Hopefully some of the huge amount of organic and inorganic chemistry done during the frankly inflationary decade of the sixties will provide new clues for the synthetic polymer chemists.

Fields such as the hydrodynamics of polymer solutions, light scattering from polymer solutions and many characterization methods for polymer molecules have also achieved a quasiclassical status; some such as n.m.r. methods for sequence distribution are approaching this condition within a relatively few years. Great advances have been made by the 'lattice method in interpreting the thermodynamic properties of polymer solutions. However, full understanding eludes us, just as does a complete theory of the liquid state.

The viscoelastic behavior of amorphous polymers at low strains unquestionably obeys the laws of linear viscoelasticity, another classical field. The elucidation of this behavior was highly simplified by the time-temperature superposition principle. The molecular theory of Rouse and Bueche probably explains much, but not all, of the relaxation phenomena of polymers in dilute solution. This beautiful and elegant theory is woefully misused for solid polymers, even when ingenious modifications for entanglement effects are introduced. Here the unsolved problem is: what are the true experimental facts; can anyone look at the data outside the framework of theory.

The behavior of polymers at high strains and the strength properties of polymers are basically unsolved problems.

High strain properties, strength properties, polymer crystallization, electronically and photoactive polymers, composites are fields that will progress proportionally to their successful marriage with solid state physics, ceramics and metallurgy into a new science of materials.

Historically polymer science has advanced its status by marriage with other fields: X-ray crystallography, free radical chemistry, chain reaction kinetics, just to mention a few. We can look forward to continuing connection with medicine (synthetic organs) and to multiple new connections with biochemistry (synthetic polymers with enzyme-like activity?) without forgetting previous triumphs such as the Pauling helix or the Crick-Watson model.

In summary, if polymer chemistry is to maintain its vitality, it must marry new fields and disciplines. This, like all marriages, will create unsolved problems. The partial solution of these problems will advance our science and provide material for the next Symposium on this subject.
PERMEATION OF WATER AND IONS IN IONOMERS

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INTRODUCTION

As part of a program sponsored by the Office of Saline Water on materials problems in desalination processes, a study was begun of the protection of concrete against corrosion by hot saline water (1). Concrete protected by polymeric coatings or membranes may be considered as a construction material in certain components in flash distillation desalination plants. In order to select suitable protective materials, it was assumed that low permeabilities to water and to salt ions are essential. Since little information was available it was decided to investigate the permeation behavior of water and salts in different types of polymers.

One question of interest is the role of charged species in permeation. Glass and Smith (2) have concluded that even common non-ionic polymeric membranes may exhibit selectivity to permeating ions due to residual positive or negative charges. Kumins and London (3) also included that typical polymers may similarly behave like charged membranes. Using an electron microprobe technique, the authors have confirmed such effects with polychloroprene (4), which tended to accumulate magnesium, but not sulfate, ions.

In order to study the role of charges in more detail, sodium and zinc ionomers were used as membranes for the permeation of liquid and ions typical of salt water. This paper reports preliminary results of the investigation.

EXPERIMENTAL

Two samples of ionomers were provided through the courtesy of the I. duPont de Nemours & Co., Inc. One, Surlyn 1707, contained sodium carboxylate groups; the other, Surlyn 1652, contained zinc carboxylate groups. Low-density polyethylene film was used as a control.

Permeability tests were made using a system designed to operate at elevated temperatures under pressure (see Fig. 1), and constructed of Monel alloy to avoid corrosion. Membranes were conditioned at 50-70°C in the presence of water for 24 hours and exposed to the temperature desired (between 25° and 80°C). The water vapor passed was picked up by a sweep of dry nitrogen and analyzed by a Moisture Monitor (Consolidated Electrodymanics).

Reproducibility of permeation values for a given specimen was usually to within ±15%; larger deviations can occur from specimen to specimen, however, especially with crystalline polymers. Values of P were reported as gm water passed/min/mil/cm². Permeability coefficients, P, were estimated on the assumption that the permeation process may be characterized by an Arrhenius-type expression (5):

\[ P \propto P_0 e^{-E_p/RT} \]

where EP is the apparent energy of activation for permeation. In this and other related studies (1), such a relationship was found to be valid in the temperature range used.

For the salt uptake experiments, specimens were exposed to 10% solutions of NaCl and MgSO₄ at room temperature for periods up to 3 weeks. After exposure, samples were freeze dried, sliced in a direction parallel to the diffusion axis, and examined by the electron microprobe in various locations across the specimen. Samples were examined before and after exposure; concentrations were determined at 4 points and averaged.
The precision for the analysis of a given specimen was generally within ±5%; variations from specimen to specimen were within ±15%.

As before, the electron microprobe was used to yield two types of information: reverse sample current pictures, which indicate variations in atomic number; and X-ray analyses for the various elements of interest: Na, Mg, Cl, S, Zn, and Al. The percentages of the elements were determined by comparison of the number of counts per unit time for the specimen to the number observed for a standard after correcting for background. Standards used were: metallic Zn, Al, and Mg; and NaCl and FeS2.

RESULTS AND DISCUSSION

Permeation of Water

Figs. 2 and 3 show typical permeability data for low-density polyethylene, and for sodium and zinc ionomers. Apparent energies of activation, \(E_p\), and permeability coefficients are given in Table I.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Medium</th>
<th>Apparent Activation Energy ((E_p))</th>
<th>Permeability Coefficient ((P_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Ionomer</td>
<td>Deionized water</td>
<td>18.6 (\text{Kcal/mole})</td>
<td>1.6 (\times 10^{-4})</td>
</tr>
<tr>
<td>Zn-Ionomer</td>
<td>&quot;</td>
<td>16.3 (\text{Kcal/mole})</td>
<td>5.2 (\times 10^{-5})</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>&quot;</td>
<td>14.6 (\text{Kcal/mole})</td>
<td>1.2 (\times 10^{-5})</td>
</tr>
<tr>
<td>Na-Ionomer</td>
<td>Artificial Seawater</td>
<td>17.8 (\text{Kcal/mole})</td>
<td>5.6 (\times 10^{-5})</td>
</tr>
<tr>
<td>Zn-Ionomer</td>
<td>Artificial Seawater</td>
<td>18.2 (\text{Kcal/mole})</td>
<td>4.9 (\times 10^{-5})</td>
</tr>
</tbody>
</table>

It may be seen that the ionomers are more permeable than polyethylene in deionized water. Replicate experiments suggest that the curves shown for the sodium and zinc ionomers may not differ significantly - there being a greater variability from specimen to specimen than for data obtained for a given experiment. However, the difference between the polar ionomers and the non-polar polyethylene does fall outside the range of variability. Such an increase in permeability might well be expected for a polymer containing carboxylate and -etal ions. Permeation characteristics appear to be similar in salt water, though non-ionized polymers generally are less permeable in salt water.

Values of the apparent energy of activation for the ionomers all fall in the range 16 to 19 \(\text{Kcal/mole}\), slightly higher than for polyethylene and other non-ionized polymers (1).

Thus ionomers are somewhat more permeable than polyethylene.

Microprobe Analysis

Analysis of unexposed specimens for the elements Na, Zn, Al, Mg, S, and Cl gave the following results:

Sodium ionomer: 1.5% Na
Zinc ionomer: 0.7% Zn, 0.2% Al

After exposure, the ionomers were analyzed again. Results for sodium ionomer after a 3-week exposure are given in Table II.
TABLE II.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration, % Before exposure</th>
<th>After exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.46 (±0.07)</td>
<td>1.53 (±0.07)</td>
</tr>
<tr>
<td>Mg</td>
<td>≤ 0.04</td>
<td>≤ 0.04</td>
</tr>
<tr>
<td>Cl</td>
<td>≤ 0.03</td>
<td>≤ 0.03</td>
</tr>
<tr>
<td>S</td>
<td>≤ 0.11</td>
<td>≤ 0.11</td>
</tr>
</tbody>
</table>

Clearly, no significant amount of Na is taken up by the ionomer. Analyses for the other elements all fell within the limit of detectability or background level. Similar results were obtained for the nc ionomer, with all concentrations measured falling within 10%, and usually 5% of the background levels, which themselves may vary +5%.

Thus, the ionomers do not appear to take up ions most commonly und in sea water.

**Morphology**

Figs. (4-a) and (4-b) present a typical reverse sample current structure and an X-ray scan for Na, respectively, for the sodium ionomer before exposure. In Fig. (4-a) differences in the current density transmitted through various domains in the polymer are seen as dark and light areas. Since the picture represents the reverse sample current, the dark rather regularly circular areas about 10 μm in diameter present regions of lower atomic number. Fig. (4-b), the X-ray scan structure, indicates that few sodium ions exist in the region corresponding the dark areas in the sample current picture. Thus, phase separation must have occurred with respect to ion-rich and ion-poor molecules, or segments of molecules. Such experimental evidence for segregation has not apparently been reported previously, although segregation on a smaller scale has been suggested by Longworth and Whitt (6) for ionomers. Phillips, Emerson, and McKnight (7), while studying the dielectric properties of polyethylene containing phosphonic acid groups, also postulated the existence of segregation, which is presumed to yield a dispersion of hydrogen-bonded acid-rich molecules in a matrix of acid-poor polyethylene.

In the case of the zinc ionomer, the reverse sample current picture, Fig. 5 revealed dark and light regions. However, the origin of this segregation has not yet been resolved.

The origin of the two distinct regions in the sodium ionomer would superimpose an additional morphological feature on the models proposed by Bonotto and Bonner (8) is not yet clear. It is interesting that the sample current picture for low density polyethylene (Fig. 6) also reveals globular components having about the same diameter as the dark areas in the pictures for ionomers. Further investigation using the microprobe technique should complement electron microscopy in helping elucidate the detailed nature of ionomers.
REFERENCES


ACKNOWLEDGEMENT

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Fig. 1 Permeability Equipment

Fig. 2 Permeability of Ionomers to Sea Water

Fig. 3 Permeability of Ionomers to Deionized Water
Fig. (4-a)
Reverse sample current picture for sodium ionomer (1000 x)

Fig. (4-b)
Sodium X-ray scan picture for sodium ionomer (1000 x)

Fig. 5
Reverse sample current picture for zinc ionomer (1000 x)

Fig. 6
Reverse sample current picture for polyethylene