Polarized infra-red studies of sulphochlorinated polyethylene and products of its hydrolysis

Benjamin Bikson, Joseph Jagur-Grodzinski and David Vofsi
Department of Plastics Research, The Weizmann Institute of Science, Rehovot, Israel

(*Received* 30 *April* 1980)

Band assignments in the polarized i.r. absorption spectra of sulphochlorinated polyethylene are discussed. The absorption band at 720 cm^{-1} and computer-resolved absorption spectra in the 1000–1600 cm^{-1} region have been used for conformational analysis of the reaction products. It has been concluded that *gauche* methylene sequences are preferentially attacked during the heterogeneous sulphochlorination of polyethylene. However, *gauche* and *trans* methylene sequences seem to be equally susceptible to chlorination. Analysis of the dichroic character of the i.r. absorption bands of products obtained from preoriented polyethylene films enabled us to elucidate the conformation of SO_2Cl groups attached to the polymeric chains. The orientation of the parent polyethylene is preserved to a large extent in the sulphochlorinated materials and in the products of their hydrolysis.

INTRODUCTION

Polarized infra-red spectroscopy has proved useful in the study of polymer morphology[1]. Together with X-ray diffraction and birefringence measurements it has been used for the elucidation of the structure of polyethylenes[2–4]. It allows the number of the chain elements in the crystalline and in the amorphous components to be established together with their orientation and the conformation of chain segments in the amorphous phase. New bands which arise upon introduction of chlorine or sulphonyl chloride groups into the paraffinic chain can again be used to characterize the orientation of the adjoining polymeric segments. Several investigators dealt with the i.r. spectra of chlorinated[5–7] and sulphochlorinated paraffins[8,9] and the assignment of several bands in the spectrum of a sulphochlorinated polyethylene has been given by Smook *et al.*[10]. Oriented sulphochlorinated polyethylenes have recently been prepared in this laboratory[11].

This investigation is concerned with the elucidation of the structure of sulphochlorinated polyethylenes obtained by the heterogeneous introduction of SO_2Cl and chlorine into an oriented polyethylene matrix. Here, an analysis of various features of the polarized infra-red spectra of these materials is given, and the effects of segment conformation on susceptibility to chemical attack is discussed.

EXPERIMENTAL

Sample preparation

Cold drawn samples were prepared from commercial blow extruded polyethylene film, 90 μm thick (Ipethene 323, $d = 0.921$ g cm^{-3}, *MFI* 2.0, Petrochemical Industries, Haifa) as described elsewhere[11]. Unoriented films, 30 μm thick, were prepared by compression moulding of the blow extruded Ipethene 323 films, by heating them at 180°C between Teflon sheets in a mould cut from 30 μm shim stock and sandwiched between two 1/8 in. stainless steel plates. After 10 min at 20 000 p.s.i., samples were removed from the press, quenched by immersion in cold water (20°) and dried in a vacuum oven at room temperature. The birefringence of samples prepared in this manner was less than 1×10^{-3}.

Sulphochlorination and chlorination procedures

Various polyethylene films were sulphochlorinated by bringing them in contact with carbon tetrachloride solution saturated with a gaseous mixture of sulphur dioxide– and was added continuously at a rate of 0.24 g/h per l CCl_4. performed under analogous conditions in carbon tetrachloride solution saturated with chlorine gas at 15°C. Methyl ethyl ketone hydroperoxide was used as initiator, and was added continuously at a rate of 0.24 g/h per 1 CCl_4.

Infra-red measurements

A 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° and −45° to the spectrometer slit[1]. A normal slit programme and a low scanning speed were used. The dichroic ratios were calculated from the expression:

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

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

Computer resolution of i.r. spectra

The γ_i and T_i coordinates of the i.r. transmittance curves were digitized using a D-MAC digitizer. Values of $A_i = \log(T_0/T_i)$ were calculated from the transmittances, and the computer resolution of the spectra carried out assum-

0032-3861/81/050640-07$02.00

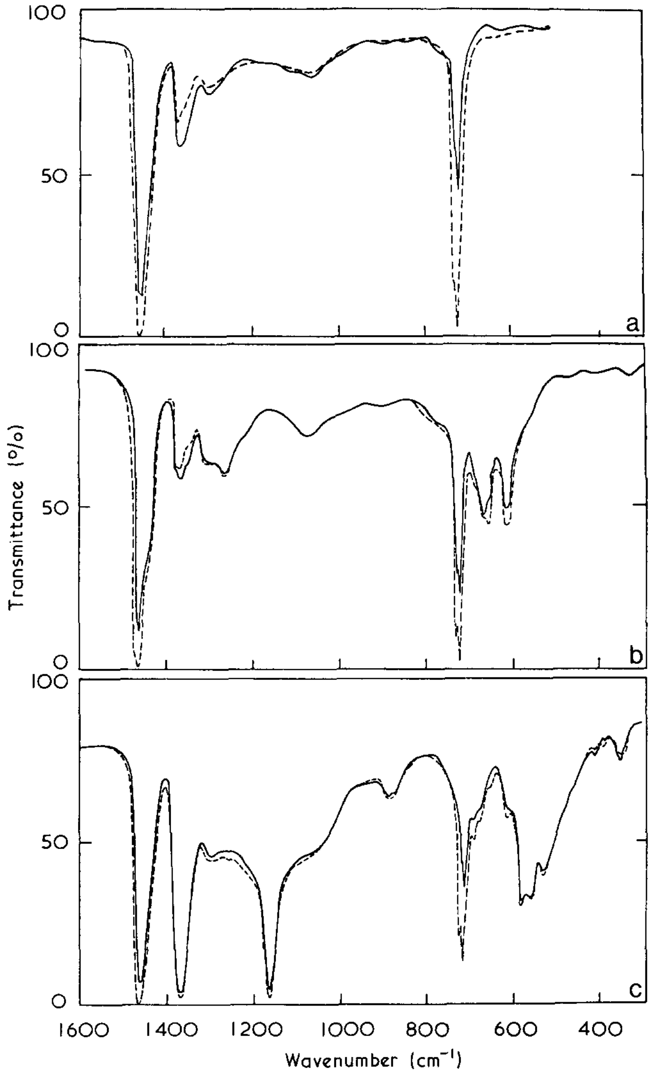


Figure 1 Polarized i.r. spectra of polyethylene and its reaction product: (a) parent polyethylene, draw ratio λ = 4.1; (b) chlorinated product, Cl = 3.2 meq g^{-1}; (c) sulphochlorinated product, SO_2Cl = 1.1 meq g^{-1}, Cl = 0.9 meq g^{-1}. Full and broken lines refer to light polarized in parallel and in perpendicular to the stretching direction, respectively

ing Lorenzian absorption peaks. The computer programme utilized a general optimization package with algorithms for minimizing the sum of squares, which may be non-linear and may have constraints imposed. Curve fit was adjusted by minimizing the discrepancy defined as $[\Sigma\Delta^2/n]^{1/2}$, where Δ is the difference between the calculated and experimental points and n is the number of points considered.

RESULTS AND DISCUSSION

Polarized i.r. spectra of a cold drawn polyethylene film and of its reaction products are shown in *Figure 1*. The dichroic character of various absorption bands in the chlorinated and sulphochlorinated films is evident. The spectrum of the chlorinated product, PC, is given to help in the assignment of the absorption bands in the sulphochlorinated material, PS, since during the sulphochlorination reaction a considerable chlorination of the polymeric chains takes place along with the sulphochlorination.

Assignment of the infra-red bands

The assignment of principal bands in these spectra is summarized in *Table 1*. It was partly based on comparison with i.r. spectra of primary and secondary paraffin sulphonylchlorides[8,9] and with the i.r. spectra of polyethylene[13], and its chlorination products of low chlorine content[5]. The dichroism of the i.r. absorption bands in the oriented sulphochlorinated polyethylene film was useful in verifying the assignments since it enabled comparison of the observed character of various absorbance peaks of the reaction product with those predicted on the basis of chain orientation in the polyethylenic precursor. The dichroic behaviour of various absorption peaks of polyethylene and its reaction products is summarized in *Table 2*.

300–600 cm^{-1} region. Precise band assignment is difficult in the 300–600 cm^{-1} region due to the multiple character of most of the bands. For example, the medium 360 cm^{-1} band is assigned to S–Cl stretching mode, but there are probably some supplementary contributions of asymmetric SO_2 rocking and SO_2 twisting modes to this absorbtion band[8].

Strong bands at 538, 565 and 558 cm^{-1} are assigned to SO_2 deformational modes. This assignment is consistent with polarization of these bands in samples prepared by sulphochlorination of oriented polyethylene films.

600–800 cm^{-1} region. Several absorptions in the 600–800 cm^{-1} region are related to the chlorinated polymeric backbone. The only strong contribution of sulphonyl chlorides to this region is at 688 cm^{-1} (the C–S stretching mode of secondary sulphonyl chlorides).

We will discuss in some detail the assignment of the C–Cl stretching mode at 610 and 660 cm^{-1} because of its importance for the conformational analysis of chlorination products. The frequency of the C–Cl stretching modes is a function of the detailed structure in the vicinity of the C–Cl bond. Spectroscopically different structures may be described merely by specifying whether the chlorine atom is *trans* to hydrogen, carbon or chlorine atoms with respect to the carbon–carbon bond. Thus, for a CHCl unit surrounded on both sides by polyethylene

Table 1 Assignment of the principal i.r. absorption bands of chlorosulphonated polyethylene

Frequency (cm^{-1})	Relative intensity	Assignment	
1472, 1463	s	CH_2	Scissoring
1450–1440	s	CH_2 (α to CHX)	Scissoring
1368	s	SO_2	Antisymmetric stretching[a]
1300–1260	m	CH (in CHX)	Deformational
1160	s	SO_2	Symmetric stretching
870	w	CH_2 (α to CHX)	Rocking
720, 730	s	CH_2	Rocking
688	m	C–S	Stretching
680–640	m	C–Cl	Stretching
615–600	m	C–Cl	Stretching
588, 565, 538	s	SO_2	Deformational
365	w	S–Cl	Stretching

s = strong; m = medium; w = weak

[a] The CH_3 deformational mode at 1378 cm^{-1}, and CH_2 wagging modes at 1368 cm^{-1} and 1355 cm^{-1}, respectively, contribute to this band absorption

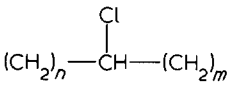
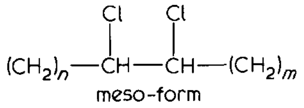
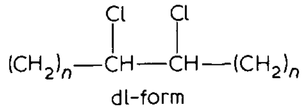
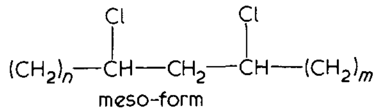
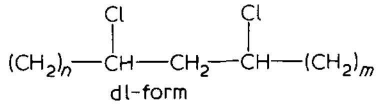
Table 2 Dichroic character of polyethylene precursor and its reaction products

Sample[a]	1472–1463	1368	1300–1280	1160	730	720	690	660	610	360
					Band (cm^{-1})					
P	⊥	∥	∥		⊥	⊥				
PS	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	∥
PC	⊥	∥	⊥		⊥	⊥		⊥	⊥	

[a] P, PS, PC = cold drawn polyethylene film and its chlorosulphonation and chlorination products, respectively

∥ and ⊥ designate a parallel or a perpendicular character of the absorption band

Table 3 Infra-red band assignment of the main configurational and conformational sequences of the chlorinated polyethylene backbone

Chemical structure	Backbone conformation[a]	C–Cl stretching (cm^{-1}) S_{HH}	S_{CH}	S_{ClH}	Model for the assignment
 $(CH_2)_n{-}\overset{Cl}{CH}{-}(CH_2)_m$	TG		663		4-Chlorooctane (ref 16)
	TT	611			
 $(CH_2)_n{-}\overset{Cl}{CH}{-}\overset{Cl}{CH}{-}(CH_2)_m$ meso-form	TTT			650	*meso*-3,4-Dichlorohexane (ref 17)
 $(CH_2)_n{-}\overset{Cl}{CH}{-}\overset{Cl}{CH}{-}(CH_2)_n$ dl-form	TG$^+$T			645	*dl*-3,4-Dichlorohexane (ref 17)
	TTT	632			
 $(CH_2)_n{-}\overset{Cl}{CH}{-}CH_2{-}\overset{Cl}{CH}{-}(CH_2)_m$ meso-form	TTTG	619	683		*meso*-2,4-Dichloropentane (ref 18)
 $(CH_2)_n{-}\overset{Cl}{CH}{-}CH_2{-}\overset{Cl}{CH}{-}(CH_2)_m$ dl-form	*TTTT*	597(B) 623(A)			*dl*-2,4-Dichloropentane (ref 18, 19)

[a] Only the main conformations for each chemical structure were considered

sequences the two main backbone conformations are *TT* and *TG*, leading to two absorption band in the i.r. spectra at 610 and 660 cm^{-1}, respectively, and assigned to S_{HH} and S_{CH} resonance modes, according to notation used by Krimm *et al.*[6,7]. In the chlorinated polyethylene backbone, especially at high chlorination levels, in addition to single CHCl units surrounded by unreacted polyethylenic sequences, the vicinal and 1,3-dichloride units are formed and must be considered in the spectral assignment of absorption peaks in this region. The spectral bands of the main conformations of these chlorinated structures in model compounds are summarized in *Table 3*. Analogous absorbtion bands in PS samples may be shifted to higher frequencies, since the force field is changed when the number of chlorine substituents in the chain is increased[14]. The frequency shift will be pronounced for vicinal dichlorides because of the coupling of the C–Cl stretching mode with low frequency skeletal modes. For example, in SRSR-2,3,6,7-tetrachlorooctane absorptions due to the S_{ClH} stretching modes are observed[14] at 650 and 690 cm^{-1}.

Quenum *et al.*[15] assumed that in chlorinated polyethylene the 660 and 610 cm^{-1} absorptions may be uniquely assigned to S_{CH} and S_{HH} stretching modes, respectively, and evaluated the conformation of the chlorinated backbone from the ratio of the integrals of these two bands. It seems, however, that since the vicinal dichloride sequences in the *trans* conformation may also contribute to the 660 cm^{-1} region, conformational analysis of chlorinated products based on the 610 cm^{-1}/660 cm^{-1} ratio will be misleading at high degrees of substitution. Indeed, inspection of the spectrum shown in *Figure 1b* reveals that the 660 cm^{-1} band may be resolved into the 660 cm^{-1} and 642 cm^{-1} peaks. We suggest that the 642 cm^{-1} peak should be assigned to vicinal dichloride sequences with *trans* backbone conformation. Integrals of the 610 cm^{-1} and of the resolved 642 cm^{-1} and 660 cm^{-1} peaks, therefore, must be used for accurate evaluation of the conformational features of the chlorinated polyethylene backbone.

The self-consistency of this approach is indicated by the analysis of the dichroic ratios of these peaks. For example, in a sample obtained by chlorination of polyethylene, cold drawn in the extrusion direction to a draw ratio of 4.1, the dichroic ratios of the 610 cm^{-1}, 642 cm^{-1} and 660 cm^{-1} peaks are 0.85, 0.79 and 0.96, respectively. The high perpendicular dichroism of the 642 cm^{-1} peak is consistent with its assignment to *trans* backbone sequences.

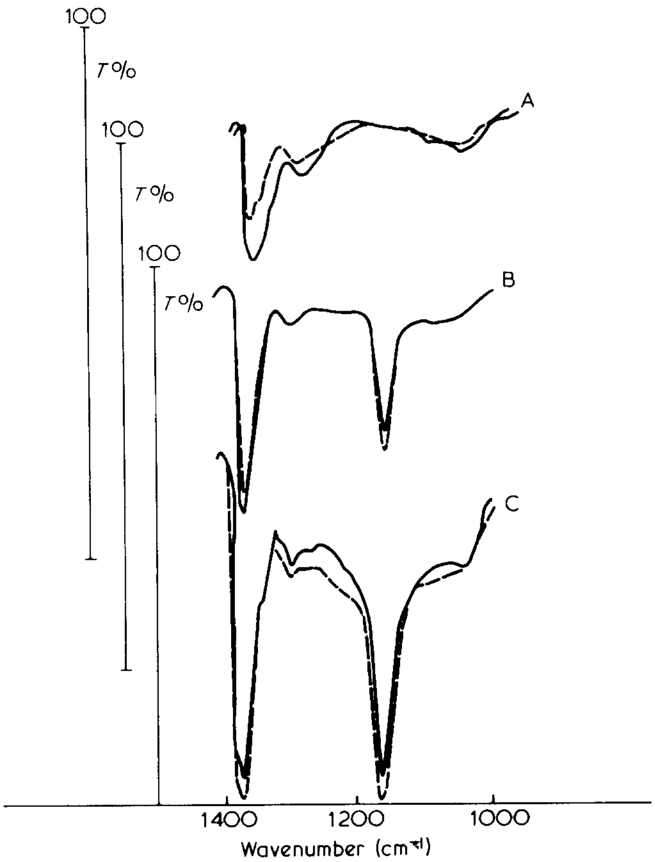


Figure 2 Effect of sulphochlorination on the dichroic character of the i.r. spectrum in the 1000–1400 cm^{-1} region. (a) Unsubstituted polyethylene, draw ratio $\lambda = 4.1$; (b) sulphochlorinated product, SO_2Cl = 0.3 meq g^{-1} (1.0% S); (c) sulphochlorinated product, SO_2Cl = 1.0 meq g^{-1} (3.2% S). Full and broken lines refer to light polarized in parallel and in perpendicular to the stretching direction, respectively

An absorption band at 730–800 cm^{-1} appears in the spectra of PC and PS at high degrees of substitution. Quenum and coworkers[15] assigned absorptions in this region to the vibrational modes of CHCl units, Gates *et al.*[16] to CH_2 rocking modes, and Krimm *et al.*[7,19] to S_{CC} stretching vibrations. Assignments suggested by Quenum *et al.* and by Gates *et al.* are inconsistent with our experimental findings, since we observe the 730–800 cm^{-1} absorption band only at high degrees of substitution. This behaviour is to be expected according to assignment suggested by Krimm *et al.*, since the latter assignment implies contributions of S_{CCl}, S_{ClS} and S_{CS} to this region.

The CH_2 rocking mode at 720 and 730 cm^{-1} of the polyethylenic precursor is also found in the products of its heterogeneous sulphochlorination and chlorination. The 720 cm^{-1} band contains components due to both crystalline and amorphous phase. The crystalline component arises from out-of-phase CH_2 rocking mode and is polarized along the *b* crystallographic axis[20,21]. The amorphous component is assigned to CH_2 rocking modes of chain segments in the *trans* conformation and is associated with sequences of more than four *trans* bonds. The amorphous component has a transition moment perpendicular to the chian axis. The 730 cm^{-1} band arises from the crystalline phase and is assigned to in-phase CH_2 rocking mode for the two chains in the unit cell; it was found to be polarized along the *a* axis of the crystal. In stretched polyethylene samples both bands possess a strong perpendicular dichroic character. This dichroism is preserved in the sulphochlorinated polyethylene samples, although at high degrees of substitution a decrease in the dichroic ratios is observed. This seems to indicate that some disorientation may be taking place as a result of extensive sulphochlorination.

800–1500 cm^{-1} region. A weak band appears at 870 cm^{-1} in the spectrum of sulphochlorinated polyethylene at high conversions; it is assigned to the $-CH_2-$ rocking mode of the $-CHCl-CH_2-CHSO_2Cl-$ and $-CHCl-CH_2-CH_2-CHSO_2Cl-$ structures. Similar assignments for the CH_2 rocking modes of methylenes adjacent to $CHSO_2Cl$, CHCl, and CCl_2 have previously been proposed[9,15,19,22].

The continuous absorption of sulphochlorinated polyethylene samples in the 1200–1300 cm^{-1} region is composed of the $-CH_2-$ wagging mode of the polymeric backbone, ≈ 1300 cm^{-1}, the weak $-CH_2-$ twisting mode, ≈ 1210 cm^{-1}, the CH deformation mode of $-CHSO_2Cl-$ units, and the CH deformation mode of $-CHCl-$ units at 1260 cm^{-1} (the absorption of the latter is strong in chlorinated polyethylene spectra).

The two strong absorption bands that appear at 1160 and 1368 cm^{-1} in the sulphochlorinated polyethylene spectra were identified[10] as the symmetric and antisymmetric stretching modes of SO_2, respectively. There is also some contribution of the CH_3 deformation mode (1378 cm^{-1}) and of the $-CH_2-$ wagging modes (1368 and 1352 cm^{-1}) to the antisymmetric stretching of SO_2 at 1368 cm^{-1}. The dichroic character of the CH_3 deformation and the $-CH_2-$ wagging modes is parallel in the spectra of oriented samples, while the SO_2 symmetric and antisymmetric stretching modes possess a perpendicular dichroic character. The contribution of CH_2 wagging modes to the SO_2 antisymmetric stretching can reverse the dichroic character of this band to parallel in the spectra of sulphochlorinated polyethylene samples with low SO_2Cl contents. Only at high conversions does the perpendicular dichroic behaviour of the SO_2 antisymmetric stretching become dominant (*Figure 2*). The characteristic splitting of the CH_2 scissoring mode appears at 1463–1472 cm^{-1} in the spectrum of polyethylene. At high degrees of conversion it is possible to distinguish between $-CH_2-$scissoring modes of the unreacted polyethylene segments (1463–1472 cm^{-1}) and of CH_2 groups near sulphochlorinated and chlorinated units (1445–1455 cm^{-1}). The band is shifted with the increase of chain substitution. The dichroic character of the new band is less pronounced than that of the CH_2 scissoring mode of the unreacted polyethylene.

Conformation of polymeric segments

The conformation of methylene sequences in polyethylene may be expected to affect their susceptibility to substitution by such bulky substituents as SO_2Cl. Indeed, inspection of molecular models reveals that attachment of SO_2Cl to a *TTT* segments is sterically hindered and requires a *trans–gauche* conformational transition (*Figures 3* and *4*). It follows that *gauche* sequences should be preferentially attacked during heterogeneous sulphochlorination of polyethylene. Such steric restrictions do not apply to chlorine substitution. The latter may be expected, therefore, to proceed indiscriminately. Conformational analysis of the i.r. spectra of polyethylene and its reaction products at low degrees of substitution provides experimental evidence for these predictions. Conformational assignments for several i.r. absorption bands of polyethylene are reported in the literature[3,4,23]. The 1303 cm^{-1} band has been assigned to the twisting mode of CH_2 in a *gauche* conformation and the wagging mode of the *GTG* and *GTG'* methylene sequences. The 1352 and 1368 cm^{-1} bands have been assigned to the wagging modes of the *GG*+*GTG* and *GTTG* methylene sequences, respectively. The scissoring and rocking modes of the long *trans* methylene sequences in the amorphous phase contribute to the 1463 and 720 cm^{-1} frequencies, respectively. In sulphochlorinated polyethylene the SO_2 antisymetric stretching at 1368 cm^{-1} absorbs strongly in the 1300–1500 cm^{-1} region. However, resolution of methylene bands becomes possible upon hydrolysis of $-SO_2Cl$ leading to formation of SO_3^-. When SO_3^- is in the form of its Rb^+ salt, the SO_3^- antisymetric stretching band at 1200 cm^{-1} is almost unperturbed by the counterion and its absorption band is relatively sharp. This peak does not contribute strongly to the absorption in the adjacent 1300–1400 cm^{-1} region, and the i.r. spectrum can be easily resolved by the computer simulation technique. Computer resolution of the i.r. absorption spectrum was first used by Pohl and Hummel[24] to obtain detailed information about the overlapping configurational and conformational bands of the C–Cl stretching modes, and is now extensively applied in infrared spectroscopy.

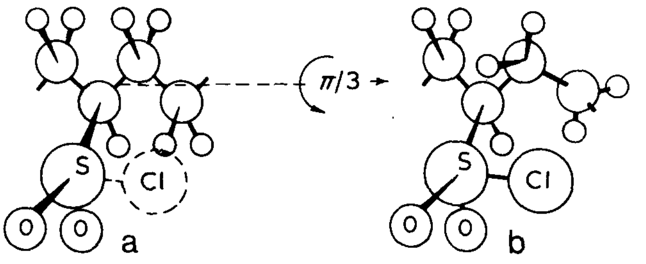


Figure 3 Spatial representations of $CH_2CHSO_2ClCH_2CH_2$ corresponding to different backbone conformations. (a) *TTT*; (b) *TGT*

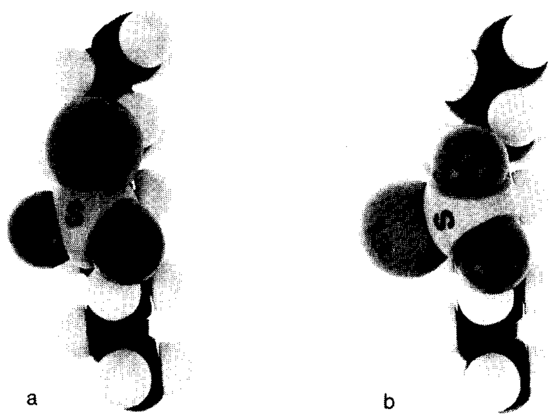


Figure 4 Molecular models of the two preferred conformations for SO_2Cl attached to a *TGT* sequence

The computer resolved spectrum of the parent polyethylene and of its sulphochlorinated product, after hydrolysis and conversion into its rubidium salt, is given in *Figure 5*. The degree of substitution of this sample by SO_2Cl and by chlorine was 1.8 and 1.5%, respectively.

The fit of the experimental points to the computer-simulated line is gratifying. The reliability of the resolution is also indicated by the fact that the line shape parameters of the resolved CH_2 and CH_3 absorption peaks in the initial polyethylene and in its reaction product deviate by less than 5% (with the exception of the 1302 cm^{-1} peak). Relative intensities of the resolved peaks and their lineshape parameters are summarized in *Table 4*.

The intensity of the absorption at 1378 cm^{-1}, corresponding to the methyl deformation mode, is not affected by the reaction. This result is consistent with the low chemical reactivity of the primary hydrogens of CH_3.

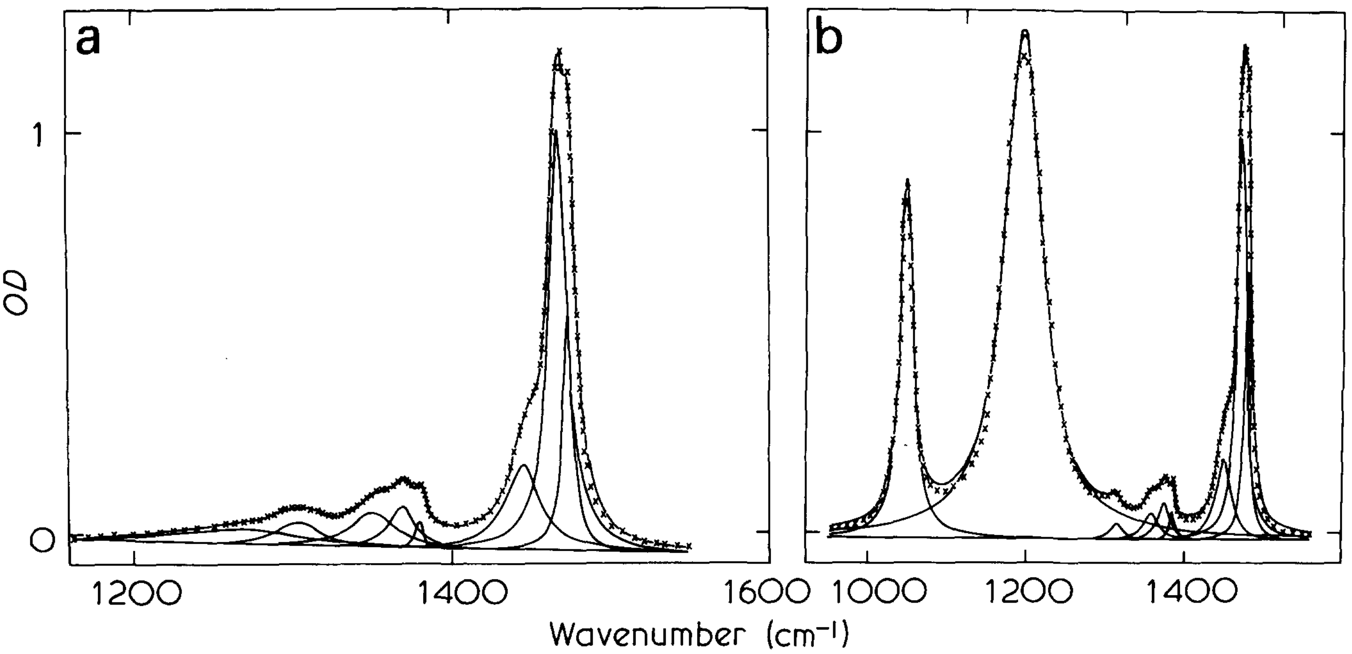


Figure 5 Computer resolved i.r. absorption spectra in the 1000–1600 cm^{-1} region. x, Experimental points; upper line –simulated spectrum. (a) Parent polyethylene; (b) rubidium salt of the product of hydrolysis of sulphochlorinated polyethylene, SO_3^- = 1.1 meq g^{-1}, Cl = 0.9 meq g^{-1}

Table 4 Intensities and line shape of the i.r. absorption bands in the computer-resolved spectra of polyethylene and its reaction products

	Degree of substitution		w CH_2 *GG*		w CH_2 *GTG* + *GG*		w CH_2 *GTTG*		δ CH_3		δ CH_2		δ CH_2		δ CH_2	
			1302 cm^{-1}[a]		1351 cm^{-1}		1368 cm^{-1}		1379 cm^{-1}		1445 cm^{-1}[b]		1463 cm^{-1}		1472 cm^{-1}	
Sample	SO_2Cl	Cl	*I*[c]	$H/\Delta_{0.5}$[d]	*I*	$H/\Delta_{0.5}$	*I*	$H/\Delta_{0.5}$	*I*	$H/\Delta_{0.5}$	*I*	$H/\Delta_{0.5}$	*I*	$H/\Delta_{0.5}$	*I*	$H/\Delta_{0.5}$
P	–	–	79	3.9	136	5.9	106	12.1	21	24	299	18	850	156	265	162
PS	0.0185	0.0155	40	4.9	82	5.8	93	13.1	20	21.8	284	19	830	155	270	169
PC	–	0.07	83	4.8	118	5.9	99	13.5	22	26.0	308	17	825	154	258	158

[a] 1307 and 1309 cm^{-1} in PS and PC spectra, respectively
[b] 1443 and 1442 cm^{-1} in PS and PC spectra, respectively
[c] *I* = integral band absorbance in arbitrary units
[d] $H/\Delta_{0.5}$ = line shape parameter; band height divided by band half width

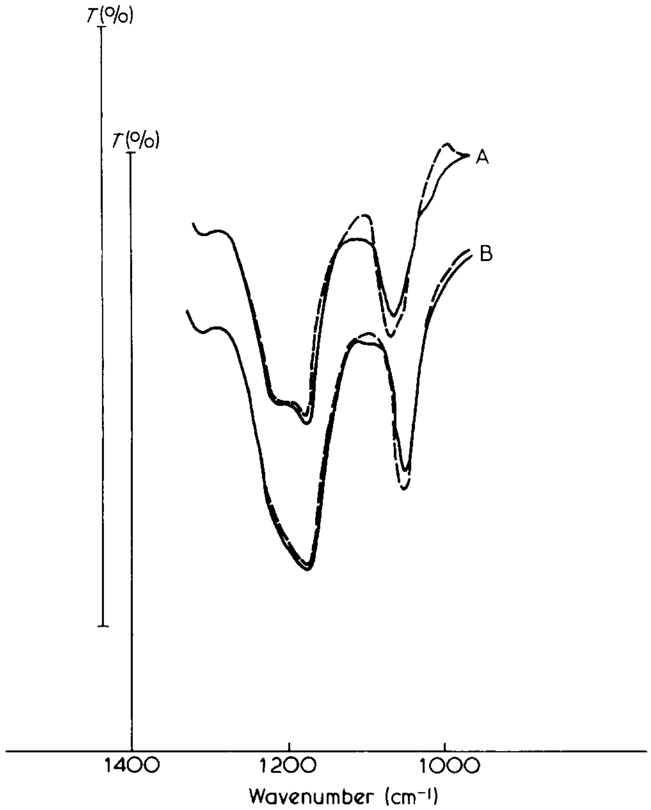


Figure 6 Effect of counterion on the polarized i.r. spectrum of the sulphonated polyethylene. SO_3^- = 0.7 meq g^{-1}, Cl = 0.6 meq g^{-1}. A, Counterion, Li^+; B, Rb^+

Furthermore, it is evident from the tabulated data that the intensities of peaks at frequencies corresponding to the absorption modes of *gauche* methylene sequences decrease by 20–35% as a result of sulphochlorination*, while those corresponding to the *trans* methylene sequences are not affected significantly, and changes in the intensities of these peaks remain within the limits of experimental error. Comparison of the effects of sulphochlorination with those due to chlorination is interesting. It may be seen from the last line in *Table 4* that even at relatively high degrees of chlorine substitution (0.07) the intensities of the absorptions due to *gauche* methylene sequences decrease by only 8–9%. These results clearly indicate that the *gauche* and *trans* sequences are equally susceptible to chlorine substitution, while the *gauche* sequences are preferentially substituted by SO_2Cl. The magnitude of the observed effects may be interpreted in terms of an exclusive substitution of *gauche* sequences by SO_2Cl during the early stages of the sulphochlorination reaction. Let us assume that the fraction of *gauche* sequences represents 20% of all methylenes and that each substitution leads to a reduction in the intensity of the *GTTG* absorption band corresponding to the elimination of absorption due to three CH_2 groups (substituted CH_2 and its two nearest neighbours). Using these assumptions we calculate that at the degree of substitution prevailing in the analysed sulphochlorination experiment, the intensity of the *GTTG* absorption peak should decrease by 32% if *gauche* sequences only are substituted by SO_2Cl and both *gauche* and *trans* sequences are indiscriminately substituted by chlorine. Thus, the estimated value is close to the experimentally observed decrease of 35% in the intensity of this peak.

Conclusions based on the analysis of the spectra in the 1300–1500 cm^{-1} region are supported by the observed changes in the intensity of the 720 cm^{-1} peak due to sulphochlorination and chlorination, respectively. Namely, this absorption band of the long *trans* sequences decreases by 7% for sulphochlorination and by 17% for chlorination (at an overall degree of substitution of 3.3%).

Chain configuration of sulphochlorinated materials

Inspection of polarized i.r. spectra of cold drawn sulphochlorinated films reveals that the C–S stretching mode of 688 cm^{-1} has a perpendicular dichroic character. This indicates that the SO_2Cl groups attached to polymeric chains are oriented perpendicular to the stretching direction. This is confirmed by the perpendicular dichroic character of the symmetric and the antisymmetric SO_2 stretching modes (see *Table 2*).

Random rotation of the SO_2Cl group around the C–S bond in sulphochlorinated polyethylene is impossible because of steric hinderance. Molecular models of the two thermodynamically preferable conformations are shown in *Figure 4*. The directions of the SO_2 stretching transition are mutually perpendicular but both are in the plane of SO_2 group. The dichroic character of SO_2 symmetric and antisymmetric stretching transitions has to be perpendicular for the A configuration of SO_2Cl group (*Figure 4*), because the SO_2 plane is oriented perpendicular to the chain axis (the stretching direction in this configuration). The dichroic character of the SO_2 antisymmetric and symmetric stretching modes has to be parallel and

---

* Quantitative interpretation of changes in intensity of the 1303 cm^{-1} peak cannot be justified because of inadequate resolution.

perpendicular, respectively, for the B configuration of SO_2Cl group. Since both SO_2 stretching modes have been found to have a perpendicular dichroic character in oriented sulphochlorinated polyethylene samples, the A structure must be prevalent in the sulphochlorinated compound.

It has been previously reported[11] that the orientation of the polymeric chains in the sulphochlorinated material is preserved during hydrolysis of the SO_2Cl groups, leading to the formation of the corresponding sulphonic acids. The polarized i.r. spectra in the 1000–1300 cm^{-1} region of the lithium and rubidium salts of such materials are shown in *Figure 6*. The Li^+ counterions shift the absorption band due to SO_3^- symmetric stretching to higher frequencies and splits the 1200 cm^{-1} band due to the antisymmetric stretching mode of SO_3^-. The effect of the counterion is much weaker in the case of Rb^+, as suggested by Zundel[25]. The parallel dichroic character of the antisymmetric stretching of SO_3^- and the perpendicular character of its symmetric vibrational mode are consistent with orientation of this group perpendicular to the polymeric chain, as expected from the orientation of the parent SO_2Cl.

ACKNOWLEDGEMENT

Dr H. Jarosh from the Computer Center of the Institute wrote the computer program for spectrum resolution; his assistance is gratefully acknowledged.

REFERENCES

1 Zbinden, R., 'Infrared Spectroscopy of High Polymers', Academic Press, New York (1964)
2 Stein, R. S. and Norris, F. H. *J. Polym. Sci.* 1956, **21**, 381
3 Reed, B. E. and Stein, R. S. *Macromolecules* 1968, **1**, 116
4 Glenz, W. and Peterlin, A. *J. Macromol. Sci.* (*B*) 1970, **4**, 473
5 Nambu, K. *J. Appl. Polym. Sci.* 1960, **4**, 69
6 Shipman, J. J., Folt, V. L. and Krimm, S. *Spectrochim. Acta* 1962, **18**, 1603
7 Opaskar, C. G. and Krimm, S. *Ibid.* 1967, **23A**, 2261
8 Hanai, K., Okuda, T. and Machida, K. *Ibid.* 1975, **31A**, 1227
9 Geiseler, G. and Bindernagel, K. O. *Z. Electrochem.* 1960, **64**, 421
10 Smook, M. A., Pieski, E. T. and Hammer, G. F. *Ind. Eng. Chem.* 1953, **45**, 2731
11 Bikson, B., Jagur-Grodzinski, J. and Vofsi, D. *Polymer* 1979, **20**, 215
12 Jagur-Grodzinski, J., Bikson, B. and Vofsi, D. 'Proc. 4th Int. Symp. on Fresh Water from the Sea' 1973, **4**, 171
13 Snyder, R. G. *J. Chem. Phys.* 1965, **42**, 1744
14 a. Demster, A. B. and Swinton, P. F. *J. Mol. Structure* 1974, **21**, 373 b. Demster, A. B. and Uslu, H. *Ibid.* 1974, **21**, 197
15 Quenum, B. M., Berticat, P. and Vallet, G. *Polym. J.* 1975, **7**, 277
16 Gates, P. N., Mooney, E. F. and Willis, H. A. *Spectrochim. Acta* (*A*) 1967, **23**, 2043
17 Stokr, J., Doskocilova, D., Sykora, S., Horhold, H. H. and Schneider, B. *Collect. Czech. Chem. Commun.* 1969, **34**, 1875
18 Schimanouchi, T. and Tasumi, M. *Spectrochim. Acta* 1961, **17**, 755
19 Krimm, S., Folt, V. L., Shipman, J. J. and Berens, A. R. *J. Polym. Sci.* (*A*) 1963, **1**, 2621
20 Stein, R. S., *J. Chem. Phys.* 1955, **23**, 734
21 Pakhmov, P. M., Shermatov, M., Korsukov, V. E. and Kuksenko, V. S. *Vysokomol. Soedin* (*A*) 1976, **18**, 132
22 Murayama, N. and Amagi, Y. *J. Polym. Sci.* (*B*) 1966, **4**, 119
23 Zerbi, G., Piseri, L. and Cabassi, F. *Mol. Phys.* 1971, **22**, 241
24 Pohl, H. U. and Hummel, D. O. *Makromol. Chem.* 1968, **113**, 203; *Ibid.* 1968, **113**, 190
25 Zundel, G. 'Hydration and Intermolecular Interation', Academic Press, New York, 1969