

Characterization of Polyethyleneimine Modified with Organotin Halides. Thermal, Solubility, and Fungal Properties

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Synopsis

Modified polyethyleneimine products are hydrophobic with products from monohalotin reactants soluble in HMPA, DMSO, CHCl_3 , and 2,4-pentanedione, while products from dihalotin reactants are insoluble in all solvents. Antifungal activity varies markedly with the nature of the tin moiety. For products from triphenyltin chloride, antifungal activity is widespread and suitable to about 40 ppb of the polymer, which is clearly acceptable for medical and industrial uses. Thus, such modified polymers can be used as retarders of fungi related rot and mildew. The products show moderate high-temperature stabilities.

INTRODUCTION

There has been a rapid growth in the use of polyethyleneimine, both pure and as a blend, in a number of diverse areas such as fabric treatments,^{1,2} ion exchange resins,³⁻⁵ sludge dispersants,⁶ and as binding adhesive agents.^{7,8}

Recently we reported the modification of polyethyleneimine utilizing organotin halides employing the interfacial technique to give products⁹ of forms I and II shown below:

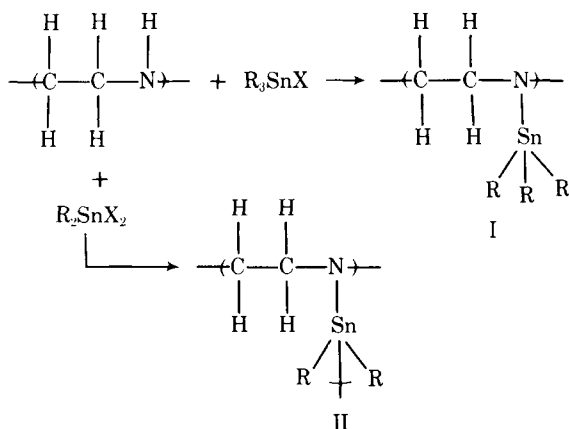


TABLE I
 Identification of Tested Products

Compound designation	Tin reactant	% Tin moiety	Compound designation	Tin reactant	% Tin moiety
1	Ph ₃ SnCl	34	6	Et ₂ SnCl ₂	33
			7		0
2	Ph ₃ SnCl	62	8	octyl ₂ SnCl ₂	32
3	Ph ₃ SnCl	72	9	benzyl ₂ SnCl ₂	72
4	Ph ₃ SnCl	83	10	butyl ₂ SnCl ₂	31
5	Ph ₃ SnCl	86	11	Ph ₂ SnCl ₂	61

 TABLE II
 Growth Inhibition as Function of Tin Moiety^a

Compound designation	<i>Penicillium</i> sp.	<i>Aspergillus fumigatus</i>
1	4+	4+
2	4+	4+
3	4+	4+
4	4+	4+
5	4+	4+
6	1+	0
7	0	0
8	±	0
9	±	0
10	±	0
11	±	0

^a 4+ = 100% inhibition, 3+ = 75%, 2+ = 50%, 1+ = 25%, ± is retarded growth, not complete inhibition; 0 = no noticeable inhibition. Control plates showed confluent growth. Colonies with DMSO were light tan, whereas without DMSO they were shades of blue-green.

 TABLE III
 Growth Inhibition as Function of Concentration for *Aspergillus flavus* (#4)

Compound designation	Initial concn, µg/ml	Zone of inhibition, ^a mm, at dilution:			
		Undiluted	1:10	1:100	1:1000
1	4.1	25	22	18	11±
2	2.0	25	22	14	10±
3	4.0	25	23	17	10±
4	5.9	25	22	19	11±
5	3.0	24	20	15	10±

^a Average from two plates to the nearest mm; ± is retarded growth, not completely inhibited.

Our interest with such modifications includes improvement of thermal stabilities, improvement of the hydrophobic nature, and imparting favorable biologic activities—mainly mildew and rot resistance. The afore would be advantageous for many coatings and fabrics applications. Here we report results aimed toward achieving these improvements.

EXPERIMENTAL

Synthesis procedures, elemental and infrared techniques and results, isolation procedures, and experimental apparatus are described elsewhere.⁹ Synthesis occurs utilizing the interfacial technique.

Polyethyleneimine (Polysciences, Inc., Warrington, Pennsylvania, MW 50,000); trimethyltin chloride, trimethyltin iodide (Orgment, Inc., Hampstead, New Hampshire); tri-*n*-butyltin chloride (Aldrich Chemical Co., Inc., Milwaukee, Wisconsin); dibenzyltin dichloride, dibutyltin dibromide, dibutyltin dichloride, diethyltin dibromide, diethyltin dichloride, dimethyltin dichloride, di-*n*-propyltin dichloride, di-*n*-octyltin dichloride, diphenyltin dichloride, tri-*n*-propyltin chloride, and triphenyltin chloride (Alfa Inorganics, Inc., Beverly, Massachusetts) were all used as received.

TABLE IV
Growth Inhibition as Function of Concentration for *Penicillium* sp. (#7)

Compound designation	Undiluted ^a	Zone of inhibition, mm, at dilution:		
		1:10	1:100	1:1000
1	30	27	19	±
2	28	26	15	±
3	30	26	19	2.5±
4	32	28	23	±
5	30	28	13	±

^a See Table III for concentrations.

TABLE V
Growth Inhibition as Function of Concentration for *Aspergillus fumigatus* (#16)

Compound designation	Undiluted ^a	Zone of Inhibition (mm) at dilution:		
		1:10	1:100	1:1000
1	34	30	15	±
2	30	27	14	±
3	32	29	17	±
4	34	30	19	±
5	34	29	11	±

^a See Table III for concentrations.

TABLE VI
Summary in Terms of Minimum Concentration Showing Zones of Inhibition (in µg/ml)

Compound designation	<i>Aspergillus flavus</i>		<i>Aspergillus fumigatus</i>		<i>Penicillium</i> sp.	
	Complete	Partial	Complete	Partial	Complete	Partial
1	0.04	0.004	0.04	0.04	0.04	0.04
2	0.02	0.002	0.02	0.02	0.02	0.02
3	0.04	0.004	0.04	0.04	0.04	0.004
4	0.05	0.005	0.05	0.05	0.05	0.05
5	0.03	0.003	0.03	0.03	0.03	0.03

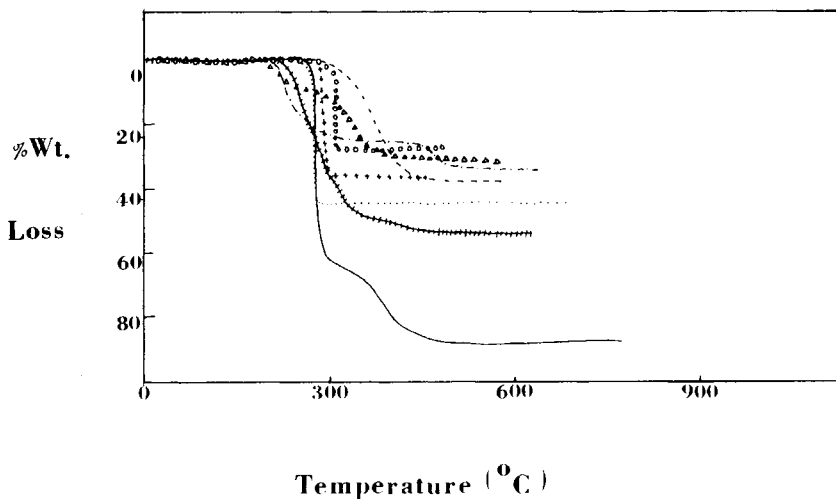


Fig. 1. TGA thermograms of products from polyethyleneimine with dibenzyltin dichloride (· · · · ·), diphenyltin chloride (—), tributyltin chloride ($\Delta\Delta\Delta$), diethyltin dichloride (000), dibutyltin dibromide (---), tripropyltin chloride (+++), and dioctyltin dichloride (+ + + +) in air.

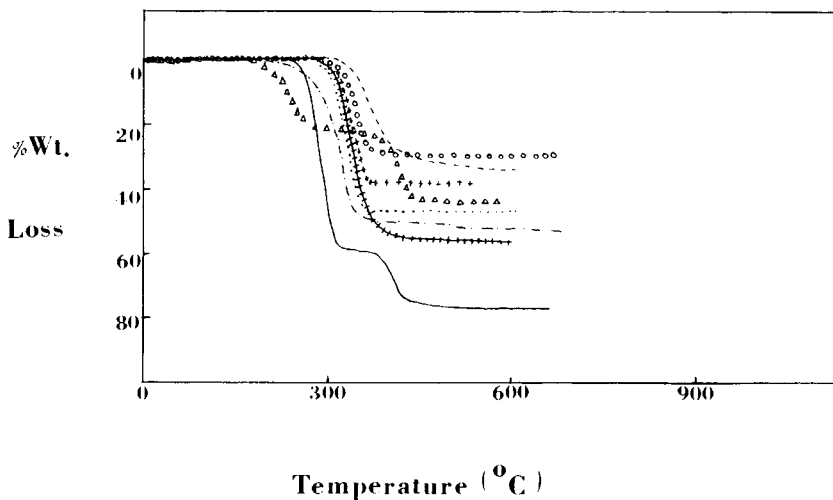


Fig. 2. TGA thermograms of products from polyethyleneimine with dibenzyltin dichloride (· · · · ·), diphenyltin chloride (—), tributyltin chloride ($\Delta\Delta\Delta$), diethyltin dichloride (---), dibutyltin dibromide (---), tripropyltin chloride (+++), and dioctyltin dichloride (+ + + +) in nitrogen.

RESULTS

Solvent Properties

Polyethyleneimine is soluble in a number of organic solvents and in most aqueous solutions including water. Products of form II are crosslinked and insoluble in all solvents studied. Products of form I are linear and soluble in HMPA, DMSO, CHCl_3 , and 2,4-pentanedione and to lesser amounts in CCl_4 and benzene. All modified products appear hydrophobic, often residing at the surface of an aqueous solution, with no signs of wetting even after vigorous shaking.

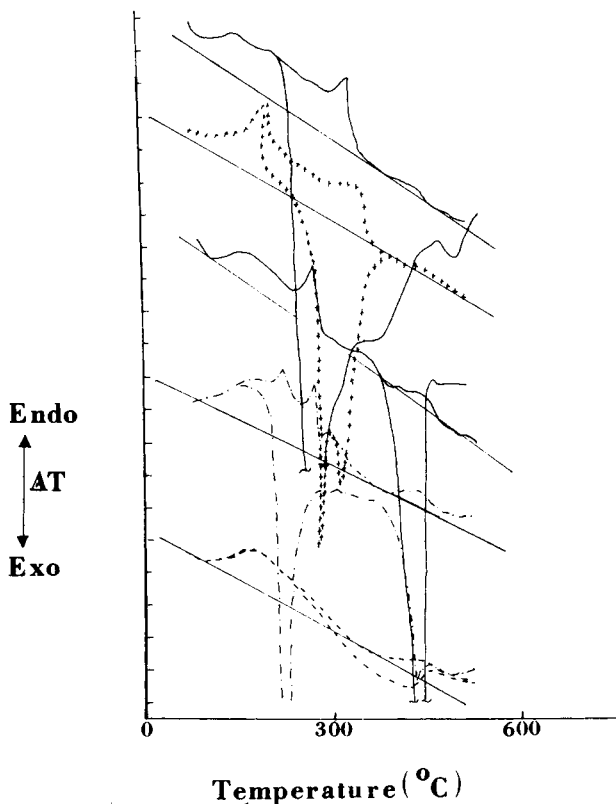


Fig. 3. DSC thermograms of products from polyethyleneimine with dibenzyltin dichloride (- . - . - .), diphenyltin chloride (—), tributyltin chloride ($\Delta\Delta\Delta$), diethyltin dichloride (000), dibutyltin dibromide (.), tripropyltin chloride (+++), and dioctyltin dichloride (+|+|+|+|+) in air (lower portion) and nitrogen (upper portion), where the straight line is $\Delta T = 0$.

This change to a hydrophobic nature is positive for applications requiring water stability, resistance, and repellency. This hydrophobic nature is general for most water-soluble polymers, such as poly(acrylic acid) and poly(vinyl alcohol), modified through condensation with organometallic halides¹⁰⁻¹³ resulting from a replacement of the "hydrogen bonding proton" by a dipolar aprotic moiety.

Preliminary Fiber- and Film-Forming Characteristics

Attempts were made to draw fibers and cast films utilizing the modified products. For instance, polyethyleneimine modified with triphenyltin chloride melts about 75°–80°C to form a clear liquid. Two compounds were tested, one containing 29% tin moiety inclusion and the second containing 80% tin moiety inclusion. Since the results are similar, only results for the 80% inclusion product will be reported. Fibers cannot be drawn from the melt. The melt adheres to glass but does not form tractable, coherent films. Small fibers can be drawn from a solution of 80% (w/w) product with 20% DMSO. Small (about 1 mm square and smaller) films can be formed from the solution of the product (80%) in DMSO when cast onto the surface of a Teflon II-coated muffin (Mirro; Manitowoc, Wisconsin) pan followed by placing the pan into a vacuum and held at 27°C and

20 torr pressure for three days. These films were not of sufficient quality to permit physical testing. Melts of the product on the Teflon surface did not yield coherent films.

Solutions can be made by mixing together the product with suitable plastizers and heating to about 80°C. The following plastizers were received as gifts and were tested: dioctyl phthalate (DP) and dioctyl sebacate (DS) (from Pfaltz and Bauer, Stamford, Connecticut) and isodecyldiphenyl phosphate (IP) (Santicizer 148) and a mixture of *N*-ethyl-*o*- and *p*-toluene sulfonamides (ES) (Santicizer 8) (from Monsanto, St. Louis, Missouri). The following amounts (w/w) of product:plastizer were tested: 1:1, 2:1, 3:1, and 6:1. One test involved melting the mixtures in test tubes and then coating the test tubes with the melt. No coherent film formation was found. The 3:1 and 6:1 products from IP and ES were tacky and appeared to offer more promise for future work. The second test involved pouring the heated mixtures onto a Teflon surface (noted above). Tacky fibers could be drawn from the 6:1 mixture with DS. None gave coherent films. Part of the problem appears to be the limited solubility of the product in the plastizers. Melts appeared clear, but small portions of product appeared on cooling. These precipitated portions appeared to be less than 25% of the added product but still signal that good melt mixing may not have occurred.

Biological Fungal Assays

The test organisms, *Aspergillus fumigatus*, *Aspergillus flavus*, and *Penicillium* species, were obtained from the College of American Pathologists. Each organism was suspended in sterile water (1×10^6 spores/ml). Appropriate dilutions were made in Sabouraud's dextrose agar and poured into Petri plates (100 mm). The best confluent growth (three to four days) resulted when employing 10^3 spores/ml. Spore concentrations of 10^3 – 10^2 spores/ml were employed for subsequent studies.

Preliminary tests were carried out by addition of about 0.1 mg polymer sample to about 3 ml DMSO for samples 1 through 5 (Table I) and a drop of the resulting solution added to Petri plates containing Sabouraud's dextrose agar seeded with either *A. fumigatus*, *A. flavus* or *Penicillium* sp. Another set of duplicate plates was treated with trace amounts (about 0.1 mg) of samples 6 through 11. Extreme inhibition was found for all the DMSO soluble products but only moderate to no inhibition for the "dry" products (Table II). "Dry tests" were conducted employing samples 1 through 5 to determine if solubilization of the product is necessary for significant inhibition. All of the "dry tests" showed inhibition to the same extent as found when the samples were dissolved in DMSO. Thus, the inhibitory properties of the polymers are not dependent on solubilization. Further inhibition is dependent on the nature of the tin moiety. Sample 7 is included as a check and is unmodified polyethyleneimine recovered from condensation with dimethyltin dichloride.

Further study concentrated on samples 1 through 5, which represent a series of triphenyltin-containing polymers with increasing amounts of tin moiety. Tables III, IV, and V contain results from such studies. Inhibition appears independent of Ph_3Sn moiety inclusion (after adjustment of solution concentration variations). Table VI contains a summation of results for complete and partial inhibition. Complete inhibition is found for concentrations of about 40 ppb,

which is clearly acceptable for medical and industrial uses involving coatings and fabrics.

The fungi tested are typical and widespread and represent a good cross-sectional test for the applicability of such modified products as retarders.

Thermal Stability

Thermal stability was studied employing a du Pont 950 thermal gravimetric analyzer (TGA) and a du Pont 900 differential scanning calorimeter (DSC) cell fitted on a du Pont 900 thermal analyzer console. Specific procedures are given elsewhere.^{10,11} Gas flows of about 0.3 l./min were employed. A Mettler H20T semimicrobalance was employed for the weighing of DSC samples. Samples were ground to a fine powder for analysis. DSC measurements were obtained using open aluminum cups allowing free flow away from the solid of volatilized gases, thus closely simulating the conditions under which TGA studies were conducted.

The products exhibit kinetically dependent stability plateaus (Figs. 1 and 2) characteristic of most organometallic polymers.¹⁰⁻¹³ While weight retention is increased over that of polyethyleneimine itself, the modified products exhibit only moderate thermal stabilities. For instance, the product from Ph_3SnCl (about 38% inclusion) shows only 20% weight retention at 500°C, whereas the product from Et_2SnCl_2 (33% inclusion) exhibits a 70% weight retention at 600°C.

While weight loss does not occur until the 200–300°C range, DSC endothermic transitions are present (Fig. 3). These transitions are identical in nitrogen and air. Infrared spectra of products heated to about 150°C showed little or no change compared to that of unheated products probably indicating occurrence of a physical rearrangement, possibly a T_g . For the product from Ph_3Sn , a new band at about 800 cm^{-1} appeared while other bands remained constant.

DSC and TGA thermograms differ greatly at higher temperatures in air and nitrogen indicative of an oxidative degradation occurring in air. Unlike a number of other tin moiety-containing organometallic polymers, tin-containing effluents do not appear to be emitted during degradation.

The products are initially white, while the degradation products (at 600°C) are white if degradation occurred in nitrogen but are yellow tan to red brown if degradation occurred in air.

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