

Synthesis and Characterization of Cellulose Triacetate and Poly(ethylene imine) Membranes Containing a Polyether Macrobicyclic: Their Application to the Separation of Copper(II) and Silver(I) Ions

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ABSTRACT: A cellulose triacetate (CTA)–poly(ethylene imine) (PEI) membrane containing a polyether macrobicyclic (cryptand) as a carrier and 2-nitrophenyloctyl ether (NPOE) as a plasticizer was prepared. The CTA–PEI–cryptand–NPOE membrane was characterized with chemical techniques as well as Fourier transform infrared, X-ray diffraction, differential scanning calorimetry, and scanning

electron microscopy. The permeation of silver and copper ions through the CTA–PEI–cryptand–NPOE membrane was comparable to that through a supported liquid membrane. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1401–1410, 2004

Key words: diffusion; membranes; synthesis

INTRODUCTION

Requirements to limit industrial waste in the environment are responsible for the increase in the number of research programs devoted to the improvement of technical processes for the separation and recuperation of valuable and toxic species. Separation processes based on membrane technologies are more sophisticated methods.¹ Classical routes include the synthesis of porous inorganic or hybrid membranes of well-defined pore sizes² and the modification of surface properties to introduce specific interactions or electrostatic repulsive–attractive effects, as for electro-dialysis membranes.³

Membranes modified through the adsorption of poly(ethylene imine) (PEI) under the effect of an electric field show improvements in their transport properties toward monovalent ions against divalent ones.^{4–6}

A solvent polymeric membrane, which consists of a polymer film containing a plasticizer, can be used as an example of a liquid membrane containing a mobile carrier. This type of membrane, however, generally exhibits low ionic permeability in comparison with

emulsion or supported liquid membranes. Therefore, much of the research on these types of membranes has centered on the development of membrane-selective ion electrodes.^{7,8} The facilitated transport of metal ions through polymeric fixed-site carrier membranes has resulted in good ion-separation selectivities and vast improvements in membrane stability in comparison with liquid membranes and polymer-stabilized liquid membranes.^{9,10} Transport studies using cellulose triacetate (CTA) membranes as polymeric matrices with high flux and good stability have recently been reported.^{11–13}

In this work, we developed a novel class of plasticized CTA membranes, modified by carrier incorporation, that were selectively permeable to copper and silver cations. The CTA–2-nitrophenyloctyl ether (NPOE)–carrier membrane was characterized with chemical techniques as well as Fourier transform infrared (FTIR), X-ray diffraction, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

EXPERIMENTAL

PEI was used as an absorbent; under the experimental conditions, PEI was a positively charged polyelectrolyte. Previous work established that PEI and porous materials could constitute a model system for investigating the relationship between diffusion into porous structures, the adsorption rate, and the molecular weight of the polymer.

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TABLE I
Characteristics of PEI

Molecular weight	pK_a	m	Specific viscosity	PR (%)	$\log K_4$
1,000,000	9.06	3.6	0.28	73	29.30

PEI is a typical polymeric amine; it has a chelating form with various metal ions. It is known to exist as a linear structure or a branched structure. Commercial branched PEI was used in this work; depending on the polymerization process, it contained primary, secondary, and tertiary amino groups in a ratio of approximately 0.25:0.5:0.25.¹⁴

PEI possesses quite a number of advantages as a polymer chelating agent, such as good water solubility and a suitable molecular weight. The chelating properties have been studied elsewhere,¹⁵ and it has been found, with both potentiometric and spectrophotometric methods, that the ability of PEI-Cu²⁺ to complex with the branched form is 10 times greater than its ability with the linear form. Moreover, the stability constants obtained for PEI-Cu²⁺ complexes are higher than those obtained for other heavy metals such as Co²⁺, Ni²⁺, Cd²⁺, Zn²⁺, and UO₂²⁺.¹⁶

In addition, PEI in an aqueous solution behaves as an effective base and is protonated at pH < 10. Some characteristics of the PEI sample used in this work are given in Table I.

The values of pK_a and the chain-expansion coefficient of the polymer (m) were estimated with the Henderson-Hasselbach modified method as follows:

$$pH = pK_a + m \log \frac{\alpha}{1 - \alpha} \quad (1)$$

where α is the neutralization coefficient.

The specific viscosity was measured at a constant temperature of 20°C with a calibrated Ubbelohde suspended-bulb viscometer. The protonation ratio (PR) of PEI in an acidic medium was ascertained, and the overall complexation constant ($\log K_4$) was determined with a potentiometric method.¹⁷

Preparation of the membranes

The CTA membranes were prepared according to the procedure reported by Sugiura and coworkers.^{18–22} In 30 mL of chloroform, 0.3 g of CTA (Fluka, Buchs, Switzerland) was dissolved. In a glass culture dish were mixed 30 mL of the CTA solution, 0.3 mL of *o*-nitrophenyl *n*-octyl ether (NPOE; Fluka), 0.075 g of 4,7,13,16,21,24-hexaoxa-1,10-diaza-bicyclo-[8.8.8]-hexacosane (222; Fluka), and 0.3 g of PEI (Fluka). The culture dish was then covered with a glass cover and

left overnight at room temperature. During the interval, the mixed solution was slowly air-dried. After the culture dish was filled with water, the resulting membrane was peeled from its bottom.

Characterization of the membranes

The prepared membranes were characterized with different physical methods. The FTIR spectra were obtained with a Nicolet 710 spectrophotometer. The DSC measurements were performed with a TA Instrument thermogravimeter in the range of 20–300°C.

The internal morphology and external morphology of the respective membranes were observed with a Hitachi S4500. X-ray analyses were recorded on a Siemens diffractometer.

Permeation procedure

The apparatus used for the permeation experiments was similar to that previously used;²³ the permeation cell consisted of two compartments that were separated by the membrane (Fig. 1). The half-cell volume was 40 mL, and the effective area was 8.04 cm².

The CTA membrane was fixed between the glass compartments. To each compartment was added 40 mL of an aqueous solution: one (compartment I) initially contained 10 mM copper nitrate; the other (compartment II) contained 40 mL of a water distillate. All the permeation experiments were performed at 25°C. The metal concentrations in the two compartments were determined by absorption atomic spectroscopy (model 2380, PerkinElmer).

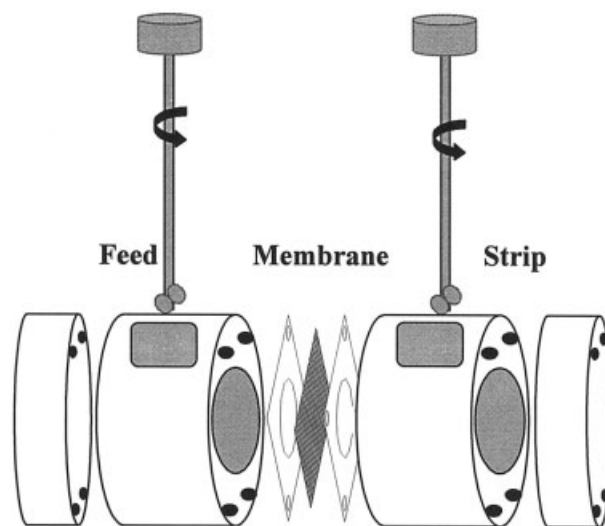


Figure 1 Scheme of the transport cell.

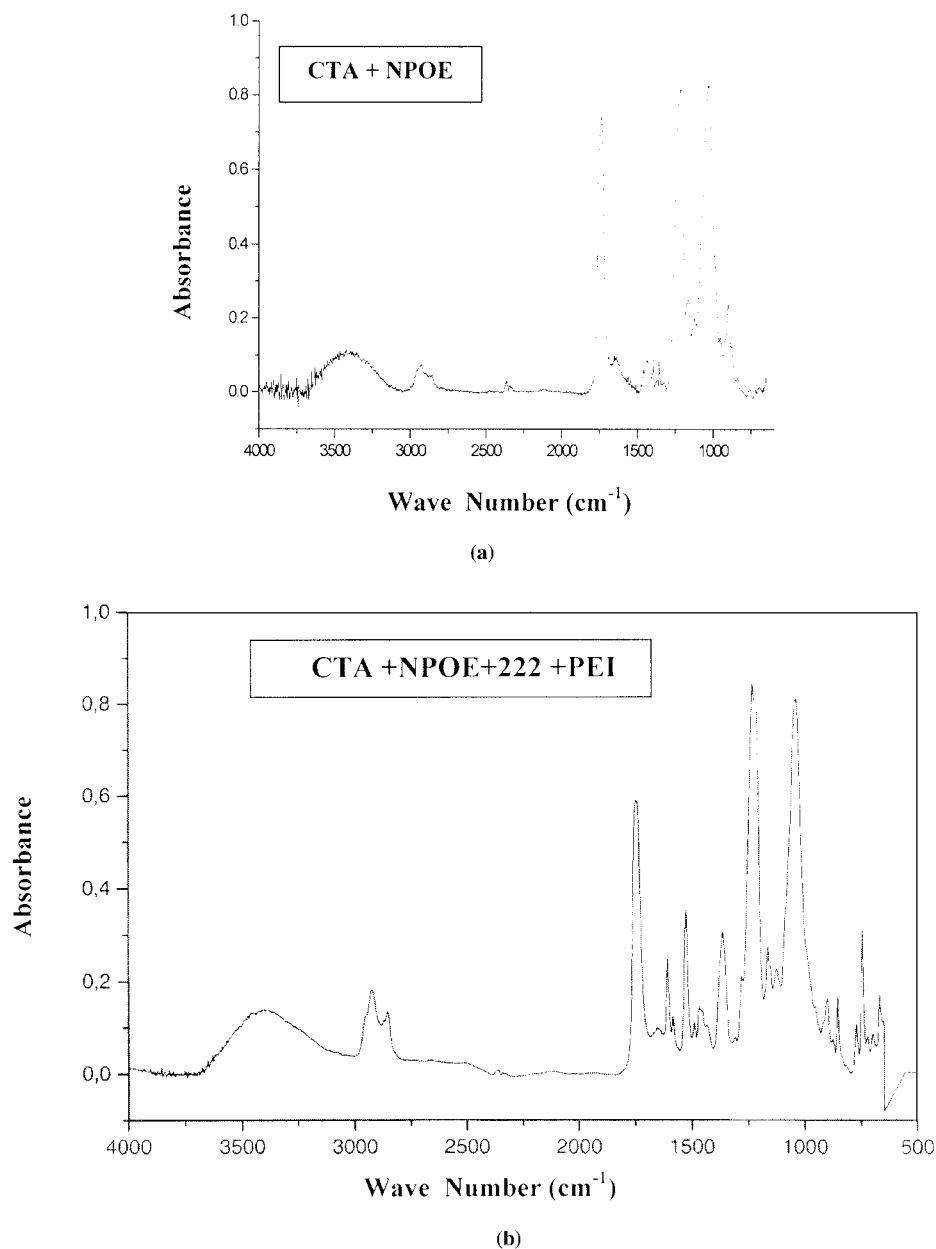


Figure 2 FTIR spectra of (a) the CTA–NPOE membrane and (b) the CTA–NPOE–222–PEI membrane.

RESULTS AND DISCUSSION

Characterization by FTIR

Figure 2(a) shows the spectrum of the CTA membrane. There is an absorption band around 1735 cm^{-1} , which can be attributed to the stretching vibration of the carbonyl group. The bands at 1216 and 1029 cm^{-1} correspond to the stretching modes of the C–O single bond.

The bands at 2940 and 2880 cm^{-1} can be attributed to C–H bonds. Bands corresponding to O–H bond stretching are generally detected between 3500 and 3100 cm^{-1} .

Figure 2(b) shows a band at 1351.8 cm^{-1} assigned to the C–N bond vibration. This may be attributed to the cryptand compound and PEI, for which the band is slightly more intense.

Table II lists the peak values and the corresponding chemical radicals obtained from the spectra of the different membranes.

The results show that all the maximum values given by the spectrum of the membrane of reference, that is, without a carrier, are present on the membranes on which the carrier molecules are fixed because CTA presents the same radicals as the cryptands and crown ethers.

TABLE II
Peak Values and Corresponding Radicals
in Different Membranes

Membrane	Peak value (cm ⁻¹)	Corresponding radical
CTA	3500	O—H
	1735	C=O
CTA-NPOE	1216–1029	C—O—C
	3480	C—H aromatic (NPOE)
	1525	NO ₂ (NPOE)
	1465	—CH ₃ of the octyl (NPOE)
	2856	—CH ₂ — (NPOE)
	1735	C=O (CTA)
	1127	C—O—C (NPOE)
	1043	C—O—C (CTA)
	1232	R—O—CH ₂ (NPOE, CTA)
	1351	C—N (NPOE)
	CTA-NPOE-222	Same bonds and 1352
CTA-NPOE-PEI-222	Same bonds and 1352	C—N (222, PEI)

Characterization by X-ray diffraction

Figure 3(a–c) shows X-ray diffraction curves for the CTA membrane, CTA-carrier membrane, and CTA-PEI-carrier membrane, respectively. On the basis of these figures, we can make the following observations.

The CTA membrane presents a single maximum at approximately 20°. This maximum can be found for all the polymers and corresponds to the van der Waals halo.^{24,25} Thus, this material presents basically amorphous characteristics.

The systems consisting of mixtures of CTA and NPOE, CTA, NPOE, and 222, and CTA, NPOE, 222, and PEI do not yield any diffraction because of the absence of crystallization within the membranes. On the other hand, this result should be attributable to the amorphous state of the structure, which permits us to eliminate the mechanism of ion transfer by an electron jump.

Two of the most likely mechanisms are carrier diffusion (amorphous structure) and fixed-site jumping (crystalline structure).²⁶ With the latter mechanism, the transporter molecules act as stepping stones, and the solute moves through the membrane by jumping from one fixed site to another. The theory of fixed-site jumping was described by Cussler et al.²⁶ and Noble,²⁷ however, very few systems have been characterized experimentally.^{26–30}

Characterization by DSC

The DSC experiments were performed with TA Instrument equipment. The scanning speed was 10°C min⁻¹.

Figure 4(a,b) presents DSC thermograms and thermogravimetric analysis (TGA) curves of the CTA membrane, respectively. The DSC curve of CTA [Fig. 4(a)] shows an exothermic reaction beginning at 180°C for CTA and ending at 200°C. This exotherm is followed by an endotherm at a higher temperature (220°C). The exothermic peak may be attributed to the combustion of CTA, whereas the endothermic peak may be attributed to the carbonization of the formed ash.³¹ On the basis of Figure 4(b), we can make the following observations.

The CTA membrane (CTA) degrades in two steps. The first step at 292°C represents the main thermal degradation of the CTA chains. The second step, starting at 476°C, represents the carbonization of the products into ash.

The CTA-NPOE membrane degrades in three steps. The first step at 138°C represents the volatilization of NPOE. The second and third steps represent degradation and carbonization of CTA at 293 and 480°C, respectively.

The same interpretation can be made for the ATG mixture (CTA-NPOE-222 and CTA-NPOE-222-PEI) thermograms in Figure 4(c,d).

SEM

A Hitachi S4500 5-kV scanning electron microscope was used to elucidate the membrane morphology. The membrane samples were prepared by freezing under liquid nitrogen (70 K) and rapid fracturing, which resulted in clean breaks for viewing the cross sections. The samples were mounted with conductive glue to metal stubs with the fractured edge up, and then they were sputter-coated with gold. These samples were viewed in the scanning electron microscope at a magnification of approximately 1000×.

The CTA membrane is characterized by well-defined pores; these pores are completely filled with NPOE and the carrier. The surfaces of the membranes with 222 or 222-PEI are smooth (Fig. 5).

The morphologies of the CTA and CTA-NPOE membranes (surface view) show that these membranes, consisting of polymeric CTA, have porous structures, and the distribution of the pores is nearly uniform (porosity = 50%). However, the CTA-NPOE membrane has a dense structure in which the pores have been filled by NPOE molecules yielding to the thick and less porous membrane.

Water-content measurement and mouillability

The water content (*H*), defined as the volume fraction of water in a wet membrane, was estimated with the following equation:

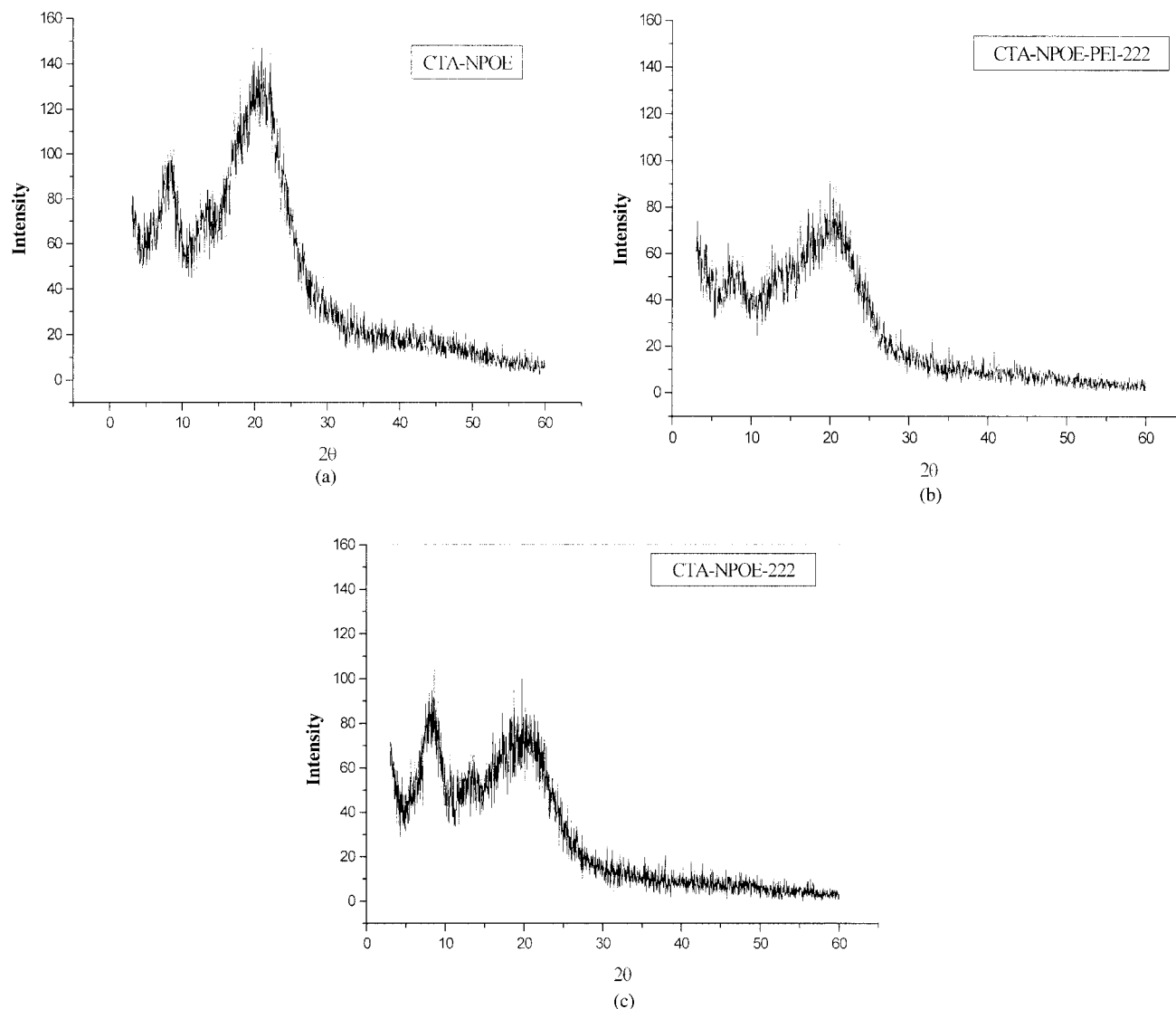


Figure 3 X-ray curves for (a) the CTA–NPOE membrane, (b) the CTA–NPOE–222–PEI membrane, and (c) the CTA–NPOE–222 membrane.

$$H = \frac{\text{Water volume}}{\text{Water volume} + \text{Polymer volume}} = \frac{(W_s - W_d)}{[(W_s - W_d) + W_d/1.2]} \quad (2)$$

where W_s and W_d are the weights of a membrane at the equilibrium swollen and dry states, respectively.

The thickness of the membrane was measured with SEM, and the contact angle was estimated with a mouillability apparatus. The results are listed in Table III.

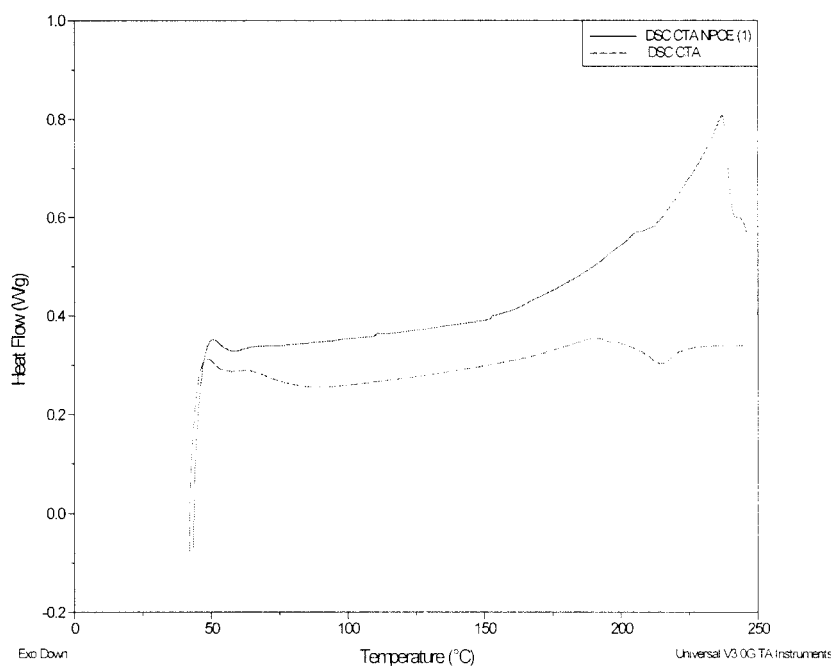
Using the same composition of polyether, we observed an increase in the density of the membrane when the cryptand and PEI were added. This rise in the density was characterized by an increase in the thickness and a reduction in the contact angle. The increase in the contact angle should be connected to the reduction of the

hydrophobicity of the resulting membrane. Thus, the addition of PEI increased the hydrophilicity of the membrane because the value remained almost constant with the addition of the cryptand.

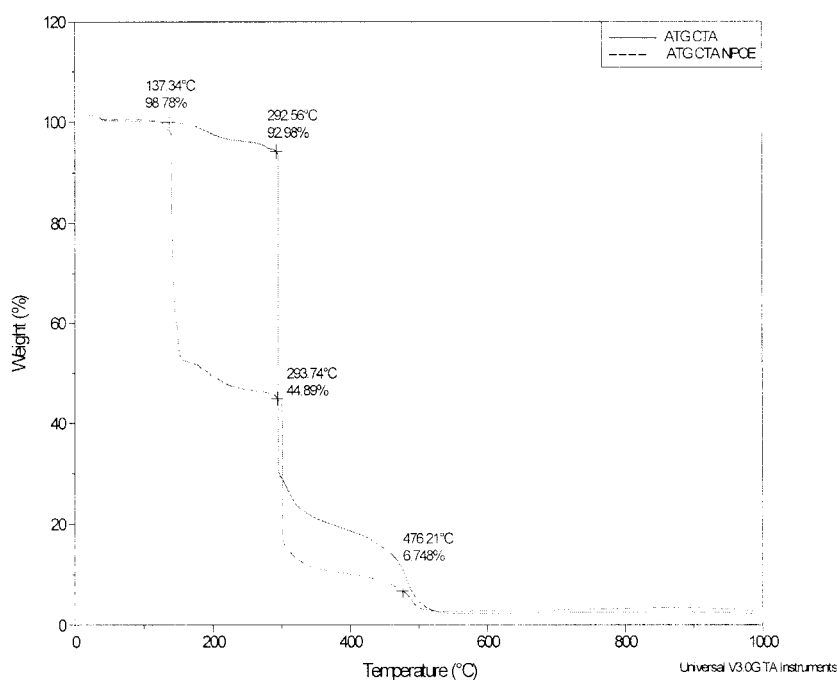
Application to the transport of silver(I) and copper(II)

A cell for copper-ion transport is described in the Experimental section. The feed compartment contained $10^{-2}M$ copper nitrate and silver nitrate, and the other compartment, called the strip, contained distilled water. The two compartments had the same volume: 40 mL.

The experiment duration was fixed to 7 days, and 0.5-mL solutions were taken at regular intervals (24 h) from the strip compartment for the determination of the copper-ion flux through the membrane.



(a)



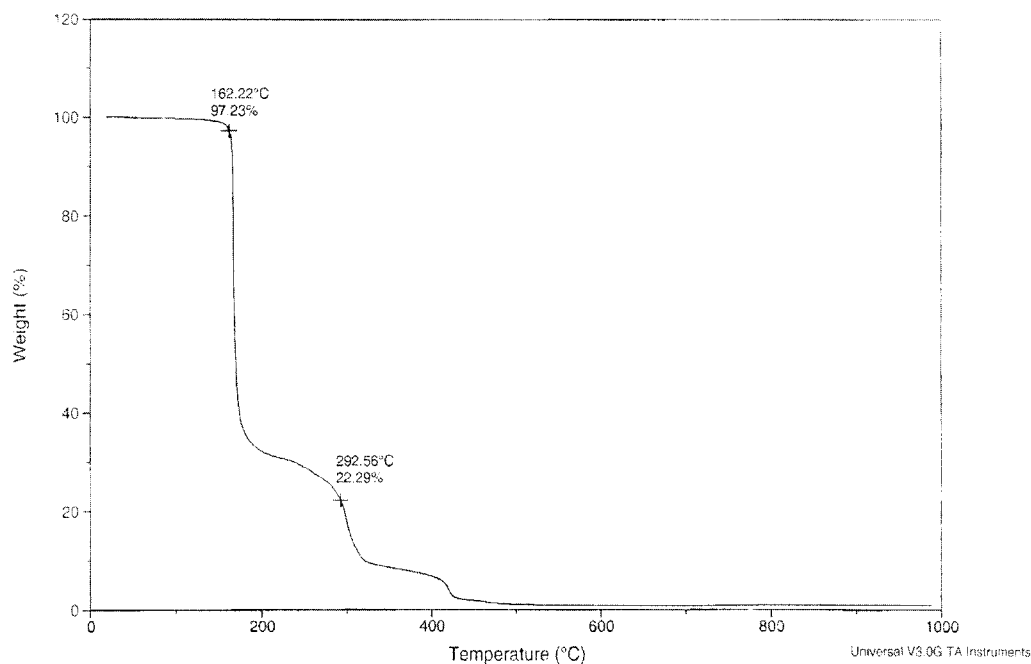
(b)

Figure 4 (a) DSC thermograms of the CTA and CTA-NPOE membranes, (b) ATG curves of the CTA and CTA-NPOE membranes, (c) ATG curve of the CTA-NPOE-222 membrane, and (d) ATG curve of the CTA-NPOE-222-PEI membrane.

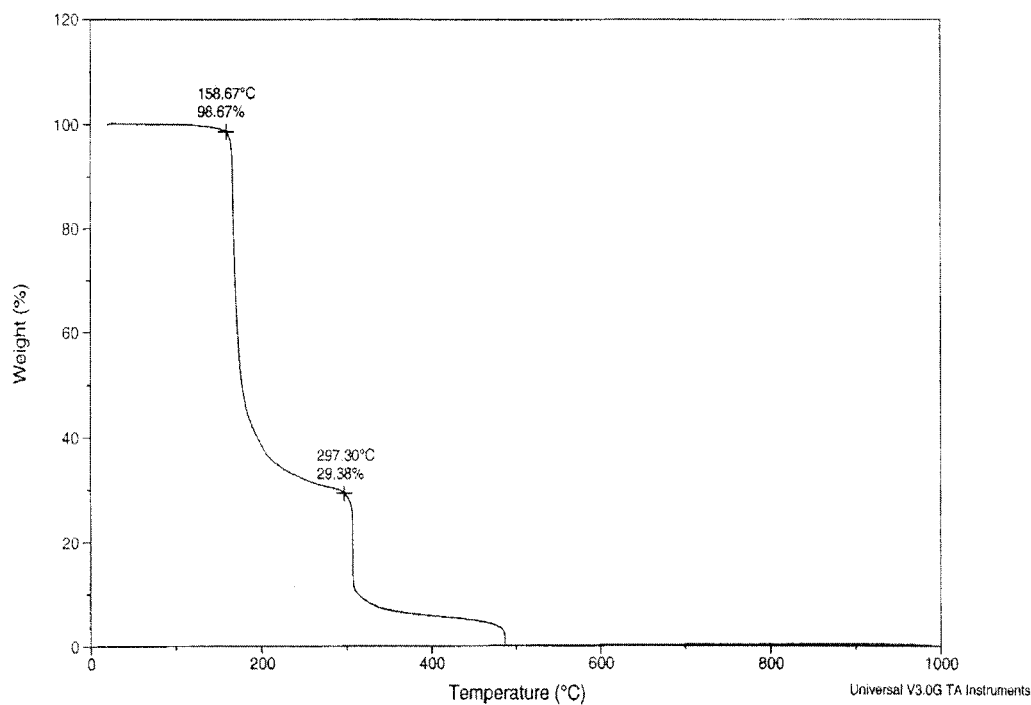
Figure 6(a,b) presents the evolution of silver- and copper-ion concentrations in the strip compartment as a function of time for supported liquid membranes and fixed-site membranes, respectively, and Figure 6(c) presents the concentration of copper ions in the

strip compartment for both membranes prepared in the absence and presence of PEI.

The increase in the concentration of silver and copper ions in the strip compartment with the time for the CTA-222 membrane indicates that transport was fa-



(c)



(d)

Figure 4 (Continued from previous page)

cilitated by the introduction of the carrier [Fig. 6(b)]. However, a maximum was obtained after 5 days. Furthermore, in all cases, the concentrations obtained with the fixed sites membrane (FSM) membrane [Fig. 6(b)] were higher than those obtained with the supported liquid membrane (SLM) mem-

brane [Fig. 6(a)]. The decreasing tendency and the formation of a plateau after this length might be linked to the saturation of the membrane with the metallic ion, which can be explained by the equality of the chemical potential values in the feed and strip compartments.

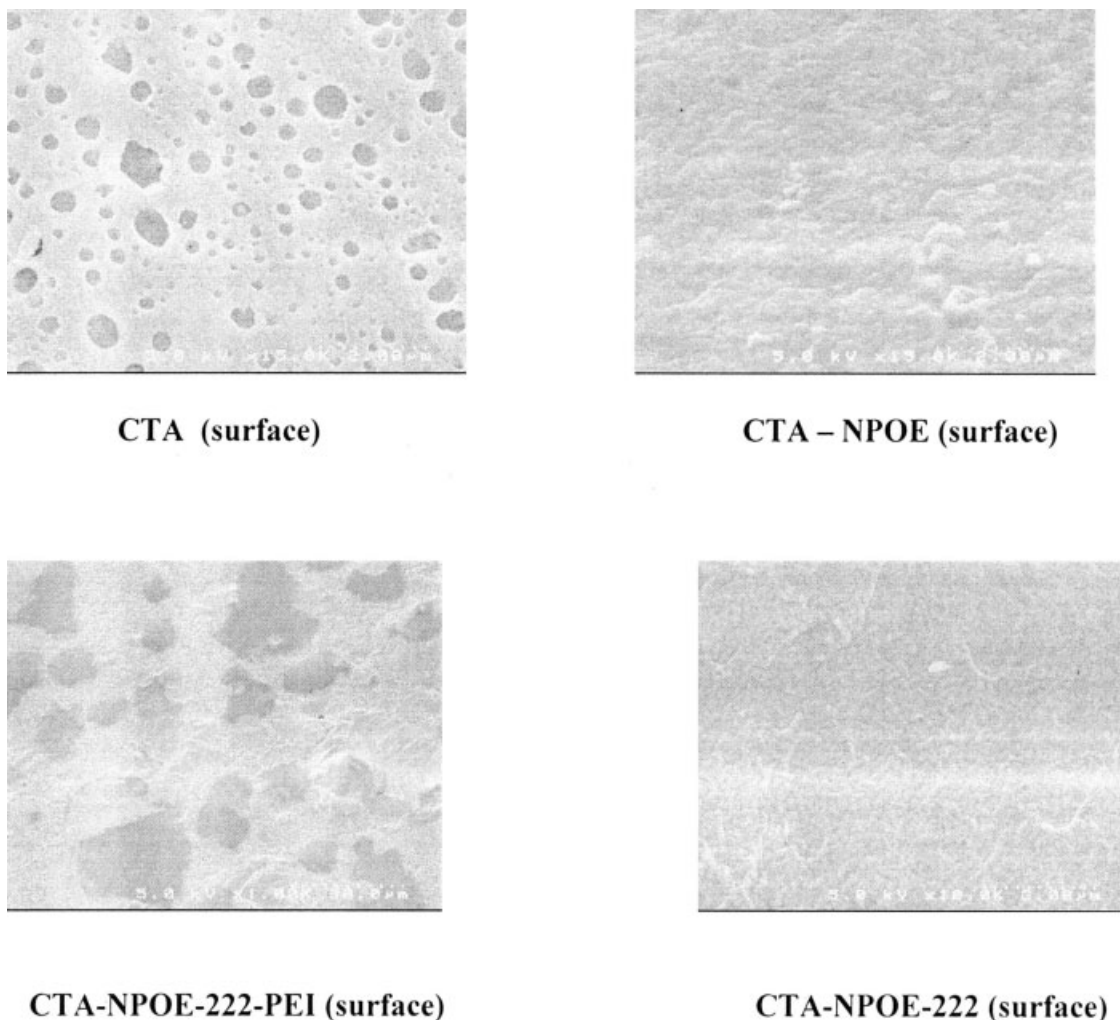


Figure 5 SEM images of various membranes.

The CTA-222-PEI membrane presented a very low variation of the concentration of copper transported. This was attributable to the presence of PEI in this membrane in comparison with the CTA-222 membrane [Fig. 6(c)].

From the concept of surface complex formation, it can be concluded that a membrane containing PEI in its structure presents a great affinity to the fixation of copper ions through the formation of chelating bonds. This complex formation contributes to the reduction of

transport through the membrane but provides a great advantage for the separation of ions from mixture solutions. Ions that have less complexing properties toward PEI are well separated from copper ions.

CONCLUSIONS

In this work, a new membrane prepared from a combination of polyelectrolytes and the addition of a cryptand as a carrier showed attractive properties

TABLE III
Thickness, Contact Angle, and Water Content Characteristics of the Prepared Membranes

Membrane	Composition (weight of polyether)	Weight/area (mg/cm ²)	Thickness (μ m)	Contact angle ($^{\circ}$)	Water content (%)
CTA-NPOE	0	6.121	15	80.5	0.96
CTA-NPOE.222	0.075	9.366	38	81	0.05
CTA-NPOE.222-PEI	0.075	9.854	42	74.2	21.03

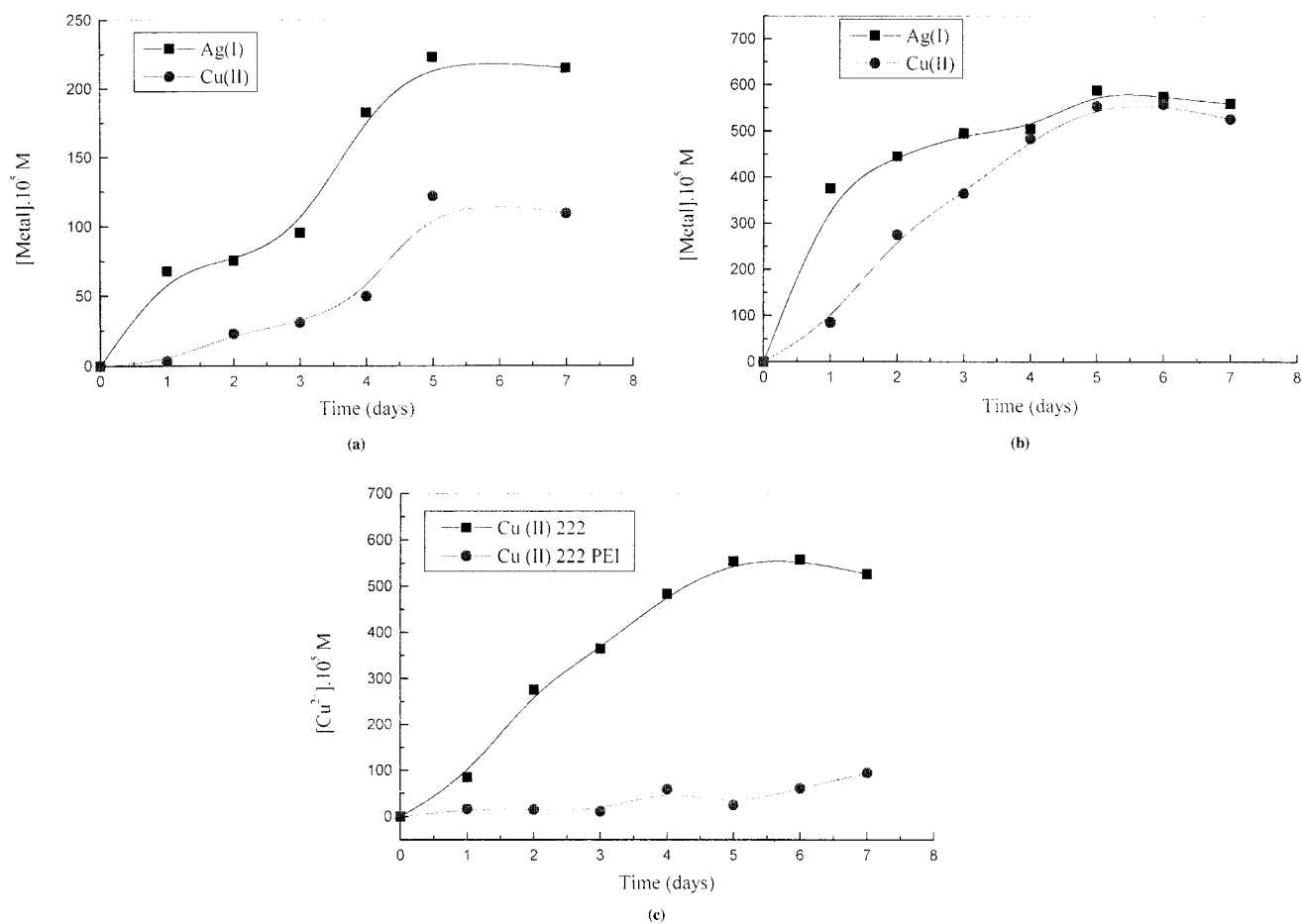


Figure 6 (a) Variation of the silver(I)- and copper(II)-ion concentrations in the strip compartment versus time ($[\text{metal}]_0 = 0.01\text{M}$; SLM; $[\text{222}] = 0.01\text{M}$; membrane support = Celgard 2500), (b) variation of the silver(I)- and copper(II)-ion concentrations in the strip compartment versus time ($[\text{metal}]_0 = 0.01\text{M}$; FSM = CTA-NPOE-222), and (c) variation of the copper-ion concentration in the strip compartment versus time ($[\text{metal}]_0 = 0.01\text{M}$; FSM = CTA-NPOE-222 and CTA-NPOE-222-PEI).

for the separation of ions with complexing properties.

An analysis method adopted for the characterization of the membrane verified the simultaneous existence of PEI and the cryptand in the membrane.

DSC measurements established the stability of the membrane as a function of the temperature. Finally, mouillability and water-content measurements allowed us to estimate a good balance of hydrophilicity and hydrophobicity properties of the resulting membrane.

We concluded that the transport efficiency was increased more with FSM than with SLM. The release of the carrier from the membrane phase to the aqueous phases with the SLM membrane was avoided with the FSM because the carrier remained fixed on the membrane matrix. Our results indicate that facilitated transport through plasticized membranes is an effective way of solving the enduring problem of membrane stability.

Further efforts will be directed to the determination of the nature of the interactions between polyelectrolytes and cryptands with other materials and analysis.

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