# Heterogeneous sulphochlorination of polyethylene. The effect of polymer morphology on the reaction rates and properties of reaction products

**Benjamin Bikson, Joseph Jagur-Grodzinski and David Vofsi**
*Department of Plastics Research, The Weizmann Institute of Science, Rehovot, Israel*
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Polyethylenes of low, middle and high density have been submitted to heterogeneous sulphochlorination in the presence of hydroperoxides as initiators. Approximately equal amounts of $SO_2Cl$ and chlorine could be attached to the polyethylenic precursors. Although the reaction kinetics are strongly affected by the initial morphology of the substrates, it has been found that maximum amounts of the $SO_2Cl$ groups which can be introduced under such conditions are determined by the fraction of the amorphous material. The reaction kinetics are also strongly affected by the presence of antioxidants.

X-ray diffraction analysis, birefringence and polarized i.r. measurements indicated that the morphology of the sulphochlorinated materials and of the products of their hydrolysis is strongly affected by the initial morphology of the polyethylenic precursors. Fluorescence probe measurements revealed that in highly oriented materials, the orientation of the amorphous regions is retained even upon water swelling of the final ion exchange membranes. It has been found that the initial morphology of the polyethylenic substrates together with the degree of the chemical modification (concentration of the introduced chlorine and $SO_2Cl$ groups) determine the properties of the products.

## INTRODUCTION

The sulphur dioxide–chlorine mixture which is known to act as an effective sulphochlorinating agent for paraffins[1] has also been used for heterogeneous sulphochlorination of polyethylene films and powders. In such systems the reaction has been initiated by u.v. light, $\gamma$-irradiation or organic peroxides[2–4]. In the latter case the polymer must be swollen by a suitable liquid, such, for example, as carbon tetrachloride[4].

Low density polyethylenes which are characterized by a low degree of crystallinity were recommended for these reactions but no attempt was made to establish any exact correlations between the morphological parameters of the precursors, the reaction rates and the properties of the reaction products. It is obvious, however, that the degree of crystallinity, size, shape, orientation and perfection of the crystallinities as well as the orientation of the polymeric chains in the amorphous regions must be of importance in such heterogeneous reactions. These parameters affect the accessibility of the amorphous regions and the character of the interphase between the crystalline and the amorphous phase. They may affect both the kinetics of the reactions and the properties of the products.

For heterogeneous reactions taking place within a polymeric network of a semicrystalline polymer some features of its initial morphology may be expected to be preserved in the reaction products. One may ask if this is true for the sulphochlorinated polyethylenes and to what extent the properties of the products are determined by the initial morphology of polyethylene.

The present investigation was undertaken to provide some answers to these questions. The sulphochlorination was performed on various polyethylenes and the morphologies of the reaction products were compared with those of the precursors.

## EXPERIMENTAL

### *Preparation of unoriented samples*

Unoriented films of low, middle and high density polyethylene were prepared by compression moulding. Ipethene 600, $d = 0.916$ g/cm$^3$, Petrochemical Industries (Israel); Scleir 8507, $d = 0.941$ g/cm$^3$, Du Pont, USA and Eltex, $d = 0.96$ g/cm$^3$, Solvay, were used. In order to eliminate the influence of antioxidants on reaction rates in films prepared by compression moulding, polyethylene samples were purified by reprecipitation. Hot xylene solutions (2% by weight) were poured into excess methanol, rinsed and dried in high vacuum at room temperature. The polymers were heated to 180°C between Teflon sheets in a mould cut from 100 $\mu$m to 30 $\mu$m shim stock and sandwiched between two 1/8 inch stainless steel plates. After 10 min at 20 000 psi, the samples were removed from the press, quenched by immersion in cold water (20°C) and dried in a vacuum oven at room temperature. The birefringence of samples thus prepared was less than $1 \times 10^{-3}$. The crystallinity of the samples was determined by d.s.c. and by X-ray diffraction analysis. Values of 24%, 38% and 54% were obtained for the low, middle and high density polyethylene films respectively.

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*Cold drawn samples*

Three types of commercial blown polyethylene films (Petrochemical Industries, Haifa) were used for drawing experiments: (a) Ipethene 100, d = 0.923 g/cm$^3$, *MFI* 0.3, (b) Ipethene 113, $d$ = 0.923 g/cm$^3$, *MFI* 0.7, and (c) Ipethene 323, $d$ = 0.921 g/cm$^3$, *MFI* 2.0. The degrees of crystallinity as determined by d.s.c. were found to be 27%, 27% and 24% for a, b and c, respectively. Ipethene 113 and 323 contained before extrusion about 300 ppm of antioxidant. Ipethene 100 did not contain any antioxidant at all. Drawing of these films in the machine direction did not cause necking, and samples of any desired draw ratio could be obtained. Films were cold drawn at room temperature in an Instron machine model TT–CM at the rate of 2 cm/min. Film samples for cold drawing were cut into 8 cm x 8 cm large squares and were marked by ink lines 1 cm apart. The percent of elongation was determined by measuring the change in distance between the lines. The identity of changes in the distances between four central lines indicated the uniformity of stretching.

*Sulphochlorination procedure*

Various polyethylene films were sulphochlorinated by bringing them in contact with a carbon tetrachloride solution saturated with sulphur dioxide–chlorine gaseous mixture as described elsewhere[4]. The reaction temperature was kept at 15°C. Methyl ethyl ketone hydroperoxide was used as initiator. It was added continuously at a rate of 0.24 g/h per l of $CCl_4$.

*Conditioning*

Samples of low density polyethylene were kept for 48 h at 51°C in $CCl_4$.

*Preparation of cation exchange membranes*

Sulphochlorinated intermediates were hydrolysed by immersion at room temperature in 1N NaOH.

*Thermal behaviour*

The behaviour of the polyethylenes and of their chlorosulphonated products in the temperature range 20°–140°C was studied using the Perkin–Elmer DSC A-1 model. The heating rate was 8°C/min. The apparent heats of fusion, $\Delta H_f$, of the polymers were calculated from the areas under the melting endotherm. (Indium was used as reference.)

Polymer crystallinity was calculated from the expression:

$$\%\ \text{crystallinity} = \frac{\Delta H_f}{65.9} \times 100 \qquad (1)$$

where, the value of 65.9 cal/g was assumed to be the heat of fusion of a completely crystalline polyethylene[5].

*X-ray diffraction analysis*

Wide-angle X-ray diffraction patterns were obtained using a pinhole flat film camera. Sample-to-film distance was 2 cm. Nickel filtered copper radiation was employed. The percentage of crystallinity was determined with a Phillips PW 1380 horizontal goniometer. The calculations were performed following the Hermans–Weidinger procedure[6].

*Infra-red measurements*

The 457A Perkin–Elmer grating spectrophotometer equipped with silver bromide polarizers was used. In order to eliminate the effects of machine polarization, it was necessary to orient both the polarizer and the sample with their axes at +45° or –45° to the spectrometer slit[7]. A normal grid setting and a low scanning speed were used. The dichroic ratios were calculated from the expression

$$R = A_{\parallel}/A_{\perp}$$

where $A_{\perp}$ and $A_{\parallel}$ are the measured absorbances for radiation polarized perpendicular and in parallel to the draw direction, respectively.

*Fluorescence polarization*

The degree of fluorescence polarization was measured with a Perkin–Elmer MPF-3L fluorescence spectrophotometer. Hitachi polarization accessories to the MPF-3L were used for polarizer and analyser. A cut-off filter was placed in front of the detector to reduce light scattering from the samples. 3-Amino-*N*-methyl pyridinium iodide (AMP) (kindly supplied by Prof. M. Shinitzky from this Institute) was used as fluorescence polarization probe for polyethylene based cation exchange membranes.

The fluorescence probe was introduced by equilibration of the membranes ($Na^+$ form) for 24 h at room temperature in 0.1N aqueous solution of AMP.

The fluoresence polarization was determined from the equation:

$$P = \frac{I_{vv} - GI_{vH}}{I_{vv} + GI_{vH}}$$

where $I$ is the photometer reading, the subscripts $v$ (vertical) and $H$ (horizontal) refer to the orientation of polarizer and analyser, respectively, and $G$ is the grating correction factor. Correction for grating polarization effect, $G$, was made following the Chen[8] procedure. The angular distribution of fluorescence polarization was determined only in the stretching and in the transverse directions. The polarization in stretching direction is denoted as $P_s$ and in transverse direction as $P_t$. The ratio $P_s/P_t$ was used for a comparison of the orientation of the samples.

*Birefringence*

This was measured by the compensation method, using a Zeiss Universal polarizing microscope equipped with Ehringhaus or Brace–Kohler compensators. The measurements were carried out at the D spectral line ($\lambda$ = 589 $\mu$m).

*Analytical procedures*

The weight percent of S and Cl in the reaction products has been determined by standard microanalytical procedures[9]. Residual traces of $CCl_4$ were carefully removed from the analysed samples by conditioning them for 24 h in ethyl ether and consecutive drying to constant weight in high vacuum ($10^{-3}$ torr) at room temperature. $N_{SO_2Cl}$ and $N_{Cl}$ in meq/g were calculated from the results of elemental analysis using $N_{SO_2Cl}$ = % S/3.2 and $N_{Cl}$ = % Cl/3.55 – $N_{SO_2Cl}$.

Rates of hydrolysis were calculated from the concentrations of $Cl^-$ in the 1N NaOH solutions used for the hydrolysis. Chloride titrator (Aminco, USA) was used in these determinations. The progress of hydrolysis was also checked in a semi-quantitative way by following changes in the i.r. spectra of the hydrolysed films.

The specific volume of the amorphous phase in the polyethylene samples was calculated from the equation

$V_a^{sp} = (1 - f)/0.87$, where 0.87 is the density of the amorphous phase[10] and, $f$, is the fraction of crystallinity determined by d.s.c. or X-ray (see above). The concentration of $SO_2Cl$ was calculated using the relationship $[SO_2Cl] = N_{SO_2Cl}/(1 - 0.0995 N_{SO_2Cl} - 0.0355 N_{Cl}) V_a^{sp}$. In this calculation we assumed that the volume of the amorphous phase remains constant during the reaction. Such as assumption was based on the observation that the dimensions of the samples are not affected by the sulphochlorination reaction.

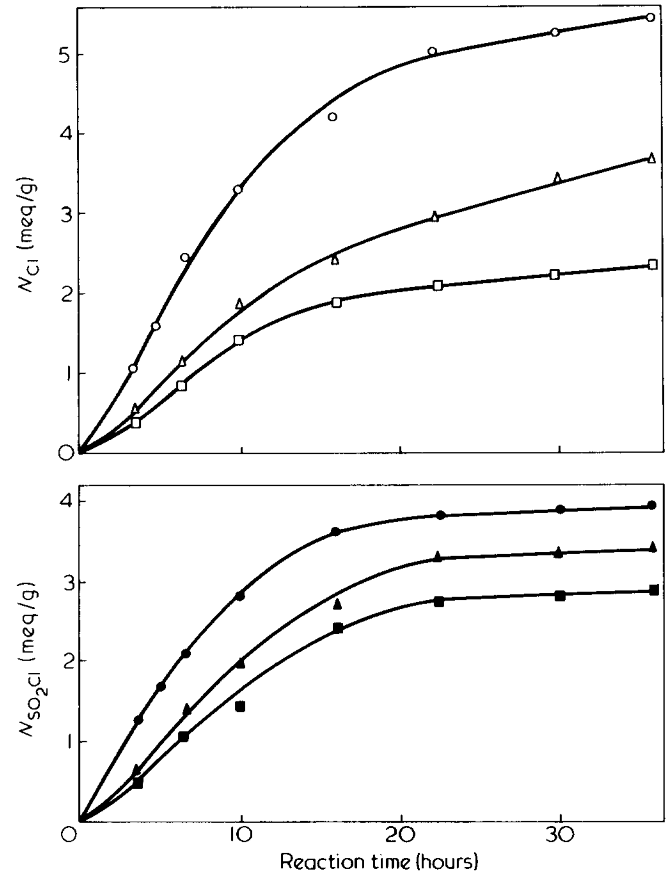


*Figure 1* Concentration of $SO_2Cl$ and Cl as function of reaction time for various unoriented polyethylene samples free from antioxidants (film thickness 35 μm). ○, ● – low density PE, △, ▲ – middle density PE, □, ■ – high density PE

## RESULTS AND DISCUSSION

Totally unoriented films prepared by compression moulding were submitted to sulphochlorination. Thus, effects due to changes in the degree of crystallinity could be separated from those due to other morphological parameters of the system. Results of these experiments are summarized in *Figure 1* and in *Table 1*. It is evident that the maximum amounts of the sulphonyl chloride groups, which can be attached under such conditions to the paraffinic backbone, decrease with the increase in the degree of crystallinity of the polymers. Apparently, the crystallites are virtually inaccessible to the attacking radicals and form a protective barrier around the amorphous regions susceptible to the attack. The observed differences in the rates of sulphochlorination, may be related to differences in the rates of diffusion of the reactants into the amorphous regions surrounded by crystallites. Obviously, as the fraction of crystallites increases, the diffusive path of small molecules penetrating the polymeric network of the amorphous regions becomes more tortuous.

One could argue at this point that the observed differences in the rates of sulphochlorination should be attributed to differences in branch frequencies rather than to differences in the morphological parameters of the samples. We exclude this possibility for the following reasons; although the fraction of the reactive tertiary hydrogens increases as a result of branching, such hydrogens cannot be substituted by $SO_2Cl$ groups for steric reasons. The latter observation, which was reported by Asinger *et al.*[11], has been presently confirmed by sulphochlorination of isobutane solutions (Matheson, Research Purity) in $CCl_4$ at 15°C, under conditions closely resembling those prevailing during the sulphochlorination of polyethylenes. N.m.r. analysis of the reaction products indicated that *only primary* hydrocarbons were substituted by $SO_2Cl$ (for 95–97% conversions of isobutane into products). At the same time over 30% of the tertiary hydrogens was substituted by chlorine. Thus, on purely statistical grounds branching should cause a *decrease* and not an *increase* in the rates of sulphochlorination.

One may ask, however, if a possible increase in the length of the kinetic radical chains, due to the presence of the reactive tertiary hydrogens, may not outweigh the statistical factors.

Experimental evidence to the contrary has been provided by sulphochlorination of poly(4-methyl-1-pentene).

*Table 1* Sulphochlorination of unoriented polyethylene films. $SO_2Cl$ and Cl content after prolonged reaction times

| Sample | Reaction time (hours) | Sulphonyl chloride content (meq/g) | Chlorine content (meq/g) | $\frac{[SO_2Cl]}{[Chlorine]}$ | $[SO_2Cl]$ meq/ml of amorphous phase* |
|---|---|---|---|---|---|
| Ipethene 600 (low density) | 22.5 | 3.8 | 5.0 | 0.76 | 9.8 |
| | 30 | 3.85 | 5.2 | 0.74 | 10.2 |
| | 38 | 3.85 | 5.4 | 0.715 | 10.4 |
| Scleir (middle density) | 22.5 | 3.25 | 2.9 | 1.12 | 8.0 |
| | 30 | 3.3 | 3.4 | 0.97 | 8.4 |
| | 38 | 3.38 | 3.6 | 0.94 | 8.8 |
| Eltex (high density) | 22.5 | 2.75 | 2.0 | 1.37 | 7.9 |
| | 30 | 2.8 | 2.2 | 1.27 | 8.2 |
| | 38 | 2.83 | 2.3 | 1.23 | 8.4 |

* Calculated on the assumption that the volume of the amorphous phase remains constant during the reaction

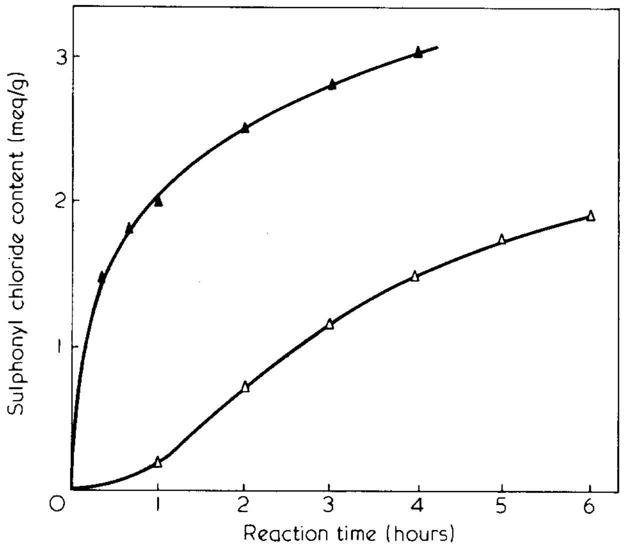
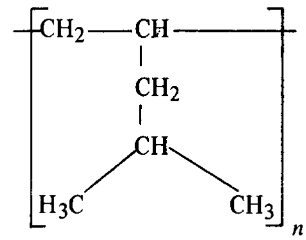


*Figure 2* The effect of conditioning on the sulphochlorination rates of the unoriented low density polyethylene films. Film thickness – 55 μm; △, unconditioned and ▲, conditioned samples



PMP

Samples of this polymer in the form of a gel in $CCl_4$ have been sulphochlorinated under identical conditions to those prevailing during sulphochlorinations of polyethylenes. The rate of sulphochlorination of PMP has been found to be more than 50% slower than the rate of sulphochlorination of the low density polyethylene (antioxidant free Ipathene 600 powder swollen by $CCl_4$). At the same time, the rate of chlorination of PMP was twice as fast as that of the polyethylene sample.

Inspection of data in *Table 1* shows that nearly identical results are obtained for the low, middle and high density polyethylenes after long reaction periods, if the concentration of the $SO_2Cl$ groups is calculated per volume of the amorphous regions of the samples. Such behaviour is consistent with the assumption that only the amorphous regions are attacked under our experimental conditions. This conclusion is also consistent with the results of Korosy and Zeigerson[12] and with our X-ray diffraction measurements which do not show any changes in the X-ray diffraction pattern of the sulphochlorinated samples due to changes in the degree of crystallinity.

The observed increase in the relative intensity of the amorphous halo can be ascribed to the enhanced scattering of the amorphous regions in presence of the sulphur and chlorine atoms. The concentration of chlorine and $SO_2Cl$ groups attained in the 'plateau' regions of the kinetic curves correspond to a first approximation to the substitution of every third methylene group by $SO_2Cl$ or Cl. At this point further substitution with $SO_2Cl$ becomes impossible for steric reasons. Indeed, reactions carried out on 1-chloropropane, which was used as a model compound, indicated that even a prolonged exposure did not lead to substitution with $SO_2Cl$ of the methylenes in $\alpha$ position to the sulphochlorinated carbons. No such restrictions apply, however, to the chlorination reaction. It may be seen from *Figure 1* and *Table 1* that a slow chlorination continues after the concentration of the sulphonyl chloride groups had approached its maximum value. The analysis of the n.m.r. spectra of such materials indicated a considerable increase of the $-CCl_2-$ groups at this stage of the reaction.

In column 5 of *Table 1* are listed the $[SO_2Cl]/[Cl]$ ratios obtained in various samples after long reaction times. While for the high density materials sulphochlorination is slightly favoured over chlorination, the reverse becomes true for the low density samples. This may be attributed to the considerable amount of tertiary hydrogens in the low density materials. Such hydrogens are more easily substituted by chlorine than the secondary or primary ones, but because of steric hindrance are immune to substitution by $SO_2Cl$ (see also the discussion in the preceding paragraph).

### *Effects due to conditioning*

Some samples of low density polyethylene were conditioned before the sulphochlorination by immersion in $CCl_4$ for 48 hours at 51°C. Such conditioning causes an increase in the swelling of the polyethylene by $CCl_4$ and should increase the accesibility of the amorphous regions. This apparently is the reason for the increase in the reaction rates due to conditioning (*Figure 2*). Again, the increase is much greater for the low density than for the higher density polyethylenes. The pronounced effect of the conditioning on the reaction rates and on the properties of the final products (*Table 2*), indicates that such treatment must strongly affect the morphology of the polymer. D.s.c. measurements of the heat of fusion of the conditioned and of the unconditioned samples indicated that the degree of crystallinity remained unchanged as results of the treatment. (Heat of fusion was not affected by the conditioning, $DH_f = 15.8$ cal/g.) However, it can be seen from the X-ray diffraction patterns shown in *Figure 3* that the 110 and 200 reflections became significantly sharpened. Apparently, during conditioning which is carried out at temperatures just below the critical solubility temperature of the polymer in the solvent, rearrangement in the crystalline phase of the polymer has taken place. As result of such rearrangement the crystallites become larger and their perfection increases. Hence, crosslinking of the amorphous phase, due to its entangle-

*Table 2* Water content and conductivity of cation exchange membranes prepared from Ipethene 600

| IEC meq/g | Water content % | Specific conductivity* (25°C) $ohm^{-1}$ $cm^{-1}$ x $10^3$ |
|---|---|---|
| Membrane prepared from 'unconditioned' polyethylene | | |
| 1.05 | 12.5 | 2.4 |
| 1.7 | 24 | 8.3 |
| 2.1 | 33.5 | 14.3 |
| 2.45 | 42 | 19.2 |
| Membrane prepared from 'conditioned' polyethylene | | |
| 1.05 | 18 | 5.5 |
| 1.7 | 31.5 | 14.2 |
| 2.15 | 44 | 24.4 |
| 2.5 | 59 | 32.8 |

* In 0.1 KCl at 1 kHz. A conductivity cell described by Steymans[22] and 1373A Automatic Capacitance Bridge (General Radio, USA) were used in the measurements

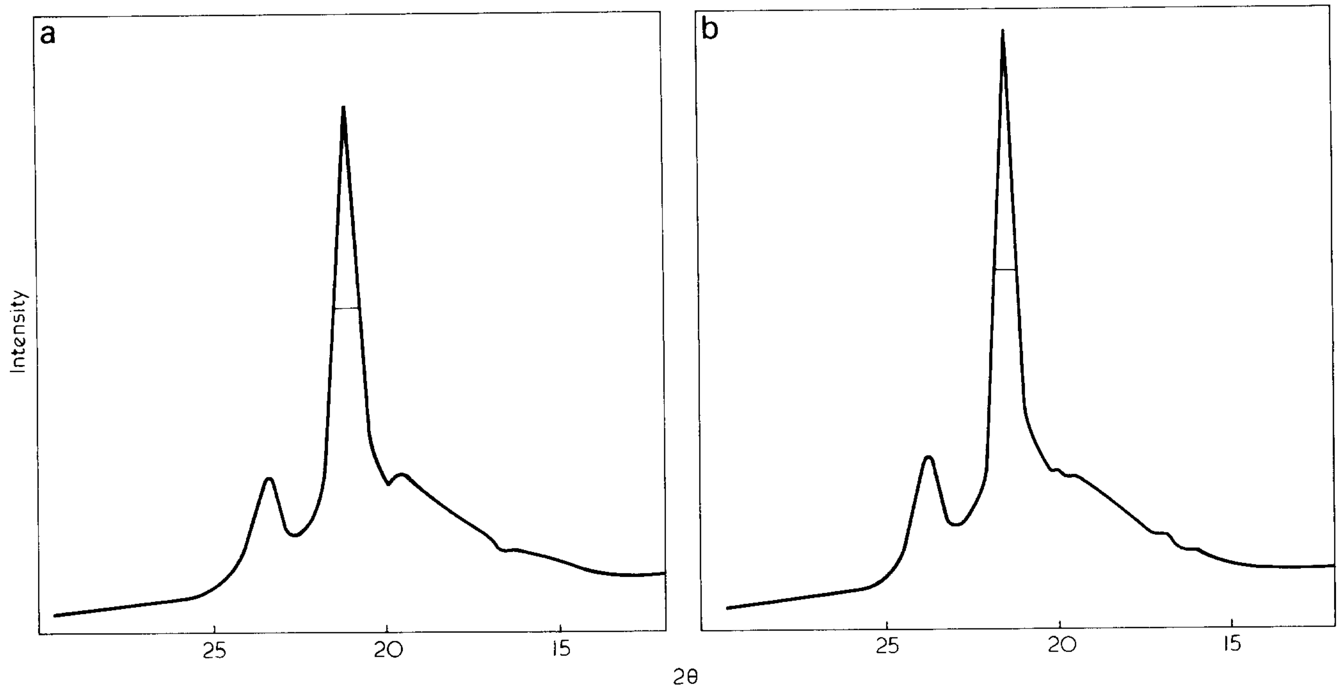


*Figure 3* X-ray diffraction patterns of low density polyethylenes before (a) and after (b) conditioning

ment with the crystalline regions, diminishes. This conclusion is consistent with changes in the mechanical characteristics due to conditioning. Namely, the ultimate elongation increases from 450% to 480% while the tensile strength decreases by 2–3%.

Conditioning of polyethylenes in a suitable swelling agent, was described previously by Michaels *et al.*[13]. These authors improved the permeability characteristics of polyethylene films by conditioning them in xylenes. Though they stated that both degree of crystallinity and crystalline morphology may be affected by such treatment, their experimental evidence based on density measurements and X-ray diffraction analysis, pointed to changes in the crystallite perfection and orientation only. To explain these results they assumed that changes induced in the degree of crystallinity are reversible and only irreversible changes in crystallite morphology persist at room temperature. In any case we performed the sulphochlorination reactions at 15°–20°C, therefore, we are not concerned with the possible transient membrane morphologies at more elevated temperatures. Thus, the effect of conditioning in our systems seem to be analogous to that reported for xylene.

Consideration of properties of the products of the sulphochlorination reaction seems to indicate that changes induced by conditioning in the morphology of the starting polyethylenes are preserved in the sulphochlorinated materials. Cation exchange membranes obtained by the hydrolysis of the sulphochlorinated intermediates also 'remember' the initial conditioning. Inspection of data summarized in *Table 2* reveals that ion exchange membranes produced from conditioned samples are characterized by water uptakes and ionic mobilities considerably larger than those of membranes of equal ion exchange capacity produced from the unconditioned ones.

### *Cold drawn films*

The morphology of the original commercial samples and changes induced by their cold drawing were determined using X-ray diffraction, i.r. polarized light and birefringence techniques. The results of X-ray measurements are illustrated by *Figure 4*. It is obvious that a considerable orientation of the crystallites has been achieved at the drawing ratio λ = 4.1. This is in agreement with other investigations reported in the literature[14]. Results of i.r. measurements shown in *Figure 5*, confirm this conclusion and provide information about the orientation in the amorphous phase which is clearly indicated by the dichroic character of the 1380 cm$^{-1}$ and 1352 cm$^{-1}$ bands assigned[15] to the $-CH_3-$ deformation and $-CH_2-$ wagging modes, respectively. Interesting information is provided by the inspection of the 720–730 cm$^{-1}$ bands which were assigned to the $-CH_2-$ rocking mode[14]. The long *trans-trans* $-CH_2-$ sequences in the amorphous region absorb at 720 cm$^{-1}$ only. The crystallites absorb at 720 cm$^{-1}$ when the radiation is polarized in parallel with the *b* crystallographic axis and at 730 cm$^{-1}$ for radiation polarized in parallel with the *a* crystallographic axis of the crystallites[16]. It has been reported that during extrusion of polyethylene the

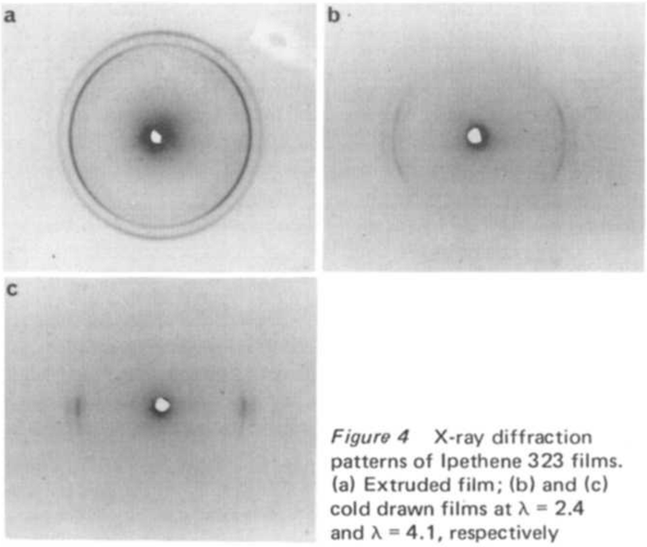


*Figure 4* X-ray diffraction patterns of Ipethene 323 films. (a) Extruded film; (b) and (c) cold drawn films at λ = 2.4 and λ = 4.1, respectively

crystallites are oriented with *a*-axis in parallel to the machine direction[17]. Consequently, in the original unstretched samples (*Figure 5a*) the 730 $cm^{-1}$ peak is slightly higher than the 720 $cm^{-1}$ peak, for light polarized in parallel to the machine direction.

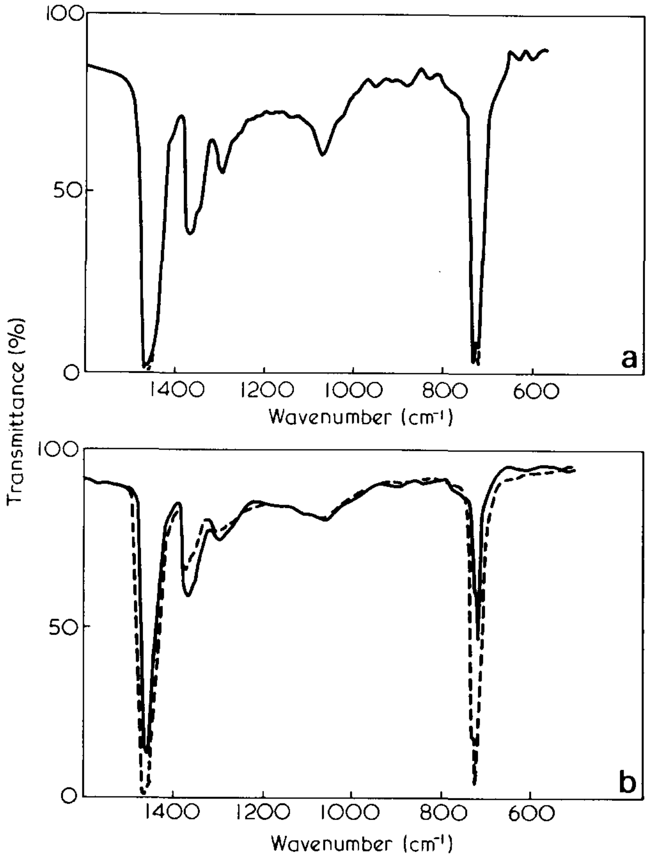


*Figure 5* Polarized infrared spectra of the polyethylenes. Full and dotted lines refer to light polarized in parallel and perpendicular, to the machine or stretching direction. (a) Extruded Ipethene 323 film. (b) Same film cold drawn, $\lambda = 4.1$

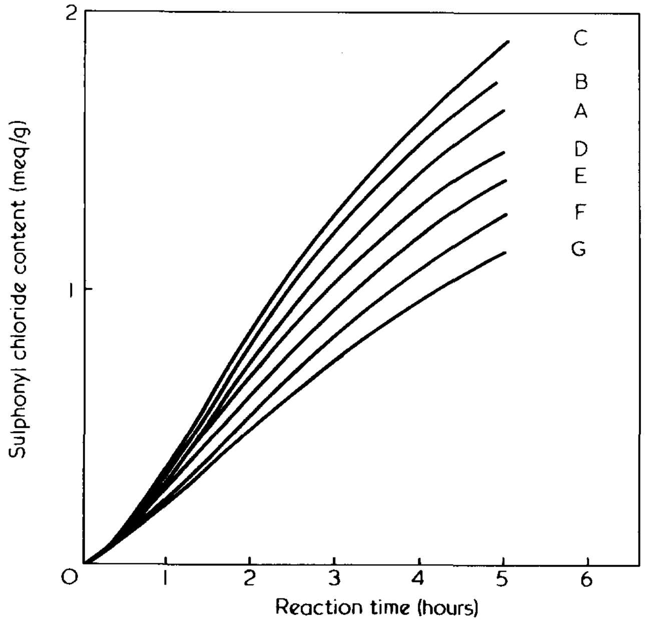


*Figure 6* Concentration of $SO_2Cl$ as function of reaction time for cold drawn Ipethene 323. A, extruded film ($\lambda = 1$); B, $\lambda = 2.3$; C, $\lambda = 3.2$; D, $\lambda = 3.9$; E, $\lambda = 4.25$; F, $\lambda = 4.7$; G, $\lambda = 5.21$. Film thickness = 90 $\mu m/\lambda^{1/2}$

The situation is, however, drastically changed as result of cold drawing. The dominant character of the 720 $cm^{-1}$ peak for light polarized both in parallel and perpendicular to the stretching direction and the strong dichroic character of this peak must be attributed to the reorientation of the crystallites and to the orientation of the chains in the amorphous phase in the stretching direction. The reorientation of the crystallites is also indicated by the reversal of the dichroic character of the 730 $cm^{-1}$ peak.

The results of the sulphochlorination experiments indicate that cold drawing of polyethylene affects significantly the course of reactions. It has been shown by Glenz and Peterlin[14], that the crystallinity of cold drawn polyethylene films remains constant up to draw ratios of 7. Changes in the reaction rates, noted by us at draw ratios of up to 5.2, should be attributed to changes in orientation only. The slow-down of the reaction rates (curves A and D–G in *Figure 6*), may be explained in terms of restricted diffusion. The differences become even more evident when unstretched and stretched samples containing antioxidant and those free from it are compared (see *Figure 7*). In the stretched samples the molecules of the antioxidant become trapped between the oriented chains and inhibit effectively the reaction, while they are washed out or destroyed at the onset of the reaction in the unoriented samples. Thus, the presence of antioxidant amplifies the effect of orientation on the reaction rates.

The apparent increase in the reaction rates at low draw ratios (curves B and C in *Figure 6*), is probably due to the fact that in this region the geometrical factors outweight the effects due to orientation (membrane thickness decreases from 90 to 50 $\mu m$ at $\lambda = 3.2$).

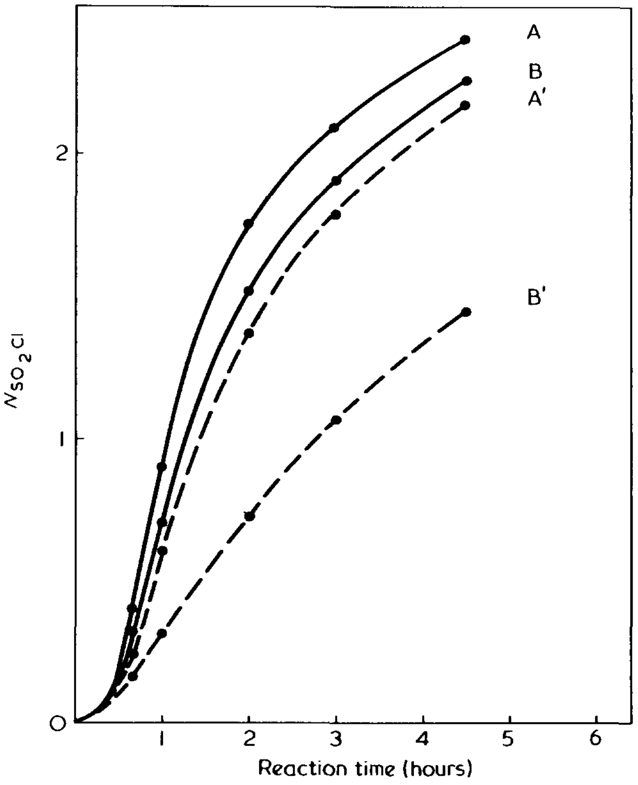


*Figure 7* The effect of antioxidant on the sulphochlorination rates for the extruded and cold drawn films. Full and dashed lines refer to the extruded (100 $\mu m$ thick) and cold drawn (50 $\mu m$ thick, $\lambda = 4.1$) films, respectively. AA' – Ipethene 100 free from antioxidant. BB' – Ipethene 113, contains ca. 350 ppm of antioxidant

### *Morphology of the sulphochlorinated films*

The birefringence of the sulphochlorinated samples obtained from the oriented polyethylene precursors (see line C in *Figure 8*) indicates that at least part of the orientation induced by cold drawing of polyethylene is preserved during the sulphochlorination process. The comparison of the X-ray diffraction patterns shown in *Figures 4* and *9* leads to similar conclusions with respect to the orientation of the crystallites.

More detailed information about the morphology of the sulphochlorinated materials was obtained from the analysis of their i.r. polarized light spectra. As may be seen from *Figure 10*, the dichroic character of the 1470 cm$^{-1}$ and 720 cm$^{-1}$ peaks corresponding to the $-CH_2-$ scissoring and rocking modes, respectively, is not changed very significantly as result of sulphochlorination. A dichroic character is also noted in the new band appearing at 870 cm$^{-1}$ which we assign to the $-CH_2-$ rocking mode of the $CH_2$ groups in $\alpha$ position to the chlorinated or sulphochlorinated sites. Orientation of the polymeric chains in regions modified by chlorination or by sulphochlorination is also indicated by the dichroic character of the 610 cm$^{-1}$, 690 cm$^{-1}$, 1160 cm$^{-1}$ and 1370 cm$^{-1}$ bands which are assigned to the

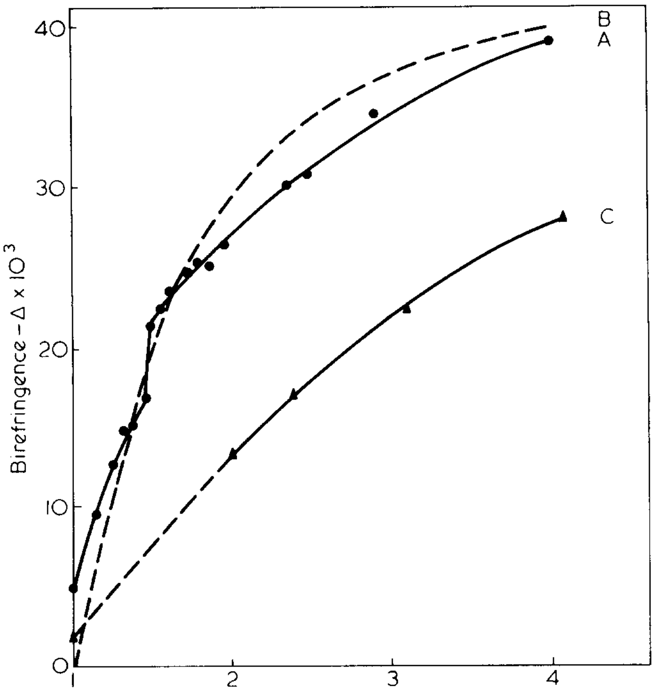


*Figure 8* The birefringence of polyethylene films and its sulphochlorinated product as function of the cold draw ratio. A, Ipethene 323; B, from Norris and Stein[18]; C, Sulphochlorinated Ipethene 323, 2.4 meq/g $SO_2Cl$

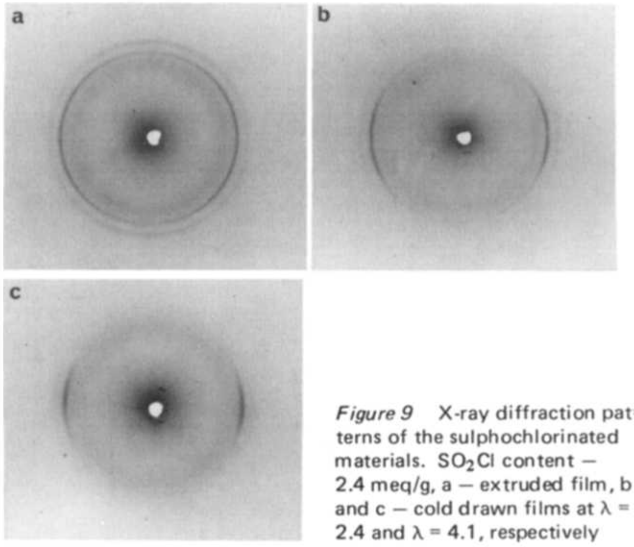


*Figure 9* X-ray diffraction patterns of the sulphochlorinated materials. $SO_2Cl$ content – 2.4 meq/g, a – extruded film, b and c – cold drawn films at λ = 2.4 and λ = 4.1, respectively

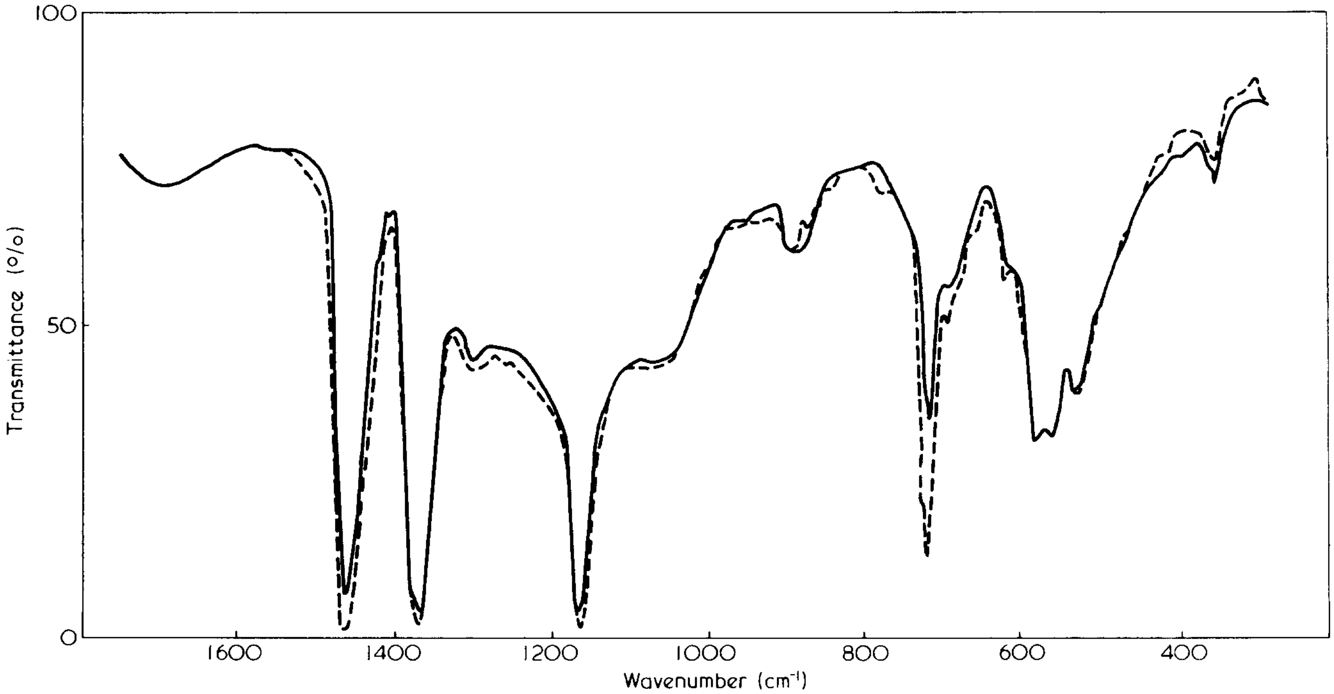


*Figure 10* Polarized infrared spectra of the sulphochlorinated materials. $SO_2Cl$ – 1.8 meq/g, Cl – 2.8 meq/g. Full and dotted lines refer to light polarized in parallel and perpendicular to the extrusion or stretching direction

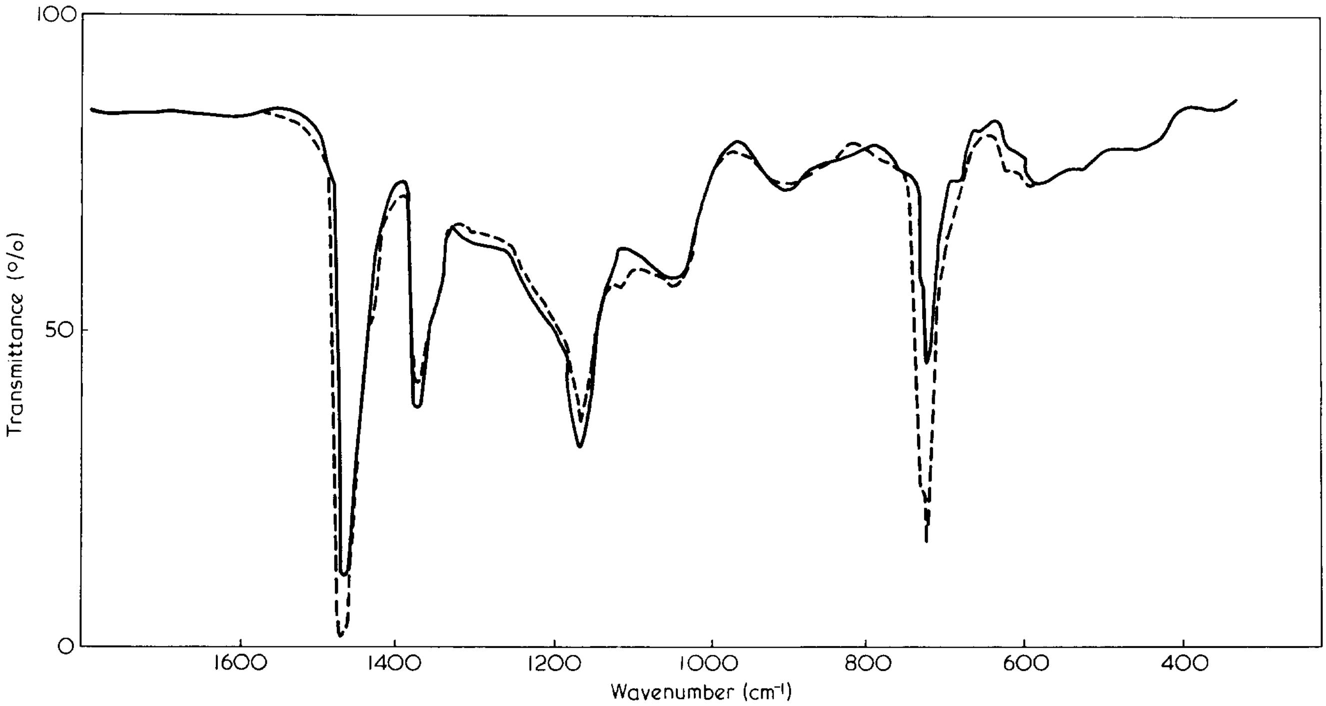


*Figure 11* Polarized infrared spectra of an ion exchange membrane in its acidic form. IEC = 0.8 meq/g. (Membrane prepared from Ipethene 323, $\lambda$ = 3.9). Full and dotted lines refer to light polarized in parallel and in perpendicular to the stretching direction, respectively.

C–Cl and C–S stretching and to the symmetric and asymmetric stretching of the $SO_2$, respectively[19,20].

Attention is drawn to the perpendicular dichroic character of these bands. Stronger absorption of light polarized in the direction perpendicular to the stretching could be expected from consideration of the orientation of the Cl and $SO_2Cl$ groups in respect to the paraffinic chains. A more comprehensive discussion of the polarized i.r. spectra of various chlorosulphonated polyethylenes and information provided by such analysis will be given elsewhere[21].

### *Ion exchange membranes*

Hydrolysis of the sulphochlorinated materials yields cation exchange membranes. Their polarized i.r. spectra are shown in *Figure 11.*

The effect of the organization of polymeric chains on the diffusivity of small molecules, which was noted during the chlorosulphonation step, is again evident from the rates of hydrolysis of various chlorosulphonated samples. Rates of such heterogeneous hydrolysis depend on the diffusion of water and NaOH molecules to the active sites, and must be affected by the morphology of the polymeric network.

Differences in the rates of hydrolysis due to orientation of the polymeric chains in the sulphochlorinated films proved to be very large, particularly at relatively low sulphochlorination levels. Thus, immersion in 1N NaOH for 24 h at room temperature was sufficient for hydrolysis of 99% of the sulphonyl chloride groups in an unoriented sample while more than 3 weeks were required to achieve this result in a highly oriented sampled. (The initial $-SO_2Cl$ content was 1.1 meq/g.)

Swelling of the membranes by water, accompanying their hydrolysis, tends to lead to irreversible disorientation. This may be seen from the X-ray diffraction patterns in *Figure 12* and from the birefringence results in *Figure 13.* Organization is preserved, however, in samples which were initially very strongly orientated ($\lambda > 3.9$). In such membranes the orientation of crystallites is maintained upon swelling with water, even for high concentration of ionic groups (see *Figure 12c, d*). This, however, is not always true for the amorphous regions.

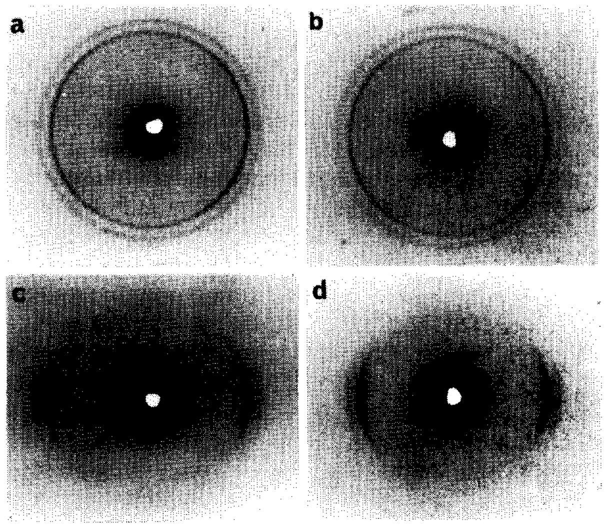


*Figure 12* X-ray diffraction patterns of hydrolysed membranes. (a) prepared from extruded film, IEC = 1.85 meq/g; (b) and (c) prepared from cold drawn films at $\lambda$ = 2.4 and $\lambda$ = 4.1, respectively. IEC = 2.4 meq/g. (d) film shown in (c) before drying. Samples shown in (a), (b), (c) were dried in high vacuum after hydrolysis

Information about the orientation of the amorphous phase in water swollen membranes has been obtained from the fluorescence probe measurements. Large fluorescent organic cations, which were used in these experiments cannot penetrate into crystallites. Their orientation reflects on the orientation of polymeric chains in the amorphous regions only. It is evident from data summarized in *Table 3* that at very high ion exchange capacities the orientation of the

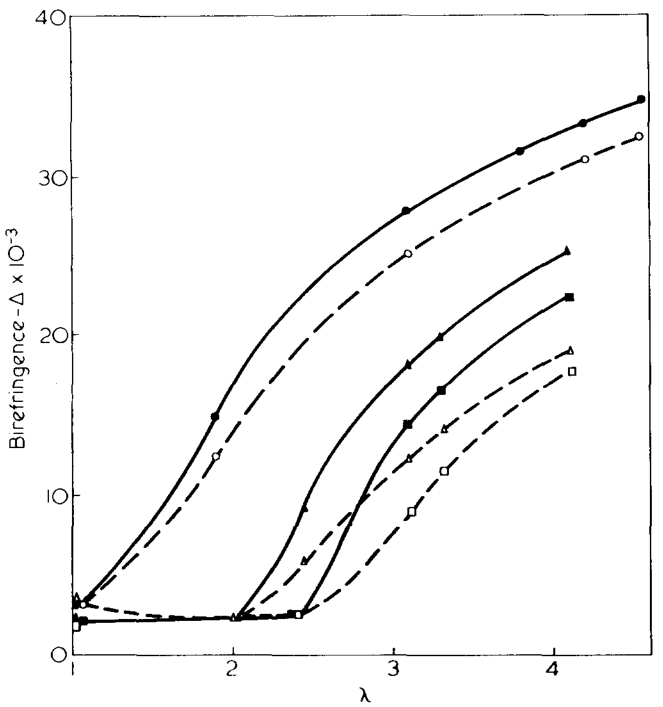


*Figure 13* The birefringence of the ion exchange membranes prepared from Ipethene 323 as function of the cold draw ratios of the polyethylenic precursors. Dotted and full lines refer to water swollen membranes before drying and to dried membranes respectively. ○, ● – IEC = 1.1 meq/g; △, ▲ – IEC = 2.4 meq/g; □, ■ – IEC = 2.8 meq/g

*Table 3* Fluorescence probe polarization measurements[a] of water swollen ion exchange membranes

| Sample | | | | |
|---|---|---|---|---|
| IEC meq/g | λ | $P_s$ | $P_t$ | $P_s/P_t$ |
| 0.8 | 3.9 | 0.220 | 0.111 | 1.98 |
| 0.8 | 5.0 | 0.248 | 0.095 | 2.6 |
| 1.1 | 1.9 | 0.170 | 0.147 | 1.16 |
| 1.1 | 3.9 | 0.204 | 0.112 | 1.82 |
| 1.1 | 5.0 | 0.230 (0.365)[b] | 0.099 (0.136)[b] | 2.32 (2.68)[c] |
| 1.85 | 4.1 | 0.035 (0.18)[b] | 0.031 (0.155)[b] | 1.13 (1.16)[c] |

[a] Emission wavelength 420 nm. Excitation wavelength 360 nm

[b] Numbers in brackets refer to samples frozen to 0° C

[c] The effect of the rotational depolarization of the fluorescent probe on the $P_s/P_t$ ratio does not seem to be very significant.

amorphous phase nearly vanishes upon swelling of the hydrolysed products with water. However, at ion exchange capacities not exceeding 1.1 meq/g the orientation attained upon cold drawing of the polyethylenic precursor to 300–400%, prevails also in the hydrolysed membranes. Water uptakes of such membranes do not exceed 12%.

Because of possible changes in the organization of polymeric networks of the membranes as result of water swelling during hydrolysis, the effect of cold drawing of the precursors on the water uptake of the final ion exchange membranes is rather complicated. At high drawing ratios the original orientation of the polymeric chains is preserved at least partially in the exchange membranes and as expected water uptake decreases with the increase in λ. The anisotropy of such membranes is reflected by the anisotropy of their electrical resistance. Thus, membrane of ion exchange capacity of 2.4 meq/g prepared from film cold drawn to λ = 4.1 have an electrical resistivity of 27.8 ohm.cm in parallel and of 39.5 ohm.cm perpendicular to the stretching direction. However, as may be seen from *Figure 14*, water uptake may reach maximum at intermediate values of λ. The position of such a maximum is dependent on the ion exchange capacity of the membrane. This rather unexpected behaviour may be explained as follows: in partially oriented samples the sulphochlorination will be preferentially directed towards the remaining unoriented regions. The distribution of the hydrophilic sulphonic groups in the final membrane may, therefore, be quite uneven, and high local concentrations of ionic groups may be attained in certain regions. In such regions, large water clusters will be formed and the overall water uptake will increase.

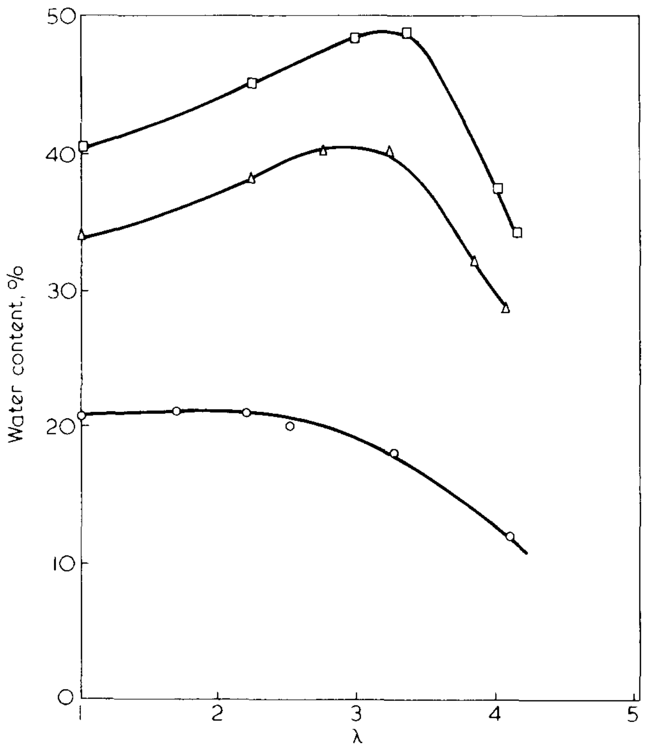


*Figure 14* Water uptake of the ion exchange membrane as function of the cold draw ratios of the polyethylenic precursors. Membranes in the Na$^+$ form with ion exchange capacities (IEC) of 1.8–2.8 meq/g. ○ – 1.8 meq/g; △ – 2.4 meq/g; □ – 2.8 meq/g

It is also interesting to note that the water swelling characteristics correlate with the birefringence results. Namely, as may be seen from *Figure 13*, the membranes begin to show birefringence only at λs close to those corresponding to the maximum water uptakes.

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