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Synthesis and Characterization of a Series of Alternating Copolymers (Oligomers) Containing Organophospha-λ^5-azene Backbone Moieties

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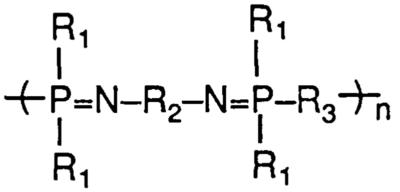
ABSTRACT: The Staudinger reaction of bis(diphenylphosphino)alkyl or aryl compounds with 1,4-diazidobenzene at room temperature in benzene solution was shown to produce poly(organophospha-λ^5-azenes), which are alternating copolymers (oligomers) with the general formula $(=P(Ph)_2-R-P(Ph)_2=N-C_6H_4-N=)_n$ where R = $(CH_2)_n$, n = 2-5, or R = p-C_6H_4. The CP/MAS ^{13}C and ^{31}P NMR spectra were consistent with the proposed structures and showed a small amount of P=O end groups in addition to the P=N ^{31}P resonances. The diffuse reflectance FT-IR spectra showed the typical P=N absorptions characteristic of phospha-λ^5-azenes along with some azido end group absorptions. The thermogravimetric analyses (TGA) of these polymers showed that they were reasonably thermally stable up to about 300°C, and differential scanning calorimetry (DSC) provided the glass transition temperatures, T_g. The T_g's for the polymethylene containing polymers were in the range 103-124°C and appeared to decrease with increasing length of the polymethylene chain. Approximate molecular weights of these insoluble polymers were obtained by end group analysis using the integrated areas from the ^{31}P NMR spectra (ratio of P=O and P=N groups) and assuming that P=O and N_3 were the end groups.

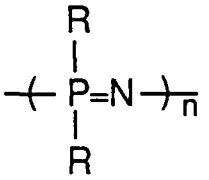
Introduction

Our interest in the preparation and study of phospha-λ^5-azenes over the past several years[1-10] has led us to examine the synthesis and properties of alternating copolymers of the type **1** shown below. While it is well known that polymers of the type **2**, with completely inorganic backbones, have interesting and commercially useful properties, depending on the substituents, R,[11] the only way the properties of these polymers can be altered is by changing the R groups. In structures of type **1**, however, we not only retain the advantages of the phosphazene linkages and can vary the phosphorus substituents, R_1, we can also now vary the spacer groups R_2 and R_3. This should allow the altering of properties such as the glass transition temperature and the thermal stability. This means that we should be able to prepare polymers with more desirable and more readily controllable properties.



$$\left(P(R_1)_2{=}N{-}R_2{-}N{=}P(R_1)_2{-}R_3 \right)_n$$

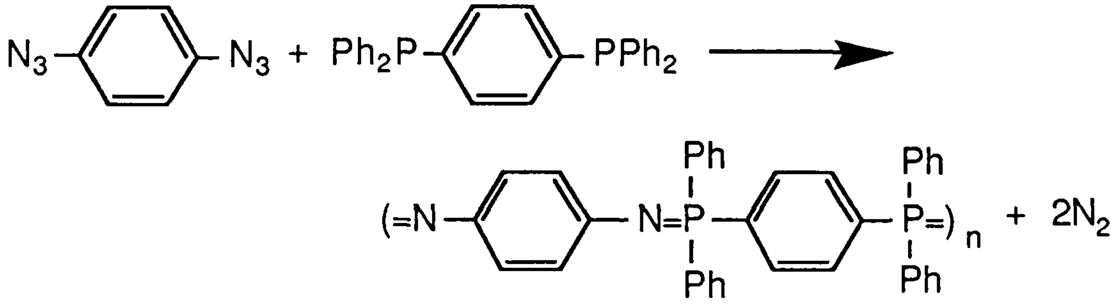
1



$$\left(P(R)_2{=}N \right)_n$$

2

A search of the literature has revealed only a handful of references to polymers of this type and only one where the spacer groups R_2 and R_3 are organic. Herring[12] reported the synthesis of **3** from 1,4-bis(diphenylphosphino)benzene and 1,4-diazidobenzene via the Staudinger reaction (eqn. 1).[13]

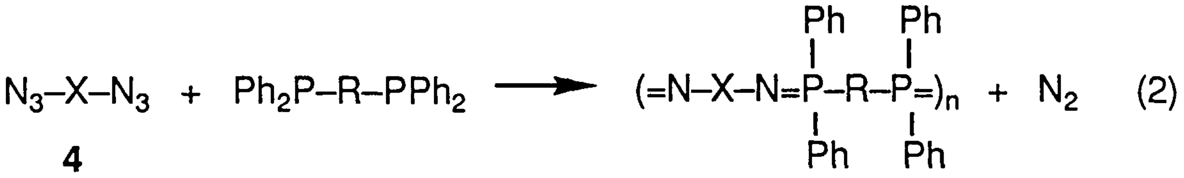


3

(1)

Unfortunately, only thermal stability data were presented for the product. The structure was not proven nor was a molecular weight obtained.

The only other reports of preparation of polymers of type **1** all involve the Standinger reaction of bisphosphines containing organic groups (R) between the phosphorus atoms but bis-azides (**4**) all of which contain inorganic groups and atoms (X) between the nitrogen atoms.[14-18] These produce polymers **5** with only one spacer group organic (R) and the other (X) containing inorganic groups and atoms (eqn. 2).



$$N_3{-}X{-}N_3 + Ph_2P{-}R{-}PPh_2 \longrightarrow (=N{-}X{-}N=\overset{Ph}{\underset{Ph}{P}}{-}R{-}\overset{Ph}{\underset{Ph}{P}}=)_n + N_2 \qquad (2)$$

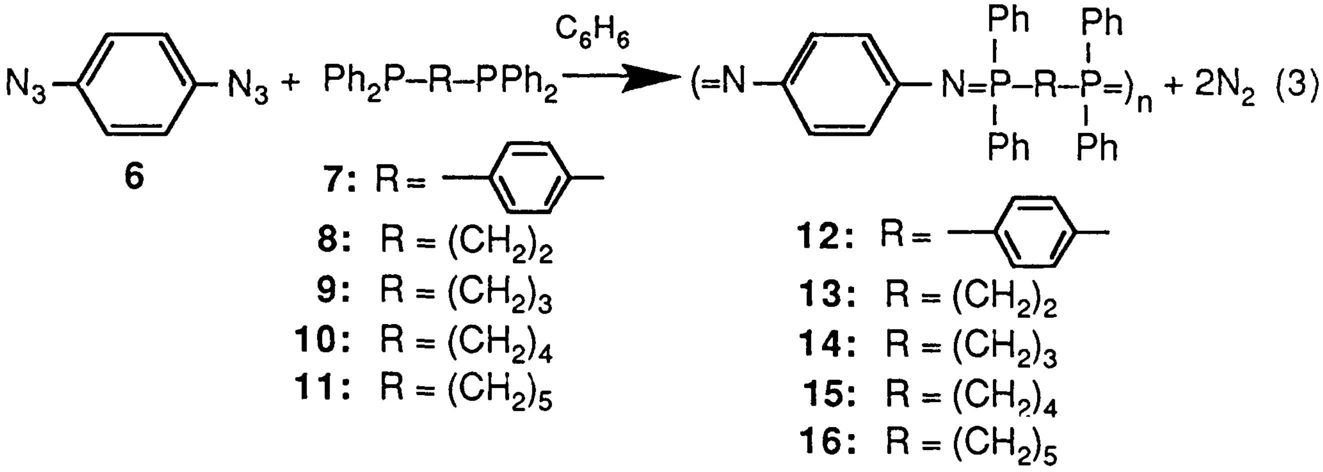
4

5

In this paper we describe the preparation and properties of a series of polymers of type **1** where the groups attached to phosphorus, R, were phenyl, the group separating the nitrogen atoms, R_2, was *p*-phenylene, an organic group, and the group between the phosphorus atoms was systematically varied.

Results and Discussion

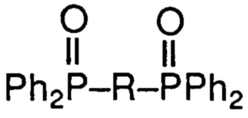
Reaction of 1,4-diazidobenzene (**6**)[12] with 1,4-bis(diphenylphosphino)benzene (**7**), 1,2-bis(diphenylphosphino)ethane (**8**), 1,3-bis(diphenylphosphino)propane (**9**), 1,4-bis(diphenylphosphino)butane (**10**) and 1,5-bis(diphenylphosphino)pentane (**11**) in benzene gave the alternating copolymers **12-16** respectively (eqn. 3). These polymers were insoluble in common organic solvents such as tetrahydrofuran, diethyl ether, dimethylsulfoxide, dimethylformamide and



dimethylacetamide and so spectroscopic analysis was done on solid samples.

Diffuse reflectance FT infrared spectroscopic analysis of the polymers **12-16** showed the P=N stretch as a broad peak at 1303-1311 cm^{-1} (Table 1) as expected.[19] In addition all polymers showed a band at 2117-2125 cm^{-1} (Table 1) which was indicative of an azide end group.[20] In the case of **12**, heating just below the decomposition point at 320°C diminished the 2117 cm^{-1} absorption but it was still present even after fifteen minutes.

^{31}P solid state CP/MAS NMR spectroscopy showed the P=N phosphorus at approximately δ 5 to -3 ppm (relative to external $NH_4H_2PO_4$) similar to where it appears in monomeric phospha-λ^5-azenes.[3,4] In all cases there was an additional small absorption at δ 24-31 which is where the corresponding oxides would appear[21] and this functionality would of necessity be an end group. The chemical shift of polymer **12** at δ -2.7 is about 7 ppm upfield from the chemical shifts of the polymethylene polymers **13-16** and is most likely an electronic effect of the *p*-phenylene ring between the phosphorus atoms in **12**.[3,4,21] The same trend is observed in the oxide end groups where the ^{31}P shift of the P=O group in **12** appears about 6 or 7 ppm upfield of the other systems **13-16**. This is the same trend which is observed in the bis-oxides, **17**, where the compound with



$$Ph_2\overset{\overset{\displaystyle O}{\|}}{P}-R-\overset{\overset{\displaystyle O}{\|}}{P}Ph_2$$

17

the *p*-phenylene group between the phosphorus atoms (R = *p*-C_6H_4) shows $\delta_{^{31}P}$ shielded relative to the case where R = $(CH_2)_n$.[8,21] Also, compounds frequently show more than one solid state NMR band because of "solid state effects," that is, the atoms may appear in crystallographically non-equivalent sites or may show residual dipolar coupling of the spin-1/2 nucleus to an adjacent quadrupolar nucleus such as ^{14}N.[22]

^{13}C CP/MAS NMR spectra of **12-16** showed the aryl carbon atoms in the range of δ 128-143 (Table 1). In all cases there was a peak downfield at ca. δ 142-143 (Table 1) and this must be due to the ipso carbon to which the nitrogen in attached.[4] Polymers **13-16** showed the aliphatic carbon resonances at δ 14-30 (Table 1), which is within the expected range.

Thermogravimetric analysis (TGA) indicated that the polymers were reasonably thermally stable to temperatures above 300°C in a nitrogen atmosphere. Table 2 shows the thermal data including the temperature for the onset of decomposition (the procedural decomposition temperature),[23] and the temperature and rate for the maximum in the decomposition rate, obtained from the derivative TGA trace. The weight loss for **12-16** was a single step with no observable plateaus (no other peaks in the DTGA trace) with < 5% residue at 1000°C. The residue, if any, was not analyzed. Also shown, for comparison, are the procedural decomposition temperatures for the starting phosphines **7-11**. The bis-azide starting material, **6**, had a procedural decomposition temperature of 100°C. As expected, the polymer with the two *p*-phenylene units in the backbone, **12**, is the most thermally stable. Further, thermal stability appears to increase with increasing chain length in polymers **13-16**.

In order to obtain glass transition temperatures (T_g) for these polymers (**12-16**) duplicate samples were heated in an oven at 280°C (320°C for **12**) and allowed to equilibrate. One of the duplicate samples of each was cooled autogenously to room temperature (method A) while the other was rapidly cooled in liquid nitrogen (method B). Differential scanning calorimetry (DSC) was run on each of the samples from –90°C to 280°C (320°C for **12**) at 20°C/min. Table 3 shows the average values for T_g. We were not able to observe a glass transition for polymer **12** while for polymers **13** and **14** a clear T_g could only be observed using method A. There is an error of about ±5°C in T_g and even so, it appears that the polymer with the longest, most flexible spacer, **16**, has the lowest T_g. As the spacer group gets shorter T_g appears to increase modestly, which is what one would expect.[24]

For none of the polymers could a T_m be observed since they began decomposing before a melting temperature could be reached.

Because of the insolubility of these systems in common organic solvents the molecular weights could not be obtained by solution methods such as GPC. With several assumptions, the molecular weights (M_n) could be calculated using end group analysis. By assuming one end group was the azide and the other was phosphine oxide and then integrating the ^{31}P CP/MAS NMR spectrum we could get the ratio of end to internal phosphorus atoms. This provided the molecular weights shown in Table 3 and these range from ca. 1800-2600. The modest molecular weights are most likely due to the insolubility of these compounds since they precipitate out of solution before they can achieve a larger molecular weight.

Summary and Conclusions

A series of poly(organophospha-λ^5-azenes), **12-16**, which are alternating copolymers (oligomers) with the general formula $(=P(Ph)_2–R–P(Ph)_2=N–C_6H_4–N=)_n$ has been synthesized from the corresponding bisphosphines, **7-11**, and 1,4-diazidobenzene (**6**). These insoluble polymers have been characterized by CP/MAS ^{13}C and ^{31}P NMR and FT-IR spectroscopy and by thermal analysis including TGA and DSC. They appear to be reasonably thermally stable, and all showed temperatures for the onset of decomposition of 300°C or greater. Glass transition temperatures were observed for polymers **13-16**. They were all between 103 and 124°C and appeared to decrease with increasing chain length in the spacer group, R. Since the IR spectra showed residual azide groups and the ^{31}P NMR spectrum showed some P=O groups, the molecular weights (M_n) were calculated by end group analysis, assuming N_3 and P=O end groups. The modest molecular weights, which were in the range 1800-2600, were probably the result of the insolubility of the polymers in the reaction solvent.

Work on other, more soluble polymers containing both phospha-λ^5-azene and organic groups in the backbone is continuing.

Experimental Section

General Methods . IR Spectra were recorded on a Biorad-Digilab FTS-40 FT-IR spectrometer using a resolution of 8 cm^{-1}. Diffuse reflectance spectra were done in KBr powder using a SpectraTech DRIFTS accessory. CP/MAS NMR spectra were obtained on a Bruker MSL-300 NMR spectrometer at 75.5 and 121.5 MHz for ^{13}C and ^{31}P respectively using a Doty Scientific probe with 5mm silicon nitride rotors and a spinning speed of 11.1-11.4 kHz. The magic angle was checked with glycine and the ^{13}C chemical shifts were referenced against the carbonyl carbon of glycine ($\delta_{C=O}$ = 177.0)[25] which was in turn referenced against the methylene carbon of adamantane (δ_{CH_2} = 29.5).[26] The ^{31}P chemical shifts were referenced against $NH_4H_2PO_4$ (δ = 0.00). The TGA and DSC analyses were done on a DuPont 9900 thermal analysis system. 1,4-Diazidobenzene (**6**) was prepared by literature methods[12] as was the bisphosphine **7**.[27] Bisphosphines **8-11** were commercial samples (Organometallics, Inc). All were checked for purity by mp and ^{31}P NMR spectroscopy prior to use.

Synthesis of Polymers 12, 13, 15 and 16. In a 100 mL round-bottomed, three-necked flask, equipped with a magnetic stirrer, argon inlet, addition funnel, reflux condenser and drying tube, was put 1-2 mmol of the bisphosphine dissolved in 30 mL of benzene. Note: benzene is a cancer suspect agent. To this was added one equivalent (1-2 mmol) of 1,4-diazidobenzene (**6**) in 30 mL of benzene dropwise, over a period of about 10 min. During the addition the solution became colored and a gas was evolved. The reaction mixture was stirred overnight. The solid which formed was filtered, extracted with boiling benzene and filtered hot. It was vacuum dried and stored in a desiccator until used. Yields: **12**, 0.26 g, 46%, orange powder; **13**, 0.48 g, 91%, greenish yellow powder; **15**, 0.62 g, 90%, yellow powder; **16**, 0.74 g, 43%, yellow powder. Additional infrared bands, not shown in Table 1, for **12**, **13**, **15** and **16**, are presented in Table 4.

Synthesis of Polymer 14. The synthesis of polymer **14** was the same as for the other polymers except that after stirring overnight the reaction mix was refluxed for 3 h prior to extracting with boiling benzene and hot filtration. It, too, was vacuum dried and stored in a desiccator; yield: 0.11 g, 18%, olive green powder. Additional IR bands are presented in Table 4.

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Table 1. Spectroscopic Properties of Polymers 12-16

Polymer	IR (cm^{-1})[a] P=N	IR (cm^{-1})[a] N_3	CP/MAS NMR (δ, ppm) $^{31}P^{b}$ P=N	CP/MAS NMR (δ, ppm) $^{31}P^{b}$ P=O	CP/MAS NMR (δ, ppm) $^{13}C^{c}$
12	1312	2118, 2095	–2.7	24.4	143.4, 132.3, 129.1
13	1308	2121	5.4	31.1	143.3, 130.4, 121.1, 24.3
14	1304	2118	4.0	29.9	143.3, 131.6, 30.7, 23.0, 15.0
15	1304	2118	4.1, –3.0	30.8	143.3, 129.3, 23.5
16	1304	2118	1.4	30.8	142.2, 131.5, 30.1, 23.3

a) Diffuse Reflectance FT-IR; taken in KBr powder.

b) Downfield from external $NH_4H_2PO_4$.

c) Using external glycine as standard; $\delta_{C=O}$ 177.0.

Table 2. Thermogravimetric Analysis Data of 7-16

Compound	Onset of Decomp. (°C)	DTGA T_{max} (°C)[$rate_{max}$(%/min)]
7	275	400 [18]
8	200	340 [27]
9	225	340 [30]
10	250	380 [30]
11	250	360 [27]
12	350	430 [25]
13	300	350 [30]
14	320	400 [16]
15	320	425 [40]
16	330	440 [30]

Table 3. Glass Transition Temperatures (T_g) and Molecular Weights (M_n) of 12-16

Polymer	T_g (°C)^a	Molecular Weight^b
12	c	1830
13	119^d	2100
14	124^d	2580
15	112^e	2570
16	103^e	2030

a) Obtained by DSC.

b) Obtained by integration of the ^{31}P NMR spectrum and assuming P=O and N_3 end groups.

c) T_g not observed.

d) Obtained by Method A (see text).

e) Average of results obtained by Methods A and B.

Table 4. Additional IR Bands for Polymers 12-16[a]

Polymer	IR Bands (cm^{-1})
12	3051, 1589, 1497, 1435, 1107, 829, 748, 717, 694
13	3051, 2919, 1599, 1493, 1435, 1111, 834, 818, 725, 694
14	3051, 2941, 1601, 1489, 1435, 1281, 1111, 829, 740, 714, 694
15	3051, 2943, 1600, 1493, 1435, 1285, 1111, 829, 745, 714, 694
16	3051, 2940, 1600, 1493, 1435, 1111, 829, 745, 718, 694

a) Bands not shown in Table 1