

PHOTOCHEMICAL SULFOCHLORINATION OF POLYVINYLTHIOPHENE

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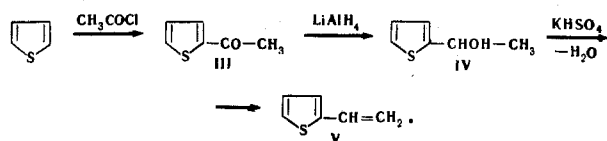
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A study is made of the photochemical sulfochlorination of polyvinylthiophene, and the optimum conditions for introducing the chlorosulfonyl group determined.

Of recent years there has been extensive use of simultaneous introduction of chlorine atoms and chlorosulfonyl groups into macromolecules to impart to polymeric materials a number of valuable properties [1, 2]. The present paper represents a first study of sulfochlorination of polyvinylthiophene (I), with a mixture of sulfur dioxide and chlorine initiated by ultraviolet light. The literature contains a very limited amount of information about the properties of I. It is known that the latter can be prepared by polymerizing 2-vinylthiophene both by a radical and by an ionic mechanism [3-5]. We used thermal polymerization to prepare I.

The starting 2-vinylthiophene (V) was prepared thus from thiophene:



It may be mentioned that the above reduction of 2-acetylthiophene with lithium aluminum hydride gave a good yield of the corresponding alcohol. 2-Vinylthiophene polymerizes at 160° C to give a high yield of polymerization product. The I molecule contains 8-10 thiophene rings in the side chains.

It was of undoubted theoretical interest to elucidate the nature of the process of photochemical sulfochlorination of I, and the effect of macromolecule

structure on the distribution of chlorine atoms and chlorosulfonyl groups at the various bonds. Also investigated were the effects of temperature and time of irradiation on reaction rate. Research led to the preparation of modified I compounds containing 42-56% chlorine and 12-14% sulfur. Change in temperature over the range 20°-60° C has a considerable effect on the process of sulfochlorination of I (Table 1). Rate of reaction increases with increase in temperature, reaching a maximum at 40°. Further increase in temperature cuts the quantity of SO₂Cl groups, and promotes straight chlorination. This can be explained by the decrease in solubility of the gases, especially SO₂, in the liquid phase on heating. On raising the temperature the degree of straight chlorination at first decreases, reaching a minimum at 40°, then increases.

By studying the relationship between sulfochlorination of I and illumination time, it was found that the reaction is practically complete in the first 5-10 minutes. Further illumination only increases the extent of straight chlorination, leading to decreased SO₂Cl group content. Table 2 gives the results of some of the most characteristic runs.

A mole ratio SO₂:Cl₂ = 3.6:1, which favored introduction of the SO₂Cl group into the I molecule [2], was used when studying sulfochlorination of I. Intensity of stirring substantially affecting the kinetics of the process, in all runs the magnetic stirrer turned at the same speed.

From data in the literature [6], it is known that CH groups are chlorinated (sulfochlorinated) considerably more readily than methylene groups. It can

Table 1

Effect of Temperature on Sulfochlorination of Polyvinylthiophene

Temperature, °C	Irradiation time, min	Amounts of the gases passed in g		Product content, % of				Extent of straight chlorination**, %	Mass of polyvinylthiophene taken, g	Mass of sulfochlorinated polyvinylthiophene, g
		SO ₂	Cl ₂	S (total amount)	Cl (total amount)	O	SO ₂ Cl group*			
20	15	10.28	2.85	13.15	51.88	2.52	7.83	49.09	0.42	0.71
30	15	10.28	2.85	13.71	48.65	2.70	8.39	45.67	0.42	0.69
40	15	10.28	2.85	16.06	47.86	3.21	9.98	44.30	0.61	1.54
50	15	10.28	2.85	16.40	48.98	2.87	8.92	45.80	0.61	1.49
60	15	10.28	2.85	12.83	48.90	1.90	5.91	47.79	0.61	1.76
20	30	20.56	5.70	12.25	53.04	1.50	4.66	51.38	0.42	0.71
30	30	20.56	5.70	12.56	51.85	2.07	6.43	49.56	0.42	0.84
40	30	20.56	5.70	12.78	51.02	3.19	9.92	47.48	0.61	1.72
50	30	20.56	5.70	12.87	51.51	2.36	7.34	48.89	0.61	1.68

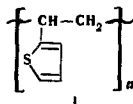
*The chlorosulfonyl group content (%) was calculated from the product's O content.

**The extent (%) of straight chlorination was determined by taking the total chlorine (%), then allowing for the amount of Cl present in chlorosulfonyl groups. Thus the first run gave a product containing 51.88% Cl and 2.52% O. The amount of oxygen corresponds to 2.79% Cl in chlorosulfonyl groups, hence there was 49.09% Cl present due to straight chlorination.

Table 2
Effect of Illumination Time on the Sulfochlorination of Polyvinylthiophene

Illumination time, min	Amount of gases passed in, g		Product content, %				Extent of straight chlorination, %	Mass of polyvinylthiophene taken, g	Mass of sulfochlorinated polyvinylthiophene, g
	SO ₂	Cl ₂	S (total amount)	Cl (total amount)	O	SO ₂ Cl group			
5	3.43	0.95	14.56	41.95	4.60	14.30	36.85	0.42	0.80
10	6.87	1.90	14.55	42.33	4.92	15.29	36.87	0.42	0.77
15	10.29	2.85	13.71	48.65	2.70	8.39	45.67	0.42	0.69
20	13.72	3.80	12.63	50.53	2.41	7.49	47.86	0.42	0.78
30	20.57	5.71	12.56	51.85	2.07	6.43	49.56	0.42	0.84
60	41.16	11.41	12.52	52.25	1.96	6.09	50.08	0.42	0.80
90	61.71	17.12	12.43	56.33	0.36	1.12	55.94	0.42	0.82

be assumed that what is most active in the sulfochlorination of I is the alkyl chain, consisting of alternating methylene and CH groups.



The results obtained show that the CH groups of the polymer chain primarily undergo sulfochlorination, and that the secondary chlorination is due mainly to the methylene groups and to the possible chlorination of the thiophene ring itself. This is confirmed by the high degree of straight chlorination of I, and by IR spectra data, given in the figure.

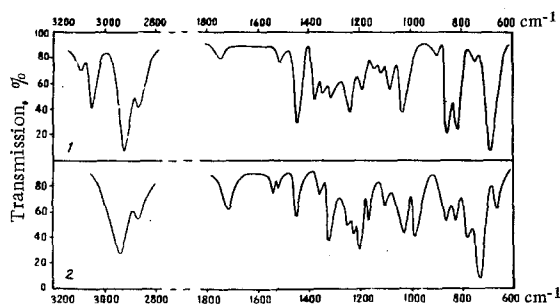


Fig. IR spectra: 1) Polyvinylthiophene; 2) sulfochlorinated polyvinylthiophene.

With sulfochlorinated polyvinylthiophene II, the CH group valence vibrations band intensity in the 2900–2960 cm^{-1} region is less than for I; the CH_2 group deformation vibrations band intensity in the 1420–1460 cm^{-1} region is also less for II than for the initial polyvinylthiophene. Characteristic absorption bands in the 1325 and 730 cm^{-1} regions must be ascribed to SO_2Cl group and C–Cl bond vibrations respectively.

EXPERIMENTAL

2-Acetylthiophene (III). 52 g (0.2 mole) freshly-distilled SnCl_4 was added over a period of 40 min, to a mixture of 16.8 g (0.2 mole) thiophene and 15.7 g (0.2 mole) AcOCl in benzene, cooled to 0° C. The reaction product was hydrolyzed with 10% HCl , the benzene layer separated off, dried, the benzene distilled off, and the residue vacuum-distilled, to give 22.1 g (87.7%) III, bp 89°–90° (9 mm), n_D^{20} 1.5671.

2-(α -Hydroxyethyl)thiophene (IV). 25.2 g (0.2 mole) III in dry ether was added dropwise into excess LiAlH_4 in ether at such a rate that the ether refluxed steadily. Excess hydride was decomposed with water, and the product hydrolyzed with 10% HCl , yield 23.4 g (91.7%), bp 94°–97° (12 mm), n_D^{20} 1.5442. The literature [8] gives: bp 91°–93° (11 mm), n_D^{20} 1.5422.

2-Vinylthiophene (V). This was prepared by dehydrating 38.4 g (0.3 mole) IV at 180°–190° C (100 mm) in the presence of 1.5% by weight KHSO_4 and 1% by weight of hydroquinone. The distillate was dissolved in ether, and the water separated off. The ether layer was dried and fractionated, to give 16.1 g (48.8%) 2-vinylthiophene, bp 64°–65° (49 mm); d_4^{20} 1.0475;

n_D^{20} 1.5738. Found: C 65.32; 65.67; H 5.64; 5.76; S 29.31; 29.14%; MR_D 34.61. Calculated for $\text{C}_6\text{H}_6\text{S}$: C 65.45; H 5.46; S 29.09%; MR_D 33.57.

Polymerization of 2-vinylthiophene. 10 g (0.09 mole) V was placed in a thick-walled ampul, after which it was evacuated, and filled with N. The ampul was heated for 4 hr in a glycerol bath at 160° C. After cooling the product was a pale-orange viscous mass. It was dissolved in 15 ml CHCl_3 , and with vigorous stirring, precipitated with 200 ml petrol ether. After two further precipitations, the polyvinylthiophene I was vacuum-dried to constant weight. Yield 8.9 g (89.4% by weight), mp 85°, M 800 (Rast in camphor). It was a white amorphous powder, readily soluble in benzene, acetone, CHCl_3 , and dichloroethane, insoluble in water, EtOH, and petrol ether.

Sulfochlorination of I. 40 ml of a 1.5% (in some runs 1.0%) solution of I in CCl_4 was placed in a cylindrical quartz vessel. A magnetic stirrer was used to stir and heat. The chlorine and SO_2 were passed through H_2SO_4 washbottles, CaCl_2 drying tubes, and graduated flowmeters, and thence to a mixer. The chlorine feed rate was 1 mole/sec, that of SO_2 4 ml/sec (mole ratio $\text{SO}_2:\text{Cl}_2 = 3.6:1$).

UV light from a PRK-2 quart-Hg lamp 30 cm from the reaction vessel was used to start the sulfochlorination of I. The reaction was run for various illumination times and at various temperatures. Tables 1 and 2 give the results.

The sulfochlorinated polyvinylthiophene II was precipitated with petrol ether, and vacuum-dried to constant weight. It formed a pale-yellow powder, readily soluble in acetone, dichloroethane, and benzene, insoluble in water, EtOH, and petrol ether, mp 210°–220° C (for II prepared at 30° using an illumination time of 15 min).

The IR spectra were determined with an IKS-14 instrument, using tablets with KBr.

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