

## Investigation by Electron Microscopy and X-Ray Diffraction of the Microstructure of Permselective Membranes Made from Polyethylene

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### Synopsis

Ion-permselective membranes containing polyethylene in their base material have been examined by direct transmission electron micrography and x-ray diffraction. All of the electron micrographs showed white lines of about 100 Å. thickness between somewhat thinner black lines composed of granules. These lines often occur as black-white-black triplets. We tentatively explain these structural elements by assuming that they are cross sections of the crystallite platelets, characteristic for polyethylene, reacted on both of their faces during sulfochlorination. It is known, that these platelets are about 100 Å. thick. X-ray diffraction experiments also showed the characteristic lines of polyethylene crystallites, their intensity decreasing after sulfonation. The velocity of heterogeneous sulfochlorination of polyethylene sheets decreases abruptly when the film contains 6% S and 7% Cl (after hydrolysis). This means six substituted sites on a chain element across the platelet for a 100% crystalline film and accordingly less for a partially amorphous material. It is known that five CH<sub>2</sub> groups of each chain element are exposed at the surface of the platelets, in good agreement with our findings.

In the course of a series of experiments on electron micrography of permselective membranes,<sup>1</sup> we found that membranes made of polyethylene by sulfochlorination and subsequent chemical reactions show a very specific and interesting structure. These membranes were developed in our laboratory.<sup>2,3</sup> In view of the fact that they were the only ones we were able to examine quite thoroughly, we are going to report on our results separately in this paper.

Polyethylene can be sulfochlorinated topochemically in a gas mixture of chlorine and sulfur dioxide, or dissolved in a chlorinated solvent into which the same gases are introduced. The reaction is photochemical. Sheets of sulfochlorinated polyethylene can be hydrolyzed by alkali to cationic, sulfonic acid membranes. They can also be reacted with polyvalent amines so that they form a sulfonamide bond and carry basic groups as anionic membranes. Amino groups in such membranes may be alkylated in order to obtain quaternary ammonium groups.

### Electron Microscopy

The membranes were embedded in Epon resin and sectioned to 400-500 Å. thickness on a Porter-Blum microtome with 45° glass knives. They

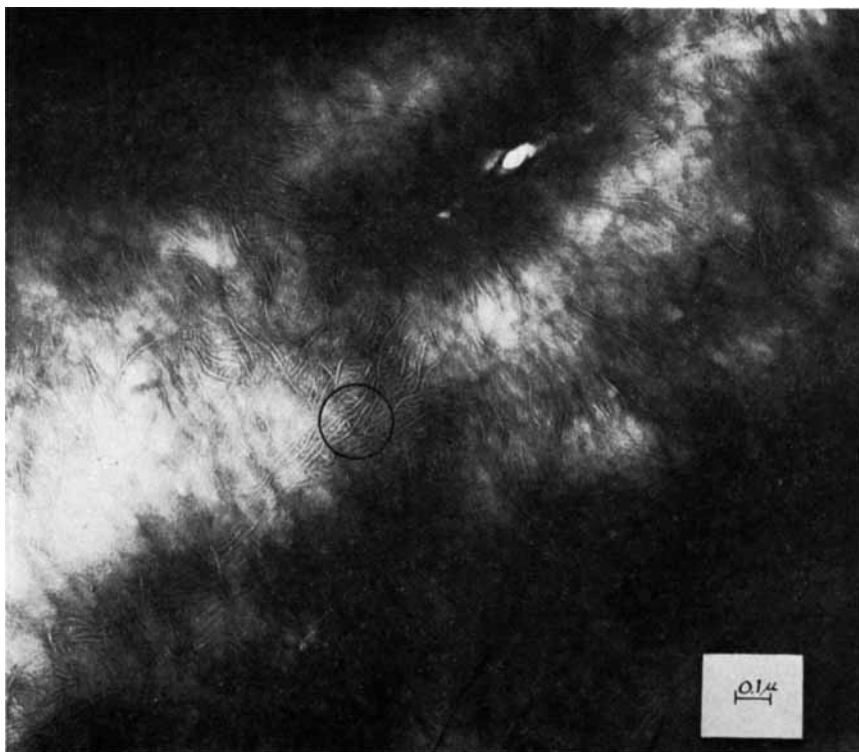


Fig. 1. Polyethylene sulfonic acid, membrane,  $H^+$  form. Encircled: structural elements which could be cross-sections of fibers.

were viewed and photographed on an RCA EMU-3C type electron microscope. The maximum direct enlargement was 43,200 times.

The recurring feature common to all membranes made from polyethylene is a series of black and white lines in the electron micrographs. The white lines were always about 50–100 Å broad. In general the breadth of the black lines was somewhat less, rarely down to one-half of that of the white lines. Sometimes they were even broader than the white lines. They can be easily found on Figure 1 which is a section of a polyethylene sulfonic acid film in the hydrogen form. The only electron-absorbing atoms in this material are the S atoms of the  $SO_3H$  group and Cl atoms which enter the polyethylene in a photochemical reaction parallel to sulfochlorination. The remainder is the hydrocarbon matrix with much weaker electron absorption.

The same structure recurs somewhat more strongly contrasted in the  $Ag^+$  and  $Pb^{++}$  forms of the membranes (Fig. 2). Such a structure has not yet been observed in direct transmission electron micrographs of sectioned polyethylene films. However, striation of 500–1000 Å width was observed by Andrews<sup>4</sup> on  $OsO_4$  stained sections. A similar structure was observed by Anderson<sup>5</sup> on broken surfaces of deep-cooled polyethylene

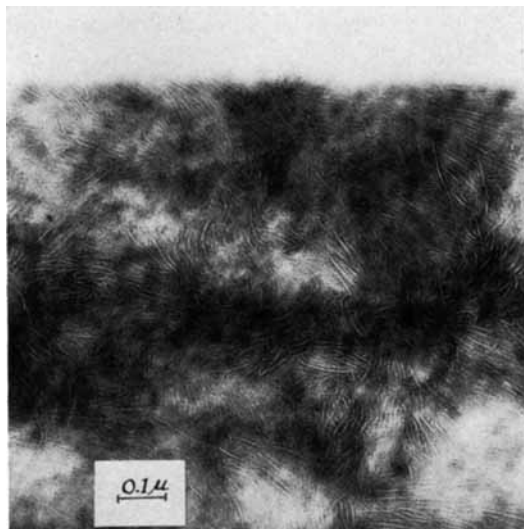


Fig. 2. Polyethylene sulfonic acid membrane,  $Pb^{++}$  form, rinsed.

after shadow casting and by Reding on etched polyethylene on using shadow-cast carbon replicas.<sup>6</sup>

Prof. Dannon at the Weizmann Institute first called our attention to these black and white lines, especially to the fact that they are arranged on the micrographs often in black-white-black triplets. These lines look like fibers. They can be found on all electron micrographs of membranes made from polyethylene. Sometimes they are abundant, sometimes black-white-black-white- etc. bundles are more abundant, but the triplets are always present. Multiple black-white-black-white lines also occur on membranes made by sulfochlorinating polyethylene in solution, casting it to films, and hydrolyzing the latter (Fig. 3). To some extent the lines also occur in membranes produced by the American Machine & Foundry Co. Their membranes are made from a polyethylene-polystyrene matrix.

Throughout all micrographs the black lines are composed of black dots of 20–40 Å diameter. We cannot tell whether this is their real dimension or whether they are smaller, but have not been resolved in the electron microscope. A satisfactory explanation of this dot structure has not been found and will be discussed later.

In looking for an interpretation of the triple line structure which appears to be characteristic, we have to choose between two assumptions. What is observed could be a fiber of organic material coated with heavier active groups. It could also be the cross-section across platelets coated on both sides with such groups. If they were fibers lying in the plane of the section, one ought to expect that they also occur in other orientations, cutting the plane of the section at different angles. These would yield elliptic or circular cross-section of the same diameter as the triple lines, white in the middle and black all around. Such structures have only been seldom

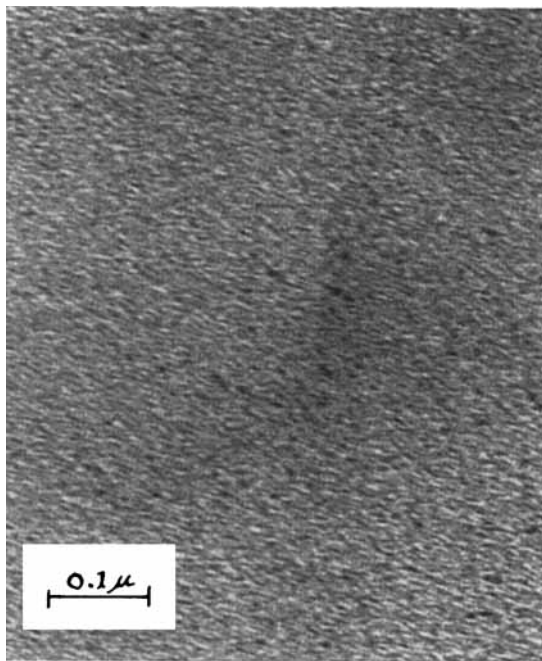


Fig. 3. Cast polyethylene sulfonic acid membrane,  $Pb^{++}$  form, rinsed.

observed in our electron micrographs (Fig. 1). Most series of the micrographs never showed them at all. It therefore seems that in most cases the second alternative explanation is valid. We are looking at sections of platelets containing matrix material within and having undergone substitution by sulfonic acid groups or their salts on their surface.

This is in perfect accordance with Keller's findings concerning the internal structure of polyethylene.<sup>7,8</sup> He found that polyethylene crystallizes from solution or from its melt in platelets in which the hydrocarbon chains are folded back upon themselves after about 80  $CH_2$  units perpendicular to the surface. Sets of such long, meandering folded chains are packed beside each other in the platelets (Fig. 4). The similarity of the structure of such polyethylene to long-chained paraffin crystals was investigated by Bunn.<sup>9</sup> The characteristic wide-angle x-ray reflections of polyethylene were accordingly explained.

Keller observed that the crystalline platelets often start from a common center from which they diverge in spherulithic structures.<sup>10</sup> The same can be observed on Figure 5.

Our results fit the assumption, that sulfochlorination begins at the surface of the platelets. It does not proceed very far into their body, between the hydrocarbon chains. Keller et al.<sup>11</sup> found, by means of x-ray diffraction, that chlorination of polyethylene also begins at the surface of the platelets. We know from chemical analysis of our membranes that for each  $SO_2Cl$  group introduced into polyethylene 1-4 additional atoms of

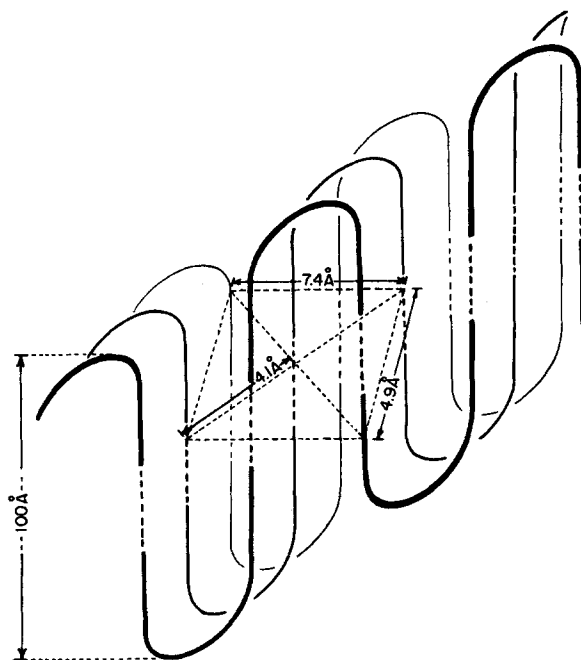


Fig. 4. Meandering folded chain structure of polyethylene platelets.

chlorine always enter as a result of direct photochemical chlorination. These Cl atoms would naturally begin to be attached at the platelet surface, and they too would add to the electron absorbing, staining, material in the micrographs. Sulfonic acid groups and chlorine atoms would together account for the two black lines adjoining the white middle line. The line itself, would be due to the hydrocarbon crystal body of the platelets.

However, the two black lines are at least half as thick as the white line between them. A surface layer on the platelets would not be thicker than perhaps 5–10 Å., even allowing for the curvature of the folding  $\text{CH}_2$  chain. The observed thickness is about five to ten times as large. It may be due to the fact that we certainly do not observe the platelets edge-on, but more or less with their surface at an angle to the electron beam. Those platelets lying flat in the plane of the section would not show up at all. Their surface absorption would contribute to the general background. But those standing nearly perpendicular to the section, nearly parallel to the impinging electrons, would show their surface coating in perspective, thicker than it really is. This could be one reason for the thickness of the black lines as discussed by Andrews.<sup>4</sup> Another reason could be that the chemical attack proceeds from the surface of the platelets towards their interior, pushing apart the  $\text{CH}_2$  chains from their folded order. Finally an amorphous reacted region could be between the platelets.

On all our micrographs we saw that black and white lines often occur in larger numbers, one beside the other. Had we not encountered the triple line structure discussed above, we could easily explain these multiple parallel lines as parallel tubular channels carrying the active groups. In cross-section we would expect to find black dots as sections of the channels, on a white background on the hydrocarbon matrix. Such black dots are actually found in many places, but they are mostly arranged in what we call the black lines. In view of the triple line structure, we can just as well explain the multiple parallel lines by assuming that they represent the cross-section of a stacked parallel series of platelets reacted on their faces.

We now have to discuss the granular structure of the black lines we have been speaking about. This structure is not always visible to the same ex-

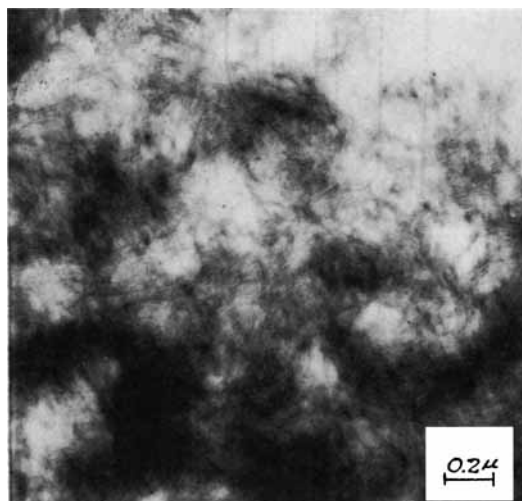


Fig. 5. Spherulitic structures in polyethylene sulfonic acid membranes,  $Pb^{++}$  form, rinsed.

tent, but present. The diameter of these granules is around 30 A., which is an order of magnitude above atomic dimensions. They can certainly not be due to individual active sites. Perhaps they are related to Anderson's type II, irregular, corrugated lamellae,<sup>5</sup> though the distance between the corrugations is larger by at least an order of magnitude, than the distance between the dots we see. Perhaps  $SO_2Cl$  groups tend to be introduced into the matrix in groups one near to the other. Their total number per unit volume is much too small to ascribe them to single active sites, remembering that our membrane has a capacity of 1.6 meq./g. It may be that two or more platelet systems lie one above the other, in the thick sections (about 500 A.). The dots could be intersections of two systems of black lines. As things stand today, we really cannot tell what these spots represent.

### X-Ray Diffraction

The crystal structure of very long-chain normal paraffin hydrocarbons and of polyethylene has been examined by Bunn.<sup>9</sup> The elementary cell is orthorhombic with  $a_0 = 7.40$ ,  $b_0 = 4.93$  and  $c_0 = 2.534$  Å. The paraffin chains are parallel to the  $c$  axis. Four of them, with their zigzag parallel to each other, lie along the edges of the unit cell. A fifth, with its zigzag perpendicular to that of the four others, lies in the middle. In polyethylene the chains fold back upon themselves in the (110) plane, forming an arch of about 5 CH<sub>2</sub> groups, the chain itself being always parallel to  $c$  (Fig. 4). The strongest wide-angle x-ray reflections are 110, 200, and 020 with the Bragg spacings corresponding to half the diagonal in the  $a$ - $b$  plane: 4.102 Å. and to half the unit cell edges  $a_0$  and  $b_0$ : 3.696 Å. and 2.467 Å.

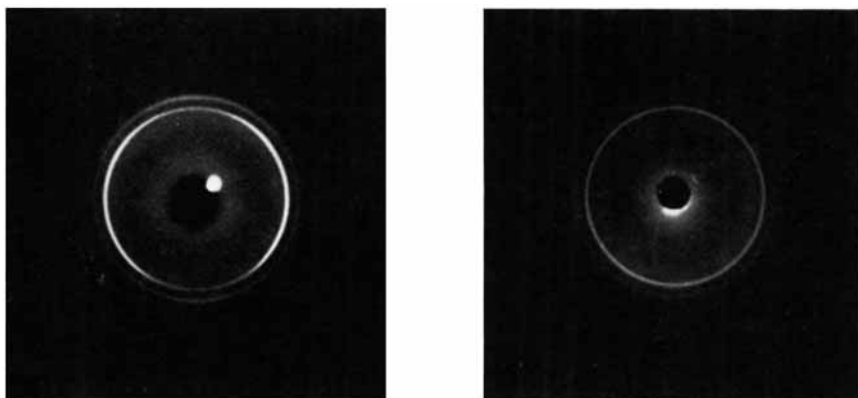


Fig. 6. X-ray diffraction diagrams: (a) polyethylene film; (b) membrane made from the same film by sulfochlorination and hydrolysis.

We measured x-ray diffractions of sulfonated membranes and their different salts at the Hebrew University, Jerusalem with the kind help of Dr. Y. Meir. The main result of these experiments was the corroboration of Dr. A. Keller's previous findings: topochemical sulfochlorination and subsequent hydrolysis or amination of a polyethylene sheet do not eliminate its characteristic crystalline diffraction diagram (Fig. 6). This means that the crystallites in polyethylene survive its sulfochlorination, probably because they are primarily attacked on their flat faces. We arrived at this same conclusion from the triple line structure found in the electron micrographs.

The second result of the x-ray diffraction experiments was no less interesting. We found that the second maximum of the diagram corresponding to the reflection 200 can definitely be observed on polyethylene which has been sulfochlorinated in trichloroethylene solution and cast into films (Fig. 7). This fact can hardly be explained by assuming that the crystalline platelets have absolutely vanished in solution. Then a perfectly random chemical attack would have had to ensue along the entire chain

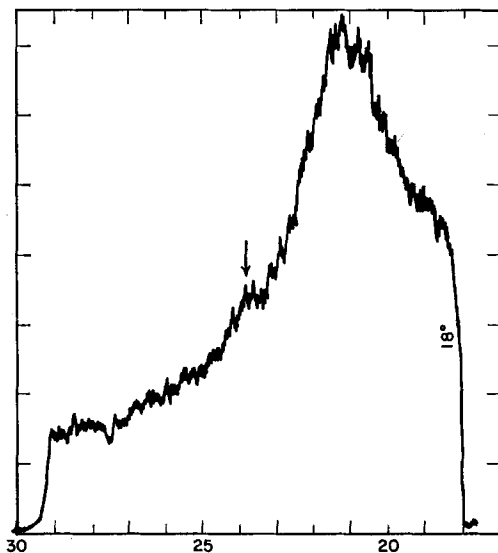


Fig. 7. X-ray diffractogram of a cast polyethylene membrane. Note the side maximum exactly at the  $2\theta$  value of the 200 reflection in addition to the main maximum of the 110 reflection.

length and the randomly substituted chain would have been unable to re-fold into the platelets of unsubstituted polyethylene. The assumption, however, that the platelets have been partially conserved in solution is also very strange, and certainly needs further confirmation. For reasons beyond our control we are unable to continue these experiments but would gladly provide cast film material to anybody interested in the problem.

Our electron micrograph of cast sulfonated polyethylene membranes (Fig. 3) is admittedly of very poor quality. We have not been able to detect the characteristic triple line structures which, we think, belong to the crystalline platelets on a series of such micrographs. But a structure of black-white-black-white multiple lines recurs, whatever it may represent. Also, the lines are often composed of dots which can also be arranged in another set of weaker lines at an angle to the strong ones. Whether we look at superposed structures at an angle to one another and whether these structural elements are fibers or platelets is entirely open to discussion. We can do no better than offer to give film samples to anyone, more versed in electron microscopy than we have been, who is interested in following up this investigation.

We also investigated whether counterions of different size and/or valency disturb the x-ray diagram of polyethylene sulfonate films by pushing apart the folds of the meandering chains in the crystallites. We did not find any effect of these counterions on the diffraction diagram. The diffraction lines were weakened by substitution of H with metal ions, but the weakening was due to absorption and background scattering of x-rays by



the counterions. To prove this, a film which contained the counterions was placed as an additional filter before the Geiger counter, while a film in its  $\text{SO}_3\text{H}$  form was the diffractor. Subsequently the position of the two films was interchanged.

### Kinetic Evidence

The question of platelets reacting on their faces can be attacked from an entirely different point of view also. We had determined years ago for other reasons, the time curves of sulfochlorination of polyethylene. Figure 8 shows, for instance, the increase of S and Cl contents in an 0.1 mm. film of polyethylene sulfochlorinated in the light of incandescent lamps in a 2:1 mixture of  $\text{SO}_2$  and  $\text{Cl}_2$  gas. After reaction, the films were hydrolyzed in alkali; the percentage values refer to these hydrolyzed films which are already cation-active membranes. The chlorine is always introduced by direct photochemical chlorination, parallel to the sulfochloride groups. Both reactions begin probably at the surface of the platelets.

The velocity of sulfochlorination suffers a sharp break at 6% S, that is, at about 1.9 meq./g.  $\text{SO}_2\text{Cl}$  or  $\text{SO}_3\text{H}$ . At the same time, 7% (2.0 meq./g.) chlorine was introduced by direct chlorination. For reasons of stoichiometry, 74% (53 meq./g.).  $\text{CH}_2$  has remained in the material as hydrocarbon chain. According to Keller's finding the platelets are about 100 Å. thick, that is, the straight parts of the parallel meandering chains contain about 80  $\text{CH}_2$  groups across a platelet. We found approximately 1.9  $\text{SO}_3\text{H}$  groups and 2 Cl atoms for 53  $\text{CH}_2$  units; so that 80 units accommodate about 2.9  $\text{SO}_3\text{H}$  groups and 3 Cl atoms. To sum up, this means nearly six substituted  $\text{CH}_2$  groups for each chain element of 80  $\text{CH}_2$  groups,

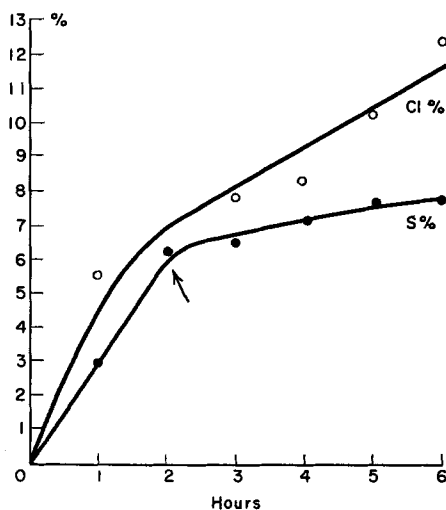


Fig. 8. Sulfur and chlorine contents of polyethylene sulfonic acid membranes as a function of reaction time. Topochemical sulfochlorination.

assuming that 100% of the polyethylene is arranged in platelets. Geil<sup>12</sup> built such meandering CH<sub>2</sub> chains from atomic models. He found about 5 CH<sub>2</sub> groups belong to the curved fold if the straight chains are set 4.1 Å apart from each other, as they are in polyethylene. Our low-density polyethylene certainly contains amorphous regions more easily attacked by the reactants. Therefore less than six substitutions remain for the folds. The break, however, is so sharp that it certainly marks the transition from an easy to a difficult substitution.

After having passed this break in the sulfochlorination curve, sulfochlorination and chlorination proceed, but more slowly, because the substitution has to take place between the straight hydrocarbon chains, pushing them apart. The velocity of the chlorination decreases to a lesser extent, since the Cl atom is much smaller than the SO<sub>2</sub>Cl group and can slip in more easily between the distended chain ends. Peterlin and Meinel<sup>13</sup> found a break in the velocity curve of polyethylene single crystal oxidation by concentrated HNO<sub>3</sub> at a much higher percentage of attacked CH<sub>2</sub> groups.

In brief, from the results of electron microscopy, x-ray diffraction, and kinetic experiments we conclude that sulfochlorination of polyethylene proceeds primarily in the amorphous phase and on the surface of its crystalline platelets. Accordingly, the interconnected aqueous network of permselective membranes made by the above process is also situated in these regions.

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## References

1. F. de Körösy and E. Zeigerson, *Israel J. Chem.*, **4**, 85 (1966).
2. F. de Körösy and J. Shorr, *Athens Symposium: Fresh Water from the Sea*, Dechema Monographs, Vol. 47, 1962, p. 477.
3. F. de Körösy and J. Shorr, *Israel Pat.* 14720; *Brit. Pat.* 981562.
4. E. H. Andrews, *J. Polymer Sci. B*, **3**, 353 (1965).
5. F. H. Anderson, *J. Appl. Phys.*, **35**, 64 (1964).
6. F. P. Reding and E. R. Walter, *J. Polymer Sci.*, **38**, 141 (1959).
7. A. Keller, *Phil. Mag.*, **2**, 1171 (1957).
8. A. Keller and A. O'Connor, *Nature*, **180**, 1289 (1957).
9. C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).
10. A. Keller, *J. Polymer Sci.*, **17**, 301 (1955).
11. A. Keller, W. Matreyek, and F. H. Winslow, *J. Polymer Sci.*, **62**, 291 (1962).
12. P. H. Geil, *Polymer Single Crystals*, Wiley, New York, 1963, p. 83.
13. A. Peterlin and G. Meinel, *J. Polymer Sci. B*, **3**, 1059 (1965).

### Résumé

Membranes ion-permselectives qui contiennent polyéthylène dans leur matériel de base ont été examinées par transmission directe dans le microscope électronique et par diffraction des rayons X. Les électronmicrogrammes de toutes ces membranes ont montrées des lignes blanches d'environ 100 Å d'épaisseur emplacements entre deux lignes noires composées des granules. Ces lignes s'arrangent beaucoup de fois en triplets noir-blanc-noir. Nous essayons d'expliquer ces éléments structurels les considérant comme des sections à travers les plaques cristallines caractéristiques pour la polyéthylène, qui ont subis la sulfochlorination sur leur deux surfaces. On sait que ces plaques ont environ 100 Å d'épaisseur. Les diagrammes obtenus par diffraction de rayons X ont aussi montrées les lignes caractéristiques des cristallites de polyéthylène, leur intensité étant plus faible après la sulfochlorination. La vitesse de la sulfochlorination hétérogène des films polyéthylènes diminue abruptement quand les films contiennent 6% S et 7% Cl (après hydrolyse). Ça donne six substitutions sur chaque élément de la chaîne à travers les plaques cristallines pour un film de 100% cristallinité et respectivement moins pour une matière partiellement amorphe. On sait que cinq groupes  $-\text{CH}_2-$  du chaque élément de la chaîne est exposé à la surface des plaques de qui est en accord avec nos résultats.

### Zusammenfassung

Es wurden ion-permselective Membrane welche Polyethylen in ihrem Matrix enthalten, elektromikroskopisch in direkter Transmission und mit Röntgenstrahlen-Diffraction untersucht. Auf allen Elektronmikrogrammen erschienen etwa 100 Å breite weisse Linien welche von je zwei schwarzen, aus Punkten bestehenden, Linien begrenzt waren. Oft waren diese Linien in schwarz-weiss-schwarze Triplets eingeordnet. Wir erklären diese Strukturelemente versuchsweise, indem wir annehmen, dass sie Querschnitte der für das Polyethylen charakteristische Kristall-Plättchen darstellen welche an ihren beiden Flächen sulfochloriniert wurden. Solche Plättchen sind bekanntlich etwa 100 Å dick. Röntgen-Beugungsbilder zeigten auch die charakteristischen Linien der Polyethylen Kristallite obwohl sie in der sulfonierten Membranen etwas schwächer waren. Die Geschwindigkeit der heterogenen Sulfochlorinierung von Polyethylen Filmen fällt plötzlich, wenn der S Gehalt 6% und der Cl Gehalt 7% (nach Hydrolyse) erreicht hat. Das würde heissen dass sechs Stellen an jedem Kettenelement des Plättchens substituiert wurden falls man 100% Kristallinität des Filmes annimmt und entsprechend weniger für teilweise amorphes Material. Es ist bekannt dass fünf  $-\text{CH}_2-$  Gruppen jedes Ketten-elementes an der Oberfläche der Plättchen frei liegen, in guter Übereinstimmung mit dem Befunde.

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