The average rates for the restricted and nonrestricted ions moving across the two selected membranes were studied as follows: The membrane sample was held between two rectangular tanks with $25 \times 45 \times 72 \text{ mm}^3$ each. The effective area of the membrane sample was $40 \times 60 \text{ mm}^2$. An equal volume (about 80 mL) of the 0.100 mol L^{-1} solutions of the selected electrolytes, namely, $\text{NH}_4\text{Cl}/\text{KNO}_3$, was added simultaneously into the individual compartments of the divided cell. After standing for 24 h at 20°C , a suitable volume of the solution in each of the compartments in the divided cell was collected, and the quantity of the nonrestricted ions (cations) moved across and the amount of the restricted ions (anions) that leaked through the membrane sample were determined.

The amount of ammonium ion in the KNO_3 compartment was determined by the indophenol spectrophotometric method.⁷ The concentrations of the chloride ion in the sample collected from the KNO_3

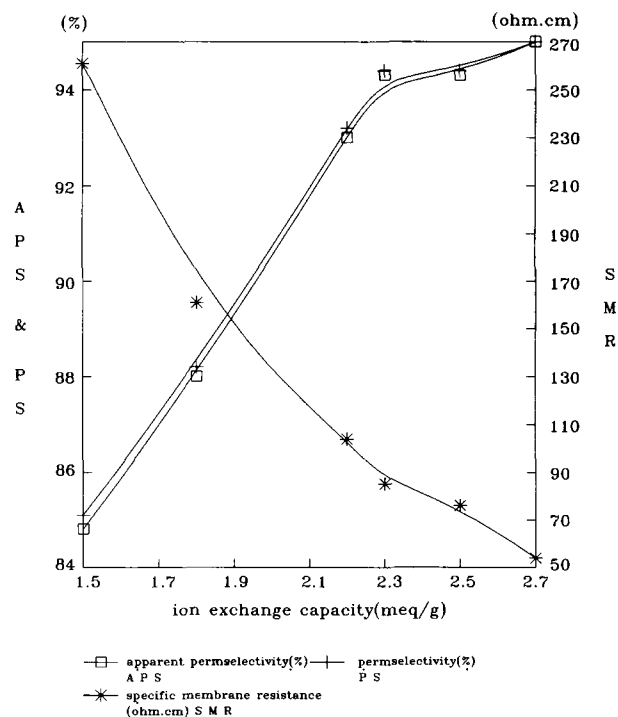


Figure 2 The relationship between the ion-exchange capacity and the permselectivity, apparent permselectivity, and the specific membrane resistance.

Table IV Temperature Effect on the Electrical Resistance (e.r.) of the Acetal-based Membranes Fabricated from 85% of Sulfonated Polystyrene Crosslinked with 1, 4, and 7% of Divinyl Benzene

Degree of Crosslinking	Electrical Resistance	20°C	30°C	40°C	50°C
7%	Membrane area e.r. (ohm cm ²)	3.7	3.0	2.8	2.1
	Specific membrane resistance (ohm cm)	67	55	51	38
4%	Membrane area e.r. (ohm cm ²)	3.6	2.9	2.5	1.9
	Specific membrane resistance (ohm cm)	55	45	39	29
1%	Membrane area e.r. (ohm cm ²)	3.4	2.5	2.1	1.9
	Specific membrane resistance (ohm cm)	34	25	21	19

compartment and also the nitrate ion in sample collected from the NH₄Cl compartment were analyzed using an ion-exchange chromatographic method.⁸ Finally, the concentration of potassium ion in the sample collected from the NH₄Cl compartment was determined using an atomic absorption spectrophotometric method.⁹

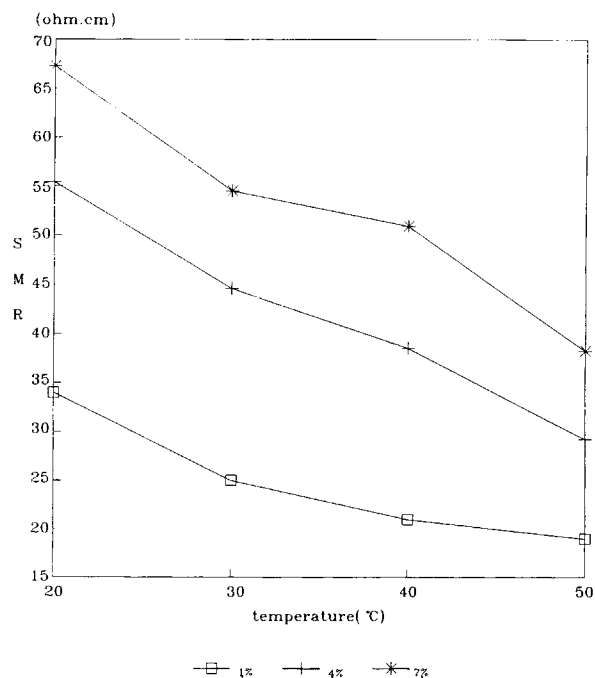
RESULTS AND DISCUSSION

The data given in Table I report the ion-exchange capacity and the water content of the SPDB resin. The hydrophilic nature of the SPDB resin was greatly affected by the degree crosslinked by divinyl benzene, as expected. The dimensional stability of the wet acetal-based membrane in 85% (w/w) resin of sulfonated polystyrene crosslinked with 1%, 4%, and 7% (w/w) of divinyl benzene and also the Shanghai 3361 membrane was quite good. All acetal-based membranes were curled up due to the uneven deformation as the water content was removed from the wet membranes.

Table V Average Rates of the Nonrestricted Ions Moved Across and the Restricted Ions Leaked Through the Acetal-based Membrane of the 85% of Na-SPSDVB (7% Crosslinked) and the Shanghai 3361 Membrane of Na-SPSDVB in the NH₄Cl/KNO₃ System During a Standing Period of 24 h at 20°C

Electrolytes:	Membrane: Average Rate (meq h ⁻¹ cm ⁻²)	
	Acetal-based	Shanghai 3361
NH ₄ ⁺	7.6 × 10 ⁻²	7.6 × 10 ⁻²
Cl ⁻	2.5 × 10 ⁻²	1.5 × 10 ⁻²
K ⁺	10 × 10 ⁻²	12 × 10 ⁻²
NO ₃ ⁻	2.7 × 10 ⁻²	2.3 × 10 ⁻²

Table II shows the longitudinal stretchability after wetting. The stretchability of the acetal-based membrane was dependent on the degree of crosslinking in the resin used. For the sulfonated polystyrene crosslinked with 1% divinyl benzene, the acetal-based membrane could not be successfully fabricated unless its thickness was nearly doubled in comparison with the others. The dimensions of the dried membranes with a low degree of crosslinking were difficult to determine due to the irregular change in their shape. The mechanical strength of the 1% crosslinked acetal-based membrane was very poor, and several cracks were observed on the dry membrane.

**Figure 3** The specific membrane resistance of the 85% Na-SPSDVB permselective membrane fabricated from three different degrees of crosslinked sulfonated polystyrene/divinyl benzene resin at 20, 30, 40, and 50°C.

Some physical and electrical characteristics of the fabricated acetal-based membrane and the Shanghai 3361 strong cation-exchange membrane are given in Table III. It was found that the gel water content depended mainly upon the degree of crosslinking and the hydrophilic ability of the resin used for fabrication. The ion-exchange capacity of the fabricated membrane depended on the percentage of ion-exchange resin contained, as expected. The relationships between the degree of crosslinking of the Na-SPSDVB used and their specific membrane resistance and gel water content are given in Figure 1. For the 7% DVB-crosslinked sulfonated polystyrene, the specific membrane resistance and the apparent permselectivity of the acetal-based membranes with a resin content higher than 70% were comparable with or even better than those of the Shanghai 3361 membrane. The relationships between the ion-exchange capacity of the fabricated membrane and the permselectivity, the apparent permselectivity, and the specific membrane resistance are given in Figure 2. The permselectivity, the apparent permselectivity, and the specific membrane resistance of the studied membrane were affected by the ion-exchange capacity and the amount of Na-SPSDVB contained in the studied membrane.

Table IV shows the electrical resistances of the fabricated membranes consisting 85% of NA-SPSDVB resin with 1, 4, and 7% of divinyl benzene measured at 20, 30, 40, and 50°C. For the membranes fabricated with three different degrees of crosslinking, a similar pattern of an electrical resistance-temperature plot was obtained for the membrane fabricated from the three Na-SPSDVB resins of 1, 4, and 7% crosslinked divinyl benzene (Fig. 3).

The permeabilities of the nonrestricted ions and cations and the restricted ions and anions, exchanged across the selected Na-SPSDVB mem-

branes to the opposite compartment in the studied system, are given in Table V. Mostly, the permeability of the nonrestricted ions, such as the ammonium or potassium ion, was found to be greater than those of the restricted ions and anions, such as the chloride or nitrate ion. Obviously, the fabricated Na-SPSDVB and also the Shanghai 3361 membranes are not ideally ionselective; in addition to the cations moved across, a substantial leak of the chloride or nitrate ion occurs through the membrane.

The authors are indebted to the Research Committee of Hong Kong Baptist University for financial support.

REFERENCES

1. H. Strathmann, *J. Sep. Process Technol.*, **5**, 1-13 (1984).
2. H. Strathmann, *Sep. Purif. Methods*, **14**, 41-66 (1985).
3. W. S. W. Ho and K. K. Sirkar, Eds., *Membrane Handbook*, Van Nostrand Reinhold, New York, 1992, pp. 255-262.
4. W. P. Innes, W. H. Toller, and D. Tomasello, *Plat. Surf. Finish.*, **65**, 36-40 (1978).
5. X. C. Zhu, *Polym. Commun. (China)*, **2**, 238 (1957).
6. W. S. W. Ho and K. K. Sirkav, Eds., *Membrane Handbook*, Nostrand Reinhold, New York, 1992, pp. 239-244.
7. V. D. Adams, *Water and Wastewater Examination Manual*, Lewis, Chelsea, 1990, pp. 116-118.
8. Waters Chromatography Division, *The IC-PAK Column and Guard Column: Care and Use Manual*, Millipore Corp., Milford, Ma 1988.
9. E. Rothery, *Operation Manual: SpectrAA-10*, Varian Techtron Pty., Mulgrave, 1995.

Received May 26, 1994

Accepted February 25, 1995