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Experimental and Theoretical Study of the Hydrolytical Stability of Isolable Poly(2,2′-dioxy-1,1′-biphenoxyphosphazene)s with [NPCl$_2$] Units

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ABSTRACT: The reaction of $[NPCl_2]_n$ with substoichiometric amounts ($x < 0.5$) of the biphenol $(HO)_2C_{12}H_8$ and K_2CO_3 followed by precipitation into cold water allowed the isolation of the stable chlorine-containing copolymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NPCl_2]_x\}_n$ (**1**) [$(O_2C_{12}H_8)$ = 2,2′-dioxy-1,1′-biphenyl], with $x = 0.12$ (**1a**), 0.28 (**1b**), and 0.43 (**1c**), having M_w of the order of 10^6, and the chain structure of strictly alternating copolymers. Larger x values resulted in the formation of hydrolyzed insoluble materials with no controlled composition. The polymers **1** could be hydrolyzed in THF/water solutions at rates that varied from very slow ($x = 0.12$ at room temperature) to very fast ($x = 0.43$ at reflux). However, in water suspensions the polymers **1** with $x < 0.5$ are not chemically affected, and only a reduction of the average M_w (as measured by GPC) could be observed at 100 °C. Molecular dynamics simulations were performed on model compounds of polymer **1**. The results of these calculations explain the hydrolytic behavior of the polymer.

Introduction

The polyphosphazenes are very interesting compounds in basic and applied material science.[1] In earlier works[2] we discovered that the reaction of $[NPCl_2]_n$ in THF with 2,2′-dihydroxy-1,1′-biphenyl ($HO-C_6H_4-C_6H_4-OH$) in the presence of K_2CO_3 occurred without cross-linking giving, depending on the stoichiometric ratios, the linear and very soluble $[NP(O_2C_{12}H_8)]_n$ or solutions of the partially substituted intermediates $\{[NP(O_2C_{12}H_8)]_{1-x}(NPCl_2)_x\}_n$, which could be subsequently reacted with functionalized phenols or biphenols to give a variety of polyphosphazenes with cyclic dioxyarene repeating units.[3]

It has been long known that the presence of P−Cl bonds makes a polyphosphazene chain sensitive to degradation by hydrolysis[4]—a fact that has been found advantageous for biomedical applications.[4b] In fact, more recent works have demonstrated that the hydrolysis of the homopolymer $[NPCl_2]_n$ is fast and generates first NP−OH groups that cause insolubility by interchain H-bond interactions rather than by P−O−P cross-linking.[5] Many reports have appeared showing that biologically active water-soluble polyphosphazenes obtained by incomplete macromolecular substitution from $[NPCl_2]_n$ undergo hydrolytic degradation at rates increasing with the residual Cl contents,[6] and the preparation of hydrolytically stable derivatives with formula $[NP(OC_6H_4-Bu^t)_{1.2}Cl_{0.8}]_n$ has been recently published.[7] Herein we report the preparation of various chlorine-containing 2,2′-dioxybiphenylphosphazenes that can be isolated as very stable intermediates resistant to hydrolysis from 0 to 100 °C in aqueous media where they are insoluble, although they are hydrolyzed in THF/water solutions at rates that are faster as x increases. The isolation of the solid polymers **1** (Scheme 1) allowed the unexpected observation of a positive deviation of the glass transition temperatures from the additive rule on biphenoxyphosphazene copolymers.

In order to understand the hydrolytic behavior of polymer, molecular dynamics simulations were performed on model compounds of polymer **1** both in water and in THF/water mixtures.

Experimental Section

All reactions were carried out under a dry N_2 atmosphere. K_2CO_3 was dried at 140 °C prior to use. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. The 2,2′-dihydroxybiphenyl (Aldrich) was used as purchased.

The THF solutions of the polymer $[NPCl_2]_n$ were prepared following the method already described.[8]

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-300 and Avance 300 and 600 Mz instruments, using $CDCl_3$ as solvent unless otherwise stated. ^1H and $^{13}C\{^1H\}$ NMR are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4. C, H, and N, analyses were performed with a Perkin-Elmer 240 microanalyzer. Chlorine analyses were performed by Galbraith Laboratories. GPC were measured with a Perkin-Elmer equipment with a model LC 250 pump, a model LC 290 UV, and a model LC 30 refractive index detector. The samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium bromide in THF through Perkin-Elmer PLGel (Guard, 10^5, 10^4, and 10^3 Å) at 30 °C. Approximate molecular weight calibration were obtained using narrow molecular weight distribution polystyrene standards. T_g values were measured with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer. Thermal gravimetric analyses were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under constant flow of nitrogen.

X-ray diffractograms were measured with PANalytical X'Pert Pro, using Kα_1 Cu radiation (1.5406 Å) at 45 kV−40 mA, with a X'Celerator detector with 2.122°. The scans were $\theta/2\theta$ from 2 to 560°2θ at 0.033° intervals at 300 s per interval.

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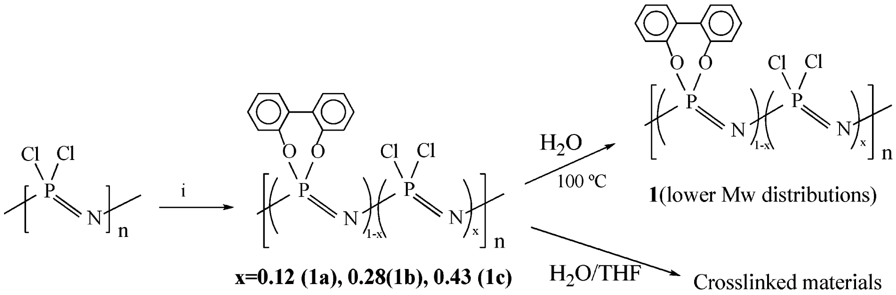
Scheme 1[a]



[a] (i) 2,2′-Dihydroxybiphenyl/K_2CO_3/THF.

Preparation of $\{[NP(O_2C_{12}H_8)]_{1-x}(NPCl_2)_x\}_n$ (1). The following procedure for the preparation of **1b** ($x = 0.28$) is representative of the corresponding to the other derivatives but modifying the molar ratios accordingly.

To a THF solution of $[NPCl_2]_n$ (50 mL, 2.85 g, 24.2 mmol) THF (200 mL), 2,2′-$HOC_6H_4C_6H_4OH$ (3.11 g, 16.7 mmol), and K_2CO_3 (9.22 g, 66.7 mmol) were added, and the mixture was refluxed for 17 h with vigorous mechanical stirring. The resulting mixture was poured into water (1.5 L) with ice and filtered to give a precipitate that was washed with isopropyl alcohol and diethyl ether. The solid was dissolved in THF (600 mL), and the solution was filtered and concentrated at reduced pressure until the formation of a viscous liquid that was poured portion-wise (Pasteur pipet) into water (1 L). Two further reprecipitations from THF/isopropyl alcohol and THF/hexane gave **1b** as a white material that was dried 24 h in vacuum at room temperature. Yield: 3.34 g, 68%. Anal. Calcd for $C_{8.64}H_{6.76}NO_{1.44}PCl_{0.56}$ (197.3 g/mol): C, 52.5; H, 2.92; N, 7.09; Cl, 8.84. Found: C, 51.1; H, 3.0; N, 7.0; Cl, 10.0. IR (KBr) cm^{-1}: 3066 w, 3038 vw (ν-CH−arom), 2961 vw (ν-CH−aliph from solvents retained), 1605 w, 1583 vw, 1501 m, 1477 s (ν-C=C−arom), 1439, 1369 br (not assigned), 1272 sh (ν-C−OP), 1246 vs 1191 vs, br (ν-PN), 1096 s (ν-P−OC), 943 vs, br (δ-POC), 786 s, 752 s, 717 m (out-of-plane CH deformations), 608 s, 590 m, 538 s br (other). $^{31}P\{H\}$ NMR ($CDCl_3$) δ: −4.3 br $[NP(O_2C_{12}H_8)]$, −20.9 br $[NPCl_2]$. Ratio $NP(O_2C_{12}H_8)/(NPCl_2)$: exptl 0.7/0.3. ^1H NMR ($CDCl_3$) δ: 7.3, 7.1 m br ($O_2C_{12}H_8$). $^{13}C\{H\}$ NMR ($CDCl_3$): $\delta = 151$ br, 150.6 d br $[C_1{-}O_2C_{12}H_8]$, 131 vbr, 128 vbr, 125 vbr ($O_2C_{12}H_8$). GPC: M_w 615 000, $M_w/M_n = 5.7$. TGA: −2% from room temperature to 170 °C (solvents retained), followed by a continuous loss (total −52%) with three maxima with similar intensity at 400 °C, 500 °C (middle intensity), and 710 °C. Residue at 800 °C: 46%. DSC: $T_g = 128$ °C ($\Delta C_p = 0.18$ J/(g K)).

Polymer 1a ($x = 0.12$). Yield: 82%. Anal. Calcd for $C_{10.56}H_{7.04}NO_{1.76}PCl_{0.24}$ (215.4 g/mol): C, 58.8; H, 3.27; N, 6.50; Cl, 3.9. Found: C, 58.9; H, 3.4; N, 6.5; Cl, 3.1. $NP(O_2C_{12}H_8)/(NPCl_2)$ by ^{31}P NMR: 0.86/0.14. GPC: M_w 510 000, $M_w/M_n = 4.4$. TGA: −1.3% from room temperature to 210 °C (solvents retained); −5.3% from 210 to 430 °C, −35% centered at 525 °C. Residue at 800 °C: 58.4%. DSC: $T_g = 149$ °C ($\Delta C_p = 0.19$ J/(g K)).

The M_w could be decreased without chemical alteration in water suspension to 490 000 (10 days at room temperature), 350 000 (1 h, reflux), 173 000 (7 h, reflux), and 115 000 (5 h, reflux). Further heating maintained the M_w near this value.

The hydrolysis in THF/H_2O was studied dissolving 50 mg of the polymer in 10 mL of THF and adding 1.5 mL of water. The process was carried out both at room temperature and at reflux and was followed by ^{31}P NMR.

Polymer 1c ($x = 0.43$). Yield: 68%. Anal. Calcd for $C_{6.84}H_{4.56}NO_{1.14}PCl_{0.86}$ (180.4 g/mol): C, 45.5; H, 2.52; N, 7.76; Cl, 16.9. Found: C, 45.2; H, 2.6; N, 7.2; Cl, 15.1. Ratio $NP(O_2C_{12}H_8)/(NPCl_2)$ by ^{31}P NMR: 0.56/0.44. GPC: M_w 500 000 (6.0). TGA: −5% from room temperature to 170 °C (solvents retained), followed by a continuous loss (total −32%) with three maxima at 400 °C (the most intense), 500 °C (the weakest), and 730 °C. Residue at 800 °C: 63%. DSC: $T_g = 101$ °C ($\Delta C_p = 0.19$ J/(g K)).

The M_w could be decrease without chemical alteration in water suspension to 380 000 (15 h, room temperature), 200 000 (1 h, reflux), and 70 000 (7 h, reflux). Further heating maintained the M_w near 70 000.

The hydrolysis was studied as indicated above for polymer **1a**.

Results and Discussion

The reaction of $[NPCl_2]_n$ in refluxing THF with substoichiometric amounts ($1 - x$) of $(HO)_2C_{12}H_8$ in the presence of an excess of K_2CO_3 (Scheme 1) followed by precipitation into ice−water (see Experimental Section) gave the copolymers $\{[NP(O_2C_{12}H_8)]_{1-x}(NPCl_2)_x\}_n$ (**1**) [$x = 0.12$ (**1a**), 0.28 (**1b**), and 0.43 (**1c**)] where $[(O_2C_{12}H_8) =$ 2,2′-dioxy-1,1′-biphenyl], which were isolated in 70−80% yields as white stable solids. The GPC chromatograms were bimodal with a more intense band at the higher M_w and an average M_w of the order of 0.5×10^6 and PDI of ca. 4−6 (Experimental Section).

The x values observed were close within the experimental errors (see below) to those expected from the amounts of biphenol used. Using quantities of $(HO)_2C_{12}H_8$ ($1 - x$) below 0.5, the same procedure gave the expected THF solution of the corresponding $NPCl_2$ copolymers, but after the precipitation step into water, only not well characterized insoluble materials that retained solvents were obtained.

The analytical and spectroscopic data for **1** were in accord with their composition. Thus, the x values were chosen as the best averages more consistent with the CHN and Cl analysis found and with the relative intensities of the signals corresponding to the two monomeric units in the ^{31}P NMR spectra in CD_3Cl solution that appeared as two broad multiplets: one centered near −5 ppm for the $NP(O_2C_{12}H_8)$ and other near −21 ppm for the $NPCl_2$. Considering all the data, the values have an uncertainty of ±0.03 units.

A comparison of the IR spectra of **1** with that of the completely substituted homopolymer $[NP(O_2C_{12}H_8)]_n$ showed not only the expected increase of the relative intensity of the band at 1245 cm^{-1} in the ν(PN) region as x increases (the reported value for the homopolymer $[NPCl_2]_n$ is 1240 cm^{-1})[9] but also noticeable changes in the δ(POC) region (950 cm^{-1}),[10] a band which is absent in the spectrum of the $[NPCl_2]_n$.

The ^1H NMR and, especially, the ^{13}C NMR spectra of **1** indicated that the biphenoxy groups are sensitive to the presence of the $[NPCl_2]$ units in the chains. Thus, the ^1H NMR spectra in chloroform showed that while three maxima are observed in the broad multiplet of the hydrogen of the aromatic rings in $[NP(O_2C_{12}H_8)]_n$ (7.2, 7.0, and 6.9), only two (7.3 and 7.1) are found in the case of **1**, indicating that the lower frequency peak is shifted to higher values and overlapped with the more intense central one. The ^{13}C NMR revealed a clear difference between the C_1 carbons of the most abundant $NP(O_2C_{12}H_8)$ units, which appeared as a singlet at 151 ppm, and those of the smaller fraction of them that are near the $[PCl_2]$ units (a doublet at 150.5 ppm).

The X-ray diffractograms showed a broad peak at wide angles indicating the formation of a mesophase only for **1a** and **1b**. Although the interplanar distances could not be measured accurately, they were clearly between 10 and 11 Å, i.e., lower than that of the homopolymer $[NP(O_2C_{12}H_8)]_n$ (12.1 Å).[11] It is known that the presence of composition defects in the phosphazene chains originated by incomplete macromolecular substitution of chlorines may prevent the appearance of mesophases,[12] but the limiting residual chlorine might depend on the type of phosphazene units present in the polymer, which explains the thermotropic behavior of **1a** and **1b** ($x = 0.12$ and 0.28) and the absence of mesophases in **1c** ($x = 0.43$).

As expected, the thermal stability, as estimated from the TGA curves at 10 °C/min, showed more complexity and less stability as the fraction of reactive $NPCl_2$ units increases. Thus, the thermogram of a polymer $[NP(O_2C_{12}H_8)]_n$ having only 1.3% chorine (i.e., **1** with $x = 0.05$) showed only a sharp weight loss (−49%) between 320 and 660 °C (centered at 507 °C), approaching that of the chlorine-free biphenoxyphosphazene homopolymer with only ppm of residual Cl.[11] In the case of **1a** ($x = 0.12$), however, the thermogram showed a first decomposition (5%) from 210 to 430 °C, which was partially overlapped with the main loss (−35%) centered at 525 °C. In the cases of **1b** and **1c**, various overlapped decomposition processes were evident, resulting in an almost continuous loss (−52% for **1b** and −32% for **1c**) from ca. 300 to 800 °C, with three relative maxima of decomposition rates at ca. 400, 500, and 720 °C, the first of which was more pronounced for the more chlorine-containing **1c**. It is known that above 250 °C poly(aryloxy)-phosphazenes depolymerize in more volatile cyclic oligomers, and above 400 °C chemical decomposition with cross-linking occurs.[13] Considering the thermal behavior of the $[NP(O_2C_{12}H_8)]_n$ homopolymer,[11,14] it is clear that the presence of the P−Cl bonds reduces the thermal stability of the copolymers, a fact early observed studying the thermal breakdown of diphenoxyphosphazene[15] that was attributed to the volatilization of chorobenzene.

As observed in other cases,[6] the chlorine content also determines the hydrolytic stability of **1**. In THF/water solutions, where the hydrolysis leading eventually to insoluble gels was clearly observed, the monitoring by ^{31}P NMR revealed that the reaction rate depended on x and on the temperature, varying from very slow in the case of **1a** ($x = 0.12$) at room temperature to very fast for **1b** ($x = 0.43$) at reflux. As the hydrolysis of the homopolymer $[NPCl_2]_n$ is always fast,[5] the higher resistance to water of **1** might be due to a protection of the $NPCl_2$ units by the hydrophobic $NP(O_2C_{12}H_8)$ units (see later). This can explain why polymers **1** with x much higher than 0.5, where diads and triads of $NPCl_2$ units are present, are more hydrolytically unstable and could not be isolated pure.

We also observed that stirring at room temperature a suspension of **1a** in water produced no chemical alterations and only a very small decrease of the average M_w (by GPC) (Experimental Section) due to an increase of the intensity of the band corresponding to the lower M_w fraction. No chemical changes occurred while heating the aqueous suspension at the boiling temperature (nearly 100 °C), but this time the reduction of the M_w was more pronounced, and the final GPC chromatogram was sharp and monomodal. The same effects were observed with **1c** ($x = 0.43$) although the reduction of the average M_w was more intense, falling from 400 000 to a plateau at 70 000 in 7 h at reflux (not altered after another 7 h).

It is possible that the changes in the M_w distribution, as measured by GPC, observed in the boiling water suspension are attributable to the temperature rather than to the water. Similar thermal degradation has been observed for the homopolymer $[NP(O_2C_{12}H_8)]_n$, which, freshly prepared might have some degree of branching.[14] Branching is, together with the presence of P−Cl bonds, one of the possible defects (or weak points) that were early proposed as responsible for the thermal behavior of polyphosphazenes.[15] The evident resistance of **1** to hydrolysis in the water suspensions even at 100 °C is probably due to the protection of the $NPCl_2$ units by the hydrophobic $NP(O_2C_{12}H_8)$ mentioned above, which, in the solid state, must be even more efficient (see later).

The glass transition temperatures of **1** (measured by DSC), which were unaffected by the treatment with boiling water, varied linearly with the composition given by x in the available range (0−0.5). (The value for $x = 0.05$, which is 155 °C, could be measured in a polymer $[NP(O_2C_{12}H_8)]_n$ having 1.3% residual chlorine content.) This confirms that they can be considered as random copolymers and that the $x = 0.5$ derivative (extrapolated $T_g = 94$ °C) is similar to a strictly alternating copolymer.[16] However, contrary to the other phosphazene copolymers with biaryloxy units,[16] the deviations from the additive values were positive instead of negative. (The average T_g value of the homopolymers $[NP(O_2C_{12}H_8)]_n$ (161 °C) and $[NPCl_2]_n$ (−63 °C)[17] is 49 °C.) It is known that both positive and negative deviation from the additive rule values may be found in random acrylic copolymers because the T_g on random copolymers depends not only on the polymer composition (chain stiffness and volume additivity) and distribution of the monomeric units along the chain but also on the possible monomer−monomer interactions and on the difference between the two extreme T_g values.[18] At present, it is not possible to advance a satisfactory explanation to the dependence of the T_g with composition in the polymers **1**, but it could be related with the interactions of the $[NPCl_2]$ and $[NP(O_2C_{12}H_8)]$ units along the chains which are absent in the two extreme homopolymers.

Theoretical Calculations. *Molecular Dynamics (MD) Software and Procedures.* The Amber molecular modeling package,[19] including the Amber force field, was employed for all the molecular dynamics (MD) simulations presented below. This force field has been previously used in the analysis of the same kind of molecules studied in the present work.[14,20] Coulombic potentials were computed by the Ewald sum procedure.[19] Partial charges were assigned to every atom by means of the MOPAC package and the AM1 procedure.[21] A time step $\delta = 1$ fs (i.e., 1×10^{-15} s) was employed for the integration algorithm.

All the MD simulations were performed on periodic boundary condition systems under NVT conditions, with the temperature being kept constant by means of the Berensen[19,22] thermostat with a coupling factor of 1000 fs. Several exploratory calculations were performed at different temperatures ranging from 300 to 500 K. Finally, it was decided to perform all the calculations at 500 K in order to increase the atomic velocities, thus facilitating the passage over energetic barriers and consequently improving the statistical sampling of all the configurational space.

Molecular Systems. The target molecule in the present work was an oligomer containing 27 phosphazene repeat units. The central unit (number 14 along the chain) was $-[N-PCl_2-]$ while all other units had a biphenoxy group attached to the phosphorus atom. This is a good model compound for polymer chains containing $N-PCl_2$ units which are isolated along the chain. Two different systems, both having periodic boundary conditions, were studied. System A contained one oligomer and 2200 molecules of water packed into a cubic box of side $L =$

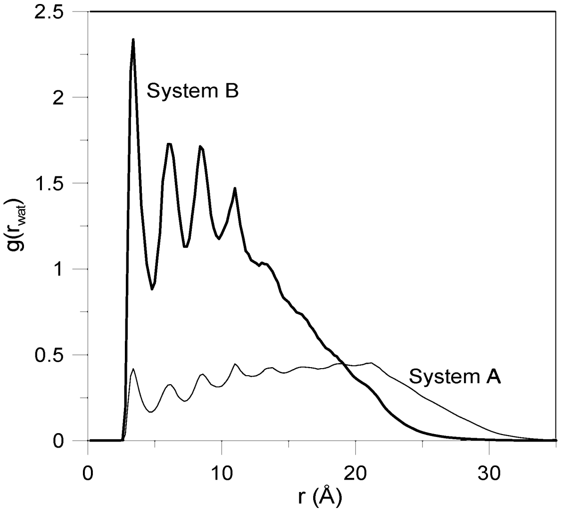


Figure 1. Radial correlation function $g(r_{\mathrm{wat}})$ for the distances between Cl atoms and water molecules for systems A (pure water as solvent) and B (THF and water). See text for details.

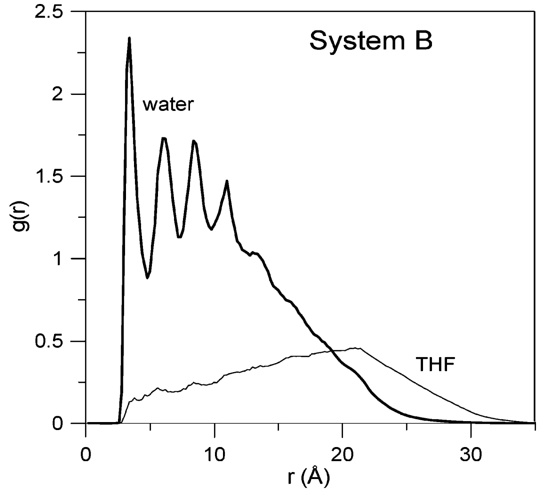


Figure 2. Radial correlations functions for distances between Cl and water molecules (r_{wat}) and Cl to THF molecules (r_{THF}) computed for system B.

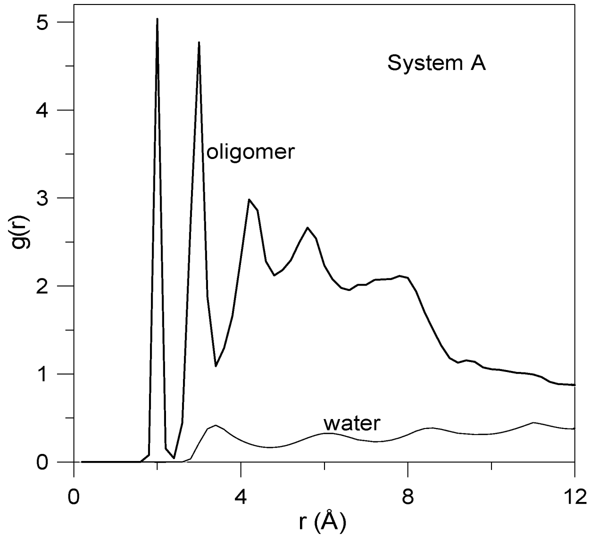


Figure 3. Radial correlation functions computed on system A for distances Cl to oligomer atoms (r_{oli}) and Cl to water molecules (r_{wat}).

42.34 Å. System B contained one oligomer and 500 molecules of THF and 250 molecules of water packed into a cubic box of side $L = 42.63$ Å. The concentration, in grams of oligomer by volume of the solution, is roughly the same in both systems.

Each system was initially built within a rather large box having approximately twice the final side length. The size of these initial boxes was progressively decreased by a combination of MD and energy minimization steps performed as follows: After each decrease of the side box, a 60 ps (i.e., 60×10^{-12} s) MD simulation was performed during which the system was slowly warmed up from 0 to 500 K, equilibrated at this temperature during ~20 ps, and then slowly cooled to 0 K. Then, the energy of the system was minimized with respect to all internal coordinates with a combination of steepest descendent al conjugated gradient algorithms.[19] Once the system has reached the desired volume, it was slowly warmed from 0 to 500 K, employing 100 ps in this process. Finally, the production stage was started which consisted in 4×10^6 integration cycles (i.e., a time span of 4000 ps), during which the coordinates of the system were recorded at intervals of 1 ps, thus producing a total of 4000 configurations of the system that were employed in the posterior analysis. Results obtained during the warming step were not employed in the analysis.

Results. The present analysis was focused on studying the distances between the two Cl atoms in the central unit of the oligomer and different kinds of atoms within the system over all the configurations recorded during the production stage. Thus, r_{oli} indicates distances from Cl to the rest of atoms contained in the oligomer chain, r_{wat} is the distance from Cl to the molecules of water (in fact, to the oxygen atom of each water molecule), and r_{THF} represents distances from Cl to the oxygen atom of THF molecules. These distances were employed to compute the radial correlation function $g(r)$ defined as the ratio between the probability of finding two particles at a distance $r \pm \delta r$ and the same probability computed assuming that the particles are randomly distributed. A value $\delta r = 0.1$ Å was employed in the present work. The values of the different $g(r)$ functions are represented in Figures 1−4.

Figure 1 represents the $g(r_{\mathrm{wat}})$ function for the distances between Cl atoms and water molecules in both A and B systems. According to these results, there is a strong correlation for the position of the water molecules with respect to the Cl atoms in system B for distances r of ca. 3−12 Å. The correlation is much weaker in the case of system A. Thus, the few molecules of water contained in system B together with THF molecules are able of getting into much closer proximity to the Cl atoms of the oligomer than the molecules of water contained in system A where the solvent is pure water.

Figure 2 shows the values of $g(r_{\mathrm{wat}})$ and $g(r_{\mathrm{THF}})$ for system B. It clearly shows that Cl atoms have a strong preference for water molecules rather than THF. It seems that THF molecules are no able of getting very close to the Cl atoms, but they force the water molecules into close proximity of Cl atoms.

Figure 3 shows the values of $g(r_{\mathrm{oli}})$ and $g(r_{\mathrm{wat}})$ for system A. The two very sharp peaks exhibited by $g(r_{\mathrm{oli}})$ at $r \approx 2$ and 3 Å are produced by the first (P atom) and second (two N and the second Cl) neighbors of each Cl atom. The distance to these atoms does not depend on any rotation and changes very little along the MD trajectory and consequently produces very strong correlations. Comparison of the two lines of Figure 3 clearly indicates that Cl atoms strongly prefer to be surrounded by other atoms of the oligomer than by the water molecules of system A.

Figure 4 contains the three functions for system B. As it is apparent from this figure, correlations with water molecules at $r \approx 2$−3 Å are much smaller than correlations with first and

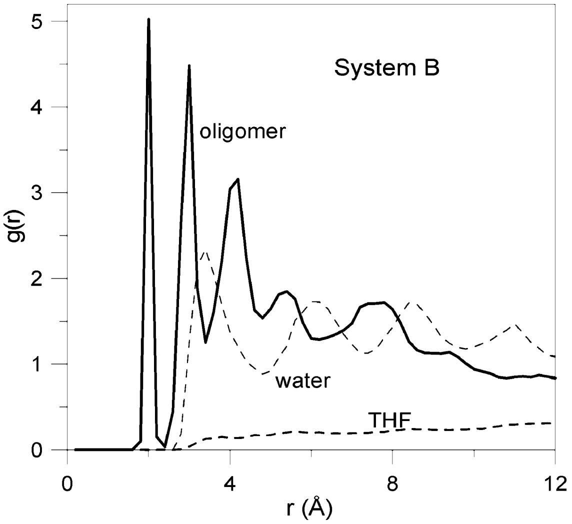


Figure 4. Radial correlation functions computed on system B for distances Cl to oligomer atoms (r_{oli}) and Cl to water molecules (r_{wat}) and Cl to THF molecules (r_{THF}).

second neighbors. But at distances of ca. 3−3.5 Å water molecules are preferred over atoms of the oligomer. Finally, the correlations for both oligomer atoms and water molecules are very similar for values of r larger than 4.5 Å. Correlations with the THF molecules are much weaker than those with either water or atoms of the oligomer.

These results explain why the $NPCl_2$ units are stable in pure water because the P−Cl bonds are protected by the atoms of the polymeric chain and less accessible to the water molecules; i.e., their hydrolytic activity[1,4a] is decreased. However, the dichloro units are hydrolyzed in water/THF mixtures because the THF molecules facilitate the approach of water molecules to the P−Cl bonds.

Conclusion

This paper demonstrates the possibility of isolating stable chlorine-containing phosphazenes that can be used as synthetic intermediates (by macromolecular substitution) for copolymers with regular distribution of two different units. It also includes an experimental study of reactivity with water, whose main feature, i.e., the fact that polymers containing a few dichloro units are stable in contact with water and yet they are hydrolyzed in THF solutions containing small amounts of water, is explained by theoretical calculations based on molecular dynamics simulations.

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