A Simplified and Convenient Laboratory-Scale Preparation of ^{14}N or ^{15}N High Molecular Weight Poly(dichlorophosphazene) Directly from PCl_5

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Abstract: A simple and convenient one-pot synthesis of THF solutions of high molecular weight poly(dichlorophosphazene) $[NPCl_2]_n$, or the ^{15}N isotopomer $[^{15}NPCl_2]_n$, starting directly from PCl_5 and NH_4Cl or $^{15}NH_4Cl$ in a solution of 1,2,4-trichlorobenzene in the presence of sulfamic acid and calcium sulfate dihydrate, is described. The solutions of $[NPCl_2]_n$ in THF, which are obtained free of poly(tetrahydrofuran) by preparing them in the presence of K_2CO_3, can be reacted directly with phenols, biphenols, or even $HO\text{-}CH_2CF_3$ in the presence of K_2CO_3 or Cs_2CO_3 to obtain, after a very simple workup, the corresponding polyphosphazene derivatives almost free of chlorine.

Keywords: inorganic polymers · poly(dichlorophosphazene) · polyphosphazenes · synthetic methods

Introduction

The preparation of poly(dichlorophosphazene) $[NPCl_2]_n$ (PDCP), is of paramount importance in the chemistry of polyphosphazenes because it is the key starting material for the synthesis of these potentially useful polymers.[1] The main reactions leading to poly(dichlorophosphazene) are: a) the ring-opening polymerization of the trimer $[N_3P_3Cl_6]$;[2, 3] b) the polycondensation of $Cl_3P{=}NP(O)Cl_2$;[4] and c) the polycondensation of $Cl_3P{=}NSiMe_3$.[1b] The latter method is the most convenient one, but only when polymers with a reproducible molecular weight in the range 10^4–10^5 are required.

The ring-opening polymerization of $[N_3P_3Cl_6]$[2] is usually carried out in the molten state, sometimes in the presence of a catalyst (for a recent review see reference [3]). However, as described by Magill and co-workers[5] the reaction can be also accomplished in solution by using 1,2,4-trichlorobenzene (b.p. 214 °C) as solvent in the presence of $CaSO_4 \cdot 2H_2O$ as promoter, and $HSO_3(NH_2)$ as catalyst. Therefore, taking into account that the $[N_3P_3Cl_6]$ is obtained from the reaction of PCl_5 with NH_4Cl,[6] it might be possible to obtain the poly(dichlorophosphazene) in one pot, directly from those reagents and in the presence of the promoter and the catalyst. Herein we describe a procedure for the laboratory-scale synthesis of poly(dichlorophosphazene) with a molecular weight of the order of 10^6, which may be very useful for research in this field. There are many previous reports on the preparation of poly(dichlorophosphazene) from PCl_5 and NH_4Cl either in solution or in the solid state,[7, 8] most frequently leading to low molecular weight materials, and recently a novel method to prepare high molecular weight poly(dichlorophosphazene) in 100% yield, in two steps starting directly from PCl_5 and $(NH_4)_2SO_4$ in the solid state has been patented.[9] The simplicity of the method presented herein for the synthesis of $[NPCl_2]_n$ and for the substitution of its chlorine atoms by OR groups may facilitate the preparation of new functionalized high molecular weight polyphosphazenes, which could be of interest in materials science,[1a, 2] and of their transition-metal complexes,[1c, 1d] which may be useful as supported catalysts.[1e, 1f]

Experimental Section

General remarks: All the preparations were carried out under nitrogen, unless otherwise stated. K_2CO_3 (Panreac) and Cs_2CO_3 (Aldrich) were dried at 140 °C prior to use, and NH_4Cl (Aldrich) was dried in a dissicator over P_2O_5 (Panreac). 1,2,4-Trichlorobenzene was used freshly distilled. PCl_5 (Aldrich) was purified by sublimation. THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Petroleum ether refers to that fraction with a boiling point in the range 60—65°C. $^{15}NH_4Cl$ (99% ^{15}N, Isotec Inc.), the trimer $[N_3P_3Cl_6]$ (Fluka), the biphenol $HO{-}C_6H_4{-}C_6H_4{-}OH$ (Aldrich), $CaSO_4 \cdot 2H_2O$ (Panreac), and sulfamic acid (Aldrich) were used as purchased. The $CF_3CH_2{-}OH$ (Aldrich) was distilled over anhydrous $CaSO_4$.

The IR spectra were recorded with a Perkin–Elmer Paragon 1000 spectrometer. Wavenumbers are given in cm^{-1}. NMR spectra were recorded on Bruker AC-200 and AC-300 instruments. ^{1}H and ^{13}C{^{1}H}

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Chem. Eur. J. 2003, 9, 3833–3836 DOI: 10.1002/chem.200304750

NMR spectral data are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR, ^{15}N NMR, and ^{19}F NMR spectral data are given in δ relative to external 85 % aqueous H_3PO_4, liquid NH_3, and $CFCl_3$, respectively. Coupling constants are given in Hz. C, H, N analyses were performed with a Perkin Elmer 240 microanalyzer. Cl analyses were performed by Galbraith laboratories. GPC were measured with a Perkin Elmer instrument 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 was obtained by 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 analysis were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of $10\,^{\circ}C\,min^{-1}$ from ambient temperature to 800 °C under a constant flow of nitrogen.

Preparation of solutions of $[NPCl_2]_n$ in THF

1. From $[N_3P_3Cl_6]$ (The Magill method): The trimer $[N_3P_3Cl_6]$ (20 g, 57.53 mmol) and 1,2,4-trichlorobenzene (16 mL) were placed in a 250 mL three-neck round-bottom flask containing a reflux condenser, a gas inlet, and a magnetic stirring bar. The catalyst, $HSO_3(NH_2)$ (42.3 mg, 0.44 mmol) and the promoter, $CaSO_4 \cdot 2H_2O$ (37.5 mg, 0.22 mmol) were added and the mixture was refluxed while stirring and slowly bubbling dry N_2 through it all the time, until the reaction mixture became sufficiently viscous (this occurs normally after 45 – 60 min; we noted that the exact time depended on the particular experiment and, therefore, it must be observed carefully. (This is a very important aspect because before that point the molecular weight is not high, and soon afterwards the polymer starts to precipitate as a gel due to cross-linking.) During the process, the formation of foams is usually observed. The reaction mixture thus obtained was allowed to cool to room temperature and added in portions (using a Pasteur pipette) to warm petroleum ether (ca. 50 °C; 500 mL) under vigorous stirring and under nitrogen. The liquids were decanted (see note in reference [10]) and the remaining white solid was washed twice with petroleum ether (30 mL) and mixed with solid dried K_2CO_3 (0.5 g; to neutralize any acidic residues and thus preclude the formation of PTHF). Then THF (100 mL) was added to the mixture to form a solution of $[NPCl_2]_n$ over the solid potassium carbonate.

The concentration of the resulting solution of $[PNCl_2]_n$ in THF was determined by weighing the residue of the solid left by evaporating an aliquot of 3 mL to dryness. The total amount of polymer normally obtained was in the range 5 – 7 g (ca. 25 – 35 % yield based on $[N_3P_3Cl_6]$).

2. From PCl_5 and NH_4Cl: The following procedure is representative of all the experiments done. For a summary of the results and the scales (see note 1 in reference [11]) see Table 1.

In a 250 mL three-neck flask equipped with a refrigerant and a glass N_2 inlet, a mixture of PCl_5 (20.0 g, 96.0 mmol), well dried solid NH_4Cl (5.14 g, 96.0 mmol), $CaSO_4 \cdot 2H_2O$ (21 mg, 0.12 mmol), $HSO_3(NH_2)$ (23 mg, 0.24 mmol) (see note 2 in reference [11]) and very freshly distilled 1,2,4-trichlorobenzene (17 mL) was heated with stirring, while N_2 was bubbled slowly through the solution until the reaction system reached the reflux temperature (after about 45 min; evolution of HCl(g) (a well aired hood must be used)). Then the refluxing was maintained for 3.5 h (see note 3 in reference [11]). The resulting mixture was allowed to cool and was poured in portions (with a Pasteur pipette) into vigorously stirred warm hexane (500 mL) (see note 4 in ref. [11]), which led to an off-white gummy precipitate that was washed twice with hexane and mixed with solid K_2CO_3 (0.2 g). THF (100 mL) was added to the mixture to form a clear solution of $[NPCl_2]_n$ standing over the solid carbonate.

The concentration of the resulting THF solution was determined by weighing the residue of solid $[NPCl_2]_n$ left by evaporating an aliquot of 3 mL to dryness. The concentrations were of the order of $34\,g\,L^{-1}$ (total amount of polymer 3.4 g, 31 % yield based on PCl_5).

Preparation of N^{15}-$[NP(O_2C_{12}H_8)]_n$ (1b): K_2CO_3 (4.83 g, 35 mmol) and 2,2′-$HOC_6H_4C_6H_4OH$ (2.41 g, 13 mmol) were added to a solution of $[^{15}NPCl_2]_n$ (1 g, 8.62 mmol, prepared from PCl_5 and $^{15}NH_4Cl$) in THF (20 mL), and the mixture was refluxed with stirring for 15 h. The mixture was poured into water (0.5 L) to give a white precipitate that was washed with water (3 × 50 mL) and extracted with THF. The solution was filtered through celite and concentrated to a viscous liquid that was poured into water (0.5 L). The product was similarly reprecipitated once from THF/2-propanol and once from THF/petroleum ether to give a white solid that was dried in vacuo at 70 °C for two days. Yield: 0.96 g (48 %).

^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 6.8, 6.9, 7.2$ ppm (br); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, H_3PO_4): $\delta = -5.9$ ppm (br); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, TMS) : $\delta = 123, 126, 129, 130, 149$ ppm; ^{15}N NMR ($CDCl_3$, 25 °C, NH_3): $\delta = 65.5$ ppm; IR (KBr): $\tilde{\nu} = 3065$w, 3032w, 1604w, 1583w, 1500m, 1477m, 1439m, 1340br, 1272m,1245vs, 1192vs, 1096s, 951s, 917m, 786m, 750m, 717m, 609m, 590w, 536m cm^{-1}; M_w (GPC): 600. 000 ($M_w/M_n = 3.0$); elemental analysis calcd (%) for $C_{12}H_8O_2{}^{15}NP$ (230.171): C 62.6, H 3.5, N 6.5; found: C 61.5, H 3.5, N 6.1.

Preparation of $[NP(OCH_2CF_3)_2]_n$ (2a): THF (100 mL), solid Cs_2CO_3 (69 g, 212 mmol), and freshly distilled $HOCH_2CF_3$ (15.4 mL, 212 mmol) were added to a solution of $[NPCl_2]_n$ (100 mL, $82\,g\,L^{-1}$, 70.7 mmol) in THF. The mixture was stirred at room temperature for 4.5 h and poured into water (2.5 L). The resulting white precipitate was washed with water until neutral pH (ca. 3 × 200 mL), dried under reduced pressure, extracted with sufficient THF, filtered through celite, concentrated to a viscous liquid, and reprecipitated into water. The sample was further purified by reprecipitation from THF/hexane. The final product was dried at room temperature under reduced pressure (10^{-3} Hgmm) for one week to give spectroscopically and analytically pure **2a** as a white solid (17 g, 76 %).

^1H NMR ($[D_6]$acetone, 25 °C, TMS): $\delta = 4.7$ ppm (q, $^3J(H,F) = 7$ Hz); $^{31}P\{^1H\}$ NMR ($[D_6]$acetone, 25 °C, H_3PO_4): $\delta = -6.3$ ppm (br); $^{13}C\{^1H\}$ NMR ($[D_6]$acetone, 25 °C, TMS): $\delta = 124$ (q, $^1J(C,F) = 277$ Hz, CF_3), 64 ppm (q, $^2J(C,F) = 38$ Hz, CH_2); ^{19}F NMR ($[D_6]$acetone, 25 °C, $CFCl_3$): $\delta = -75.3$ ppm; IR (KBr): $\nu = 2975$m, 1459m, 1423m, 1282s, 1252s, 1172vs, 1082vs, 964s, 879m, 844m, 662m, 565m, 523, 512m cm^{-1}; $M_w = 1 - 1.7 \times 10^6$, $M_w/M_n = 1.7$ (see text); elemental analysis calcd (%) for $C_4H_4F_6NO_2P$ (243.044): C 19.8, H 1.7, N 5.8; found: C 20.2, H 1.8, N 5.6.

Preparation of $[^{15}NP(OCH_2CF_3)_2]_n$ (2b): Cs_2CO_3 (8.4 g, 26 mmol) and $HOCH_2CF_3$ (1.9 mL, 26 mmol) were added to a solution of $[^{15}NPCl_2]_n$ (1 g, 8.62 mmol), prepared from PCl_5, in THF (50 mL), and the mixture was stirred for 15 h at room temperature. The mixture was poured into water (0.5 L) to give a white precipitate that was washed with water (3 × 50 mL) and extracted with THF. The solution was filtered through celite and concentrated to a viscous liquid that was poured into water (0.5 L). The product was similarly reprecipitated once from THF/2-propanol and once from THF/petroleum ether to give a white solid that was dried in vacuo at 30 °C for two days. Yield: 1.34 g (64 %).

^1H NMR ($[D_6]$acetone, 25 °C, TMS): $\delta = 4.7$ ppm br; $^{31}P\{^1H\}$ NMR ($[D_6]$acetone, 25 °C, H_3PO_4): $\delta = -6.5$ ppm; ^{19}F NMR ($[D_6]$acetone, 25 °C, $CFCl_3$): $\delta = -75.3$ ppm; ^{15}N NMR ($CDCl_3$, 25 °C, NH_3): $\delta = 62.7$ ppm; IR (KBr): $\tilde{\nu} = 2975$m, 1458m, 1421m, 1287s, 1220s, 1174vs, 1083vs, 963s, 877m, 840m, 816w, 661m, 564m, 517m cm^{-1}; M_w(GPC): 1 000 000, $M_w/M_n = 3.3$, elemental analysis calcd (%) for $C_4H_4F_6{}^{15}NO_2P$ (244.044): C 19.7, H 1.7, N 6.1; found: C 19.2, H 1.9, N 6.0.

Results and Discussion

The synthesis of PDCP in solution: It is known that the ring-opening polymerization of $[N_3P_3Cl_6]$ in refluxing 1,2,4-trichlorobenzene (b.p. 214 °C) is promoted by the presence of calcium sulfate dihydrate and catalyzed by sulfamic acid.[5] Reaction of the resulting poly(dichlorophosphazene) with sodium aryloxides, or directly with phenols and M_2CO_3 (M = K or Cs)[12] affords the hydrolytically stable aryloxy derivatives $[NP(OAr)_2]_n$ with a molecular weight of the order of 10^6. According to Magill's work, no branching occurs in the linear polyphosphazenes formed by this procedure, and the yield of poly(dichlorophosphazene) obtained is about 30 %.

As the $[N_3P_3Cl_6]$ is formed in the reaction of PCl_5 with NH_4Cl,[7] it should be possible to obtain the poly(dichlorophosphazene) in one pot, directly from these reagents and in the presence of the promoter and the catalyst. We confirmed this hypothesis by repeating Magill's experiments but starting from an equimolar mixture of PCl_5 and NH_4Cl. As shown by the data for its hydrolytically stable polyphosphazene derivatives (see below), the poly(dichlorophosphazene) obtained had very similar characteristics to that formed starting from $[N_3P_3Cl_6]$. The yield based on PCl_5 was about 30%, which, in practice, represents a much higher yield than that obtained by using $[N_3P_3Cl_6]$ as the starting material. Monitoring the reaction by ^{31}P NMR spectroscopy revealed the rapid disappearance of the PCl_5 and the formation of $[N_3P_3Cl_6]$, $[N_4P_4Cl_8]$, $[N_5P_5Cl_{10}]$, and other small oligomers as intermediates. We also observed the presence of $[NPCl_2]_n$ from the very beginning of the process. Various experiments showed that the absence of the promoter and/or the catalyst decreased the yield to 20% and that carrying out the reaction without the use of an N_2 atmosphere had little effects on the final yield.

However, above 100 g of PCl_5 the scaling up of the laboratory procedure brought many technical problems, and safety hazards. The most important problem was the sublimation of the PCl_5 that caused obstructions within the reactor and that on occasions led to small explosions. The results are summarized in Table 1.

Table 1. Summary of the preparation of solutions of $[NPCl_2]_n$ in THF.

PCl_5 [g]	$[NPCl_2]_n$ [Av g]	Yield [%]	Number of experiments
12	2.1	32	6
22–29	3.6–4.8	30	10
48	9.2	35	4
96	15.7	30	1
250	27.3	20	5[a]

[a]Numerous experimental problems caused by the sublimation of PCl_5.

All our attempts[13] to achieve safe larger laboratory scales were unsuccessful, although by conducting the reaction sequentially using two solvents of different boiling point to prevent the sublimation of the PCl_5 led to procedures with yields approaching 40% in scales of the order of 50 g. Therefore, all these observations show that if this method were to be extended to a large-scale industrial process many technical modifications would be required.

Synthesis of polyaryloxyphosphazenes from the $[NPCl_2]_n$ in solution: As shown previously, the direct use of the phenol and K_2CO_3 or Cs_2CO_3 as proton abstractors in the direct reactions of poly(dichlorophosphazene) with phenols have important advantages from a synthetic point of view.[12] However, when these substitution reactions were carried out in THF as solvent the isolated products were frequently contaminated with polytetrahydrofuran (PTHF), a problem that could be resolved by forming the initial solution of the poly(dichlorophosphazene) in THF in the presence of solid K_2CO_3.[14]

Therefore, to determine the characteristics of the $[NPCl_2]_n$ obtained in THF by the method described above, we treated it with the biphenol 2,2′-dioxybiphenyl and K_2CO_3 to obtain the linear uncrosslinked polymer $[NP(O_2C_{12}H_8)]_n$ (**1a**), previously reported by us.[15] The molecular weight and the thermal behavior (T_g) of the product was almost identical to the that of the polymers obtained starting from $[NPCl_2]_n$ prepared by Magill's method. Therefore, the $[NPCl_2]_n$ that results from our new procedure has a much higher molecular weight than that obtained by polycondensation of $Cl_3P{=}NSiMe_3$ as described in reference [1b].

Moreover, we also noted that the direct method which used cesium carbonate worked well with the acidic alkyl alcohol $HOCH_2CF_3$ at room temperature, giving the long-known polymer[16, 17] $[NP(OCH_2CF_3)_2]_n$ (**2a**) in good yield and purity in less than 5 h (see Experimental Section). The high molecular weight observed by GPC for **2a** confirms that the molecular weight of the $[NPCl_2]_n$ obtained starting from PCl_5 is of the order of 10^6, although it must be taken into account that the molecular weight of $[NP(OCH_2CF_3)_2]_n$ is normally overestimated by GPC.[13]

Finally, the method described herein proved to be very convenient to obtain the ^{15}N phosphazene polymers **1b** and **2b**, starting from $[^{15}NPCl_2]_n$ prepared from $^{15}NH_4Cl$. As expected, the molecular weight, thermal behavior, and spectroscopy of **1b** and **2b** were almost identical to their ^{14}N counterparts. Small differences were observed in the ^{31}P NMR and ^1H NMR spectra, which exhibited broader signals, and more conspicuous ones in the IR spectra (KBr pellets). The broad absorption centered at 1400 cm^{-1} in the IR spectrum of **1a**[18] was less broad and centered at 1350 cm^{-1} in the IR spectrum of **1b**. Similarly, in the case of the trifluoroethoxy derivatives the spectra showed a very clear isotopic shift in one of the strong absorptions in the PN stretching region,[19] which appeared at 1252 cm^{-1} in the ^{14}N derivative **2a** and at 1220 cm^{-1} in the ^{15}N isotopomer **2b**. This suggests that this band is attributable to PN stretching modes that are rich in N contributions.

As expected, the $^{15}N\{^1H\}$ NMR spectra showed a strong signal near $\delta = 65$ ppm, which is close to the values reported for other polyphosphazenes.[20]

Aknowledgement

We are grateful to the Spanish FYCIT (Project PB-EXPO1-15) and DGITYT (Project MCT-01-BQU-3676) for financial support.

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[10] Note, the liquids should not be discarded because the 1,2,4-trichlorobenzene and the valuable [$N_3P_3Cl_6$] can be easily recovered from them.

[11] Note 1: In scales higher than 50 g of PCl_5, the initial sublimation of this compound is associated with some problems that become more acute in the 250 g scales. Note 2: Using no promoters lowers the yield to 10 – 15 % and also the molecular weight. Note 3: Maintaining the N_2 bubbling, if the reaction time is prolonged more than the 3.5 h crosslinking begins to be very extended. If the reaction times are lower, less yield and lower molecular weight result. Note 4: This operation should be carried out under a dry atmosphere with dried and distilled hexane; this prevents the partial hydrolysis of the polymer that would in turn give insoluble crosslinked products

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Received: January 21, 2003
Revised: April 1, 2003 [F4750]