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Polyphosphazenes combining dioxybiphenyl and butyl-amino substituents, a series with unusually high TGA residues and glass transition temperatures with negative deviation from additivity

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ABSTRACT

The new copolymeric series $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(NHBu^n)_2]_x\}_n$ ($O_2C_{12}H_8$=2,2′-dioxy-1,1′-biphenyl) with $x = 0.1$(**1a**), 0.31(**1b**), 0.43(**1c**), 0.63(**1d**) were prepared by the alkali carbonate-assisted sequential macromolecular substitution from $[NPCl_2]_n$. The thermal gravimetric analysis (TGA) revealed that although the stability decreased with x, the final residues (ca. 50% at 800 °C under N_2; 30% at 900 °C under air; and 15% at 1100 °C under oxygen) were unusually high. The variation of the glass transition temperatures with x showed negative deviation from the additive values (Fox equation), probably due to the losing of hydrogen bonding contribution as x is decreased.

1. Introduction

Polyphosphazenes are inorganic macromolecules that can be synthesized by different routes allowing a remarkable variety of chemical composition and structures [1,2]. Among the two-substituent phosphazenes $[NPA_{1-x}B_x]_n$ the un-crosslinked copolymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NPB_2]_x\}_n$ ($O_2C_{12}H_8$=2,2′-dioxy-biphenyl) having λ^5-phosphorus-heterocycles $P(O_2C_{12}H_8)$ in the repeating units (polyspirophosphazenes) (Chart 1) form a simpler system because of the bidentate nature of one of the substituents. Many examples of polyspirophosphazenes have been described [3]. They exhibit very high glass transition temperatures, particularly when x is below 0.2 (the homopolymer, with $x = 0$, has a $T_g = 161$ °C). This is probably due to strong π-interactions between chains, as pointed out by Ainscough et al. on the basis on crystallographic studies with related cyclic models [4].

Polyspirophosphazenes are easily obtained by refluxing a THF solution of $[NPCl_2]_n$ with 2,2′-dihydroxy-1,1′-biphenyl (HO–C_6H_4–C_6H_4–OH) in the presence of K_2CO_3 to give 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 in the presence of Cs_2CO_3 (alkali carbonate-assisted sequential macromolecular substitution). However, only a few derivatives have been prepared having aminophosphazene groups [5,6]. In this work we describe the synthesis of the new series of copolymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(NHBu^n)_2]_x\}_n$ (**1**) having butylamine-phosphazene units (B = $NHBu^n$ in Chart 1). The thermal behaviour (by TGA under different conditions) revealed high pyrolytic residues that can be compared with those left by different chlorine containing polyphosphazenes making them potential self-extinguishing [7]. The results have also provided a good example of negative deviation of the glass transition temperatures from the additive rule, that could be explained by the increasing difficulty in the formation of H-bonding interactions as x decreases.

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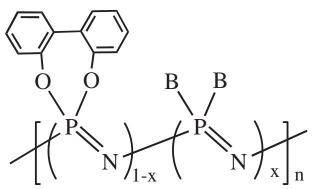

Chart 1. Structure of copolymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NPB_2]_x\}_n$.

2. Experimental section

All reactions were carried out under a dry N_2 atmosphere. K_2CO_3 and Cs_2CO_3 were 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′-dihydroxy-biphenyl (Aldrich) and the *n*-butylamine (Aldrich) were used as purchased. The intermediate polymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NPCl_2]_x\}_n$ (x <0.5) [8] or its THF solutions from $[NPCl_2]_x$ [9], were prepared following the methods already described.

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker DLX-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, N, analyses were obtained with Elemental Vario Macro. 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% by weight 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 analysis 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 or to 900–1100 °C under air or under oxygen.

X-ray diffractograms were measured with PANalytical X'Pert Pro, using $K\alpha_1$ 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.

2.1. Synthesis of $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(NHBu^n)_2]_x\}_n$ (1)

The following procedure for the preparation of **1a** (x = 0.10) starting from solid $\{[NP(O_2C_{12}H_8)]_{1-x}[NPCl_2]_x\}_n$ (x <0.5) is representative of those corresponding to other derivatives after modifying the molar ratios.

A solution of $\{[NP(O_2C_{12}H_8)]_{0.9}[NPCl_2]_{0.1}\}_n$ (0.2 g, 0.94 mmol, 0.19 mmol Cl) in THF (50 mL) was mixed with solid Cs_2CO_3 (0.20 g, 0.6 mmol) and cooled to 0 °C. Then NH_2Bu^n (0.07 mL, 0.096 g, 1.3 mmol) was added and the mixture was allowed to reach room temperature, stirred for 54 h, filtered and concentrated to a viscous liquid that was precipitated into water (100 mL). The solid was re-dissolved in THF (100 mL) and re-precipitated in the same way from THF/IPA and THF/Hexane, to give **1a** as a white solid (0.17 g, 80.3%).

The following procedure for the preparation of **1b** (x = 0.31) starting from $[NPCl_2]_n$ is representative of that corresponding to the other derivatives after modifying the molar ratios.

A solution of $[NPCl_2]_n$ (2 g, 17.3 mmol) in THF (150 mL) was mixed with solid $(HO)_2C_{12}H_8$ (1.93 g, 10.4 mmol) and K_2CO_3 (4.3 g, 31 mmol) and stirred under reflux for 16 h. Then $NHBu^n$ (5.6 mL, 4.14 g, 55.8 mmol) and Cs_2CO_3 (13.5 g, 42 mmol) were added and the mixture was stirred for 72 h at room temperature, filtered and concentrated to a viscous liquid that was precipitated into water (100 mL) (decanted overnight). The solid was washed with water (10 × 100 mL) dried at 40 °C overnight, re-dissolved in THF (600 mL) and re-precipitated in IPA to give **1b** as a white solid (3 g, 80%), that was dried at 70 °C.

Analyses: (%) C, H, N, found (calcd), and % residual Cl. (**1a**): 58.1(61.9), 3.90(4.09), 7.60(7.46), 0.14%Cl; (**1b**): 57.1(59.4), 5.5(5.4), 9.4(10.4), 0.54%Cl; (**1c**): 55.6(58.0), 5.27(6.19), 12.0(12.2), 0.35%Cl; (**1d**): 53.9(55.5), 6.40(7.59), 15.6(15.4), 0.18%Cl.

MW(PDI) by GPC: (**1a**): 570,000(5.9); (**1b**): 580,000(5.2); (**1c**): 700,000(4.7); (**1d**): 552,000(4.4).

IR (KBr) cm^{-1} (KBr pellets): 3390w.br. (ν-NH-free), 3350–3300w.br. (H-bonding-ν-NH), 3066w, 3031vw (ν-CH-arom.), 2955, 2929 and 2869 (ν-CH-Bu^n), 1604w, 1583vw, 1501m, 1477s (ν-C=C-arom.), 1438m, 1414m, 1374s.br. (not assigned), 1272sh. (ν-C-OP), 1241vs 1193vs, br. (ν-PN), 1118m, 1096s (ν-P-OC), 1037w, 1012vw (nor assigned) 931-900vs, br. (δ-POC), 782s, 750s, 717m (out of plane CH deformations), 610s, 591m, 535s.br. (not assigned). The (ν-PN) and (δ-POC) frequencies and the intensity of the absorption at 1414 cm^{-1} changed with x. The H-bonding-ν-NH band is more intense and has lower frequency as x increases.

$^{31}P\{H\}$NMR ($CDCl_3$) complex multiplet with δ max: (**1a**): −2, −5, −6; (**1b**): −0.4, −4.2; (**1c**): −1.4, −4.3; (**1d**): 2.5, 0.8, −0.5, −4.3.

^1HNMR ($CDCl_3$) δ: 6.7–7.2m, br. ($O_2C_{12}H_8$), 2.43m, 0.95m, 0.61m ($N-CH_2CH_2CH_2CH_3$). The HN signal was overlapped with the 2.4 multiplet.

$^{13}C\{H\}$NMR (THF): δ = 149br, 130, 129.7, 129.5, 128.9, 125.0, 123.2 ($O_2C_{12}H_8$), 40.5, 20.2, 26.7, 33.6, 40.5 ($N-CH_2CH_2CH_2CH_3$).

TGA residues % left at 800 °C under N_2, 900 °C under air, 1100 °C under oxygen: (**1a**): 49, 22, 16; (**1b**): 49, 27, 15; (**1c**): 49, 26, 13; (**1d**): 46, 26, 13.

The T_g's were measured by DSC from the well defined heat capacity steps. DSC, T_g°C: (**1a**): 129; (**1b**): 76; (**1c**): 50; (**1d**): 2.

3. Results and discussion

Refluxing $[NPCl_2]_n$ in THF with 2,2′-dihydroxy-1,1′-biphenyl ($HO-C_6H_4-C_6H_4-OH$) in the presence of K_2CO_3 (Scheme 1) gave the partially substituted intermediates