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New Acid-Polyfunctional Water-Soluble Phosphazenes: Synthesis and Spectroscopic Characterization

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NEW ACID-POLYFUNCTIONAL WATER-SOLUBLE PHOSPHAZENES: SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION

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ABSTRACT

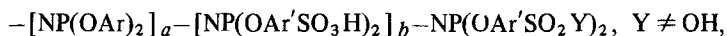
Poly[bis(phenoxy)]phosphazene sulfonic acid and its mixed substitution derivatives containing *N*-methylsulfonamide, sulfonylaminoacetic, and free sulfonic acid functions have been obtained and characterized by IR and ^1H -, ^{31}P -, ^{13}C -NMR spectroscopy. The polymers are all water soluble. Poly[bis(4-benzoylphenoxy)]phosphazene sulfonic acid could not be obtained due to chain degradation during the synthesis.

INTRODUCTION

Phosphazenes, $-(\text{NPX}_2)_{-n}$, are a unique class of inorganic compounds of the fifth group elements which may be obtained over a wide range of molecular weights (n 3-15 000) and, depending on the nature of the substituent ($\text{X} = \text{OR}, \text{OAr}, \text{NRR}', \text{R}, \text{Ar}$) offer broad opportunities for useful applications [1]. The water-soluble polymers are potentially interesting [1] as ligands of transition metal molecules [2] in homogeneous catalysis, carriers for bimolecules and drugs [3], and polyfunctional resins. So far, water-solubilizing substituents have been reported to be basic or neutral functions (e.g., NHCH_3 , glucose residues, $\text{OCH}_2\text{CH}_2\text{OCH}_3$). The only reported example of acid phosphazene ($\text{X} = \text{OC}_6\text{H}_4\text{COOH}$) [4] is a water-insoluble material. Polyphosphazenes containing strong acid functions are not known.

The sulfonic ($-\text{SO}_3\text{H}$) function is strongly acid and is often used in polymer chemistry in order to provide parent polymers with hydrophilic functions [5]. Most recently, a brilliant example of similar use has been reported with a phosphorus sulfonic acid compound in the field of homogeneous catalysis. Tris(*m*-sulfophenyl)phosphine has been shown to be an efficient ligand for achieving dissolution or extraction from organic media of hydrophobic transition-metal complexes in water [6].

In this context, the sulfonation of high molecular weight poly[bis(aryloxy)]-phosphazenes, $-\text{[NP(OAr)}_2\text{]}_{-n}$, appeared to us most intriguing. Due to the reactivity of the pendent substituents, these compounds offered opportunity to obtain, by sulfonation, new nitrogen, phosphorus, and sulfur inorganic compounds: $-\text{[NP(OAr)}_2\text{]}_a-\text{[NP(OAr}'\text{SO}_3\text{H)}_2\text{]}_b-$. Their molecular weight was the basis for the preparation of polyfunctional molecules with mixed substituents:



which contained enough sulfonic functions in free acid form to impart water solubility.

EXPERIMENTAL

Materials and Reagents

Poly[bis(phenoxy)] phosphazene [7] (PBPP) and poly[bis(4-benzoylphenoxy)] phosphazene [8] (PBBPP), synthesized according to the literature, had weight-average molecular weights (\bar{M}_w) of 4.7×10^6 and 1.9×10^6 , respectively. All other reagents were C. Erba RPE products.

Preparation of Sulfonic Acid Polymers (SA)

PBPP (8 g) is dissolved in 150 mL *sym*-dichloroethane, and to it is added at room temperature 2.9 mL freshly distilled (from 20% oleum) SO_3 , under stirring and N_2 blanketing, to yield a precipitate. After 7 h, 50 mL H_2O is added; the precipitate dissolves and layer separation is allowed to proceed over a fortnight. To the dark aqueous layer is added fresh dichloroethane; it is refluxed under stirring and separated again. Evaporation of the combined organic layers to dryness leaves no residue. Separation of the reaction product from sulfuric acid due to unreacted SO_3 is accomplished by adding to the dark aqueous phase 10 M KOH to pH 7.5, filtering, bringing the mother liquor to pH 9 with more KOH, and adding KCl up to 0.30 g/mL concentration to precipitate the sulfonated polymer product as its K^+ salt. The solid is filtered, washed with EtOH to a negative Cl^- test, taken up in water to yield 1% solution, and percolated through Dowex 50W-X8, H^+ form resin (Baker Chemical Co.). After elution, the resin is washed with water to neutral pH and the collected eluates are evaporated to dryness to yield 7.4 g of product (SA).

PBBPP (4.4 g) and 0.83 mL SO_3 were reacted for 3 h as above. When base was added during product recovery, evolution of ammonia was observed. The end product had significantly lower nitrogen content (C/N elemental ratio = 55) than the starting polymer (C/N found = 25.5) and was not investigated further.

Preparation of Mixed-Substituent Polymers in *N*-Methylsulfonamide, Sulfonylaminoacetic, and Sulfonic Acid Forms (SAMSA and SAMSAASA)

SA is converted to the sulfonyl chloride form (SCI) by refluxing 7.4 g of the above sulfonic acid polymer with 60 mL SOCl_2 and 1.5 mL dimethylformamide. After 90 min, gas evolution ceases and nearly all the polymer dissolves. Upon separation of the insoluble residue (0.25 g), the clear solution is evaporated at 40–50°C under reduced pressure to yield 7.2 g of the

polymer in sulfonyl chloride form (SCI). Contrary to SA, SCI is soluble in acetone.

SCI (3 g) in acetone (10 mL) is added dropwise to 1 g glycine in 50 mL water and 25 mL acetone containing 3.4 g NaHCO_3 , under stirring and cooling in an ice bath. CO_2 evolves, and a precipitate forms. After filtration, the sticky solid product dissolves in acetone and yields a film (2.6 g) upon room temperature solvent evaporation. The IR spectrum of this product is similar to that in Fig. 1(c) below 1600 cm^{-1} and to that in Fig. 1(d) above 1600 cm^{-1} . The product, stored in capped polyethylene vials at room temperature, is not stable and evolves an odorless gas. Taking it up in water yields a suspension which is filtered and washed repeatedly with water. Room-temperature vacuum evaporation and drying of the washings yields 0.2 g residue. The water-insoluble product, SAMSA(C), was dried under vacuum at room temperature to yield 2.2 g.

The same reaction was carried out by heating to reflux temperature for 30 min after the addition of SCI to glycine. In this case, products yields were as follows: 2.4 g of SAMSA(H), insoluble in water but soluble in acetone, and 0.24 g of SAMSAASA, which was extracted by washing the raw solid precipitated during the reaction with water.

Measurements

X-ray powder diffraction patterns were obtained on polymer films by use of Philips PW 1050 x-ray powder diffractometer. TGA and DSC scans were performed in 100 mL/min N_2 at $10^\circ\text{C}/\text{min}$ by use of Du Pont 1090 instruments. \bar{M}_w measurements were obtained by a Sophica spectrogoniodiffusometer [8]. IR spectra were recorded on a Perkin-Elmer 782 spectrometer on films deposited from solution by evaporation on AgCl plates. Samples recovered from TGA scans were analyzed as KBr pellets. ^1H - and ^{13}C -NMR spectra were recorded on a WP-80 Bruker spectrometer operating in the Fourier-transform mode at 80 and 20.149 MHz, respectively. ^{31}P -NMR spectra were recorded on an XL-200 spectrometer operating in the Fourier-transform mode at 80.961 MHz. The assignment of aromatic ^{13}C resonance bands in the spectra of sulfonated phosphazenes were obtained on the basis of the additivity of substituent effects ($\Delta\delta$, ppm) on the chemical shifts (δ , ppm) of aromatic compounds [9]. By taking benzene as standard ($\delta_{\text{S}} = 128.7$ ppm) and benzenesulfonic acid ($\delta_{\text{B}} = 126.3, 129.8, \text{ and } 132.2$ ppm at the *ortho*, *meta*, and *para* carbons and $\delta_{\text{B}} = 143.6$ ppm at the C-S carbon), the $-\text{SO}_3\text{H}$ effect ($\Delta\delta = \delta_{\text{B}} - \delta_{\text{S}}$) at each carbon was calculated: $\Delta\delta$ is 14.9 ppm at the

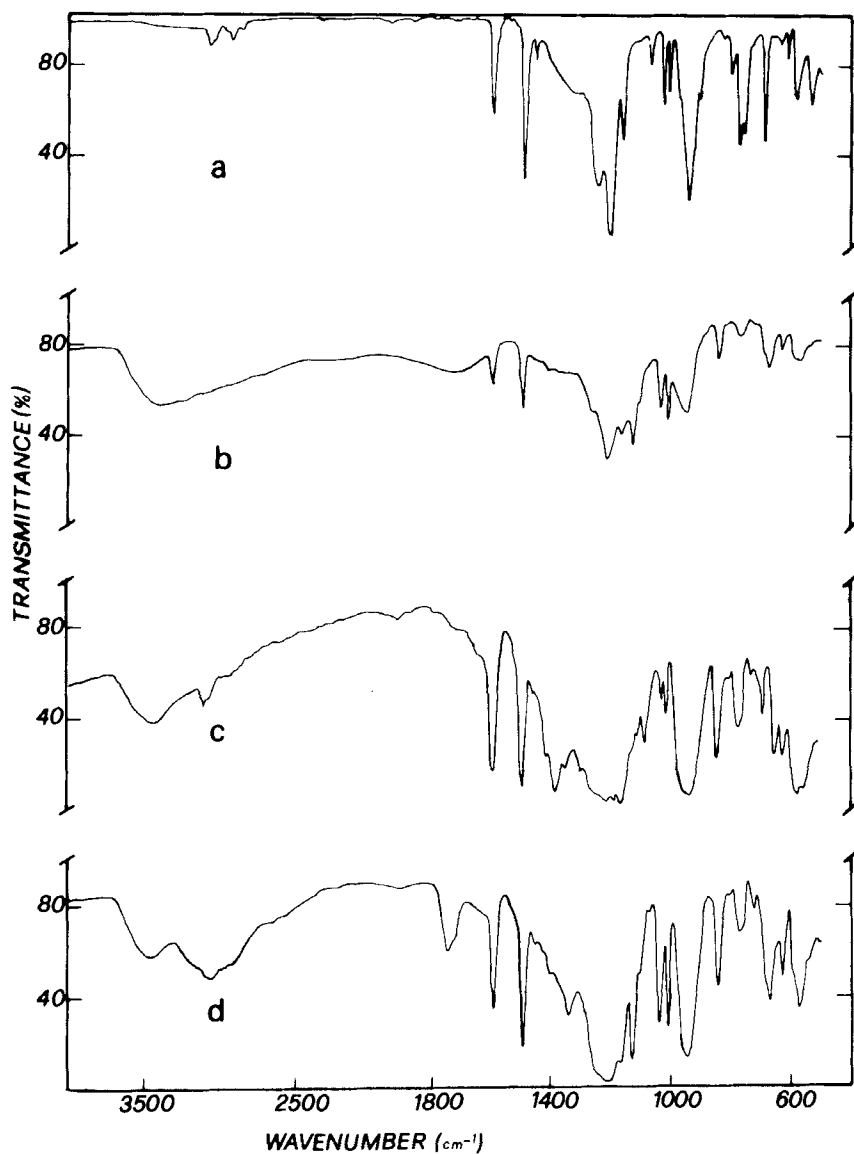
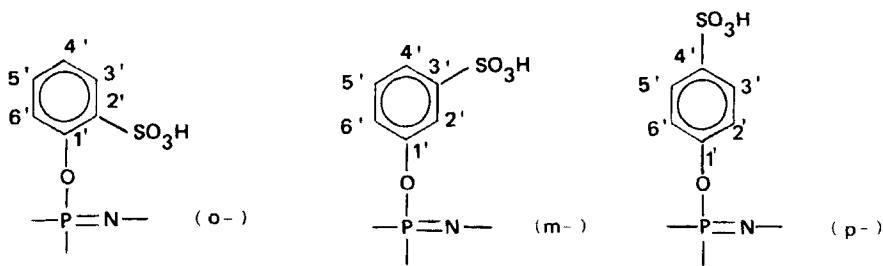
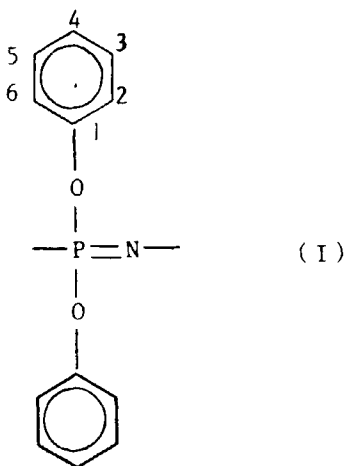


FIG. 1. IR spectra of poly[bis(phenoxy)]phosphazene (a) and of its acid derivatives: II (b), IIIH (c), and IV (d).

carbon bearing the C-S bond, -2.4 ppm at the carbons in the *ortho* position, 1.1 ppm at the carbons in the *meta* position, and 3.6 ppm at the carbon in the *para* position. The three isomers for the sulfophenoxy ring of the phosphazenes:



were then considered. The ^{13}C chemical shifts of poly[bis(phenoxy)]phosphazene:



were obtained experimentally (Table 4) and assigned, by analogy with other aromatic compounds bearing $\equiv\text{C}-\text{OP}$ bonds [10], as follows: δ is 151.6 ppm for the C_1 carbon bearing the C-O bond, 121.5 ppm for the *ortho* carbons (C_2 , C_6), 128.8 ppm for the *meta* carbons (C_3 , C_5), and 123.5 ppm for the *para* carbon (C_4). The corresponding ^{13}C chemical shifts (δ_{o-} , δ_{m-} , δ_{p-}) were then calculated for the sulfo-substituted phenoxy isomers by adding the above $\Delta\delta$ values to the ^{13}C experimental δ values of poly[bis(phenoxy)]-phosphazene: $\delta_{o-} = 149.2$ (C_1'), 136.4 (C_2'), 126.4 (C_3'), 124.6 (C_4'), 128.8

(C_{5'}), 122.6 (C_{6'}) ppm; δ_m = 152.7 (C_{1'}), 119.1 (C_{2'}), 143.7 (C_{3'}), 121.1 (C_{4'}), 129.9 (C_{5'}), 125.1 (C_{6'}); δ_p = 155.2 (C_{1'}), 122.6 (C_{2'}, C_{6'}), 126.4 (C_{3'}, C_{5'}), 138.4 (C_{4'}) ppm. Line assignments in the spectra of Table 4 were made according to the closest fit of the experimental to the calculated values. Confirmation of the selected structure was sought by means of IR spectroscopy.

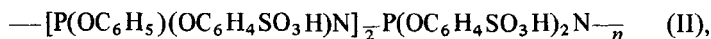
The product structures (I-IV in Table 2 and in the Results section) were derived on the basis of the closest fit of the proposed structure to both elemental microanalytical data (Table 1) and NMR relative proton ratios (Table 3). No more than one substituent per phenoxy ring was assumed. Elemental carbon ratios, as obtained in the ¹³C-NMR spectra, were also considered to support the product structures. Because of variable nuclear Overhauser enhancement and spin-lattice relaxation time, quantitative ¹³C measurements were performed only for carbons not bearing C-H bonds and under the following instrumental conditions: spectral width 5000 Hz, acquisition time 0.81928 s, pulse width 1.1 μ s (30°C), pulse delay 2.5 s. The microanalytical data (Table 1) showed some discrepancies from the structures suggested by NMR spectroscopy (Table 3), most likely because of incomplete combustion of the phosphazene samples [11] during analysis.

The polymer structures II-IV are idealized representations. In reality, the distribution of substituents in the polymer chain is not known. The structures, therefore, are more realistically identified by the mol/mol ratio of sulfo substituents to total phenoxy rings as in Table 2.

RESULTS AND DISCUSSION

Product Molecular Weight

According to expectations, the reaction of poly[bis(phenoxy)] phosphazene (PBPP) and SO₃ at SO₃/-P(OC₆H₅)₂N- mole-to-mole ratio 2.0 in dichloroethane was found to yield the water-soluble sulfonic acid derivative (SA), whose repeating unit is ideally represented by Structure II,



where the sulfo-phenoxy rings have the *meta* structure. The product weight-average molecular weight (\bar{M}_w), determined in water solution, was found to be $\sim 10^6$. The number of repeating units (n in II) was thus about 1000, which is equivalent to about 3000 ---P=N--- units. The same number of ---P=N--- units per mole of polymer was found for the other derivatives of II. By comparison, the parent polymer I had \bar{M}_w 4.7×10^6 and about 20 300 ---P=N--- units. The

TABLE 1. Found Elemental Concentrations and Atomic Ratios for Poly[bis(phenoxy)] phosphazene (PBPP) and Its Acid (-A) Reaction Products

| Product | Composition, wt% | | | | | | Atom/atom ratios | | | | | |
|----------|------------------|------|------|-------|-------|--|------------------|------|-----|-----|-----|--|
| | C | H | N | P | S | | C | H | N | P | S | |
| PBPP | 60.56 | 4.52 | 5.89 | 13.00 | 0.00 | | 12.0 | 10.7 | 1.0 | 1.0 | 0.0 | |
| SA | 38.80 | 3.70 | 3.77 | 8.32 | 11.50 | | 12.0 | 13.6 | 1.0 | 1.0 | 1.3 | |
| SAMSA(C) | 35.64 | 3.95 | 3.97 | 7.55 | 11.00 | | 12.2 | 16.1 | 1.2 | 1.0 | 1.4 | |
| SAMSA(H) | 36.75 | 2.54 | 4.34 | 8.60 | 11.58 | | 11.0 | 9.1 | 1.1 | 1.0 | 1.3 | |
| SAMSAASA | 31.35 | 3.14 | 5.20 | 6.90 | 9.06 | | 11.7 | 14.0 | 1.7 | 1.0 | 1.3 | |

TABLE 2. Proposed Structure, Theoretical Elemental Ratio, and Solvents for Poly[bis(phenoxy)] phosphazene (PBPP) and Its Acid (-A) Reaction Products

| Product structure ^a | Ratio of sulfo substituent to total phenoxy rings, mol% | | | | Theoretical elemental ratio, atom/atom | | | | | Solvents ^b |
|--------------------------------|---|-----------------------|---|------|--|-----|-----|-----|-----|-----------------------|
| | -SO ₃ H | -SO ₂ NHMe | -SO ₂ NHCH ₂ COOH | C | H | N | P | S | | |
| PBPP I | 0 | 0 | 0 | 12.0 | 10.0 | 1.0 | 1.0 | 0.0 | 0.0 | bz, THF |
| SA II | 66.6 | 0 | 0 | 12.0 | 10.0 | 1.0 | 1.0 | 1.3 | 1.3 | w, ethanol |
| SAMSA(C) IIIC | 58.3 | 8.3 | 0 | 12.2 | 10.5 | 1.2 | 1.0 | 1.3 | 1.3 | w, ethanol |
| SAMSA(H) IIHH | 50.0 | 16.7 | 0 | 12.3 | 11.0 | 1.3 | 1.0 | 1.3 | 1.3 | alk, ace |
| SAMSAASA IV | 33.3 | 6.1 | 27.3 | 13.2 | 12.2 | 1.7 | 1.0 | 1.3 | 1.3 | w |

^aAs represented in the text.

^bbz = benzene, THF = tetrahydrofuran, alk = aqueous alkali, ace = acetone.

TABLE 3. ^1H Magnetic Resonance Chemical Shifts and Relative Proton Concentrations for Products of Table 2^a

| Structure | Solvent | $\delta_{1\text{H}}$ and relative proton concentration (n_{H}) | | | | | |
|-----------|------------------|---|-------------------------------|-----------------------------|---------------------------------------|---------------------------------------|------|
| | | $-\text{CH}_3$ | $-\text{CH}_2-$ | Ring protons | $100\text{CH}_3/\text{CH}^{\text{b}}$ | $100\text{CH}_2/\text{CH}^{\text{b}}$ | f |
| I | DCE ^c | | 6.8 | | 0.0 | 0.0 | 0.0 |
| II | D ₂ O | | 6.8(2H) | 7.5(1H) | 0.0 | 0.0 | 0.0 |
| III(C) | NaOD | 2.65(3H) | 7.15-7.30(37.6H) ^d | 7.8(17.7H) | 5.8 | 5.4 | 0.0 |
| III(H) | NaOD | 2.60(3H) | 7.05-7.20(17.1H) ^d | 7.7(7.9H) | 11.5 | 12.0 | 0.0 |
| IV | D ₂ O | 2.55(0.67H) | 3.80(2H) | 6.72-6.85(11H) ^d | 4.2 | 3.9 | 12.6 |

^a δ in ppm; reference, TMS.^bMethyl to total ring (CH_3/CH) and methylene to total ring (CH_2/CH) proton, theoretical (t) and found (f) ratios, multiplied by 100.^c*syn*-Dichloroethane.^d ν values taken at the peaks of two broad merging bands.

TABLE 4. ^{31}P and ^{13}C Chemical Shifts for Table 2 Products^a

| Structure | $\delta_{^{31}\text{P}}$ | $\delta_{^{13}\text{C}}$ | | | | | | | | | |
|-----------|--------------------------|--------------------------|-----------------|------|----------------|-----------------|--------------------|---------------------------------|--------------------|--------------------|-------|
| | | CH ₃ | CH ₂ | COOH | C ₁ | C _{1'} | C _{3'} | Other ring carbons ^b | | | |
| I | -19.1 | | | | 151.6 | | | 128.8 | 123.5 | 121.5 | |
| II | -19.1 | -20.0 | | c | | 152.1 | 140.0 ^d | 130.2 | 128.2 | 126.6 ^d | 121.6 |
| III(C) | -19.0 | -20.2 | 38.2 | | 151.5 | 153.4 | 140.4 | 130.4 | 128.1 | 125.8 | 121.5 |
| III(H) | -18.8 | -20.3 | 38.0 | | c | c | c | 130.8 | 129.0 | 122.7 | 121.5 |
| IV | -20.1 | -20.4 | 39.4 | 40.9 | 170.7 | 151.5 | 140.1 | 130.4 | 128.1 ^d | 125.7 | 121.4 |

^a δ in ppm recorded in the same solvents as in Table 3; ^{31}P shifts referred to external H_3PO_4 ; ^{13}C shifts referred to internal TMS for I; all others taken from external dioxane and converted to TMS by using the factor $\delta_c = 67.4$ ppm.

^bAssignments given in text.

^cValues not assignable due to background noise.

^dVery weak and broad.

units per mole data indicate that although a significant shortening of chain length occurs upon sulfonation of poly [bis(phenoxy)] phosphazene, the products are still high molecular weight polymers.

In contrast, the reaction of poly [bis(4-benzoylphenoxy)] phosphazene with SO_3 led to a product which, during recovery, evolved ammonia. The elemental analysis indicated loss of at least 50% of the initial nitrogen, thus showing considerable degradation of the polymer backbone.

In the IR spectra of the products, the P=N absorption bands (ν 1310-1200 and 830-770 cm^{-1}), the relative intensity (i.e., the ratio of the ring-stretching band absorbance at 1600-1400 cm^{-1} to the P=N band absorbance) correlated with the extent of degradation caused by the reaction on the initial polymers. In the product obtained from PBBPP, the P=N bands appeared at higher frequency and with much lower relative intensity than in the initial polymer. In contrast, the IR spectrum of the more stable SA product did not show significant changes in the position and relative intensities of its P=N bands compared to those of the parent polymer (PBPP).

Product Structure

For the polymer II, the chemical composition of the repeat unit was derived based on the agreement between the experimental and the theoretical relative concentrations of $-\text{SO}_3\text{H}$ (Tables 1 and 2). The ^1H -resonance spectrum of II was not suitable for obtaining the concentration of $-\text{SO}_3\text{H}$ due to band broadening and to the difficulty to derive individual proton assignments. The ^1H -NMR spectrum of the parent polymer (I) exhibits one narrow (width at half height, $w_{1/2}$ 6 Hz) proton resonance line at 6.8 ppm (Table 3), showing that the chemical shift differences between the protons in the same ring and between protons of different rings are negligible or nil. On the other hand, the spectrum of SA (Table 3) contained two broad, poorly resolved bands centered at 6.8 and 7.5 ppm. Proton deshielding in the aromatic ring, due to the electron-withdrawing $-\text{SO}_3\text{H}$ group, is expected [12]. Thus the low-field resonance band at 7.5 ppm is assigned to the most deshielded protons of the sulfonated phenoxy ring. The high-field signal, broader ($w_{1/2}$ 112 Hz) than that of PBPP with equal chemical shift, is likely to include resonance contributions from the unsubstituted phenoxy rings protons and from other protons in the sulfonated phenoxy rings.

The quality of the spectrum did not allow further in-depth interpretation. A similar situation occurred in the ^{31}P resonance spectra (Table 4): two broad bands for the SA polymer centered at -19.13 and -20.03 ppm, one for the

parent polymer at -19.09 ppm. Comparison between the phosphorus spectra allows us to conclude that the main band at -19.13 ppm represents mostly skeleton phosphorus atoms which bear unsubstituted phenoxy rings and that the upfield signal at -20.03 ppm represents phosphorus bonded to the sulfo-phenoxy ring.

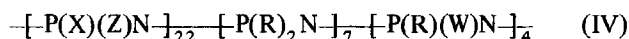
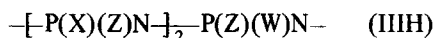
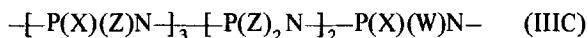
More definitive assignments were possible in the ^{13}C spectra (Table 4). The parent polymer (I) exhibited one resonance line at 151.6 ppm, which is assigned to the C_1 carbon bearing the $\text{C}-\text{OP}$ bond [10]. The other signals pertain to C_2 and C_6 (121.5 ppm), C_3 and C_5 (128.8 ppm), and C_4 (123.5 ppm). The SA spectrum showed three new signals at 152.12 , 140.0 , and 130.2 ppm. To this product, structure II was assigned rather than others having the sulfonic substituents *ortho* or *para* to the oxygen-bonded carbon, based on comparison of experimental and calculated (see Experimental section) ^{13}C δ values: δ 152.12 for C_1' (calc 152.7), 140.0 for C_3' (calc 143.7), 130.2 for C_5' (calc 129.9). The other signals of I have been assigned based on the same order of deshielding as those calculated for the *m*-sulfo-phenoxy ring structure: δ 121.6 for C_2' (calc 119.1), 125.6 for C_6' (calc 125.1), and 128.2 for C_4' (calc 121.1). The C_1 of the unsubstituted phenoxy ring in II was not well identified in the background noise. However, the spectra of the SA derivatives (III and IV) showed this signal with the same δ as the parent polymer (I). Similarly, the C_2 - C_6 signals of the unsubstituted phenoxy ring in II did not appear separately from the C_2' , C_5' , and C_4' signals because of the coincidence of chemical shift values and/or because of low intensity.

The *meta*-substituted phenoxy ring structure is also supported by IR spectroscopy. Figure 1(a) reports the spectrum of I, whose absorption frequencies (ν in cm^{-1}) are assigned [13, 14] as follows: 1310 , 1240 , and 770 ($\text{P}-\text{N}$); 1200 , 940 , and 800 ($\text{P}-\text{O}-\text{C}$); 1600 - 1400 ($\text{C}-\text{C}$ stretching); 1300 - 1000 (in-plane $\text{C}-\text{H}$ bending); 900 (out-of-plane $\text{C}-\text{H}$ bending). SA (Fig. 1b) shows the following new absorptions, which are consistent with the presence of sulfonic acid functions and substituted phenoxy rings: 3410 and 1710 (very broad, assigned respectively to the $\text{O}-\text{H}\cdots\text{O}$ stretching and bending vibrations in hydrated sulfonic acids, $-\text{SO}_3^-\text{H}_3\text{O}^+$) [15]; 1260 and 1125 ($\text{S}=\text{O}$ stretching) [16]. The location of the bands, which is mostly sensitive to substitution in the aromatic ring, lies between 650 and 850 cm^{-1} , where the out-of-plane $\text{C}-\text{H}$ stretching bands fall [17]. In this range, I has bands at 690 , 775 , 760 , and 800 cm^{-1} ; and II exhibits bands at 685 , 760 , and 840 cm^{-1} . Specifically, the two bands at 840 and 760 cm^{-1} [17] identify the *m*-substituted phenoxy ring structure in agreement with the ^{13}C spectra.

Very poor crystallinity was indicated for the SA polymer by its x-ray diffraction powder pattern: two very broad bands covering the 2θ range of 5.0 - 12.0 and 13.0 - 29 were observed. TGA scans under N_2 demonstrated that the

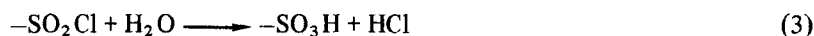
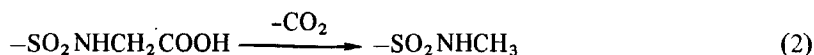
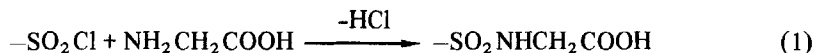
weight loss was about 10% up to 280°C and extensive thermal degradation started at 300°C, reaching its maximum rate at 350°C. Loss of crystallinity and lowering of the thermal stability typically occur in polymers upon sulfonation.

The presence of the sulfonic functions was further confirmed by their reactivity. Titration of an aqueous solution of the polymer with 0.1 N NaOH and phenolphthalein gave 3.6 meq acid/g polymer, which is the theoretical value for the polymer containing 10% water. Refluxing SA with excess thionyl chloride gave the product in the sulfonyl chloride form (SCI), as confirmed by two very strong IR absorptions at 1375 and 1160 cm^{-1} (S=O stretching in sulfonyl chlorides) [18]. SCI was dissolved in acetone and reacted with excess glycine and NaHCO_3 in a water-acetone solution to yield the mixed-substituent water-soluble polymers SAMSA (III) and SAMSAASA (IV) of Tables 1 and 2, whose structures are ideally represented as follows:



where X = $-\text{OC}_6\text{H}_5$, Z = $-\text{OC}_6\text{H}_4\text{SO}_3\text{H}$, W = $-\text{OC}_6\text{H}_4\text{SO}_2\text{NHCH}_3$, R = $-\text{OC}_6\text{H}_4\text{SO}_2\text{NHCH}_2\text{COOH}$, and the sulfo-substituted phenoxy rings (Z, W, and R) have the *meta* structure.

The products suggest that in the reaction between SCI and glycine, the functional groups react as follows:



No effort was made either to study in detail the parameters which influence each of the above reactions or to obtain polymers with one functional group. The aim was the characterization of the reaction products and the study of their solubility properties. The products structures (III and IV) fit the ^1H magnetic resonance relative ratios (Table 3) better than the elemental analysis data (Table 1). The aromatic proton signals appeared in the NMR spectra with more or less similar patterns as for the SA polymers. The ali-

phatic proton signals were quite sharp. Their chemical shifts (2.60-2.65 ppm for methyl protons and 3.80 ppm for methylene protons) were well separated from the aromatic downfield bands. Thus the relative concentrations (Table 2) of *N*-methylsulfonamide and sulfonilamminoacetic acid functions were obtained from the aliphatic/aromatic proton ratios of Table 3.

The polymer acid functions were confirmed by titration with alkali. The ^{31}P resonance spectra (Table 4) of the mixed substituent polymers had a poor diagnostic value similar to the spectra of the SA polymer.

The ^{13}C resonance spectra (Table 4) clearly showed the methyl, methylene, and carboxylic carbon signals at 38.0-39.0, 40.9, and 170.7 ppm, respectively. In the aromatic carbon resonance range, the spectral pattern of III and IV was similar to that of II, except that, in the spectra of the former compounds, the C_1 signal of the unsubstituted phenoxy ring could be picked out from the background noise. In this case, the elemental carbon ratios obtained from the integrals of the signals which belong to the carbons not bonded to hydrogen (i.e., COOH , C_1 , C_1' , and C_3') were in fair agreement with the theoretical values for the Table 2 structures: for III, $\text{C}_1/\text{C}_1' = 0.53$ (found); $\text{C}_1/\text{C}_3' = 0.51$ (found); $\text{C}_1/\text{C}_1' = \text{C}_1/\text{C}_3' = 0.5$ (theor.). For IV, $\text{C}_1/\text{C}_1' = 0.40$ (found); $\text{C}_1/\text{C}_3' = 0.44$ (found); $\text{C}_1/\text{C}_1' = \text{C}_1/\text{C}_3' = 0.50$ (theor.); $\text{COOH}/\text{C}_1' = 0.5$ (found); $\text{COOH}/\text{C}_3' = 0.57$ (found); $\text{COOH}/\text{C}_1' = \text{COOH}/\text{C}_3' = 0.41$ (theor.).

The IR spectrum (Fig. 1c) of SAMS(A), which was obtained from the reaction at the reflux temperature, exhibits the following absorption frequencies associated with the $-\text{SO}_2\text{NH}-$ functions [18], as in IIIH: $\nu = 1365$ and 1160 cm^{-1} ($\text{S}=\text{O}$ stretching), 1080 cm^{-1} ($\text{S}-\text{N}$ stretching), $500-600\text{ cm}^{-1}$ ($\text{S}=\text{O}$ deformation). In the spectra of SAMS(C), IIII, which was obtained at low temperature, and of SAMS(AA), IV, the $-\text{SO}_2\text{NH}-$ absorptions were much less intense, in agreement with the lower concentration of these functions. The $-\text{COOH}$ group in SAMS(AA) is responsible for the broad absorption maximum at 3050 cm^{-1} (OH stretching) and the band at $1720-1740\text{ cm}^{-1}$ in Fig. 1(d).

Except for the parent polymer, all the products are soluble in hydrophilic solvents (Table 2). The polymer solubility properties seem to be mostly related to the relative content of free acid functions. The product containing the highest concentration of *N*-methylsulfonamide functions, SAMS(A), shows somewhat less hydrophilic behavior relative to the other products; it dissolves in water only upon neutralization of the acid functions with alkali.

The results certainly point out that sulfonated polyphosphazenes are not indiscriminately stable. Stability seems mostly related to the nature of the pendent substituent. Poly[bis-(4-benzoyl)] phosphazenesulfonic acid could

not be isolated due to high chain degradation during sulfonation. Also, the phenoxy-sulfonylaminoacetic acid substituent was found to be unstable over long time periods. Nevertheless, the isolation of the products of this work demonstrates that sulfonic functions are water-solubilizing substituents of polyphosphazenes and reactive sites for binding other molecules to the polymer. The work certainly offers challenging scope for developing and studying new inorganic materials as water-soluble resins or carriers of molecules having a variety of other functional groups in addition to the water-solubilizing substituent.

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