Properties of Dioxybiphenyl- and Chiral Dioxybinaphthylphosphazene Copolymers with Propyl−Carboxylate−Phenoxy Units and the Randomization of the Substitution Reactions of Poly(dichlorophosphazene)

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ABSTRACT: The reaction of $[NPCl_2]_n$ first with 2,2'-dihydroxybiphenyl and K_2CO_3 or (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthyl and Cs_2CO_3, and subsequently with $HO-C_6H_4-CO_2Pr^n$ and Cs_2CO_3, gave the phosphazene copolymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O-C_6H_4-CO_2Pr^n)_2]_x\}_n$ [x = 0.2 (**1a**), 0.35 (**1b**), 0.5 (**1c**), 0.7 (**1d**), and 0.85 (**1e**)] and the chiral analogues $\{[NP(O_2C_{20}H_{12})]_{1-x}[NP(O-C_6H_4-CO_2Pr^n)_2]_x\}_n$ [x = 0.2 (**2a**), 0.4 (**2b**), 0.45 (**2c**), 0.5 (**2d**), 0.55 (**2e**), 0.7 (**2f**), and 0.8(**2g**)]. The study of their properties as a function of the composition have revealed systematic changes in the electronic structure of the macromolecules, in the interplanar distances of their mesophases and in glass transition temperatures. The latter variation has demonstrated the strictly alternating nature of the copolymeric structures in the series **1** and **2**. This is an experimental evidence supporting that the substitution of Cl in the $[NPCl_2]_n$ with the bifunctional reagents or 2,2'-dihydroxybiphenyl and (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthyl as promoted by alkali carbonates are essentially random for all values of x and that the chirality of the binaphthyls has no stereochemical effect.

Introduction

The polyphosphazenes are one of the most studied inorganic macromolecules due of their academic and industrial interest.[1] During the last few years, the activity in this field has shown an increase, partly due to the development of new methods of synthesis, both from $[NPCl_2]_n$ or from other precursors.[1,2] In an earlier paper, we reported[3] that the polydichlorophosphazene reacts directly first with 2,2'-$(HO)C_6H_4-C_6H_4(OH)$ and subsequently with para-substituted phenols $OH-C_6H_4-R$ in THF in the presence of K_2CO_3 affording a new type of phosphazene copolymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O-C_6H_4-R)_2]_x\}_n$ having high thermal stability and elevated transition temperatures and that the method could be extended to the preparation of novel chiral polymers with 1,1′-binaphthyl-2,2′-dioxyphosphazene units.[4] The versatility of this synthetic method for phosphazene random copolymers gives new opportunities to carry out systematic studies of their properties as a function of composition and structure. At the same time, the analysis of the spectroscopic data yields useful information to characterize related insoluble or cross-linked materials.

In this work we describe the synthesis of various phosphazene copolymers with cyclic repeating units $[NP(O_2C_{12}H_8)]$ and $[NP(O_2C_{20}H_{12})]$ combined with the functionallized phenoxyphosphazene units $[NP(O-C_6H_4-CO_2Pr^n)_2]$ and a systematic study of their physical, spectroscopic and thermal properties as a function of their composition. The study has revealed the glass transition temperature vary with the copolymer composition in the way predicted by the Barton equation for strictly alternating random copolymers,[5] proving that the chlorine substitution reactions of the reactive $[NPCl_2]_n$ with the biphenol and binaphthol, occur in an strictly randomized manner for all molar ratios and that, in the latter case, there are no enantiomeric effects capable of inducing an incomplete randomness of the process.

Experimental Part

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 biphenol $HO-C_6H_4-C_6H_4-OH$ (Aldrich), the *R*-(+)-binaphthol $HO-C_{10}H_6-C_{10}H_6-OH$ (VWR international), and the phenols $HO-C_6H_4-CO_2Pr$ (Aldrich) were used as purchased. The starting polymer $[NPCl_2]_n$ was prepared as described elsewhere.[2]

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-200, AC-300, and Avance 300 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. Coupling constants are in Hz. C, H, 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 analysis were performed on a Mettler TA

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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. To study the individual decomposition steps in more detail, the samples were also heated first from 20 to 400 °C at 10 °C/min and maintained at this temperature until the weight loss was stabilized (1−3 h). Then they were heated again from 400 to 800 °C at 10 °C/min and maintained at 800 °C for an additional 0.5 h.

SEM photographs were taken with a JEOL JSM 6100 microscope.

The X-ray diffraction was measured between 25 and 300 °C with a Bragg−Brentano $\theta/2\theta$ Siemens D-500, using the Cu Kα (λ = 1.5418 Å), equipped with a Temperature Camera Anton Paar TTK (−196 to +300 °C).

The specific optical rotations [α] were measured with a Perkin-Elmer 343 polarimeter at the wavelength of the D line of Na or with a Perkin-Elmer 241 polarimeter at 578, 546, and 436 nm, near 25 °C in $CHCl_3$.

Preparation of {[NP(O$_2$C$_{12}$H$_8$)]$_{1-x}$[NP(O−C$_6$H$_4$−CO$_2$Pr^n)$_2$]$_x$}$_n$ (1). The following preparation for polymer **1c** (x = 0.5) can be extended to the other derivatives using a mmol of $[NPCl_2]_n$ in the THF solution obtained by the method described in ref 2 (which usually contains on the order of 0.01 g/mL), diluting it to 150−200 mL with more THF, and adding $a(1 - x)$ mmol of 2,2'-(HO)C$_6$H$_4$−C$_6$H$_4$(OH) and $4a(1 - x)$ mmol of K_2CO_3 for the first step (22−14 h with reflux) and, subsequently, $2.32ax$ mmol (16% excess) of $HOC_6H_4CO_2Pr$ with $2.32ax$ mmol of C_2CO_3 for the second step (14−22 h with reflux). This procedure, but only with the second step, includes the homopolymer **1f** (x = 1). In the cases with $x > 0.5$ the products were purified by reprecipitation from THF/water (twice) and THF/hexane and not from THF/isopropyl alcohol because of the partial solubility in the latter solvent. The yields of the purified products ranged from 40% (**1e**) to 72% (**1a**).

To a THF solution of $[NPCl_2]_n$ (200 mL, 1.99 g, 17.32 mmol) were added 2,2'-(HO)C$_6$H$_4$−C$_6$H$_4$(OH) (1.61 g, 8.66 mmol) and solid K_2CO_3 (4.79 g, 34.6 mmol), and the mixture was refluxed with mechanical stirring for 14 h. The ^{31}P NMR showed two broad complex signals in the regions −6 to −7 and −22 ppm, with the relative intensities 0.5. Then, $HOC_6H_4CO_2Pr$ (3.63 g, 20.1 mmol) and Cs_2CO_3 (6.94 g, 20.1 mmol) were added, and refluxing was continued for another 24 h. The reaction mixture was poured into water to give a precipitate that was filtered, washed with water (2 × 100 mL) and dried. The purification was performed by dissolving the product in THF (600 mL) to give a clear solution that was concentered at reduced pressure until the formation of a viscous liquid that was poured portionwise (Pasteur pipet) into water (1 L), followed by two further reprecipitations from THF/isopropyl-alcohol and THF/hexane. The final white material was dried 3 days in vacuo at 20°C. Yield: 3.1 g (57%).

Analytical data, M_w, T_g (DSC), TGA and spectroscopic data are given in Tables 1−4.

IR (cm^{-1}, KBr pellets): The given ranges are the extreme values corresponding to the variation in the series from x = 0 to x = 1. 3064−3072 w [$\nu_{CH-aryl}$]; 2965−2969 m, 2876−2881 w [$\nu_{CH-alkyl}$]; 1716−1721, absent for x = 0 to vs for x = 1 [ν_{CO}]; 1603, w for x = 0 to vs for x = 1, 1501−1504 s, 1478−1465, s for x = 0 to w for x = 1 [$\nu_{C=C}$, aryl rings]; 1278−1275, m for x = 0 to vs for x = 1, 1245−1250, s for x = 0, to sh for x = 1, 1192−1211, vs for x = 1 to s for x = 1 [ν_{PN}]; 1115−1110, absent for x = 0 to vs for x = 1, 1096 s [ν_{POC}]; (951−940 vs, br) [δ_{POC}].

^{1}H NMR ($CDCl_3$): 7.5−6.5 m, br ($C_{12}H_8$ and C_6H_4); 4.1 m, br (OCH_2); 1.7m, br ($-CH_2-$); 1.0m, br. (CH_3).

^{13}C NMR($CDCl_3$): 166 (CO), 155 ($C_1-OC_6H_4$), 131 ($C_{3,3'}-OC_6H_4$), 126 ($C_4-OC_6H_4$), 120 ($C_{2,2'}-OC_6H_4$); 148 ($C_2-C_{12}H_8$), 130−122 ($C_{12}H_8$); 66 (OCH_2); 22 ($-CH_2-$); 10 (CH_3).

Preparation of {[NP(O$_2$C$_{20}$H$_{12}$)]$_{1-x}$[NP(O—C$_6$H$_4$—CO$_2$Pr^n)$_2$]$_x$}$_n$ (2). The following preparation for polymer **2g** (x = 0.8) is based on that of the already reported **2a** (x = 0.2),[6] and can be extended to the other derivatives using a mmol of $[NPCl_2]_n$ in 100−250 mL of THF, with $a(1 - x)$ mmol of R-(+)-2,2'-(HO)$_2$C$_{20}$H$_{12}$ and $4a$ mmol of Cs_2CO_3, refluxing for 4 to 14 h for the first step, checking by ^{31}P NMR the presence of the two broad complex signals in the regions −6 and −20 with relative intensities given by x, and adding $3ax$ mmol (50% excess) of $HOC_6H_4CO_2Pr$ followed by a 22 h reflux for the second step. In some of the cases, the Cs_2CO_3 was added in two parts, one of 2.2−3.3 times the mmol of biphenol for the first step and another for the second step, to complete the total amount of $4a$ mmol. The reaction mixture was poured into water to give a precipitate that was filtered, washed with water (2 × 100 mL) and dried. In the cases with $x > 0.5$ the products were purified by reprecipitation from THF/water (twice) and THF/hexane and not from THF/isopropyl alcohol because of the partial solubility in the latter solvent. The yields varied from 54 to 85%.The x actually obtained in the final products could be slightly different from those intended (see text).

To a THF solution of $[NPCl_2]_n$ (95 mL, 1.66 g, 14.3 mmol) were added R-(+)-2,2'-(HO)$_2$C$_{20}$H$_{12}$ (0.82 g, 2.87 mmol) and solid Cs_2CO_3(4.92 g, 15.1 mmol), and the mixture was refluxed with mechanical stirring for 14 h. The ^{31}P NMR showed two broad complex signals in the regions −6 and −20 with relative intensities 0.8. Then, $HOC_6H_4CO_2Pr$ (6.2 g, 34.3 mmol) and more Cs_2CO_3 (13.7 g, 57.2 mmol) were added, and refluxing was continued for another 22 h. The reaction mixture was poured into water (1 L) to give a precipitate that was washed with water (2 × 100 mL) and filtered. The purification was performed by dissolving the product in THF and reprecipitating into water, isopropyl alcohol and hexane as described for the polymers **1**. The final white material was dried 3 days in vacuo at 20 °C. Yield: 2.98 g (54%).

Analytical, spectroscopic, M_w, T_g (DSC), TGA, and spectroscopic data are given in Tables 1−4.

IR (cm^{-1}, KBr pellets): The given ranges are the extreme values corresponding to the variation in the series from x = 0 to x = 1. 3054−3072 w [$\nu_{CH-aryl}$]; 2965−2969 m, 2877−2881 w [$\nu_{CH-alkyl}$]; 1717−1721, absent for x = 0 to vs for x = 1 [ν_{CO}]; 1602, absent for x = 0 to s for x = 1, 1506−1504 s, 1459−1465 m [$\nu_{C=C}$, aryl rings]; 1320−1311, absent for x = 1, m, 1260−1275, s for x = 0 to vs for x = 1, 1220−1215 vs [ν_{PN}]; 1109 absent for x = 0 to vs for x = 1, 1096, absent for x = 0 to vs for x = 1, 1073 vs for x = 0 to absent for x = 1 [ν_{POC}]; 966−930 vs, br [δ_{POC}].

^{1}H NMR ($CDCl_3$): 8.3−6.5 m, br ($C_{20}H_{12}$ and C_6H_4); 4.1 m, br (OCH_2); 1.7 m, br ($-CH_2-$); 0.9 m, br (CH_3).

^{13}C NMR ($CDCl_3$): 166 (CO), 154 ($C_1-OC_6H_4$), 131 ($C_{3,3'}-OC_6H_4$), 126 ($C_4-OC_6H_4$), 120 ($C_{2,2'}-OC_6H_4$); 147 ($C_2-C_{12}H_8$), 133−121 ($C_{12}H_8$); 66 (OCH_2); 22 ($-CH_2-$); 10 (CH_3).

Results and Discussion

The phosphazene random copolymers {[NP(O$_2$C$_{12}$H$_8$)]$_{1-x}$[NP(OC$_6$H$_4$CO$_2$Pr^n)$_2$]$_x$}$_n$ [x = 0.2 (**1a**), 0.35 (**1b**), 0.5 (**1c**), 0.7 (**1d**), 0.85 (**1e**)] (Scheme 1) were prepared by reacting $[NPCl_2]_n$ first with $1 - x$ equivalents of 2,2'-dihydroxybiphenyl and K_2CO_3, to form the reactive intermediate {[NPCl$_2$]$_{1-x}$[NP(O$_2$C$_{12}$H$_8$)]$_x$}$_n$, and subsequently with an excess of the phenol $HOC_6H_4CO_2Pr^n$ in the presence of Cs_2CO_3 as proton abstractor.

Similar to the copolymers **1**, the chiral binaphthoxy analogues {[NP(O$_2$C$_{20}$H$_{12}$)]$_{1-x}$[NP(OC$_6$H$_4$CO$_2$Pr^n)$_2$]$_x$}$_n$ [x = 0.2 (**2a**), 0.4 (**2b**), 0.45 (**2c**), 0.5 (**2d**), 0.55 (**2e**), 0.7 (**2f**), 0.8 (**2g**)] (Scheme 1) were prepared from $[NPCl_2]_n$ first with $1 - x$ equivalents of 2,2'-dihydroxybinaphthyl and Cs_2CO_3, and subsequently with an excess of the phenol $HOC_6H_4CO_2Pr^n$, also in the presence of Cs_2CO_3.

For comparative purposes, the homopolymer **1f**(x = 1), which was already known,[7] was also prepared, but by following the same alkali carbonate substitution method use for the rest of the series.

In all cases the analytical (Table 1) and spectroscopic data (Table 3) were in accord with their chemical formulas and the residual chlorine contents were below 0.1%. All the samples remained unaltered after being

Scheme 1. R = $CO_2CH_2CH_2CH_3$

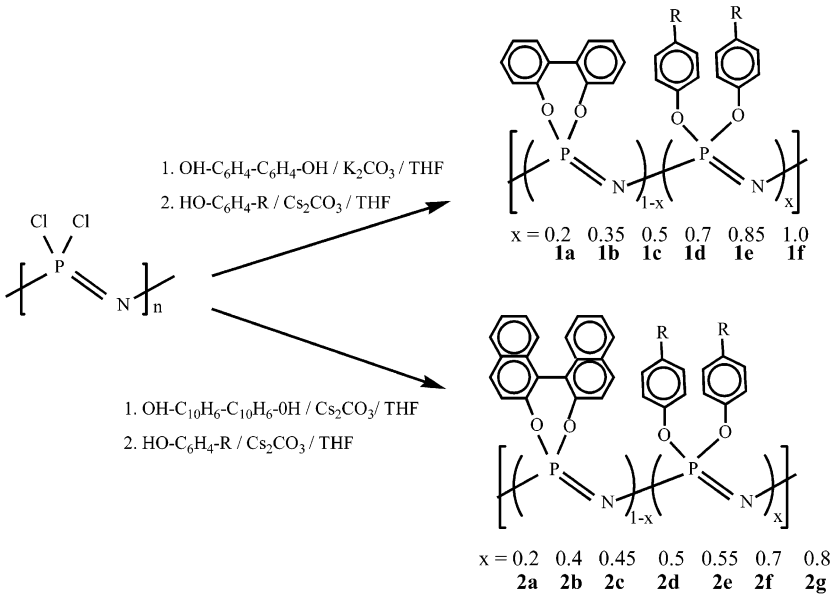


Table 1. Analytical Data for the New Polymers

compound				calcd (found)		
polymer	*x*	formula	(mass)	% C	% H	% N
1a	0.2	$C_{13.6}H_{10.8}NO_{2.8}P$	(264.01)	61.9 (62.0)	4.10 (3.90)	5.30 (5.37)
1b	0.35	$C_{14.8}H_{12.9}NO_{3.4}P$	(290.14)	61.3 (59.2)	4.48 (4.64)	4.83 (4.81)
1c	0.5	$C_{16}H_{15}NO_4P$	(316.27)	60.8 (60.3)	4.78 (4.51)	4.43 (4.52)
1d	0.7	$C_{17.6}H_{17.8}NO_{4.8}P$	(351.11)	60.2 (59.6)	5.11 (4.85)	3.99 (4.14)
1e	0.85	$C_{18.8}H_{19,9}NO_{5.4}P$	(377.24)	59.9 (58.5)	5.32 (4.99)	3.71 (3.52)
1f	1.0	$C_{20}H_{22}NO_6P$	(403.36)	59.5 (59.0)	5.50 (5.08)	3.47 (3.17)
2a	0.2	$C_{20}H_{14}NO_{2.8}P$	(344.10)	69.8 (69.1)	4.10 (3.96)	4.07 (4.14)
2b	0.4	$C_{20}H_{16}NO_{3.6}P$	(358.92)	66.9 (65.0)	4.49 (4.47)	3.90 (3.95)
2c	0.45	$C_{20}H_{16.5}NO_{3.8}P$	(362.62)	66.2 (64.3)	4.59 (4.46)	3.86 (4.02)
2d	0.5	$C_{20}H_{17}NO_4P$	(366.33)	65.6 (62.6)	4.68 (4.59)	3.82 (4.34)
2e	0.55	$C_{20}H_{17.5}NO_{4.2}P$	(370.03)	64.9 (63.4)	4.77 (5.14)	3.78 (3.89)
2f	0.7	$C_{20}H_{19}NO_{4.8}P$	(381.14)	63.0 (60.2)	5.02 (4.69)	3.67 (3.64)
2g	0.8	$C_{20}H_{20}NO_{5.2}P$	(388.55)	61.8 (59.9)	5.19 (5.13)	3.60 (3.93)

Table 2. M_w, T_g, Mesophase Interplanar Distance, and Specific Rotation

compound		mol wt	T_g	interpl dist		[α]
polymer	*x*	M_w (PDI)	(°C)	2θ (deg)	*d* (Å)	(deg)
$[NP(C_{12}H_8O_2)]_n$	0.0	600000 (3.0)[a]	160[a]	7.3[b]	12.1[b]	
1a	0.2	850000 (3.3)	113	7.5	11.8	
1b	0.35	670000 (2.5)	77	6.3	14.0	
1c	0.5	1250 000 (3.4)	41	6.0	14.7	
1d	0.7	1580 000 (3.4)	16	5.7	15.5	
1e	0.85	1590 000 (2.2)	−1	5.5	16.1	
$[NP(O-C_6H_4-COOPr)_2]_n$, **1f**	1.0	1000 000 (2.0)	−14	4.5	19.6	
R-(−)-$[NP(C_{20}H_{10}O_2)]_n$	0.0	840000 (4.0)	329[c]	6.0[c]	14.7[c]	−192
2a	0.2	1200000 (2.5)	227	6.0	14.7	−131
2b	0.4	1330000 (2.4)	134	5.4	16.4	−125
2c	0.45	1380000 (2.2)	116	5.7	15.5	−112
2d	0.5	1860000 (3.0)	92	5.6	15.7	−119
2e	0.55	1470000 (2.4)	86	5.5	16.1	−108
2f	0.7	1570000 (2.1)	33	5.0	17.6	−73
2g	0.8	1690000 (2.3)	24	5.0	17.6	−57.5

[a] Reference 3. [b] Reference 10b. [c] Reference 15.

stored at ambient temperature for one year. The optical activity of the chiral binaphthoxy derivatives was confirmed by measuring the optical specific rotation (Table 2) which changed with *x* in a similar manner as in the related series[4] $\{[NP(O_2C_{20}H_{12})]_{1-x}[NP(OC_6H_5)_2]_x\}_n$.

The physical aspect and properties of the isolated polymers varied systematically as a function of their composition. Thus, in the biphenyl series **1** the derivatives richer in $[NP(O_2C_{12}H_8)]$ units ($x < 0.5$) are brittle white solids. Their SEM (Figure 1) micrographs showed that the precipitates directly obtained by pouring the concentrated THF solution into water had a spongelike texture (Figure 1a) that, in some cases, consisted on a net of channels (Figure 1b). In the other extreme ($x >$

Table 3. IR (KBr) and ^{31}P NMR ($CDCl_3$) Data

polymer	x	ν_{CO}	ν_{NP}	δ[P(O−O)][a]	δ[P(O−Ph)$_2$][b]
$[NP(C_{12}H_8O_2)]_n$	0.0		1278 m, 1245 s, 1192 vs	−5.8	
1a	0.2	1716	1271 s, 1244 s, 1188 vs	−5.3	−23.4
1b	0.35	1716	1272 s, 1245 m, 1192 vs	−4.4	−22.4
1c	0.5	1717	1273 vs, 1243sh, 1193 s	−4.5	−21.4 to −23.0
1d	0.7	1719	1273 vs, 1248sh, 1211 s	−4.0	−21.4
1e	0.85	1720	1273 vs, 1250sh, 1211 s	−4.2	−20.2 to −22.3
1f	1.0	1721	1275 vs, 1242sh, 1211 s		−20.0
$(-)[NP(C_{20}H_{10}O_2)]_n$	0.0		1320 m, 1260 s, 1220 vs	−3.0	
2a	0.2	1717	1320 m, 1273 s, 1219 vs	−3.5	−25.0
2b	0.4	1717	1315 m, 1271 s, 1217 vs	−4.0	−22.1 to − 24.6
2c	0.45	1717	1314 m, 1273 s, 1218 vs	−3.6	−22.4 to − 24.3
2d	0.5	1718	1313 m, 1272 s, 1217 vs	−4.1	−22.4 to −24.3
2e	0.55	1718	1314 m, 1272 s, 1217 vs	−4.3	−22.0 to −24.3
2f	0.7	1718	1316 m, 1274 vs, 1215 s	−2.3	−18.7 to −22.4
2g	0.8	1719	1311 m, 1273 vs, 1215 s	−3.8	−20.3 to −22.2

[a] The chemical shift quoted is the center of a very broad band corresponding to the $[NP(C_{12}H_8O_2)]$ or $[NP(C_{20}H_{10}O_2)]$ units. [b] The chemical shift quoted is the center of a very broad band or broad multiplet, (in the range of the given values), corresponding to the $[NP(OC_6H_4COOPr)_2]$ unit.

0.5) the micrographs evidenced their gummy textures (Figure 1c). The SEM micrographs of the binaphthyl series **2** (Figure 2) revealed an spongelike morphology up to $x = 0.7$ (Figure 2a), in some cases with long channels (Figure 2b), and a gummy texture thereafter (Figure 2c).

The M_w values, as determined by GPC, were in the range $(0.7-1.9) \times 10^6$. Apparently it was higher for the polymers containing more $[NP(OC_6H_4-CO_2Pr^n)_2]$ units, especially in the series **2**. Although the behavior and the molecular shapes and sizes found for similar phosphazenes in solution[8,9,4] are too complex to allow reliable correlations between their M_w and composition, the tendency noted above could be, as least partially, connected with the fact that the reaction of $[NPCl_2]_n$ with biphenol and, to a lesser extent, with binaphthol may be accompanied by same degradation of the phosphazene main chain.[3]

The ^{31}P NMR (Cl_3CD) (Table 3) showed two broad distributions of chemical shifts for the phosphorus of both repeating units. The experimental relative intensities of those signals allowed a determination of the copolymer composition (given by x) with a precision of 0.05 units. In the cases of the binaphthyl series, the signals were broader and less symmetric, and the x values were reconfirmed in the spectra measured in DMSO-d_6 at 110 °C. As noticed in similar preparations,[4] in some of the binaphthyl derivatives, x was 0.05−0.1 units different from that originally intended.

Although the complexity of both signals and the overall chemical shifts changed as a function of x (see Table 3), in series **1** it was possible to observe a clear shift to higher frequencies for both units as x increased (from −5.3 and −23.4 ppm in **1a** to −4.2 and −20 ppm in **1e**). In the binaphthyl series **2**, the signal of the $[NP(OC_6H_4-CO_2Pr^n)_2]$ units were very broad and complex showing various peaks, the intensity of which changed with x.

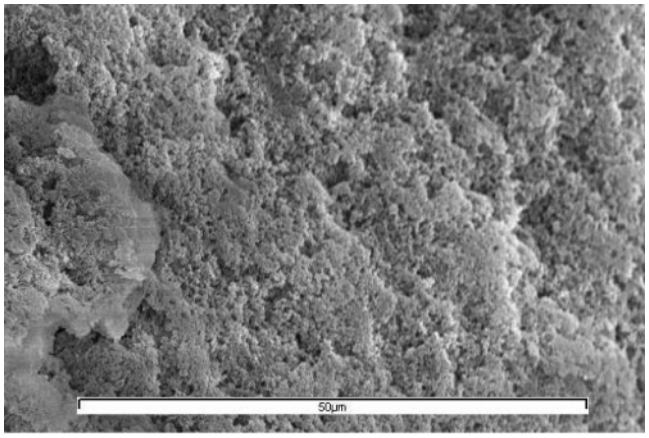
The ^{1}H and ^{13}C NMR spectra (Experimental Part) showed all the peaks expected[6] with no significant variations in chemical shifts as a function of the composition. Thus, the more relevant carbons had almost the same chemical shifts in all the polymers. The integration of the signals of the ^{1}H NMR were consistent with the values given to x in each polymer.

The IR spectra (KBr pellet, Experimental Part and Table 3) also showed the expected absorptions bands. Besides the ν_{CO} stretching (ca. 1720 cm^{-1}), the most important bands were those in the regions: 2800−3100 cm^{-1} (ν_{CH} stretching), 1500−1600 (aromatic $\nu_{C=C}$ stretching), and 1100−1300 (ν_{PN}). Interestingly, the first harmonic frequency of the carbonyl stretching was also observed, specially in the IR of the films, as a sharp weak band near 3415−3420 cm^{-1}. As expected, the relative intensities of some of the bands, specially those of the $\nu_{CH-alkyls}$, ν_{CO}, and $\nu_{C=C}$, varied accordingly with the copolymer composition, and in some cases, namely the ratios $I(3065)/I(2969)$ and $I(1716)/I(1478)$, a quantitative and almost linear correlation with x was found. This feature is potentially useful for the characterization of insoluble materials based on these types of polymers.

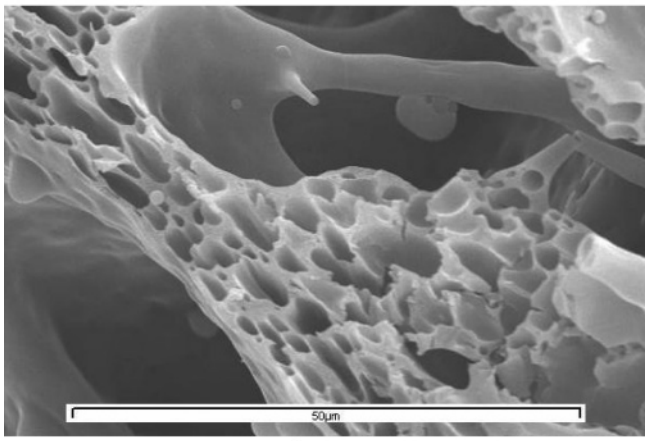
Several trends were also apparent form the IR data. Thus, the carbonyl stretching frequency progressively increased along the series **1**, from 1716 (in **1a**) to 1721 cm^{-1} in the homopolymer $[NP(OC_6H_4CO_2Pr^n)_2]_n$. A similar stepwise increase was observed for the (ν_{CH}) band of the biphenoxy group (from 3063 in the homopolymer $[NP(O_2C_{12}H_8)]_n$ to 3072 in **1e**). Significantly, the broad and multicomponent band corrresponding to the wide distribution of the vibrational modes richer in the (ν_{PN}) stretching normal coordinates (the so-called ν_{PN} region) changed in shape as a function of x, shifting the more intense absorption from 1192 cm^{-1} in the homopolymer $[NP(O_2C_{12}H_8)]_n$ to 1275 in **1f**. It was interesting to notice that in the IR spectra of the physical mixtures made with the two extreme homopolymers, all the frequencies were those of the individual components and they did not change with the composition, while their relative intensities varied as expected. Similar, but less conspicous, trends were observed in the binaphthyl series **2**.

The variation of those PN stretching frequencies may be indicating that, as might be expected, the −N=P−N=P− backbone becomes less electron rich with the higher proportion of the *n*-propyl carboxylate groups.

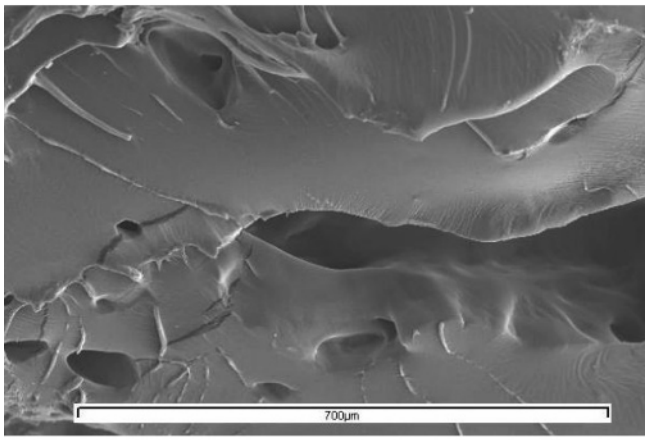
The X-ray diffraction diagrams of the solid samples obtained as precipitates (see Experimental Part) revealed in all cases the wide angle reflection typical of the phosphazene mesophases,[10] that increased in intensity with the temperature and that was less intense in the case of the dioxybiphenyl series. The 2θ values (Table 2) indicated that the interplanar distance varies with the composition (given by x) in an overall manner not very far from linear. A linear relationship between the Bragg spacing of the mesophases and the copolymer composition, found in other polyphoshazenes with dif-



a

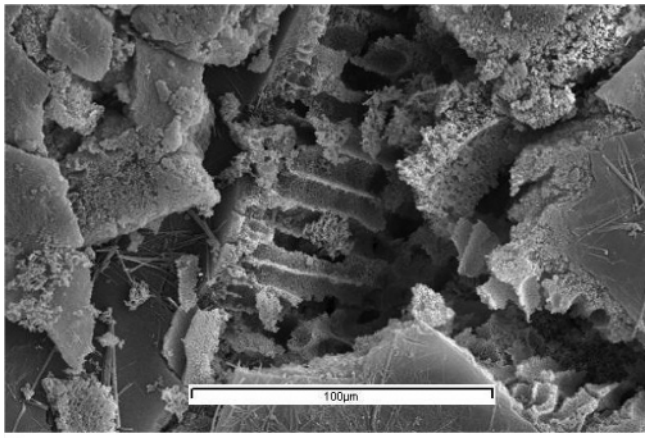


b

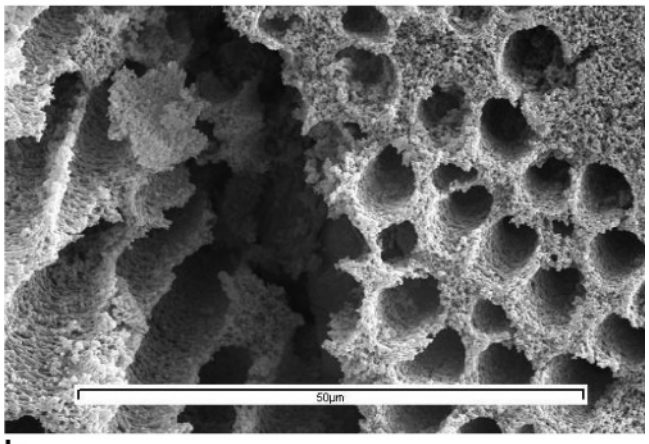


c

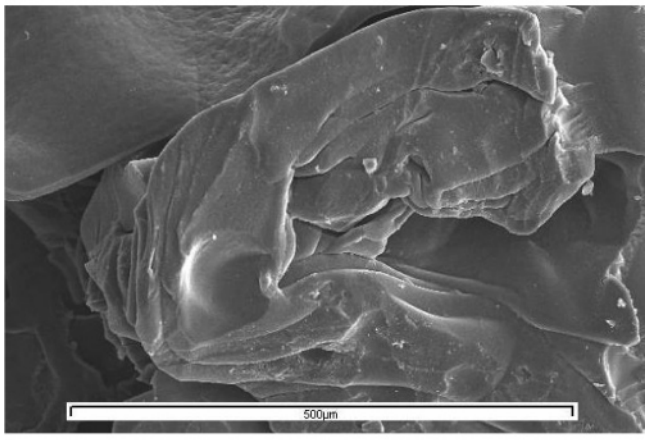
Figure 1. SEM micrographs of biphenoxyphosphazene copolymers **1**: (a) polymer **1b**; (b) polymer **1a**; (c) polymer **1e**.



a



b



c

Figure 2. SEM micrographs of binaphthoxyphosphazene copolymers **2**: (a) polymer **2a**; (b) polymer **2a**; (c) polymer **2f**.

ferent phenoxy collateral groups,[11] has been interpreted in terms of the accommodation of the bulkier substituents, which, in the case of the polymers **1**, would be the $OC_6H_5-CO_2Pr$ collateral groups.

The thermal stability of the polymers **1** and **2** was investigated as a function of their composition by TGA (Table 4). The thermograms were measured from 0 to 800 °C plus an additional heating at 800 °C for 30 min. In all cases, a drying period was observed from 30 to 300 °C with a weight loss in the range 1−3%.

In the series **1** two decomposition steps were observed. One between 300 and 400 °C and other from 600 to 800 °C. The weight stabilized at 400 °C was obtained by recording the thermogram from 0 to 400 °C and maintaining this temperature for 2 h. In the series **2** (that are expected to be more stable) the rapid weight loss that began also near 300 °C became faster in the region of 400 °C and was almost continuous to 800 °C without showing definite steps.

The first process is in the temperature region where chemical decomposition with cross-linking takes place in most polyphosphazenes,[9,12] and the shape of the curve and its derivative clearly indicated that the process was much faster as the proportion of the $[NP(OC_6H_4CO_2Pr^n)_2]$ units increased. A sharp decrease in the final

Table 4. Weight Loss and Final Residues of the Polymers Obtained by TGA

		weight loss (%)		residue (%)		
polymer	x	30−300 °C	300−800 °C	after 0.5 h at 800 °C	at 400 °C after 2 h	final residue after 0.5 h at 800 °C
$[NP(C_{12}H_8O_2)]_n$						28[a]
1a	0.2	2.5	71.5	4		22
1b	0.35	2	77	2.5	26.5	18.5
1c	0.5	3	84	4	18.5	9
1d	0.7	1	71	7.5	38	20.5
1e	0.85	2.5	74	12	40.5	11.5
1f	1	1	71	11	44.5	17
$(-)[NP(C_{20}H_{10}O_2)]_n$						53[b]
2a	0.2	1.5	56	6.5		36
2b	0.4	2.5	72	7.5		18
2c	0.45	1	72	6		11
2d	0.5	2.5	72	5		20.5
2e	0.55	1	75	3.5		80.5
2f	0.7	2	65.5	8.5		24
2g	0.8	2	67.5	8		22.5

[a] Reference 3. [b] Reference 4a.

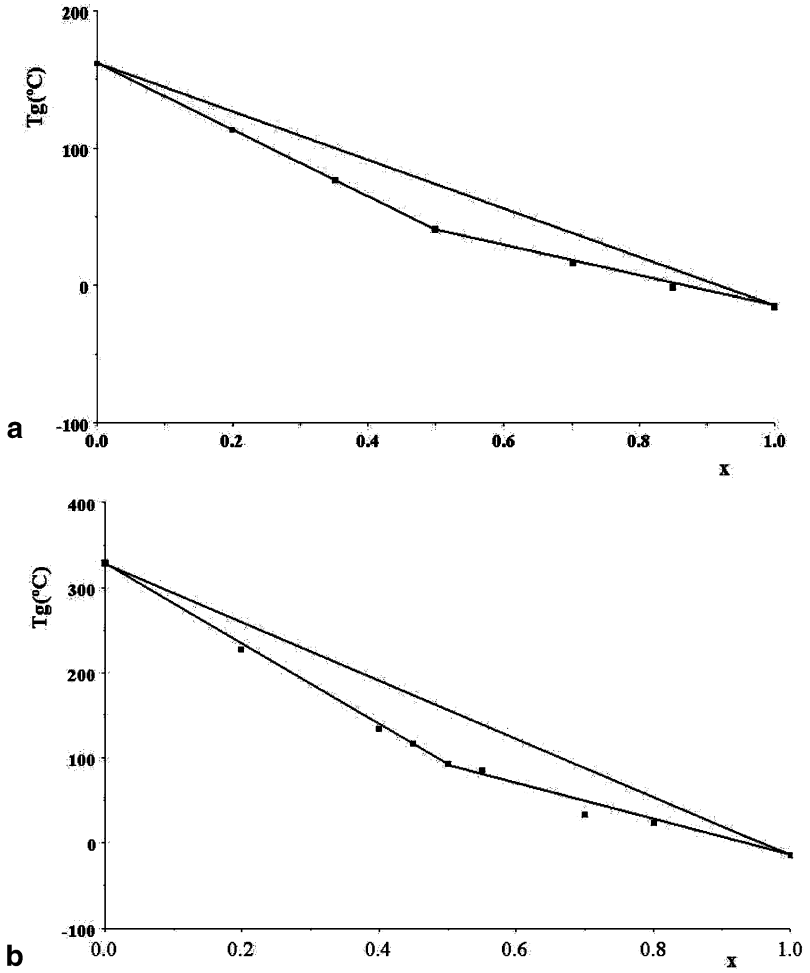


Figure 3. (a) T_g vs composition (x) for biphenoxyphosphazene copolymers **1**. (b) T_g vs composition (x) for binaphthoxyphosphazene copolymers **2**.

residue was observed from $x = 0$ to $x = 0.5$ (Table 4) followed by a much smaller and irregular variation from $x = 0.5$ to 1, indicating that the presence of the biphenoxy- and binaphthoxyphosphazene units decreases the formation of volatiles during the decomposition.

The DSC analysis of the polymers showed in all cases a clear heat capacity increase corresponding to the glass transition (Table 2) and the T_g values varied with x in an interesting manner (Figure 3, parts a and b).

In the case of polymers **1** (Figure 3a) the variation was consistent with a randomized strictly alternating distribution of the two repeating units. Thus, the Barton equation[5a] when applied to an strictly alternating copolymer[5b] of formula $[(A)_{1-x}(B)_x]_n$ [for which the theoretical run number is $R = 200x$ from $x = 0$ to 0.5 (no B−B links) and $R = 200(1 - x)$ from 0.5 to 1 (no A−A links)] predicts a plot of T_g vs x consisting on two straight lines intersecting at $x = 0.5$. Therefore, the T_g of **1c**($x = 0.5$) corresponds to the TAB parameter.[5b] This

is only to be expected considering that the behavior of the real distributions of polymers **1** is very close to that of an ideal strictly alternating copolymer. Therefore, the T_g values provide us with experimental evidence that the alkali carbonate promoted substitution of chlorines by biphenoxy groups along the chain units [$NPCl_2$] of the starting poly(dichlorophosphazene) (first step in Scheme 1) is essentially randomized for all molar ratios (x) and that the locations not vicinal to an already substituted unit [$NP(O_2C_{12}H_8)$] are preferred.

The same results were observed in the binaphthyl derivatives **2** (Figure 3b); i.e., the T_g of the $x = 0.5$ (**2d**) (92 °C) corresponded to the TAB parameter, showing the completely randomized distribution of the two phosphazene units. Therefore, also in the substitution of Cl in the reactions of $[NPCl_2]_n$ with *R*-(+)-binaphthol there are no detectable preferences for the chain sites near those already having a chiral [$NP(O_2C_{20}H_{12})$] unit, indicating that their chirality has no stereochemical effect on the reaction. Although chiral discrimination effects have been observed in crystalline cyclic phosphazenes with 2,2'-dioxybiphenyl,[13] in the case of the enantiomerically pure binaphthoxy homopolymer *R*-(−)-$[NP(O_2C_{20}H_{12})]_n$ the packing in the solid (amorphous) state[14] does not imply the strong π-stacking interactions between the aromatic binaphthyl rings that would be necessary to generate enantiomeric discrimination.

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