Polymer Bulletin 25, 95–100 (1991)

Polymer Bulletin

Membranes from polyelectrolyte complexes

H.-H. Schwarz*, K. Richau, and D. Paul

Institute of Polymer Chemistry "Erich Correns", Academy of Sciences, Kantstrasse 55,
O-1530 Teltow-Seehof, Federal Republic of Germany

Summary

Membranes were formed by the simultaneous interfacial reaction of a synthetic polycation and a cellulose based polyanion. The structure, the electrochemical properties and the permeability in dialysis and pervaporation processes of these membranes were determined.

Introduction

The formation of polyelectrolyte complexes (symplexes) is essentially a result of the electrostatic nature of the interaction between oppositely charged polyions. This interaction in the macroscopic homogeneous system, the phase transition by polysalt precipitation as well as the chemical and physical structure of symplexes have been intensively investigated from the thermodynamical and kinetical point of view (1). One application of symplexes as polymer material is the preparation of membranes. One way to obtain such membranes is the symplex formation, subsequent dissolution in a solvent and membrane formation by phase inversion (2). Symplex membranes can also be obtained following the interfacial reaction between aqueous solutions of an anionic and a cationic polyelectrolyte supported on a glass plate (3).

The aim of our study was to prepare a membrane by the simultaneous interfacial reaction of a synthetic polycation and a cellulose based polyanion and transition from the liquid (aqueous) to the solid phase. Membranes, made from Poly-(dimethyldiallylammonium) chloride and cellulose sulfate were formed by coating polyions on a support. The structure, the electrochemical properties and the permeability in dialysis and pervaporation processes of these membranes were determined.

Experimental

Materials

The polyelectrolytes selected for symplex formation were the polyanion sodium cellulose sulfate (Na-CS) made by homogeneous reaction of cellulose dissolved in N_2O_4/dimethylform-

---

*To whom offprint requests should be sent amide with $NOSO_4H$ (4), and the polycation poly(dimethyldiallylammonium) chloride (P-DMDAAC), a linear macromolecule made by radical polymerization of dimethyl-diallyl-ammonium chloride (5).

Membrane preparation

The symplex membranes were formed by the interfacial reaction between the layers of the anionic and the cationic polyelectrolyte supported on a glass plate. Initially a 0.2 mm thick film of solution of Na-CS (2 wt.-% in water) was cast on the glass plate. On this film a 0.4 mm thick film of the polycation (20 wt.-% P-DMDAAC in water) was immediatly stratified. After a reaction time of 30 minutes the glass plate with the symplex membrane was dipped into a water bath. the symplex membrane was loosened from the support, intensively soaked and dried.

Membrane characterization

The morphology of the symplex membrane was determined by electron microscopy and the topochemistry by XPS method (chemical analysis of surfaces).

Membrane potential measurements were carried out in a two-compartment thermostated cell (25 °C) with satured calomel electrodes connected to the solution by salt bridges filled with a saturated KCl solution (6) (10^{-1}n and 10^{-3}n KCl solutions, adjusted to pH = 6.0). The permeability for KCl and glucose was determined by dialysis experiments (7) using the batch principle.

The dialysis cell contains two compartments separated by the membrane and equipped in both compartments with a stirrer. The concentration of the aqueous solutions was determined by refractometry. The diffusive permeability was measured at 25 ± 0.5 °C. The dialysis results were computed according to a relation by Farrell (8).

The pervaporation experiments

- downstream pressure	- 1 Torr
- feed temperature	50 °C
- feed concentration	80 wt.-% ethanol

were carried out in a stainless-steel cell with recirculation of the feed solution. The membrane area was 19.6 cm^2 . To generate the driving force a vacuum was used at the downstream side. Permeate was condensed and frozen by liquid nitrogen.

Results and Discussion

The cross-section (thickness 5 µm) of a dried symplex membrane made from Na-CS and Poly-DMDAAC is shown in Figure 1. The porous internal structure is limited by two compact surfaces. XPS-measurements have demonstrated, that the symplex membrane has an identically chemical composition at both membrane sides.

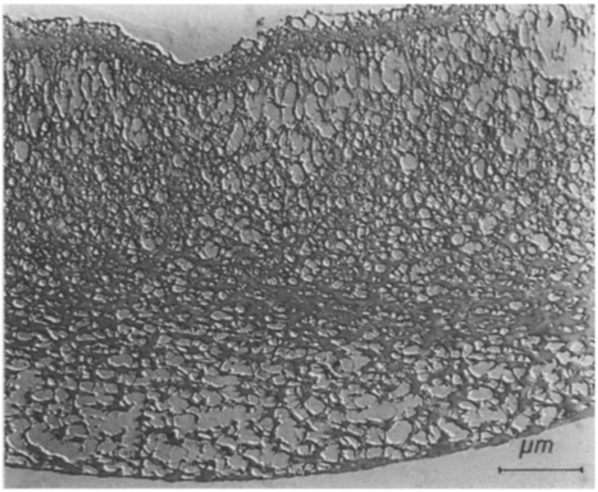

Fig.: 1

TEM micrograph of a symplex membrane from Na-CS and PDMDAAC

The distribution of the elements is shown in Table 1.

Table 1. XPS-analysis of a symplex membrane from cellulose sulfate and poly(dimethyldiallylammonium) chloride

membrane	atom-%			
surface	C	O	S	N
cellulose sulfate side	70.25	24,42	0,92	4.41
during preparation	66.31	26.26	0.91	6.52
P-DMDAAC side	70.13	24.32	0.96	4.56
during preparation	68.62	25.45	0.74	5.20

The XPS-analysis shows no significant difference between the surfaces. The polyelectrolyte components have interpenetrated completely.

In general, the membrane potential is positive (E_c = + 12.8 mV), i.e., the symplex membrane behaves as a weak anion exchanger. An orientation dependent membrane potential was not observed. The symplex from Na-CS and Poly-DMDAAC has a high chemical stability. In many solvents, for instance, ethanol, acetone, tetrahydrofurane, dimethylformamide, pyridine, chloroform, the membranes are insoluble. However in concentrated solutions of electrolytes with high ionic strength for example in HCl, 20 wt-% KSCN, 20 wt-% NaBr, the symplex was found to be soluble.

The positive charge of the symplex membrane influenced significantly the permeability of electrolytes. In Figure 2 the correlation of diffusion permeability for KCl with the electrolyte concentration is shown. The permeability increased with increasing concentration. The permeability of a typical dialysis membrane (cuprophane PM 200 from Enka) is, in contrast, independent of the KCl concentration.

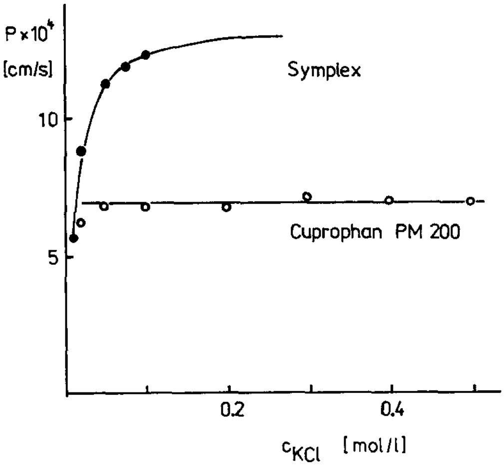

Fig.: 2

Diffusion permeability of KCl vs. electrolyte concentration

The different permeability of an electrolyte and of a neutral permeant through the symplex membrane is shown in Figure 3. In contrast to KCl the permeability of glucose is constant throughout the entire range.

Results of Philipp (1) led to the conclusion that a nearly reversible swelling of symplexes in water takes place after drying at a temperature below 100 °C and resoaking in water. Our symplex membranes show analogous results. The permeability for KCl and glucose before and after drying at 20 °C lie within the same range (see Table 2).

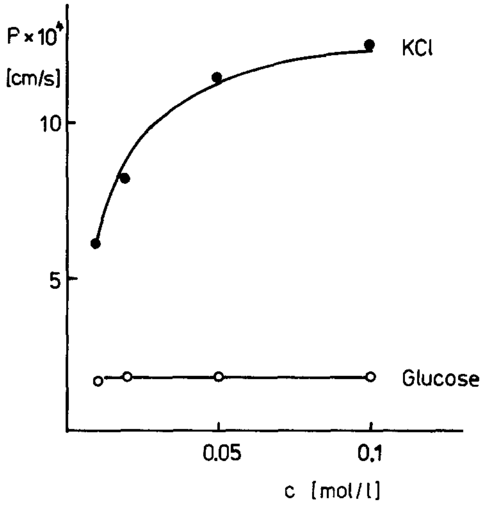

Fig.: 3
Diffusion permeability of KCl and glucose vs. feed concentration

Table 2. Diffusion permeability of symplex membranes before and after drying

permeand	$P \cdot 10^4$ / cm/s / never-dried	$P \cdot 10^4$ / cm/s / after drying and resoaking
KCl	4.8 ± 0.5	5.1 ± 0.6
glucose	1.9	1.8

Karakane et al. (8) have determined the separation of water-ethanol by pervaporation through polyelectrolyte complex composite membranes from polyacrylic acid and polycations with quarternary ammonium groups in the backbone chain. Our symplex membrane from Na-cellulose sulfate and Poly-DMDAAC was also tested for dehydration of ethanol. A permeation rate of 3.4 kg/m^2 h and a separation factor of 145 was found. A commercial pervaporation membrane from GFT, Bad Homburg (poly-(vinylalcohole)$_2$on poly-(acrylonitrile)) shows a permeation rate of 0.09 kg/m^2 h and a separation factor of 145 under the same conditions. The symplex membranes demonstrated a higher permeation rate and prooved most suitable for dehydration of organic solvents.

Acknowledgements: The authors would like to thank M. Hahn, W. Wagenknecht and B. Tiersch (Institute of Polymerchemistry) for cooperation and J. Lukas (Institute of Macromolecular Chemistry, Prague) for XPS-spectra and discussion.

References

1. B. Philipp, H. Dautzenberg, K.-J. Linow, J. Kötz and W. Dawydoff
Progr. Polym. Sci. 14, 91 (1989)
2. A. S. Michaels, Ind. Engng. Chem. 57, 32 (1965)
3. V. Gröbe, L. Hong, B. Philipp and H.-H. Schwarz
Acta Polymerica 32, 488 (1981)
4. B. Philipp and W. Wagenknecht
Cellulose Chem. Technol. 17, 443 (1983)
5. W. Jaeger, M. Hahn and Ch. Wandrey
Mitt.bl. Chem. Ges. DDR, 33, 199 (1986); EP-PS 0264710
6. V. Kudela, K. Richau, O. Ryba and H.-H. Schwarz
Coll. Czechoslovak Chem. Commun. 51, 1419 (1986)
7. H.-H. Schwarz, J. Lukas and J. Vacik
Coll. Czechoslovak Chem. Commun. 53, 1247 (1988)
8. P. C. Farrell and A. L. Babb
J. Biomed. Mater. Res. 7, 275 (1973)

Accepted August 24, 1990 C