Synthesis and Electrical Conductivity of Phosphorus-Nitrogen Compounds. V. Synthesis and Electrical Resistivity of Poly[bis(amino)phosphazenes]

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Three new poly[bis(amino)phosphazenes] of formulas $[NP(NHC_6H_{13})_2]_n$, $[NP(NHCH_2CHCH_2)_2]_n$, and $[NP(NHCH_2C_6H_5)_2]_n$ have been synthesized by direct aminolysis of $(NPCl_2)_n$. The electrical resistivity and thermal stability of a series of poly[bis(amino)phoshazenes], (NPR_2) (R: amino group), have been examined. Most polymers showed an increase in resistance with time to an equilibrium value, possibly due to space charge effects, allowance for this conductivity being ohmic up to 500(V/cm). The aliphatic amino derivatives have a lower resistivity and a lower ΔE value than the aromatic amino derivatives. The resistivity of the poly [bis(amino)-phosphazenes] was found to decrease in the order, R : $NHC_2H_5 > NHC_3H_7 > NHC_4H_9 > NHC_6H_{13} \gg N(CH_3)_2$. This seems to be predominantly due to the nature of an inductive electron supply of amino side groups. In some polymers the change of energy gap, ΔE, was observed in the range 70—90 °C. The ΔE value was usually lower in the low temperature region than in the high temperature region. All the polymers were found to decompose at about 200 °C, losing the amino side group.

Although the synthesis and chemistry of phosphazene compounds have been extensively investigated, very little[1,2] has been done to measure the electrical resistivity of these compounds. In previous papers[3,4] we reported on the electrical resistivity of the phosphonitrilic chloride, $(NPCl_2)_3$, and its derivatives.[3,4]

It was found that the resistivity of phosphazene compounds obeys an equation of the form : $\rho = \rho_0 \exp (E/kT)$, where ρ is the resistivity, E the activation energy, k Boltzmann constant, and T the absolute temperature. It has been suggested that the resistivity of $(NPR_2)_3$ was remarkably dependent upon side group R. It was found that the highest conductivities were obtained with side groups containing amino groups.

The purpose of this work is to synthesize poly[bis(amino)phosphazenes] and to measure the resistivity of the polymers. The difference in side group R of (NPR_2) is expected to affect the electrical resistivity of the polymers.

Experimental

Preparation of Poly(dichlorophosphazene). Sublimed hexachlorocyclotriphosphazene (5.000 g) and benzoic acid (0.200 g) were weighed directly into a carefully cleaned Pyrex ampoule. The ampoule was evacuated to 10^{-1} Torr for 1 h and then sealed. The sealed ampoule was placed in a furnace and heated at 210±2 °C for 4 h. After polymerization, the ampoule was opened and the conetnts were extracted with dry benzene. The solvent was removed and the unreacted materials were separated from the residue by vacuum sublimation. Linear $(NPCl_2)_n$ was obtained.

Preparation of Poly[bis(amino)phosphazenes]. Aliphatic primary amines (ethylamine, propylamine, butylamine, hexylamine, allylamine, benzylamine), secondary amine (dimethylamines), and aromatic amine (aniline) were used. The amino-substituted polymers of the structure $[NP(NHR)_2]_n$ (NHR: NHEt, $NHPr^n$, $NHBu^n$, NHPh) and $[NP(NMe_2)_2]_n$ were synthesized and purified according to the procedure given by Allcock and Kugel.[5,6] The amino-substituted polymers of the structure $[NP(NHR)_2]_n$ (NHR: $NHhexyl^n$, $NHCH_2CHCH_2$, $NHCH_2Ph_5$) were prepared as follows.

Poly[bis(mono-hexylamino)phosphazene]; $[NP(NHC_6H_{13})_2]_n$: A solution of polydichlorophosphazene (3.68 g, 0.032 mol) in tetrahydrofuran (150 ml) was added slowly to a stirred solution of mono-hexylamine (25.0 g, 0.25 mol) and triethylamine (25.3 g, 0.25 mol) in tetrahydrofuran (100 ml). The reaction was allowed to proceed at 25 °C for 5 days and then allowed to proceed at 40 °C for 7 h.

The mixture of polymer and amine salts was filtered off, and the solvent was removed from the filtrate by distillation. The residue obtained was dissolved in trifluoroethanol and the polymer was precipitated from the solution by addition of acetone. The procedure was repeated, and the polymer was dried in a vacuum over P_2O_5.

Poly[bis(allylamino)phosphazene]; $[NP(NHCH_2CH{=}CH_2)_2]_n$: This polymer was prepared by a modification of the method of Allcock *et al.*[7] A solution of polydichlorophosphazene (7.20 g, 0.062 mol) in benzene (80 ml) was added dropwise to a stirred solution of allylamine (56.50 g, 0.990 mol) and triethylamine (12.5 g, 0.124 mol) in benzene (60 ml).

The mixture was then boiled under reflux for 55 h and then allowed to stand at 25 °C for 2 days. The upper benzene layer was decanted from the amine salts and the oily bottom layer. The benzene solution was washed with water and dried over anhydrous magnesium sulfate. Filtration and evaporation of the filtrate at reduced pressure gave a white solid.

Poly[bis(benzylamino)phosphazene]; $[NP(NHCH_2C_6H_5)_2]_n$: A solution of polydichlorophosphazene (8.450 g, 0.073 mol) in benzene (70 ml) was added slowly to a stirred solution of benzylamine (46.8 g, 0.437 mol) and triethylamine (44.2 g, 0.437 mol) in tetrahydrofuran (70 ml). The reaction mixture was stirred at 25 °C for 50 h and then at 45 °C for 7 h. The mixture of polymer and amine salts was filtered off, solvent being removed from the filtrate by distillation. The residue was redissolved in acetone, and the polymer was then precipitated from the solution by addition of ehtanol and dried in a vacuum over P_2O_5.

Resistivity Measurement. All the polymers were powdered and molded pellets were used for resitivity measurements. Pellets (12 mm diameter and 1—2 mm thick) were molded at pressures up to 500 kg/cm^2). The pellets were provided with vacuumevaporated platinum–palladium alloy contacts. Among the contact materials platinum–palladium alloy seemed to give the best ohmic contacts.

The electrical resistivity was studied as a function of temperature in the range 20—180 °C. In order to get exact resistivity values, the current was measured as a function of the voltage in the range 0—90 V, with use of a guard electrode.

Physical Measurements. Molecular weights were measured by vapor pressure osmometry with a Hitachi Model-117 type osmometer using benzene as a solvent.

TABLE 1. CHEMICAL ANALYSIS OF THE PRODUCTS

Compound	Calcd(%)		Found(%)		Mol wt	Yield (%)	Appearance
	P	N	P	N			
$[NP(NH\text{-}monoC_6H_{13})_2]_n$	12.74	12.55	12.62	17.27	4.0×10^3	25	White powder
$[NP(NHCH_2CH{=}CH_2)_2]_n$	21.67	26.19	19.70	26.74	7.6×10^3	12	White powder Resinous material[a]
$[NP(NHCH_2C_6H_5)_2]_n$	11.20	16.90	12.04	16.34	—	3	White powder

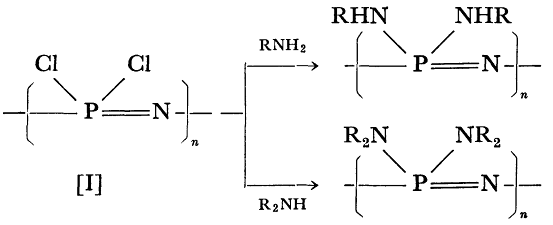
a) A small amount.

IR spectra were recorded on a Shimadzu Model-450 type spectrometer by means of the KBr disk technique.

Thermogravimetric analysis and differential thermal analysis were carried out with a Shimadzu Model DT 20-B under dry nitrogen (50 ml/min) at a heating rate of 15 °C/min.

Results and Discussion

Syntheses. In general, poly[bis(amino)phosphazenes] are synthesized by the reaction of poly(dichlorophosphazene) with a primary or secondary amine according to the following scheme.



[I] [II] [III]

We have synthesized three new compounds: poly(mono-hexylaminophosphazene), poly(allylamino phosphazene), and poly(benzylaminophosphazene).

Excess amines and triethylamine were used as hydrohalide acceptors for the steric property of these bulky amines. The results of chemical analysis and molecular weights of the products are given in Table 1.

We see that the elemental compositions of the polymers correspond satisfactorily to the expected structures.

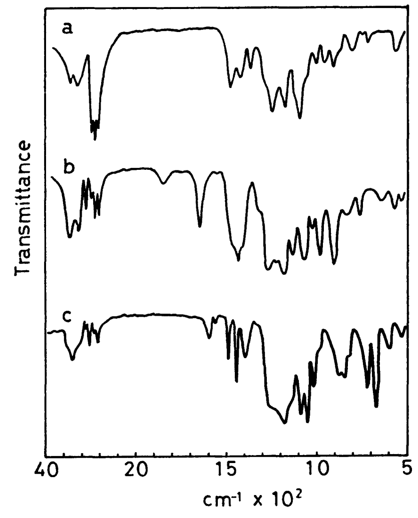


Fig. 1. IR spectrum of the products.
a: $[NP(NH\text{-}mono\text{-}C_6H_{13})_2]_n$,
b: $[NP(NHCH_2CH{=}CH_2)_2]_n$,
c: $[NP(NHCH_2C_6H_5)_2]_n$.

The IR spectra of the products obtained from the reaction of poly(dichlorophosphazene) with monohexylamine, allylamine, benzylamine are shown in Fig. 1. All the polymers exhibit a characteristic P=N stretching absorption in the region 1200—1260 cm^{-1}.

The assignments for the main peaks are as follows (frequncies in cm^{-1}): for $[NP(NHR_2]_n$ where R is mono-C_6H_{13}, 1260 (P–N), 1180, 1100 (C–N), 905 (P–N, C–N), 1467, 1370($-CH_3$), 3360, 3250, (N–H), CH_2-$CH{=}CH_2$, 1260, 1230(P–N), 1190, 1080(C–N), 915, 995, 1420, 1640, 3080, (allyl), 3220(N–H), CH_2–C_6H_5, 1220, 1250(P–N), 1180(P–N, C–N), 1070, 1090(C–N), 1450, 1500, 1580, 1600($-C_6H_5$), 2900, 2850($-CH_2$), 3345(N–H). The results indicate that the monohexylamino, allylamino, and benzylamino derivatives are of open chain structure similar to that of the $(NPCl_2)_n$.

The complete replacement of chlorine atoms of poly(dichlorophosphazene) by monohexylamine or benzylamine required severer conditions than those reported for ethylamine, methylamine, propylamine, *etc.* This seems to be associated with steric hindrance of side group.

All the polymers are soluble in mineral acid, trifluoroethanol or benzene, but not in common organic solvents or water. The solubility of the polymers indicates that the meterials are not cross-linked. The polymers seem to have a linear structure. It was found from IR spectra, chemical analysis, and UV spectra that the five polymers prepared by the method of Allcock are consistent with the expected structure, $[NP(NHR)_2]_n$ (NHR: NHEt, NHPr^n, NHBu^n, NHPh) and $[NP(NMe_2)_2]_n$.

Thermal Stability. The thermal stability of the eight poly[bis(amino)phosphazenes] were examined by TGA and DTA. The results are given in Figs. 2 and 3. The polymers begin to decompose at about 200 °C, a remarkable weight loss being observed between 250 and 400 °C. On the other hand, in the ethylamino, propylamino, butylamino, mono- hexylamino, allylamino, and diethylamino derivatives, the broad endothermic peaks appear between 200 and 400 °C. In the phenylamino and benzylamino derivatives the endothermic peaks appear between 400 and 470 °C.

In the decomposition of all the polymers at 400 °C, the corresponding amines to side groups were detected by gas chromatography. Decomposition took place with elimination of appropriate amines. The endothermic peaks appearing above *ca.* 500 °C might be due to breakdown of phosphorus nitrogen bonds. In the ethylamino, propylamino, butylamino, and monohexylamino derivatives, exothermic peaks which seem

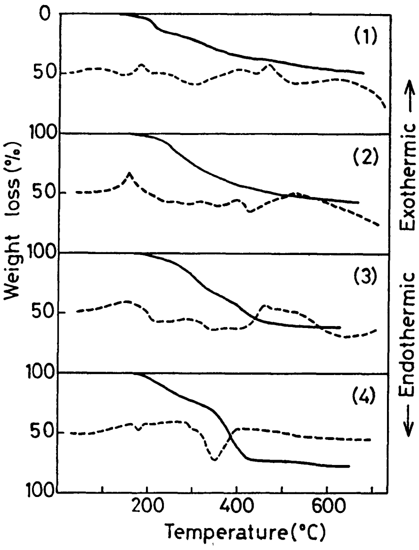


Fig. 2. TGA and DTA curves for poly[bis(amino)-phosphazenes], $[NPR_2]_n$.
(1): $R=NHC_2H_5$, (2): $NHC_3H_7{}^n$, (3): $NHC_4H_9{}^n$, (4): NH-mono-C_6H_{13}.
——: TGA, ----: DTA.

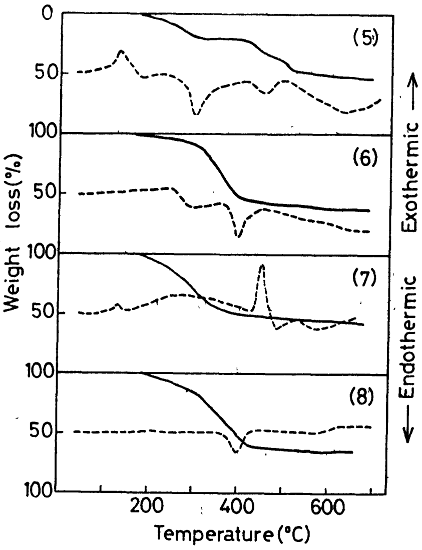


Fig. 3. TGA and DTA curves for poly[bis(amino)-phosphazenes], $[NPR_2]_n$.
(5): $R=NHCH_2CHCH_2$, (6): $N(CH_3)_2$, (7): NHC_6H_5, (8): $NHCH_2C_6H_5$.
——: TGA, ----: DTA.

to be oxidation of the alkyl groups appear between 150 and 175 °C. In the allylamino derivative, the sharp exothermic peak appears at 125 °C. This is probably due to the addition polymerization of the allylamino side group similar to that reported for $[NP(NHCH_2CH{=}CH_2)_2]_3$ and $[NP(NHCH_2CH{=}CH_2)_2]_4$ by Allcock *et al.*[7]

D. c. Resistivity. The results of initial measurements of all the samples were not reproducible.

Several thermal cycles for each sample were carried out in order to obtain reproducible results. A typical example is shown for dimethylamino derivative in Fig. 4.

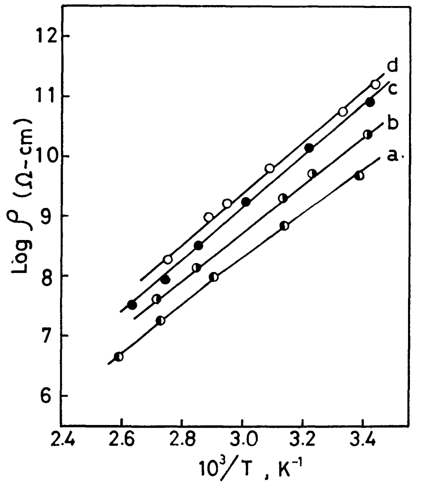


Fig. 4. Temperature dependence of resistivity of $[NP(N(CH_3)_2)_2]_n$.
a: Ascend first time, b: ascend second time,
c: ascend third time, d: desend third time.

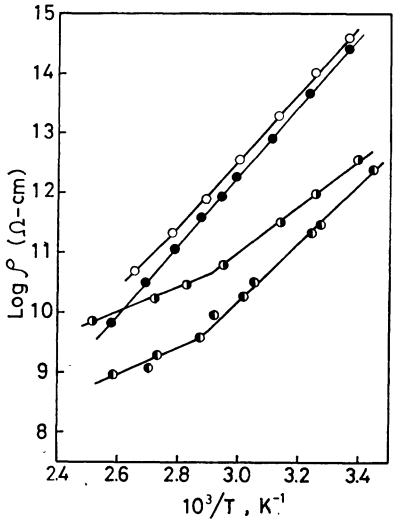


Fig. 5. Temperature dependence of resistivity of poly-[bis(amino)phosphazenes], $[NPR_2]_n$.
○: $R=NHC_2H_5$, ●: $R=NHC_3H_7{}^n$,
◑: $R=NHC_4H_9{}^n$, ◐: R=NH-mono-C_6H_{13}.

Lower resistivity was always observed in the initial runs.

Initial heating curves are usually of anomalous low ΔE and frequently curved, due to the evaporation of moisture or solvents. Reproducible results were obtained after several thermal cycles had been carried out.

The results are given in terms of log ρ *vs.* $1/T$ (Figs. 5 and 6).

The results can be expressed by the relationship $\rho=\rho_0\exp(\Delta E/2RT)$. The calculated energy gaps ΔE and values of log ρ_0 are given in Table 2. Some curves show a break point in the range 70—90 °C. A break point was found by measurements on other polymers.[8] The break point is usually associated with thermal decomposition of the sample.

However, our investigations of thermal stability show-

TABLE 2. VALUES OF RESISTIVITY, ENERGY GAP, AND log ρ_0

Side group^a) R		Temp (°C)		Energy gap ΔE (eV)	log ρ_0 (Ω cm)	ρ (20 °C) (Ω cm)
(1)	NHC_2H_5	25	90	2.20	−4.1	8.1×10^{14}
(2)	$NHC_3H_7{}^n$	25	120	2.30	−5.3	6.3×10^{14}
(3)	$NHC_4H_9{}^n$	20 70	70 125	1.54 0.84	−0.7 +4.5	4.5×10^{12}
(4)	NH-monoC_6H_{13}	20 75	75 120	1.95 0.84	−4.5 +3.5	1.8×10^{12}
(5)	$NHCH_2CHCH_2$	20 43	43 75	1.69 0.53	−3.0 +6.2	2.8×10^{11}
(6)	$N(CH_3)_2$	20	90	1.75	−3.8	1.8×10^{11}
(7)	NHC_6H_5	70 90	90 120	1.46 5.80	—	1.6×10^{15} (75 °C)
(8)	$NHCH_2C_6H_5$	85	120	(1.85)	—	1.3×10^{15} (90 °C)

a) $[NPR_2]_n$.

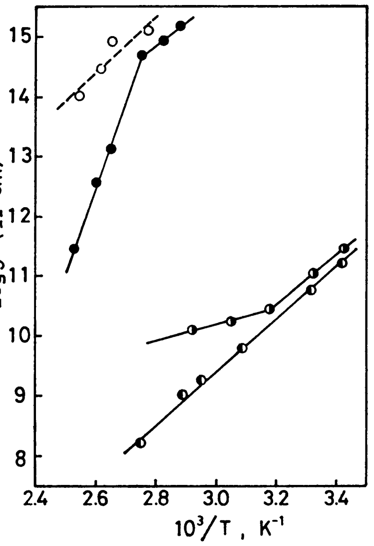


Fig. 6. Temperature dependence of resistivity of poly-[bis(amino)phosphazenes], $[NPR_2]_n$.
○: $R=NHCH_2CHCH_2$, ●: $R=N(CH_3)_2$,
◑: $R=NHC_6H_5$, ◐: $R=NHCH_2C_6H_5$.

ed no decomposition of the polymers in the range 70—90 °C. It was found that the resistivity of poly(aminophosphazenes), $[NP(NHR)_2]_n$, decreases in the order, NHR: $NHCH_2C_6H_5$, $NHC_6H_5 \gg NHC_2H_5 > NHC_3H_7 > NHC_4H_9 > NHC_6H_{13} \gg N(Me_3)_2$. Thus, the resistivity of polymers decreases with an increase in the number of C in side groups of aliphatic primary amino derivatives, and the resistivity of the secondary amino derivative, $[NP(NMe_2)_2]_n$, showed lower values than those of the primary amino derivatives. This is probably attributed to the nature of an inductive electron supply. Both the inductive electron supply from amino to phosphorus, and π effects involving donation of the nitrogen lone pair electrons into phosphorus d_{z_2} orbitals would raise the electron density at phosphorus,9) raising electrical conductivity. However, it appears that P_π–d_π bonding cannot bring about enough π-orbital overlap to cause high electrical conduction. If the π bonds in the phosphazene chain were delocalized, as suggested for cyclic oligomers,10) then the conductivity would be expected to be comparable to that of the carbon polyene polymers.

On the other hand, the values of resistivity of phenylamino and benzylamino derivatives are greater than 10^{-15} Ω cm at room temperature. The bulky side groups such as aromatic amino would be expected to reduce the interaction between molecules, as compared with aliphatic amines which possess a possible degree of rotation about the C–C single bonds. A similar behavior was reported for polyacethylenes.11) In phenylamino derivatives, the break point was observed at 90 °C corresponding to the glass transition temperature reported by Allcock and Kugel.5) The amino derivatives have low resistivity when compared to alkoxy or aryloxy derivatives.12) Thus, it appears that the high side-group polarity of amine and increased opportunities for hydrogen bonding (when NHR groups are present) decrease the resistivity of the polymers. The conductivity observed for the poly(aminophosphazenes) is assumed to be associated primarily with the electrons of its conjugated double bond.

When an external field was applied, polarization, *i.e.*, an increase in resistance with time to a steady value, occurred for most samples, the resistivity reaching equilibrium values after 30 min—1h. Although similar results have been described,13,14) it is assumed that

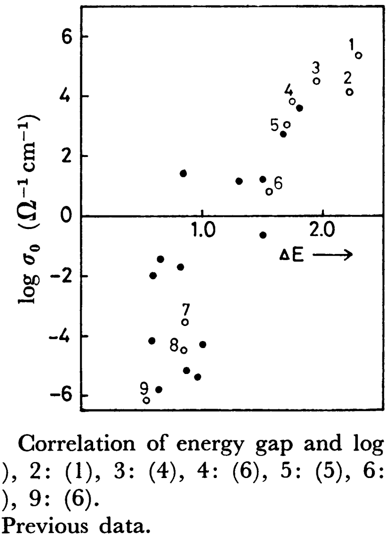


Fig. 7. Correlation of energy gap and log σ_0.
1: (2), 2: (1), 3: (4), 4: (6), 5: (5), 6: (3), 7: (4), 8: (3), 9: (6).
●: Previous data.

the effect arises from either space-charge build-up in the sample or barrier between electrode and sample.

The correlation of energy gap ΔE and preexponential factor $\log \sigma_0(=1/\rho_0)$ is shown in Fig. 7. A straight line with a large amount of scatter is obtained, suggesting the relationship $\log \sigma_0 \approx \Delta E(\mathrm{eV})-6$. The compensation law is valid for poly[bis(amino)phosphazenes]. However, it is difficult to give a physical meaning. An interpretation is given in terms of molecular motion as a condution mechanism such as presented by Gutmann and Lyons[13] and Cardew and Eley.[15] However, exprimental results are so few that a quantitative discussion of this type of conduction mechanism cannot be realized.

Most polymers showed ohm's law behavior up to *ca.* 500 (V/cm) or above.

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