

Poly(aryloxyphosphazenes) and a Flame Retardant Foam

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Synopsis

Plastics and elastomers were prepared, physical state determined by the side chains attached to the phosphorus-nitrogen backbone. The poly(aryloxyphosphazenes) displayed a high degree of flame retardancy in the uncured, unfilled state. Limiting oxygen index (*LOI*) values varied from 27 to 33 for nonhalogenated materials and from 38 to 65 for halogenated materials. These values qualify all poly(aryloxyphosphazenes) studied as flame retardants according to the generally accepted definition ($LOI \geq 27$). Materials subjected to the National Bureau of Standards Smoke Test gave encouraging results. The $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ elastomer was investigated for application as a fire retardant insulating foam. Closed-cell foams produced from this copolymer showed much improved fire retardancy and smoke generation compared to commercially available fire retardant foam insulations.

INTRODUCTION

The need for fire retardant polymers and polymer systems has increased markedly in recent years because of increased emphasis on safety and the increasing importance of enclosed environments. Elastomeric foams for thermal insulation are a basic requirement in environments such as naval vessels, aircraft, and space vehicles as well as in certain areas within ground-based structures. Poly(aryloxyphosphazenes) provide materials which have markedly reduced smoke evolution on combustion and improved fire retardancy over currently used materials.

Oligomeric phosphazene compounds have been studied for use in a variety of flame retardant applications.¹ The utility of the phosphazenes as flame retardants is due to the high percentage of phosphorus present, the simultaneous presence of large amounts of nitrogen, and the possibility of incorporation of halogen at the same time.² Polyphosphazene polymers, therefore, would be expected to be excellent flame retardant polymers.

A number of poly(aryloxyphosphazenes) with potentially useful properties have been synthesized,³ and one of these, $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$, was developed into an elastomeric, closed-cell foam with superior flame retardancy and reduced smoke emission.

TABLE I
Typical Characterization of $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ Copolymer

Yield, %	50-75	
$[\eta]_{C_6H_6}^{30^\circ C}$	2-3	
Analysis	Found, %	Calculated, %
C	63.4-65.2	64.9
H	5.3-5.6	5.4
Cl	0.02-0.1	0.0
$C_6H_5O/4-C_2H_5C_6H_4O$	47/53-50/50 (by NMR)	50/50

TABLE II³
Limiting Oxygen Index (LOI) of $[(R_1C_6H_4O)_2PN-(R_2C_6H_4O)_2PN]_n$

R_1	R_2	LOI
H	H	33
4-Cl	4-Cl	44
3-Cl	3-Cl	41
4-CH ₃	4-CH ₃	27
3-CH ₃	3-CH ₃	28
4-Br	4-Br	65
3-CH ₃	3-CH ₃	38
4-Cl	4-Cl	
H	2,4-Cl ₂	43
H	4-C ₂ H ₅	28
4-Cl	2,4-Cl ₂	59
3-CH ₃	4-CH ₃	27

EXPERIMENTAL

Synthesis of $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ Polymer

Hexachlorophosphazene was purified by distillation (120°C/10 mm Hg) and recrystallization (*n*-heptane) and was polymerized under vacuum at 250°C, generally in the presence of HCl (1 mmole/2600 g monomer). The aryloxides were prepared by the addition of sodium methoxide (10 mole % excess over P-Cl equivalents) to an equimolar solution of phenol and 4-ethylphenol (5 mole-% excess over sodium methoxide) in bis(2-methoxyethyl) ether (ca. 1.5 l./mole NaOCH₃). The methanol produced was removed by azeotropic distillation with benzene. The $[Cl_2PN]_n$ polymer, essentially free from cyclic phosphazenes, was dissolved in dry benzene (ca. 1 l. solvent/100 g polymer) and added slowly over 3 to 5 hr to a refluxing (125°C) solution of the sodium aryloxides, and temperature was maintained at 125° ± 1°C for 50 to 55 hr. The reaction mixture was cooled to 80°C or lower, and copolymer was precipitated by addition to twice the total volume of methanol or ethanol/water (10/1 v/v) and stirred for one day. The polymer was dissolved three times in 8 to 16 liters tetrahydrofuran, precipitated into 10 to 15 gallons water, and washed with methanol or isopropanol. Ranges of values of intrinsic viscosity, elemental analyses, and $C_6H_5O/4-C_2H_5C_6H_4O$ ratios as determined by NMR (in deuteriochloroform solvent) are shown in Table I.

TABLE III
Typical Properties of $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ Foam

Property	Test reference	MIL P-0015280F (SHIPS) requirement	Typical $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ foam properties
Density, lb/ft ³	ASTM D-1667-70	4.5 to 8.5	3.5 to 13
Compression resistance at 25% deflection	FED-STD-601, 12151 MOD.	2.0 to 6.0	2.0 to 7.0
Water absorption, psf, max.	4.3.6 ^a	0.1	0.02 to 0.036
Compression set, %, max.	ASTM D-1667-70	24	—
Dimensional change, length %, max.	4.3.8 ^a	7	3
Fire resistance, flame spread index, max.	ASTM E-162-67	30	14 to 24
Smoke density, flaming	NBS smoke chamber	250	49
Oil resistance	4.3.10 ^a	no softening or visible swelling	no softening or visible swelling
Tensile strength, psi, min.	FED-STD-601, 4111	40	20 to 48
Ultimate elongation, %, min.	FED-STD-601, 4121	100	70 to 120
Tensile strength of cemented joints before aging, min.	4.3.13.1 ^a	no bond failure	no bond failure
Flexibility at 28°F, initial,	4.3.14.1 ^a	no cracking	no cracking
after heat aging 7 days/180°F	4.3.14.2 ^a	no cracking	no cracking
Thermal conductivity, Btu/in. (hr sq ft °F) ⁻¹	ASTM C-177-63	0.30	0.318
<i>K</i> factor, max.			
Water vapor permeability, perm-in., max.	ASTM C-355-64	0.30	0.16

^a MIL P-0015280F (SHIPS).

Synthesis of Other Poly(aryloxyphosphazenes)

Other poly(aryloxyphosphazenes) were prepared using procedures similar to that for $[(C_2H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ copolymer described above. Some of the polyphosphazenes synthesized are listed in Table II along with *LOI* values. Poly(alkylaryloxyphosphazenes) were decidedly more soluble than their unsubstituted or halogenated counterparts.

Preparation of Elastomeric Vulcanizates and Foams

Vulcanizates were prepared from $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ copolymer using a high-intensity rubber mixer and a two-roll rubber mill. Polymer, pigments, and plasticizers were blended in the mixer, and peroxide curing agents

TABLE IV
 $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ Vulcanizate Formulations

	A	B	C
Copolymer, phr	100	100	100
Burgess KE, phr	100	—	—
Calwhite, phr	—	40	—
Hydral 710, phr	—	—	100
Elastomag 170, phr	6	5	5
DiCup 40KE, phr	4	—	—
Varox powder, phr	—	5	5.7
Benzoyl peroxide, phr	—	—	4
Cure			
Press, min/°F	15/300	15/290	15/290
Oven, hr/°F	24/212	24/212	24/212
Tensile strength, ^a psi	2410	1420	670
Elongation, ^a %	80	330	150

^a ASTM D3196T.

were added to the mixed stock on the mill. Samples were molded in an electrically heated horizontal cut-off mold 0.050 in. deep.

Foams were prepared by mixing polymer and pigments in the mixer and adding peroxide curing agents, blowing agents, and activators on the mill at or below room temperature. Milled stock was molded in an electrically heated mold, using a full charge, under confining pressure for a short time (2 to 10 min) before being placed in a forced-air oven for final expansion. Foams were compounded to meet a U.S. Navy specification, MIL P-0015280F (SHIPS), shown in Table III.

RESULTS AND DISCUSSION

The $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ copolymer was selected for development into an insulating foam because of its fire retardancy without the presence of halogen and because of its elastomeric character.

Prior to preparation of foam compositions, several vulcanizates were formulated to obtain physical/mechanical property data on the copolymer batches. Properties of three representative but unoptimized formulations are shown in Table IV. These results indicate that the $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ copolymer shows promise for applications where moderate tensile strength and flame retardancy are required.

After a brief traverse of various foaming agents, curing agents, and foaming methods, foams of $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ were prepared⁴ using a mixed peroxide curing system and a chemical blowing agent, azodicarbonamide. Typical formulations and properties are shown in Table V. Formulation C in Table V was chosen as the most desirable for the intended application due to its excellent flame retardancy. Comparison of the NBS smoke test values of a foam prepared using this formulation with a commercial fire retardant foam is shown in Table VI. The maximum smoke density, D_{max} , of the $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ foam is about one fifth that of the commercial foam. Also, the value for time to $D_s = 16$ for the $[(C_6H_5O)_2PN-(4-$

TABLE V
Typical $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ Foam Formulations

	A	B	C
Copolymer, phr	100	100	100
Calwhite, phr	40	—	—
Hydral 710, phr	—	100	200
Elastomag 170, phr	5	5	5
Varox powder, phr	5	5	8
Benzoyl peroxide, phr	1	1.5	2
Zinc stearate, phr	—	0-10	8-26
Celogen AZ-130, phr	15	15-21	30
B IK, phr	10	10-15	20
Density, lb/ft ³	3.9-9.8	3.6-10	6-13
Compression resistance at 25% deflection, psi	1-4	2-5	2-7
Tensile strength, psi	—	20-50	20-30
Ultimate elongation, %	—	80-120	65-80
LOI	25-26	31	38-48

TABLE VI
NBS Smoke Test, Flaming Condition

	Commercial fire retardant foam	$[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ foam
Density, lb/ft ³	6	6.7
LOI	29	48
D_{max}	250	49
Time to $D_s = 16$, min	0.2	1.5
R_m , max. rate, min ⁻¹	149	10
HCl, ppm	20	0
CO ₂ , %	0.5	0.3
CO, ppm	350	100
HCN, ppm	20	10
Weight loss, %	34.2	15.9

^a Meets MIL P-0015280F (SHIPS).

$C_2H_5C_6H_4O)_2PN]_n$ represents a very considerable gain in egress time from a room in which a fire is consuming this foam as compared to the commercial foam. In addition, the surface flammability of this foam, as determined by ASTM E 162, was better than the surface flammability of a commercial material, as shown in Table VII.

Though $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ foams were formulated to provide maximum flame retardancy, they also had to have adequate physical properties for their intended application as an insulating foam. A comparison of typical properties of $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ foam to the military specification MIL P-0015280F is shown in Table III.

The foams also have long-term stability to at least 300°F as demonstrated by retention of resilience and density, as shown in Tables VII and VIII. These results suggest potential use at elevated temperatures.

TABLE VII
Surface Flammability of Foams

	$[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ foam	Commercial foam ^a
Flame spread factor F_s	4.4	4.9
Heat evolution factor Q	3.9	5.0
Flame spread index, $I_s = F_s \cdot Q$	17	24

^a Meets MIL P-0015280F (SHIPS).

TABLE VIII
Compression Resistance at 25% Deflection After Isothermal Aging at 300°F

Hours	Commercial fire retardant foam ^a	Compression resistance, psi $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ Foams		
		I	II	III
0	2.5	1.7	4.0	6.7
2	1.9	1.6	—	—
6	2.3	1.7	—	—
24	12	0.7	—	—
96	25.7	1.7	—	—
	(no recovery)			
168	—	1.6	—	—
200	—	—	4.1	8.4
390	—	—	4.8	11.9
600	—	12.5	—	—
795	—	—	9.7	35.8
1128	—	—	15.5	48.2

^a Meets MIL P-0015280F (SHIPS).

CONCLUDING REMARKS

Poly(aryloxyphosphazene) foams represent an advance over current commercial flame retardant closed-cell insulating foams. Foams were prepared on a larger laboratory scale to allow field testing, which is currently in progress. Other poly(aryloxyphosphazenes) show potential for advanced applications, particularly where reduced smoke generation and increased fire retardancy are important.

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