Poly(organophosphazenes) with Chromophores as Substituent Groups[1,2]

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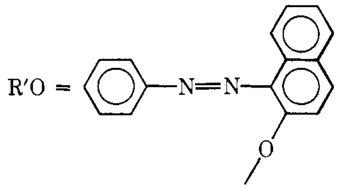
ABSTRACT: The bulky chromophoric groups, 1-phenylazonaphthalene-2-oxy (R′O) and *p*-phenylazoanilino (R″-NH), have been bound covalently to a polyphosphazene chain by the reaction of the sodium salt of 1-phenylazo-2-naphthol or *p*-phenylazoaniline with poly(dichlorophosphazene). Hydrolytically stable derivatives were then prepared by replacement of the remaining chlorine by trifluoroethoxy or methylamino groups. The UV–visible spectral characteristics of the products are described.

The first syntheses of poly(alkoxy-, aryloxy-, and amino)phosphazenes of formula $[NP(OR)_2]_n$, $[NP(NHR)_2]_n$, or $[NP(NR_2)_2]_n$ by Allcock, Kugel, and Valan[3-5] have stimulated a broad synthetic attack on polyphosphazenes in a number of laboratories.[6-18] Particular interest has been focused on mixed substituent polyphosphazenes,[7-9,11,14,17] especially those which yield technological elastomers.[14,17,18]

The principal advantage of polyphosphazenes compared to nearly all other synthetic polymers is the ease with which different substituents, and therefore different properties, can be introduced. To further explore the versatility of this system, we have attempted to introduce dye molecules as substituent groups into this polymer system. Apart from the fundamental interest inherent in the behavior of chromophores bound to an electron-rich polymer backbone, numerous technological uses exist for polymer-bound dyes.

It was considered unrealistic to expect that high polymers could be prepared that contained *only* bulky chromophores as substituents in view of the steric hindrance effects reported in earlier work.[6] Hence, the synthesis of mixed substituent polymers was attempted. The use of two particular chromophore molecules and two cosubstituent groups is described here. The chromophoric groups are 1-phenylazonaphthalene-2-oxy (R′O) (I) and *p*-phenylazoanilino (R″NH) (II), and the cosubstituents are trifluoroethoxy and methylamino.



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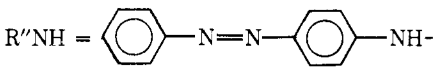
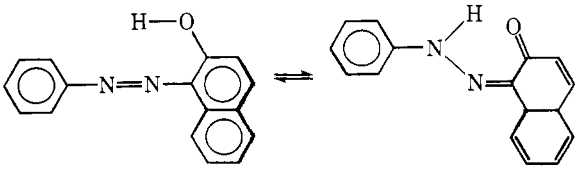


II

Spectroscopic Background. The chromophore, R′OH, was especially well-suited for this study since it exists in the two tautomeric forms, III and IV. The azo and hydrazone forms show characteristic ultraviolet–visible absorptions at ~390 and ~470 nm, respectively. These peaks overlap partially to give the broad band normally observed between 316 and 560 nm. It has been shown[19,22] that this equilibrium is highly dependent on temperature and solvent and that the hydrazone form predominates (66–95%) in the presence of polar solvents. This behavior was confirmed in the tetrahydrofuran and ethanol solvents used in this work. In these solvents the maximum absorbance appeared at 470 nm, with a shoulder at 420 nm and a small band at ~315 nm from the naphthalene ring absorbance. On the other hand, the methyl ether of III, prepared for comparison purposes, showed a principal absorbance in the 350–370-nm range that was indicative of the azo form. The ultraviolet–visible spectrum of *p*-phenylazoaniline showed a broad absorption between 300 and 500 nm, with a single maximum at 385 nm.



III IV

Syntheses. It was first demonstrated that the model compound, hexachlorocyclotriphosphazene (V), reacts with the sodium salt of R′OH to yield a mono-substituted product, $N_3P_3Cl_5OR'$ (X). The product was then converted to $N_3P_3(OCH_2CF_3)_5OR'$ (XI) and $N_3P_3(NHMe)_5OR'$ (XII) by reaction with sodium trifluorethoxide or methylamine. The authenticity of these products was confirmed by mass spectroscopic, NMR, and electronic spectral techniques.

For the polymer reactions, the substitution sequence involved the interaction of poly(dichlorophosphazene), VI, with low concentrations of the bulky chromophore molecules first, followed by the introduction of the cosubstituent. The over-all reaction sequence is shown in the conversion of V to VII, VIII, and IX.

Polymers VII, VIII, and IX were prepared and characterized (see Experimental Section). It was established that the dye molecules were bound covalently to the polymers and not merely held by acid–base forces or by entrapment. Moreover, spectral analysis indicated that an average of 0.02–0.22% of the total substituent groups were chromophore residues.[23-25] The molecular weights and molecular weight distribution of the polymers were comparable to those which contained no chromophore. Hence, significant chain shortening did not accompany the introduction of a few chromophoric ligands per chain.

However, evidence was obtained from spectroscopic studies with the model systems X, XI, and XII that prolonged exposure to the second (less bulky) nucleophile led to displacement of some of the chromophoric groups. For example, the conversion of X to XI was accompanied by roughly 53% displacement of the dye residue under the reaction conditions employed. The conversion of X to XII brought about a displacement of only 6% of the chromophoric groups. These ligand exchange processes are consistent with small molecule studies reported elsewhere,[26] and it seems clear that similar exchange reactions can occur during the synthesis of VII, VIII, and IX. However, it was not possible to introduce dye molecules into $[NP(OCH_2CF_3)_2]_n$ or $[NP(NHMe)_2]_n$ by ligand exchange with R′ONa or $R''NH_2$. Apparently, bulky ligands can be displaced by small ones, but the opposite reaction does not take place.

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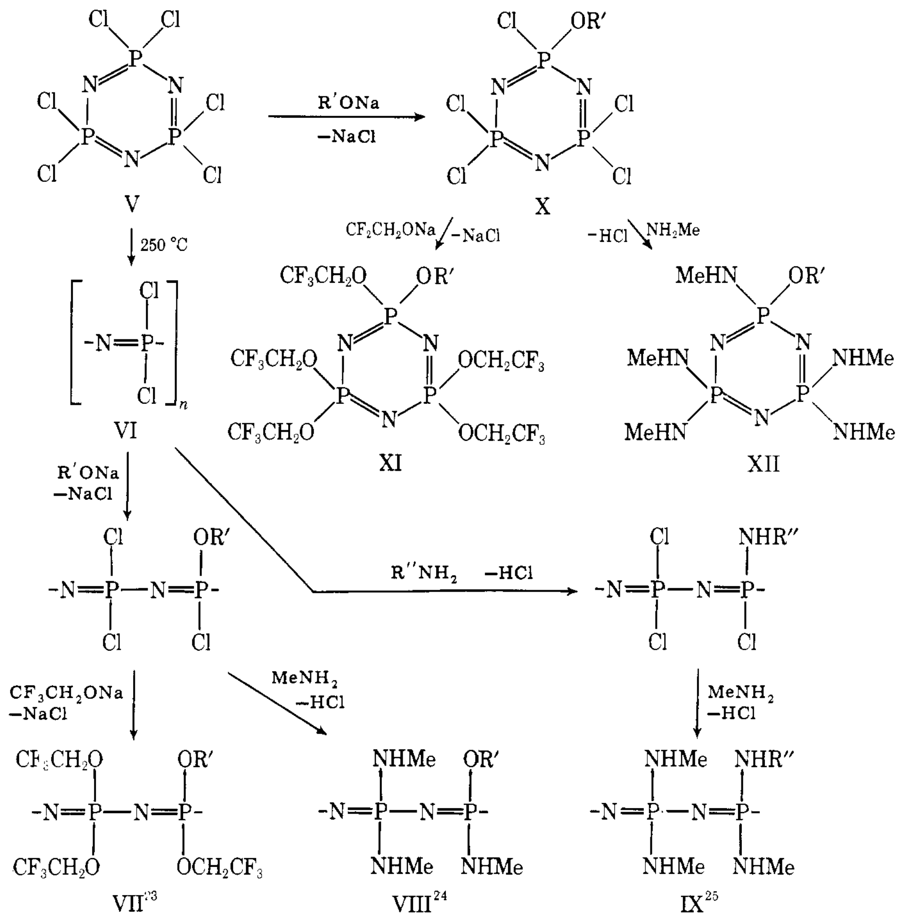

The ultraviolet spectra of polymers VII and VIII showed absorbance maxima in the ~350 to 370 nm region that were indicative of the azo form of the chromophore. The spectrum of polymer IX closely resembled that of the unbound chromophore, with only a 10-nm shift of the main peak toward shorter wavelengths. The data confirmed that the azido linkages had survived the various synthetic steps. These spectral absorptions refer only to those of the dye chromophore. Those polymers which contained methylamino substituents absorbed strongly at wavelengths shorter than about 300 nm.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (I) (El Monte Chem. Co.) was purified by sublimation at 50 °C (0.1 Torr) for 48 h, recrystallized twice from hot heptane, and resublimed twice. Samples for polymerization (~200 g) were sealed in evacuated Pyrex tubes. 1-Phenylazo-2-naphthol ("Solvent Yellow 14") (American Color and Chemical Corp.) was recrystallized twice from hot ethanol. The methyl ether of this compound was prepared with the use of methyl iodide in THF. *p*-Phenylazoaniline (Aldrich) was recrystallized once from 2% aqueous ethanol. Tetrahydrofuran (THF) (Fisher) was boiled at reflux over $LiAlH_4$ and then distilled before use. Diethyl ether (Aldrich), heptane, and benzene were dried over calcium hydride and distilled before use. Methanol (Fisher) was used as received. 2,2,2-Trifluoroethanol (Halocarbon Products) was dried over molecular sieves. Methylamine (Matheson) was condensed over sodium and distilled directly into the reaction vessel. Triethylamine was boiled over barium oxide and was distilled before use.

Analytical Equipment. Gel permeation chromatography (GPC) was carried out with the use of Waters Associates ALC-201 and ALC-GPC-501 instruments. Two column arrangements were employed: a 4 ft × $^3/_8$ in. 10^5 styragel column for use with THF solvent, and an 8 ft × $^3/_8$ in. column comprised of four 2 ft sections of 75, 175, 700, and 2000 Å controlled pore glass for use with aqueous 95% methanol or pure methanol. The columns were calibrated with the use of polystyrene standards. Ultraviolet–visible absorption spectra were obtained with the use of a Cary 17 instrument with 1-cm path-length cells. The spectra of solutions of polymers VII, VIII, and IX in THF (VII) or aqueous 95% ethanol (VIII or IX) were measured against reference solutions of the appropriate homopolymers, $[NP(OCH_2CF_3)_2]_n$ and $[NP(NHCH_3)_2]_n$. Centrifugation was effected with the use of a Sorval Superspeed RC 2-B instrument of 11 000 rpm.

Synthesis of Poly[(1-phenylazonaphthalene-2-oxytrifluoroethoxy)phosphazene] (VII). The sodium salt of 1-phenylazo-2-hydroxynaphthalene was prepared with the use of excess sodium hydride in benzene or THF solution, initially under nitrogen atmosphere for 30 min. The color of the solution changed from red-orange to deep red as the salt was formed.

A solution of sodium 1-phenylazonaphthalene-2-oxide (0.38 g, 0.0014 mol) in THF (250 mL) was filtered through a glass frit in a Schlenk-type addition funnel by a positive nitrogen pressure into a reaction vessel which contained a stirred solution of poly(dichlorophosphazene) (VI) (15.7 g, 0.14 mol) in THF (1400 mL) under dry nitrogen atmosphere. The addition took place over 30 min. After 1 h of reaction, an etheric (250 mL) solution of sodium trifluoroethoxide (39.8 g, 0.33 mol) was added slowly during 2 h. The color of the reaction mixture changed from orange-red, through brown, and then to orange during the 36 h reaction at 25 °C. The polymer was recovered by removal of the solvent at reduced pressure and precipitation into heptane. It was purified by precipitation twice from THF into distilled water and seven times from THF into heptane or benzene (yield, 16.2 g, 51%). The final precipitations showed no UV–visible spectroscopic evidence of the free dye molecules in the precipitation bath. GPC analysis suggested an $\bar{M}_n$ range from 1×10^4 to 1×10^7. UV–visible spectroscopic spectra of solutions of 0.0233-g polymer in 10 mL of THF were compared with the spectra of known concentrations of the free dye, its methyl ether, and XI. These analyses suggested that, if the polymer contained an average of 2000 repeating units (based on the center of the GPC distribution), approximately 2.5 molecules of dye were bound to each polymer molecule. The polymer formed orange-colored films that were soluble in acetone or THF.

Synthesis of Poly[(1-phenylazonaphthalene-2-oxymethylamino)phosphazene (VIII). A solution of sodium 1-phenylazonaphthalene-2-oxide (0.24 g, 1×10^{-3} mol) in THF (200 mL) was pressure-filtered under nitrogen into a stirred solution of poly(dichlorophosphazene) (VI) (11.2 g, 0.01 mol) in THF (700 mL). The total addition time was 35 min. After a further 90 min of reaction time, the mixture was transferred to an addition funnel and added dropwise during 3 h to a stirred solution of methylamine (43 mL, 0.96 mol) in THF (500 mL) at 0 °C. Atmospheric moisture was rigorously excluded. After an additional 42-h reaction, solvent was removed at reduced pressure and the polymer was isolated by precipitation into heptane. Purification was effected by dialysis in water for 48 h, centrifugation for 30 min at 10 000 rpm, and multiple precipitation from aqueous 95% ethanol into THF or heptane until no free dye could be detected spectroscopically in the precipitation medium; yield, 3.4 g, 30.4%. GPC analysis using aqueous 95% methanol solvent suggested an $\overline{M}_n$ molecular weight value of 2.8×10^6, and spectroscopic analysis indicated that an average of approximately 75 dye molecules were bound to each chain. The polymer was orange in color. It formed hygroscopic, brittle films that were soluble in water, methanol, or ethanol but only slightly soluble in 2-propanol.

Synthesis of Poly[(*p*-phenylazoanilinomethylamino)phosphazene] (IX). A solution of *p*-phenylazoaniline (0.34 g, 0.0017 mol) and triethylamine (9.8 mL) in benzene (50 mL) was allowed to react with poly(dichlorophosphazene) (VI) (20 g, 0.17 mol) under a dry nitrogen atmosphere for 35 min. The mixture was then added dropwise to a solution of methylamine (91.8 ml, 2.06 mol) in THF (700 mL) at 0 °C under a dry nitrogen atmosphere. A color change from orange-brown to bright yellow occurred at this stage, and a fine precipitate was formed. After a further 48 h of reaction, first at 0 °C and later at 25 °C, the product was isolated and purified by dialysis in water for 5 days. Subsequent precipitation eight times from methanol or ethanol into benzene or THF ensured removal of all the noncovalently bound dye; yield, 4.3 g, 23.4%. GPC analysis in methanol or aqueous 95% methanol indicated an $\overline{M}_n$ value near 1.1×10^6. UV–visible spectroscopy of solutions of 0.0205 g of polymer in 10 mL of aqueous 95% ethanol indicated that (assuming an average chain length of 15 000 repeating units) approximately six dye molecules were attached to each polymer chain. The polymer formed yellow or green, brittle, hygroscopic films that were soluble in water, methanol, or ethanol but only slightly soluble in propanol.

Synthesis of X, XI, and XII. A solution of sodium 1-phenylazonaphthalene-2-oxide (0.50 g, 0.002 mol) in THF (20 mL) was filtered under dry nitrogen into a stirred solution of V (1.40 g, 0.004 mol) in THF (25 mL). The addition was completed in 30 min and the mixture was then boiled at reflux for 24 h. The color of the solution changed from the deep red of the dye salt to yellow-orange as the reaction proceeded. Evaporation of the solvent yielded a dark orange-colored product. Mass spectral analysis of this material showed a cluster of peaks near 557 amu that corresponded to ions derived from X. A ^{31}P NMR spectrum in benzene-d_6 showed the presence of unreacted V (+19.3 ppm[27]) and peaks attributed to X at +22.4, +22.3, +21.3, +20.8, +20.1, +13.0, +11.5, and +11.3 ppm vs. 85% H_3PO_4. This peak arrangement was similar to the AB_2 pattern reported earlier for $N_3P_3Cl_5(OCH_2CF_3)$.[28] A pure sample of X, isolated by thin-layer chromatography, showed an ultraviolet–visible spectrum that was similar to those of VII, VIII, and the methyl ether of 1-phenylazo-2-naphthol. Specifically, a main absorption peak was observed from 350 to 400 nm with a weak absorption between 400 and 500 nm.

A solution of X in THF, prepared as described above, was added dropwise during 45 min to a stirred solution of sodium trifluoroethoxide, prepared from trifluoroethanol (3.45 g, 0.0345 mol) and sodium (0.63 g, 0.276 mol) in THF (41.5 mL). The mixture was stirred for a further 4 h and then heated at reflux for 16 h. The product was isolated by evaporation of the solvent. A mass spectrum showed a parent peak near 880 amu (the mol wt of XI is 877).

Compound XI was prepared by the addition of a solution of X in THF to a 60-fold molar excess of methylamine in THF at 0 °C during a period of 15 min. After 4 h at 0 °C, the mixture was stirred at 25 °C for 20 h. Methylamine hydrochloride was removed by filtration and the product was isolated by evaporation of the solvent. The electronic spectra of XI and XIII were similar to that of X, and the ^{31}P NMR spectrum showed an AB_2 pattern compatible with the expected structure.

References and Notes

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(24) The ratio of R′O/MeNH was 12–25:10000.

(25) The ratio of R″NH/MeNH was estimated to be 2:10000 from the spectral absorption intensities.

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