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Catalysts

The Synthesis of Poly-/p-Phenylene Sulphide/from Thiophenol in the Presence of Various Acidic Catalysts

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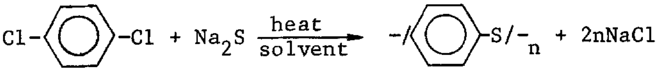
Summary

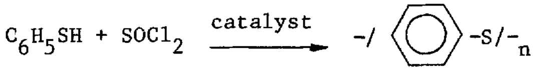
In the present work the synthesis of poly-/p-phenylene sulphide/ from thiophenol in the presence of various acidic catalysts has been investigated. Structural similarity of the obtained polymers to the polymer produced by Phillips Petroleum Co. was studied.

Introduction

Poly-/p-phenylene sulphide/ (pps) is a polymer produced on industrial scale by Phillips Petroleum Co. /1-3/ in reaction of p-dichlorobenzene and sodium sulphide in a polar solvent /4-7/.



It is a high pressure process.
In our laboratory the research is carried on the synthesis of pps by oxidation of thiophenol with thionyl chloride in the presence of acidic catalysts is described.



The catalysts used were: $FeCl_3$, $AlCl_3$, BF_3, $ZnCl_2$, $SnCl_4$, $TiCl_4$, WCl_6, $SoCl_5$ and H_2SO_4.

Experimental

Thionyl chloride /0,25M/ was added dropwise to a solution of thiophenol /0,25M/ and catalyst /0,025M/ in 22,2 cm^3 benzene. The reaction mixture was then heated at boiling temperature for 12 hours.
Then each reaction mixture was purified from the catalyst separately and from the crude product three fractions were isolated /table 1/: toluene soluble, hot N,N-dimethylformamide /DMF/ soluble and insoluble in hot DMF. The fraction insoluble in hot DMF was the expected high molecular pps which was then investigated using elemental analysis, I.R. spectra and X-ray diffraction.

Results and disscusion

Results are shown in table 1.
In each reaction a polymer was obtained with the exception of the reaction in the presence of $SbCl_5$. The unreacted thiophenol and diphenyl disulphide were isolated from the reaction mixture. All the polymers obtained have

TABLE 1

Products of the reaction of thiophenol and thionyl chloride in the presence of acidic catalysts[x/].

Catalyst / Fraction	$FeCl_3$ yield, %	$FeCl_3$ flow temp., °C	$AlCl_3$ yield, %	$AlCl_3$ flow temp., °C
Soluble in hot toluene	22,7[xx/]	-	13,1	123-140
Soluble in hot DMF	5,2	75-118	1,2	72-75
Insoluble in hot DMF	14,0	245-265	31,0	210-215

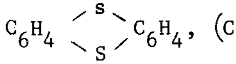
	BF_3 yield, %	BF_3 flow temp., °C	$ZnCl_2$ yield, %	$ZnCl_2$ flow temp., °C
Soluble in hot toluene	1,7	142-146	0,6	105-120
Soluble in hot DMF	1,9	142-145	0,5	53-69
Insoluble in hot DMF	1,7	182-186	3,3	256-269

Catalyst / Fraction	$SnCl_4$ yield, %	$SnCl_4$ flow temp., °C	$TiCl_4$ yield, %	$TiCl_4$ flow temp., °C
Soluble in hot toluene	3,2	56-58	1,3	142-158
Soluble in hot DMF	1,2	62-78	0,2	160-175
Insoluble in hot DMF	16,4	280-295	10,9	238-252

Catalyst / Fraction	WCl_6 yield, %	WCl_6 flow temp., °C	$SbCl_5$ yield, %	$SbCl_5$ flow temp., °C	H_2SO_4 yield, %	H_2SO_4 temp., °C
Soluble in hot toluene	0,8	90-105	-		0,6	115-125
Soluble in hot DMF	0,1	120-135	-		0,2	275-285
Insoluble in hot DMF	9,5	275-285	-		5,5	275-290

[x/] 0,25 mole of thiophenol, 0,25 mole of thionyl chloride, 0,025 mole of catalyst in 22,2 cm^3 benzene were employed.

[xx/] mixture of



$C_6H_4 \langle S, S \rangle C_6H_4$, $(C_6H_5)_2$ S and oligomers.

I.R. spectra similar to the spectrum of RYTON P-3 /fig.1./. In the range characteristic for aromatic substitution they have a strong band at 820 cm^{-1} /1,4-substituted benzene ring/ and a weak at 860 cm^{-1} /1,2,4-substituted benzene ring/. However the results of elemental analysis differ slightly from the results for a polymer with the structure $-/S-C_6H_4/-_n$. Polymers obtained in the presence of $FeCl_3$, $SnCl_4$, $TiCl_4$, WCl_6 and H_2SO_4 contain significant amounts of oxygen. Oxygen is probably contained in the form of sulphoxide groups. Observation of these groups in I.R. spectrum is difficult because the band corresponding to S=O stretching vibrations overlaps with the band 1060-1090 cm^{-1} found in the spectrum of standard pps.

The presence of S=O group is probably caused by oxidyzing action of catalysts. This hypothesis is supported by the fact that significant amounts of oxygen are present in those polymers which were obtained in the presence of the catalysts which are also strong oxidants /H_2SO_4, WCl_6, $TiCl_4$, $SnCl_4$/.

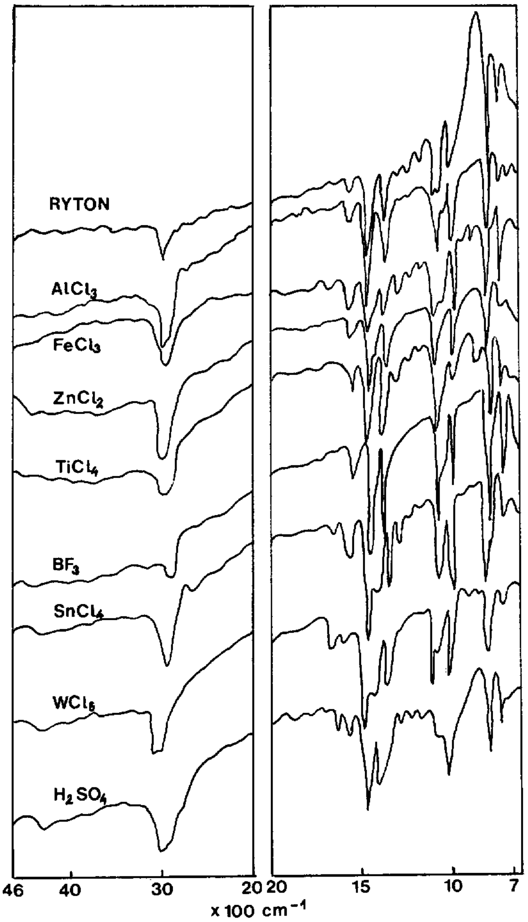


Fig.1. I.R. spectra of polymers prepared from thiophenol and thionyl chloride in the -presence of various catalysts./insoluble fractions/

In all polymers there is more then one sulphur atom per benzene ring. It is ascribed /9/ to partly cyclic structure of the polymer chain $-C_6H_3\genfrac{}{}{0pt}{}{S}{S}C_6H_2\genfrac{}{}{0pt}{}{S}{S}$. The polymers obtained in the presence of $SnCl_4$, WCl_6 and H_2SO_4 have the flow temperature similar to RYTON and the remaining ones have lower.

Considerable structural similarity of the polymers prepared in the presence of $AlCl_3$, BF_3 and H_2SO_4 to pps is suggested by their X-ray diffractograms /fig.2./. These polymers posses the degree of crystallinity respectively 49%, 68% and 48%, while RYTON P-3 79%. Taking into consideration all to compared properties it is possible to conclude that in the reaction of thiophenol with thionyl chloride in the presence of various catalysts of the Lewis acid kind and sulphuric acid, the structure most closely resembling pps is that of the polymers obtained in the presence of BF_3.

TABLE 2

Properties of poly-/p-phenylene sulphide/ - insoluble fractions obtained from thiophenol and thionyl chloride in the presence of acidic catalysts.

Property \ Catalyst		$FeCl_3$	$AlCl_3$	BF_3	$ZnCl_2$	
yield, g		14,0	31,0	1,7	3,3	
flow temperature, °C		245-265	210-215	182-186	256-269	
crystallinity, %		0	49	68	0	
elemental analysis,$^{x/}$%	C	58,73	59,90	60,76	58,47	
	H	3,04	3,16	3,84	3,36	
	S	36,26	36,17	34,08	36,99	
	O	1,97	0,77	1,32	1,18	
formula		$C_{6.0}H_{3.7}S_{1.3}O_{0.15}$	$C_{6.0}H_{3.8}S_{1.4}O_{0.06}$	$C_{6.0}H_{4.5}S_{1.3}O_{0.08}$	$C_{6.0}H_{4.1}S_{1.4}O_{0.08}$	
		$SnCl_4$	$TiCl_4$	WCl_6	$SbCl_5$	H_2SO_4
yield, g		16,4	10,9	9,5	-	5,5
flow temperature, °C		280-295	238-252	275-285	-	275-290
crystallinity, %		0	0	0	-	48
elemental analysis,$^{x/}$%	C	55,82	53,34	59,89	-	57,08
	H	3,20	3,03	3,15	-	3,60
	S	35,29	33,97	32,15	-	32,78
	O	5,70	9,76	4,81	-	7,14
formula		$C_{6.0}H_{4.1}S_{1.4}O_{0.45}$	$C_{6.0}H_{4.1}S_{1.4}O_{0.82}$	$C_{6.0}H_{3.8}S_{1.2}O_{0.40}$		$C_{6.0}H_{4.5}S_{1.2}O_{0.55}$

x/ theory $-/C_6H_4S/_n-$ - C 66,67%, H 3,70%, S 29,63%.

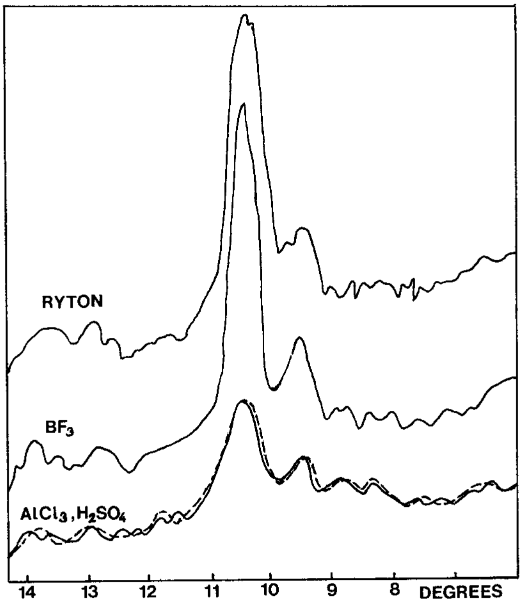


Fig.2. X-ray diffractograms of polymers obtained from thiophenol and thionyl chloride in presence of various catalysts. /insoluble fractions/

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