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Synthesis

Synthesis and Electrical Conductivity of AsF_5-Doped Poly(Arylene Vinylenes)

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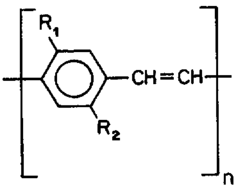
SUMMARY

A series of polymers containing 2,5-disubstituted phenylene vinylene units, and the polymer containing 1,4-naphthalene vinylene units, were prepared by polymerization of their bis(sulfonium salts) through a base elimination reaction in solution. Films of these polymers were cast from aqueous solution and chemically treated (doped) with AsF_5 vapor. The electrically conductivities of the doped films varied greatly with changes in polymer structure, with the highest value obtained of 1.8 ohm^{-1} cm^{-1} for poly(2,5-dimethoxyphenylene vinylene).

INTRODUCTION

Poly(arylene vinylenes) represent a class of conjugated organic polymers that are intermediate in structure between polyacetylene and the polyarylenes and that may exist in a very large number of structural variations. Like the former, they also show considerable promise as base polymers which on chemical activation, or doping, develop electrical conductivities of the type expected for organic metals.

We have devoted most of our efforts to the parent polymer of this series, poly(p-phenylene vinylene), PPV, which becomes highly conducting after exposure to AsF_5.(1-4) Our more recent studies in this area, however, have been involved with the preparation and evaluation of derivatives of PPV in order to better understand the relationship between polymer structure and electrical conductivity in these organic materials. For this purpose a variety of poly(arylene vinylenes) of the following structures were prepared in film form, including poly(1,4-naphthalene vinylene), PNV, and doped with AsF_5 vapor to form electrically conducting materials:



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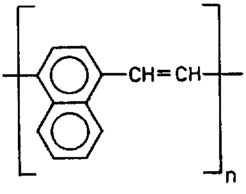

II

In the series of polymers of type I, R_1 and R_2 were either methoxy, ethoxy or methyl groups or a bromine atom.

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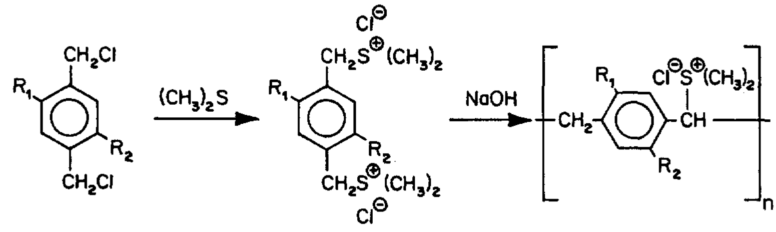
EXPERIMENTAL

The polymers prepared for this study were characterized by elemental analysis, 'HNMR spectroscopy with a Perkin-Elmer A-60 spectrometer, and by IR spectroscopy with a Perkin-Elmer 1320 spectrophotometer. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory. Solution viscosities were determined in a solution of 0.05M Na_2SO_4 in an 80/20 mixture of water and methanol at 25±0.1°C. Electrical conductivity measurements were carried out using the standard 4-probe d.c. technique on films for which the electrode contacts were made with Electrodag. Arsenic pentafluoride vapor (Ozark Mahoning Co.) was maintained at -90° during the doping experiments.

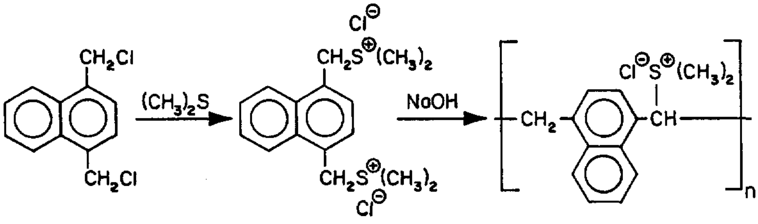
Monomer and Polymer Synthesis. The first step in the synthesis of the monomers was the preparation of the precursor, the *bis*(chloromethyl) arylene, several of which had not been previously reported. The *bis*(chloromethyl)phenylene precursors, III, were obtained according to the method of Wood(5) and Wheland(6) for the chloromethylation of aromatic compounds. 1,4-*Bis*(chloromethyl)napthalene, VI, was synthesized by refluxing 1,4-dimethylnapthalene with N-chlorosuccinimide(7)(8) in a 2/1 carbon tetrachloride/benzene solution with a trace of benzoyl peroxide, as a radical initiator, under inert conditions. The synthesis of the monomers, the *bis*(sulphonium salts), IV and VII, proceeded by the reaction of the *bis*(chloromethyl) derivatives with dimethyl sulphide under mild conditions.(9)(10) Polymerization to the intermediate water soluble polyelectrolytes, V and VIII, by reaction of the monomer with sodium hydroxide in water and purification by dialysis was described previously.(1-3)

Table 1
Elemental analyses of *bis*(chloromethylarylenes) and their *bis*(sulphonium salts)

Compounds	Elemental Analysis, %							
	Found				Calculated			
	C	H	Cl	S	C	H	Cl	S
III $R_1, R_2 = OCH_3$	51.09	5.19	30.01	-	51.06	5.10	30.21	-
IV $R_1, R_2 = OCH_3$	46.64	6.63	19.57	17.71	46.79	6.68	19.77	17.82
III $R_1, R_2 = OC_2H_5$	54.77	6.24	26.89	-	54.75	6.08	26.99	-
IV $R_1, R_2 = OC_2H_5$	49.46	7.13	18.25	16.37	49.61	7.23	18.34	16.53
III $R_1, R_2 = CH_3$	59.34	6.04	34.66	-	59.11	5.91	34.97	-
IV $R_1, R_2 = CH_3$	51.16	7.66	21.48	19.29	51.37	7.33	21.71	19.57
III $R_1 = CH_3, R_2 = Br$	40.40	3.29	26.50	-	40.29	3.25	26.49	-
IV $R_1 = CH_3, R_2 = Br$	39.81	5.29	17.98	16.17	39.79	5.35	18.11	16.32
VI	63.78	4.39	31.82	-	64.0	4.44	31.55	-
VII	55.39	6.43	20.49	17.85	55.01	6.30	20.34	18.33



III IV V



VI VII VIII

RESULTS AND DISCUSSION

The synthesis of the monomers, the arylsulphonium salts, was carried out in high yield by the reaction of an appropriate *bis*(chloromethyl) arylene with dimethyl sulphide(9,10) in a variety of polar solvents, including methanol, acetone, DMF and water, as previously described. The substituted phenylsulphonium salts were found to be more stable than the 1,4-naphthylsulphonium salt, but after several weeks of storage some degradation was also observed for the former with the loss of dimethyl sulphide.

In all cases, the base catalysed polymerization of these *bis*(sulphonium salt) monomers yielded a slightly viscous solution of the polyelectrolyte, which exhibited uv fluorescence presumably because of a partial base-induced elimination to form short arylene vinylene sequences in the polymers.(1)

The polymer solutions were freed of all low molecular weight impurities by dialysis, and films were cast by solvent evaporation at room temperature.(1) The films were heated to form the vinylene units, which occurs by the loss of dimethyl sulphide and HCl through an ElcB reaction mechanism to form the *trans* configuration of the vinylene double bond, as confirmed by the strong infrared absorbance at 970 cm^{-1}. During the elimination reaction the color of the films changed from an initially colorless appearance to a red or yellow color in the final arylene vinylenes. However, the films remained transparent throughout this conversion process.

The residual sulphur in the film, as determined by elemental analysis, indicated that some saturated units still remained. The maximum conductivities, σ_{max}, obtained for the unoriented poly(arylene vinylene) film samples after exposure to AsF_5 vapor are listed in Table 2.

The polymers in Table 2 were all of relatively moderate molecular weights, and studies are now in progress toward increasing their molecular weights so that the films may be oriented by drawing during the elimination reaction, before exposure to AsF_5, in order to increase conductivities.(2)

Table 2
Properties of intermediate polyelectrolytes and final poly(arylene vinylenes)

	Polyelectrolyte V and VIII		Poly(arylene vinylene), I and II		
				AsF$_5$ Treated Films	
Monomer	Yield, %	$[\eta]$, dl/g	Sulphur content, %	σ_{max} ohm^{-1}cm^{-1}	Appearance
IV R_1, R_2 = OCH_3	22	1.35	0.57	1.8	Multicolored metallic
IV R_1, R_2 = OC_2H_5	20	1.30	0.06	0.88	Flat black
IV R_1, R_2 = CH_3	27	2.15	0.93	3x10^{-7}	Dark green
IV R_1 = CH_3, R_2 = Br	23	1.70	3.65	5x10^{-6}	Dark brownish black
VII	20	1.40	<0.1	3.2x10^{-2}	Purple

ACKNOWLEDGEMENT

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