

The Structure of Chlorosulfonated Polyethylene

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The purpose of this work was to clarify the carbon-chlorine structure of chlorosulfonated polyethylene commercially available as Hypalon-20 synthetic rubber (Hypalon-20 is the registered trademark of E. I. du Pont de Nemours & Co., Inc. for its chlorosulfonated polyethylene). Hypalon-20 is an amorphous, vulcanizable, elastic polymer prepared by chlorinating and chlorosulfonating polyethylene. Its carbon-chlorine structure is, therefore, determined by the structure of its polyethylene precursor and by the kinetics of the chlorination. The base polymer used to prepare the chlorosulfonated polyethylene is a high pressure polyethylene which is known to contain both short and long chain branches.¹⁻³ Infrared analysis shows it to have 3 or 4 methyl groups for each 100 chain carbon atoms or a similar number of short chain branches.⁴ The length of these branches is not known accurately, but a length of four carbon atoms has been proposed as reasonable.⁵ Longer branches, arising from intermolecular hydrogen transfer, are thought to be attached to one carbon in each 100 chain carbon atoms.⁶ Unsaturation is negligible.

KINETIC ANALYSIS

Chlorosulfonation of the base polymer is carried out in carbon tetrachloride, with the use of chlorine, and a free radical catalyst. The reaction condi-

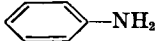
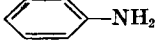
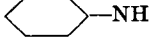
tions are adjusted to yield a material containing 31% chlorine and 1.2% sulfur. This analysis indicates that approximately 18 chlorine atoms and one SO₂Cl group are present for each 100 chain carbon atoms. Both the chlorine atoms and the SO₂Cl groups may be attached to primary, secondary, or tertiary carbon atoms in addition, secondary structures may be vicinal (—CHCl—CHCl—), 1,3-dichlorides (—CHCl—CH₂—CHCl—), or carbon-chlorine units separated by more than one methylene group.

To elucidate the distribution and structural types of chlorine atoms, the kinetic analysis developed by Salomon⁷⁻¹¹ was applied. The basis for this analysis is the variation in reaction rates between chlorides and amines as a function of (1) the structure of the chloride, (2) the basic strength of the amine, (3) the dielectric strength of the solvent, and (4) the reaction temperature.

The reagents and conditions used in this work are given in Table I.

In each of these systems the chlorides shown react completely within 150 hr., which makes it experimentally convenient to follow their rates. The sulfonyl chloride group reacts relatively fast under all conditions. Tertiary chloride reacts at a moderate rate only in Systems 1 and 2, whereas primary chloride reacts moderately only in System 3. Secondary (2°) chloride reacts very slowly under

TABLE I
Relative Rates of Amine-Chloride Reactions^a

System	Amine	Temp., °C.	Solvent, vol.-%	Chloride rate			
				Fast	Moderate	Slow	Very slow
1	 —NH ₂	50	None	—	—SO ₂ Cl, —Cl beta to —SO ₂ Cl	3°	1°
2	 —NH ₂	100	Nitrobenzene, 80%	—SO ₂ Cl, —Cl beta to —SO ₂ Cl	3°	1°	—
3	 —NH	50	Nitrobenzene, 80%	—SO ₂ Cl, —Cl beta to SO ₂ Cl	1°	—	3°

^a Data relating to primary (1°) and tertiary (3°) chlorides were taken from references 7-11.

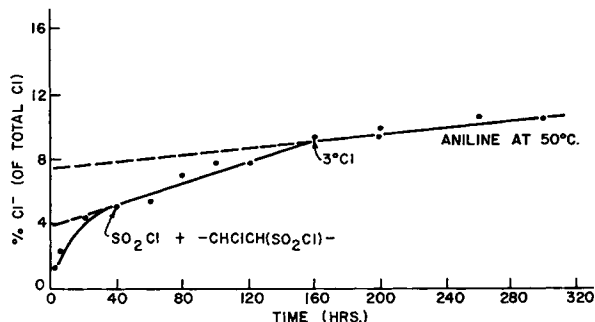


Fig. 1. Kinetic analysis of Hypalon-20.

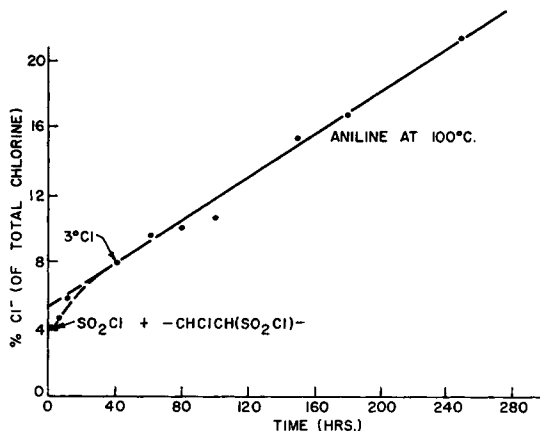


Fig. 2. Kinetic analysis of Hypalon-20.

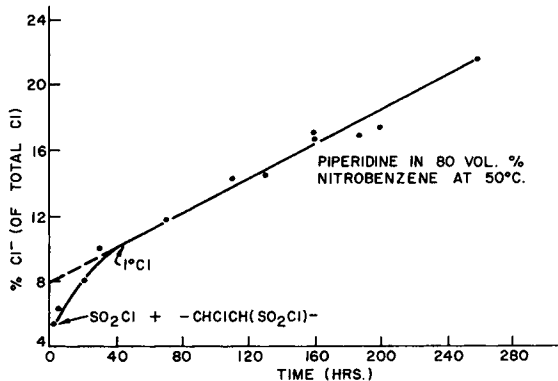


Fig. 3. Kinetic analysis of Hypalon-20.

all conditions. These differences in relative reaction rates allow the quantities of each chloride to be found experimentally.

The application of this analysis to chlorosulfonated polyethylene produced the results shown in Figures 1, 2, and 3. In Figure 1 the amount of chloride reacted is plotted as a function of reaction time for the conditions of System 1 (aniline at 50°C.). The first break in the curve is caused by the exhaustion of SO_2Cl groups and chlorides beta to them; the second break by the consumption

of 3° chloride. In Figure 2 are shown the results obtained with System 2. The first break represents both SO_2Cl and chlorides beta to them, and the second break represents 3° chloride. In Figure 3 are shown similar results for System 3, where now the two breaks in the curve represent SO_2Cl and chlorides beta to them and 1° chlorides respectively. Extrapolation of the straight sections of these curves to zero time yields quantitative measures of the chlorides present. The results are summarized in Table II.

TABLE II
Chloride Structures in Chlorosulfonated Polyethylene

Chloride	Hydrogen distribution (calc.) ^a	Chlorine distribution (calc.) ^b	Chlorine distribution (found)		
			Sys-tem 1	Sys-tem 2	Sys-tem 3
1°	5.8	2.1-2.3	—	—	2.7
3°	1.7	2.7-3.6	3.5	2.3	—
SO_2Cl + beta chloride	—	4.3 ^c	4.0	4.0	4.0
2° (by difference)	92.5	89.9-91	90.4 (avg.)		

^a Per cent of total hydrogen in polyethylene precursor calculated on the basis of 3-4 methyl groups per 100 chain carbon atoms.

^b Chlorine distribution expected from relative chlorination rates and calculated hydrogen distribution in polyethylene precursor.

^c Does not include chlorine beta to $-\text{SO}_2\text{Cl}$.

The second column in Table II shows the hydrogen structure of the polyethylene precursor for chlorosulfonated polyethylene. The third column shows the carbon-chlorine structures expected on chlorination of this polyethylene if the data and calculation of Hass¹³ for chlorination of simple hydrocarbons apply to this polymeric system. Hass' rate data were extrapolated to 70°C., the temperature at which the chlorination was carried out. At this temperature the relative chlorination rates for primary (1°), secondary (2°), and tertiary (3°) chloride are 1.0, 2.3-2.9, and 3.6-3.9, respectively. Recent work giving a 3° chlorination rate of 3.2 supports the validity of this extrapolation.¹³ It was assumed here that only a small amount of monochloride was carried to a higher chlorination state. There is close correspondence between the measured and the calculated results, indicating that the polymeric nature of the hydrocarbon did not affect the chlorination.

Sulfonyl Chloride

Sulfonyl chloride groups may also be attached to primary, secondary, or tertiary carbon atoms in the polyethylene chain.¹⁴ No attempt was made to differentiate these structures by kinetic analysis because the SO_2Cl group reacts very rapidly under all conditions. Since the calculated and experimental results for the chloride structures were in agreement, Hass' method¹² was used again, now to calculate the distribution of sulfonyl chloride groups. The extrapolation method described previously gives for the relative chlorosulfonation rates, on the basis of available literature data^{13, 16-17} primary, 1; secondary, 3; and tertiary, 6; these values give 2% primary, 94% secondary, and 4% tertiary sulfonyl chloride groups. However, there is considerable evidence that tertiary sulfonyl chloride groups are unstable^{13, 17-19} and with certain compounds do not form at all during chlorosulfonation.^{18,20} It has been shown that *tert*-butanesulfonyl chloride has a half-life of only 66 min. at 77°C.¹³ Consequently, the existence of tertiary sulfonyl chloride groups in chlorosulfonated polyethylene, prepared at temperatures of 70-77°C. is unlikely, and the distribution is probably 2.1% primary and 97.9% secondary.

Secondary Dichlorides

Most of the chlorine in chlorosulfonated polyethylene has a secondary structure as was found either by kinetic analysis or by calculation. The next problem considered was the structure of these secondary chlorides, which can exist as activated chlorides, vicinal ($-\text{CHCl}-\text{CHCl}-$), 1,3-dichlorides ($-\text{CHCl}-\text{CH}_2-\text{CHCl}-$), or as carbon-chlorine units separated by more than one methylene group.

Chlorines Beta to $-\text{SO}_2\text{Cl}$

Although the SO_2Cl group reacts with amines faster than most chloride structures, activated chlorines such as those beta to a sulfonyl chloride group will also react almost as rapidly. In Figure 4 is plotted the evolution of chloride as a function of time with piperidine as the amine and xylene as a solvent at 24°C. The amount of chlorine reacted under these mild conditions is always greater than the amount of chlorine in the SO_2Cl group. The chlorine associated with SO_2Cl was found by analyzing the polymer for sulfur. This difference, about 0.5% of the total chlorine, was assigned to the $-\text{CHClCH}(\text{SO}_2\text{Cl})-$ structure.

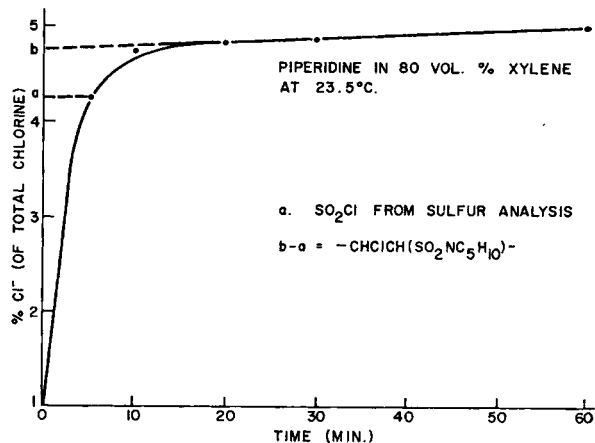
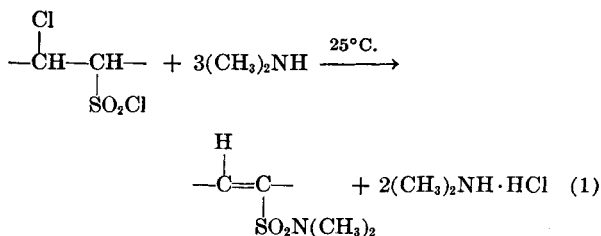


Fig. 4. Analysis for Cl^- beta to SO_2Cl .

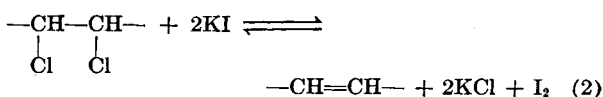
Chlorines *beta* to a carbon-bearing sulfonyl chloride function are highly activated toward base-catalyzed dehydrochlorination.²¹ When the subject polymer was treated at room temperature with a slight excess of dimethylamine, an infrared absorption band was found at 10.35μ characteristic of *trans* olefinic unsaturation in addition to the usual sulfonamide absorptions. As the sulfur content of the polymer was increased, treatment with dimethylamine resulted in a proportionate increase in the intensity of the $10.35\text{-}\mu$ band.



Both the chlorosulfonated polyethylene and its dimethylamine product have identical absorption maxima in their ultraviolet spectra appearing at 276 and 284 $m\mu$. The latter, however, had a third maximum appearing at 225 $m\mu$. This has been attributed to olefinic unsaturation in conjugation with the sulfonamide group and corresponds with an absorption maximum appearing in this same region for $\text{H}_2\text{C}=\text{CHSO}_2\text{N}(\text{C}_2\text{H}_5)_2$.²²

Vicinal Dichlorides

The reaction of vicinal dichloride with potassium iodide according to eq. (2), has previously been used as a qualitative test for this structure.^{23,24}



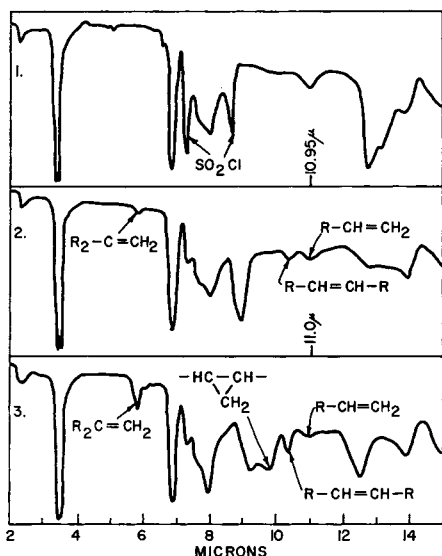


Fig. 5. (1) Hypalon-20; (2) Hypalon-20 after reaction with KI; (3) Hypalon-20 after reaction with zinc dust.

Its nonquantitative character has been ascribed to either a slow reaction rate or an unfavorable equilibrium. Either the loss of chlorine from the polymer or the appearance of I_2 may be followed. Both of these analyses gave the same result for chlorosulfonated polyethylene. A complication in the chlorosulfonated material is the possibility that I_2 is liberated by reaction of KI with SO_2Cl [eq. (3)].²⁵



To check this possibility, the polymer was first reacted with piperidine to block the SO_2Cl groups and then it was treated with KI. Identical results were obtained for both the blocked and unblocked material. The KI reaction showed 3% of the total chlorine to be reacted.

An infrared spectrum of the KI-treated polymer is shown in Figure 5-2, which should be compared

TABLE III
Infrared Analysis of Chlorosulfonated Polyethylene Treated with Zinc Dust and Potassium Iodide

Reagents	Infrared band, μ	Intensity ^a	Assignment ^b	Probable dichloride structure
KI, Zn	5.82	w	$R_2C=CH_2$	R_2CClCH_2Cl
KI, Zn	10.35	m	$RCH=CHR$	$RCHClCHClR$
KI, Zn	11.00	m	$RCH=CH_2$	$RCHClCH_2Cl$
Zn	9.8	s	Cyclopropane ring	$RCHClCH_2CHClR$

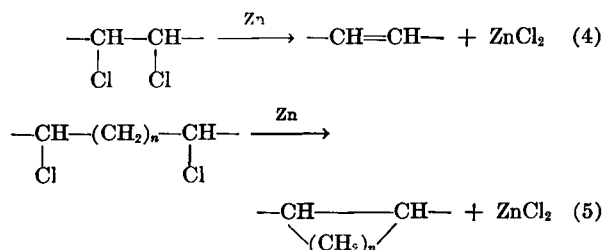
^a s = strong, m = moderate, w = weak.

^b From Bellamy (ref. 26).

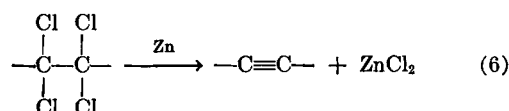
to the chlorosulfonated polymer shown in Figure 5-1. Although some changes are visible in the region of the SO_2Cl absorption, the most obvious change is the appearance of unsaturation bands in the KI-treated polymer. The assignment of these bands is given in Table III and is consistent with the reaction proposed above.

Other Dichlorides

In establishing the structure of polyvinyl chloride, Marvel²⁴ had to distinguish between vicinal and 1,3-dichlorides. His method involved reaction of the polymer with zinc dust and measuring the extent of reaction by the amount of $ZnCl_2$ formed. The infrared spectrum of the reacted polymer showed the cyclopropane ring confirming a head-to-tail arrangement, and the absence of olefinic absorption ruled out the possibility of a head-to-head or vicinal dichloride structure. His experimental procedure was applied to the subject polymer which, because of its more complicated chlorine structure, can react with zinc in a number of ways as shown by the following equations:



where $n = 1, 3, 4$, and



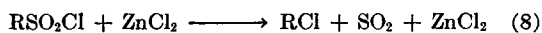
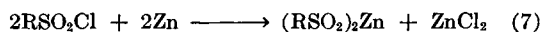
Chlorosulfonated polyethylene loses 17.7% of its chlorine on reaction with Zn dust in dioxane. On the basis of isolation of unreacted chlorines between reacted pairs this value is slightly low, although by analogy with polyvinyl chloride not more than 4%.²⁷ However, the failure of some 80% chlorine to react with Zn is unexpected in view of the preponderant amount of 1,4- and also 1,5- and 1,3-structures believed to be present.²⁸

A possible explanation is that the average, but not necessarily the representative, chlorine distribution is one chlorine for each six chain carbon atoms. This necessitates the highly unlikely formation of seven-membered rings. A further explanation is to be found in the extent and also

rate of reaction of various dihalides with Zn. High yields (72–80%)^{29,30} of cyclopropane are obtained by the reaction of 1,3-dihalopropanes with zinc dust. On the other hand, 1,4-dichlorobutane does not form cyclobutane, but yields butane in aqueous ethanol^{31,32} and undergoes a fragmentation reaction with zinc alone to give ethylene.³¹ As the number of methylenes separating the halogens is increased, the yield of the cyclization product is decreased. For example, cyclopentane is formed in undisclosed yield³³ and cyclohexane in only 44% yield³⁰ from the respective dihalides. Vicinal dihalides are more vulnerable to attack by zinc than those separated by one or more methylene groups where opportunity for free rotation permits various molecular configurations to exist, some of which are not properly predisposed sterically to favor reaction in pairs with zinc.³⁰ The hindrance to rotation decreases as the number of such methylene groups is increased³⁴ and is consistent with the lower yields noted above for the larger ring compounds. Unfortunately, yield data under comparable conditions are not available to permit a rigid comparison of the extent of reaction.

The reaction rate of zinc with 1,2- and 1,3-dihalides has been reported, but not confirmed elsewhere, to be faster than with 1,4- and 1,5-dihalides.³⁵ From yield and rate considerations and from the absence of five- and six-membered rings in the infrared spectrum of the reacted subject polymer, the reaction of zinc with chlorosulfonated polyethylene is believed to involve predominantly the reaction of the 1,2- and 1,3-dihalides.

The infrared spectrum of the zinc-treated polymer is shown in Figure 5-3. It indicates both olefinic unsaturation and cyclopropane structures, but no acetylenic band was found.²⁶ Band assignments are given in Table III. Weakening of the SO₂Cl bands and a 40% loss of sulfur from the polymer suggest the loss of SO₂Cl by the following reactions:^{36,37}



DISCUSSION

The relative rates of dichloride formation have been studied before. For example, in the chlorination of 1-chloropentane the relative rates of dichloride formation were found to be 1,4- \gg 1,5- > 1,3- > 1,2- > 1,1-.²⁸ The summary of the chlorine-carbon structures of chlorosulfonated polyethylene given in Table IV shows that the distri-

bution of these structures is consistent with the earlier work and that the "vicinal effect"^{38,39} of reduced substitution rate for hydrogens near a chlorine atom remains important in this polymeric system.

TABLE IV
Distribution and Structural Chlorine Types

Type	Structure	Total chlorine, wt.-%
Primary	R-CH ₂ -Cl	2.7
Secondary	R-CHCl-(CH ₂) _n -CHCl-R (n ≥ 2)	~71
Secondary	R-CHCl-CHCl-R	~18 ^a
Secondary	R-CHCl-CH ₂ -CHCl-R	
Secondary	R-CHCl-CH(SO ₂ Cl)-R	
Tertiary	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{C}-\text{R}' \\ \\ \text{Cl} \end{array}$	2.3-3.5
Sulfonyl chloride	R-CH ₂ -SO ₂ Cl	0.08
	$\begin{array}{c} \text{R} \\ \\ \text{CH}-\text{SO}_2\text{Cl} \\ \\ \text{R}' \end{array}$	4.20

^a The 18% may also include structures of the type R-CHCl-(CH₂)_n-CHCl-R where n ≥ 2.

EXPERIMENTAL

Kinetic Analysis

Solutions consisting of 1.000 g. of chlorosulfonated polyethylene (31.0% Cl, 1.2% S) were prepared from 2 ml. of piperidine or aniline and 8 ml. of nitrobenzene when diluted base was used and from 10 ml. of base when undiluted. Experiments were carried out in 15-ml. screw cap vials fitted with Teflon tetrafluoroethylene resin disks to prevent leakage. The vials were fastened to chain-driven rotating racks immersed in constant-temperature oil-baths maintained at 50 ± 0.1°C. and 100 ± 0.2°C. After the mixtures were heated for given periods of time, they were cooled immediately in an ice bath. The polymer was precipitated with 100 ml. of methanol and the supernatant liquid decanted and filtered. The polymer was washed with three 30-ml. portions of methanol which were filtered and combined with the above filtrate. Two aliquots of the combined filtrate were taken containing about 1 mg. each of chloride, acidified to pH 2 with nitric acid, and coulometrically titrated for chloride ion.⁴⁰ If the solutions to be analyzed contained suspended particles of polymer anomalously high chloride ion determinations resulted.

A similar procedure was used for analyzing the sulfonyl chloride content of the chlorosulfonated polymer by treatment with 25 ml. of piperidine in 100 ml. of xylene at room temperature. Since the sulfur content was under 2%, 5.000 g. of polymer was used for greater accuracy.

The piperidinated polymer was coagulated and washed as described above, dried at 50°C. and 100 mm., and analyzed.

ANAL. Calcd.: Cl 29.2%, S 1.2%, N 0.52%. Found: Cl 29.1, 29.4%; S 1.2, 1.2%; N 0.50, 0.51%.

Reaction of Chlorosulfonated Polyethylene with Zinc Dust. The procedure, with exception of work-up, is essentially that described by Marvel et al.²⁴ To a refluxing solution of 5.00 g. of chlorosulfonated polyethylene (31.1% Cl, 1.2% S) in 500 ml. of peroxide-free dioxane under a nitrogen atmosphere was added 10 g. of zinc dust. The mixture was stirred and heated at 100°C. for a total of 186 hr. The hot mixture was filtered under nitrogen to remove the zinc dust. The filtrate was treated with 600 ml. of methanol, and the precipitated polymer was washed with three 50-ml. portions of methanol. It was then dried in a vacuum desiccator at 1 mm. pressure over paraffin shavings and dissolved in CCl₄ from which films were prepared for infrared analysis. The zinc-dust filter cake was heated with 100 ml. of fresh dioxane and lastly with 100 ml. of distilled water and filtered after each operation. Aliquots from the combined dioxane-alcohol-water filtrates were analyzed for chloride ion by coulometric titration.

ANAL. Filtrate—Found: 275.6 mg. Cl⁻ (17.73% of total chlorine). Polymer. Calcd. (from Cl⁻): Cl 27.1%, S, 1.27%. Found: Cl 27.4, 27.3%, S 0.62, 0.66%.

Reaction of Chlorosulfonated Polyethylene with Potassium Iodide. A 5.00-g. sample of chlorosulfonated polyethylene (31.1% Cl, 1.2% S) was dissolved in 250 ml. of hot pentanone-2. Potassium iodide (7 g.) was added, and the mixture was stirred at reflux under a nitrogen atmosphere. At intervals 50-ml. aliquots were removed and added to a mixture of 50 ml. CCl₄ and 50 ml. of water containing 0.1 g. KI and starch indicator. The iodide was titrated to a colorless endpoint with 0.01*N* sodium thiosulfate. After a reaction time of 20 hr., a constant titer of 24.5 ml. of thiosulfate was obtained (equivalent to iodine representing 3.0% of the total polymer chlorine).

The piperidinated polymer, when treated similarly, yielded iodine equivalent to 2.9% of the total

chlorine based on the starting chlorosulfonated polymer.

Reaction of Chlorosulfonated Polyethylene with Dimethylamine. Dimethylamine (2.0 g., 0.045 mole) in 50 ml. of CCl₄ was added dropwise over a 20-min. period to a stirred, room-temperature solution of chlorosulfonated polyethylene (40 g. 0.015 mole SO₂Cl) in 500 ml. of dry CCl₄. After the amine was added, stirring was continued for 1 hr., and the reaction mixture was poured into 1500 ml. of isopropyl alcohol. The coagulated polymer was washed three times with isopropyl alcohol in a Waring Blendor, dried at 50°C. and 100 mm. and analyzed.

ANAL. Calcd.: Cl 29.7%, S 1.2%, N 0.52%. Found: Cl 29.6, 29.4%; S 1.2, 1.2%; N 0.53, 0.53%.

Infrared analysis showed the sulfonyl chloride absorption at 8.6 μ to be absent; new bands appeared at 7.57 μ and 8.75 μ characteristic of the symmetrical and antisymmetrical vibrations of the S—O bonds, and a band at 9.60 μ was due to the S—N vibration of the sulfonamide group.⁴¹ The absorbance of the transolefinic absorption at 10.35 μ ²⁶ was 5.0 ($A_{10.35}/A_{2.3}$) when referred to the absorbance at 2.3 μ to correct for film thickness.

When a chlorosulfonated polyethylene (26.6% Cl, 6.0% S) containing five times as much sulfur was treated similarly, the $A_{10.35}/A_{2.3}$ ratio was 24.5, a fivefold increase.

The 10.35- μ band appeared even when stoichiometric amounts of amine (amine/SO₂Cl molar ratio = 2/1) were used based on sulfonamide formation. It is concluded that both the sulfonyl chloride groups and the activated chlorines beta to them compete for the amine.

Ultraviolet spectra were determined on a Cary Model 14 recording spectrophotometer on films of the chlorosulfonated polyethylene and its dimethylamine product. The films were cast from 5% solutions in CCl₄, and the film thickness was adjusted to give an absorbance of 0.1 at 400 m μ . Both polymers gave absorption maxima at 276 and 284 m μ , and the dimethylamine product has a third band at 225 m μ .

Infrared Spectra

Infrared spectra were determined on a Perkin-Elmer Model 21 recording spectrophotometer. Films were deposited on NaCl windows by evaporation *in vacuo* of CCl₄ solutions of the polymers. The film thickness was adjusted to obtain an absorbance of 0.1 at 2.30 μ .

We wish to gratefully acknowledge the loan of the ultra-violet spectrum of $\text{CH}_2=\text{CHSO}_2\text{N}(\text{C}_2\text{H}_5)_2$ from C. S. Rondestvedt, Jr., and to express our appreciation to Miss D. Pfahler for preparing the infrared spectra and to Dr. R. J. Martin for the chloride ion determinations. We also wish to thank Dr. P. R. Johnson for his encouragement and helpful suggestions during the course of this work.

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Synopsis

The chlorines in chlorosulfonated polyethylene have been characterized by kinetic analysis according to the method of Salomon. It is found that 2.7% of the total chlorine is primary, 89.8% secondary, 3.5% tertiary, and 4% is sulfonyl chloride. These results are in accord with statistical calculations based on a polyethylene model containing the same methylene-to-methyl group ratio as the polyethylene precursor. The types and approximate quantities of dichlorides in the chlorosulfonated polyethylene have been determined by reactions with potassium iodide and zinc dust

Résumé

Les atomes de chlore dans le polyéthylène chlorosulfoné ont été caractérisés par analyse cinétique en accord avec la méthode de Salomon. Il a été trouvé que 2,7% du chlore total est primaire, 89,8% est secondaire, 3,5% tertiaire et 4% est du chlorure de sulfonyle. Ces résultats sont en accord avec les calculs statistiques basés sur un échantillon de polyéthylène contenant le même rapport de groupement méthylène au groupement méthyle que le polyéthylène initial. Les types et quantités approximatives de dichlorures dans les polyéthylènes chlorosulfonés ont été déterminés par réaction avec l'iodure de potassium et de la poudre de zinc.

Zusammenfassung

Die Chloratome in chlorosulfoniertem Polyäthylen wurden durch kinetische Analyse nach der Methode von Salomon charakterisiert. Es wird gefunden, dass 2,7% des gesamten Chlors als primäres, 89,8% als sekundäres, 3,5% als tertiäres Chlor und 4% als Sulfonylchlorid gebunden sind. Diese Befunde stehen mit statistischen Berechnungen für ein Polyäthylenmodell mit dem gleichen Methylene- zu Methylgruppenverhältnis wie das Ausgangspolyäthylen in Einklang. Die Art und näherungsweise die Mengen von Dichloriden im chlorosulfonierten Polyäthylen wurden durch Reaktion mit Kaliumjodid und mit Zinkstaub bestimmt.

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