Dioxybiphenyl and Chiral Dioxybinaphthyl Polyphosphazene Random Copolymers Carrying Carboxylic Acids and Their Reactions with ϵ-Caprolactam to Form Nylon-6-branched Phosphazene Materials

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Received December 2, 2004; Revised Manuscript Received February 10, 2005

ABSTRACT: The phosphazene polymers carrying phenoxycarboxylic acids $\{[NP(O-C_6H_4-CO_2H)_2]_x[NP(O_2C_{12}H_8)]_{1-x}\}_n$ [x = 0.2 (**1a**), 0.35 (**1b**), 0.5 (**1c**), 0.7 (**1d**), 0.85 (**1e**), x = 1(**2**)] and the chiral analogues $\{[NP(O-C_6H_4-CO_2H)_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$ [x = 0.2 (**3a**), 0.45 (**3b**), 0.7 (**3c**)] ($O_2C_{12}H_8$ = 2,2′-dioxybiphenyl, $O_2C_{20}H_{12}$ = R-2,2′dioxy-1,1′-binaphthyl) have been synthesized by hydrolysis of the corresponding precursors with $[NP(O-C_6H_4-CO_2Pr)_2]$ units. The new polymers have extensive H-bonding between the −COOH groups in the solid state, and those with $x > 0.5$ are very soluble in aqueous 0.5 M sodium carbonate. These polymers were used as initiators of the ring-opening polymerization of the ϵ-caprolactam (ϵ-CL) at 230 °C to give un-cross-linked polyphosphazenes, branched with short polyamide chains but having a fraction of the phosphazene units (from 20 to 35%) modified by secondary reactions.

Introduction

The polyphosphazenes are one of the most studied inorganic macromolecules, because of their academic and industrial interest.[1] In an earlier paper, we reported the preparation of the phosphazene random copolymers $\{[NP(O-C_6H_4-CO_2Pr^n)_2]_x[NP(O_2C_{12}H_8)]_{1-x}\}_n$ (x from 0.2 to 1) and the chiral analogues $\{[NP(O-C_6H_4-CO_2Pr^n)_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$ and the variation of their properties with the composition.[2] The phosphazenes with propyl-carboxylate-phenoxy units are known to undergo hydrolysis to form the COOH derivatives[3,4,5] that could be soluble in basic water and that are currently generating a great deal of interest for their biological activity.[5] Therefore, we contemplated the synthesis of other water-soluble phosphazenes carrying dioxybiphenyl or dioxybinaphthyl groups. On the other hand, it has been published that the cyclic triphosphazene $[N_3P_3(O-C_6H_4-COOH)_6]$ reacts with ϵ-caprolactam to give star-shaped polyamides attached to the phosphazene ring.[6] Therefore, another point of attention was to extend the latter reaction to high molecular weight polymers to obtain polyphosphazenes branched with polyamide chains.

In efforts to attain an advantageous combination of properties, many linear polyphosphazenes[7−15] or phosphazene films[16] have been grafted with other polymeric chains, such as short oligoethers,[7] poly(styrene),[8] poly(dimethylsiloxane),[9] PMMA,[10,11] poly(oxazolines),[12] poly(phenylene vinylene),[13] oligopeptides,[14] and others.[15] Also, many examples of the reverse approaches (branching polyphosphazene chains to organic polymer backbones[17] or on organic polymer films)[18] are well-known. However, branching with Nylon-6 has only been carried out on cyclic trimers to give star-shaped polymers.[6] Herein, we describe results that confirm the formation of linear un-cross-linked polyphosphazenes, branched with short polyamide chains by the ring-opening polymerization of ϵ-caprolactam on polyphosphazenes carrying COOH lateral groups. We also show that this process is accompanied by secondary collateral reactions, the extent of which depends on the composition of the starting phosphazene copolymers and on the molar ratio of caprolactam/COOH used.

Experimental Section

Tetrahydrofuran (THF) was treated with KOH and distilled twice from Na in the presence of benzophenone. $KOBu^t$, ϵ-caprolactam, and Nylon-6 were used as purchased (Aldrich). The starting phosphazene polymers with $-CO_2Pr^n$ lateral groups were prepared as described elsewhere.[2]

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 the solvents indicated in each case. ^1H NMR spectra are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR spectra are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hz. C, H, and N analyses were performed with a Perkin-Elmer 240 microanalyzer. GPC were measured with 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 was obtained using narrow molecular weight distribution polystyrene standards. DSC thermograms were obtained with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer. Thermal gravimetric analysis was performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from room temperature to 800 °C under constant flow of nitrogen and maintained at 800 °C for an additional $^1/_2$ h.The specific rotation $[\alpha]_D$ was measured using a Perkin-Elmer 343 Polarimeter near 20 °C. SEM photographs were taken with a JEOL JSM 6100 microscope. 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 = 1.5418Å), equipped with a temperature camera Anton Paar TTK (−196 to +300 °C).

Preparation of $\{[NP(O-C_6H_4-CO_2H)_2]_x[NP(O_2C_{12}H_8)]_{1-x}\}_n$ (1) and $\{[NP(O-C_6H_4-CO_2H)_2]_x[NP$-

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10.1021/ma047514t CCC: $30.25
Published on Web 03/23/2005

Table 1. Analytical Data and Mesophase Interplanar Distances for the Polymers 1, 2, and 3

compound					% C	% H	% N		
polymer	x	formula	(mass)	FD[a]	calcd (found)	calcd (found)	calcd (found)	2θ (deg)	d
1a	0.2	$C_{12.4}H_{8.4}NO_{2.8}P$	(247.18)	1.62	60.3 (59.2)	3.43 (4.34)	5.67 (5.38)	7.0	12.6
1b	0.35	$C_{12.7}H_{8.7}NO_{3.4}P$	(260.68)	2.68	58.5 (57.8)	3.36 (3.43)	5.37 (5.29)	6.7	13.2
1c	0.5	$C_{13}H_9NO_4P$	(274.19)	3.65	56.9 (54.4)	3.31 (3.50)	5.11 (4.93)	6.0	14.7
1d	0.7	$C_{13,4}H_{9,4}NO_{4,8}P$	(292.20)	4.79	55.1 (53.0)	3.24 (3.28)	4.79 (4.10)	5.7	15.5
1e	0.85	$C_{13,7}H_{9,7}NO_{5,4}P$	(305.70)	5.56	53.8 (51.5)	3.20 (3.27)	4.58 (4.69)	5.3	16.7
2	1.0	$C_{14}H_{10}NO_6P$	(319.21)	6.26	52.7 (50.2)	3.16 (3.26)	4.39 (4.23)	5.0	17.7
3a[b]	0.2	$C_{18.8}H_{11.6}NO_{2.8}P$	(327.27)	1.22	69.0 (66.8)	3.57 (3.22)	4.28 (4.07)	6.0	14.7
3b[b]	0.45	$C_{17.3}H_{11.1}NO_{3.8}P$	(324.75)	2.77	64.0 (62.9)	3.45 (3.16)	4.31 (4.71)	5.7	15.5
3c[b]	0.7	$C_{15.8}H_{10.6}NO_{4.8}P$	(322.23)	4.34	58.9 (56.3)	3.32 (3.47)	4.35 (4.43)	5.0	17.7

[a] mmol COOH/g of polymer. [b] Specific rotation, $[\alpha]^{30}_D$, in DMSO 1c: −83.4 (**3a**), −79.1 (**3b**), and −58 (**3c**). For **3c**, 0.5c in 0.5 M aqueous sodium carbonate: −9.

Table 2. TGA Data for the Polymers 1, 2, and 3

polymer	x	solvents (%)[a]	range (°C)	weight loss (%)	range (°C)	weight loss (%)	loss after 0.5 h at 800°C (%)	residue
1a	0.2	4.0	220−280	4.0	280−800	64	3.5	24.5
1b	0.35	1.5	230−308	12	308−800	61	2.5	23
1c	0.5	4.5	220−350	23	350−800	55	3.0	14.5
1d	0.7	1.0	140−253	8.5	253−800	43	4.0	43.5
1e	0.85	2.5	172−430	37	430−800	18	9.5	33
2	1.0	2.5	172−428	32	428−800	19.5	9.0	37
3a	0.2	1.5	115−600	52	600−800	5.5	7.5	33.5
3b	0.45	2.0	140−340	14	340−800	52.5	7.0	24.5
3c	0.7	2.0	140−250	4.5	250−800	41	9.0	43.5

[a] Weight loss from 30 °C to the beginning of the main loss.

$(O_2C_{20}H_{12})]_{1-x}\}_n$ (3). The following preparation for polymer **1c** ($x = 0.5$) can be extended to the other derivatives using always 4 mmol of $KOBu^t$ per mmol of $-OC_6H_4CO_2Pr^n$ present in the starting polymer. The procedure includes the already-known homopolymer **2** ($x = 1$). The yields of the purified products ranged from 70 to 90%.

To a solution of $KOBu^t$ (1.42 g, 12.67 mmol) in THF (25 mL), two drops of water were added, and then the mixture was cooled to 0 °C. Then a solution of $\{[NP(O-C_6H_4-CO_2Pr)_2]_{0.5}$-$[NP(O_2C_{12}H_8)]_{0.5}\}_n$ (1.0 g, 3.16 mmol; 3.16 mmol of COOPr) in THF (25 mL) was added dropwise, and the mixture was stirred first 5 min at 0 °C and then 48 h at room temperature. The reaction mixture was concentrated in vacuo to $^1/_2$ volume and poured slowly into aqueous HCl (0.5L, made with 100 mL concentrated acid and 400 mL water) to form a white precipitate that was washed with water until neutral pH was reached. The final white material was dried 3 days in vacuo at 25 °C. Yield: 0.86 g. (99%).

In the case of **1a**, it was possible to purify the product by three reprecipitations from THF/water, THF/2-propanol, and THF/hexane.

Analytical data are given in Table 1. TGA data are given in Table 2. Spectroscopic data are given below.

Polymers 1. IR (KBr pellets, cm^{-1}): 3400−3450 s, vbr, with a maximum at 3440 more defined as x increases) (ν-OH); 3065, from m to vw as x increases (ν-Carom-H); 2655w, 2530w (COOH−HOOC dimers, see text); 1692s, br (ν-CO); 1603 int increasing as x increases; 1504m, 1478 int decreasing as x increases (ν-C=C); 1245m, 1209−1195 vs, br; 1160 from w to s as x increases (ν-PN); 1097 w to m (ν-P−OC); 950−920 s, br (δ-POC); 786, 752 int decreasing as x increases; 770 int increasing as x increases (δ-PNP, δ-Carom-H); 609 w, 540 w (other). ^{1}H NMR (DMSO-*d*6): 12.7 broad (OH), from 7.4 to 6.5 vbr multiplet (aromatic protons). ^{31}P NMR (DMSO-*d*6): −5 vbr shifting to −3.5 vbr as x increases ($[NP(O_2C_{12}H_8)]$); −23 vbr, shifting to −20.3 vbr (the value for **2**) as x increases ($[NP(O-C_6H_4-CO_2H)_2]$). ^{31}P NMR (aqueous sodium carbonate 0.5M) of **1d** and **1e**: −2 vbr $[NP(O_2C_{12}H_8)]$); −20 vbr $[NP(O-C_6H_4-CO_2H)_2]$. For polymer **2**: a broad singlet at −19 ppm.

Polymers 3. IR (KBr pellets, cm-1): 3430s, vbr (ν-OH); 3055 from m to vw as x increases, (ν-Carom-H); 2650w, 2530w (COOH−HOOC dimers, see text); 1694s, br (ν-CO); 1602m, 1506m (ν-C=C); 1260sh, 1218−1214vs, br; 1160 from w to s as x increases, (ν-PN); 1070s (ν-P−OC); 960−935s, br (δ-POC); 860, 812 int decreasing as x increases; 772 int increasing as x increases, 748, 714, 695 int decreasing as x increases, (δ-CaromH); 570 s (other). ^{1}H NMR (DMSO-*d*6): 12.7 broad (OH), 7.6 vbr, 6.7 vbr (aromatic protons). ^{31}P NMR (DMSO-*d*6): −3 vbr shifting to −4 vbr as x increases $[NP(O_2C_{20}H_{12})]$; −23 vbr shifting to −20.3 vbr as x increases $[NP(O-C_6H_4-CO_2H)_2]$. ^{31}P NMR (aqueous sodium carbonate 0.5M) of 3**d**: −2 vbr $[NP(O_2C_{12}H_8)]$; −20 vbr $[NP(O-C_6H_4-CO_2H)_2]$.

Reactions of the Polymers 1, 2, and 3 with ϵ-Caprolactam. In the following general procedure, the functionalization degree (FD) is the mmol of COOH groups per gram of polymer (see Table 1).

A solid mixture of the phosphazene polymer (0.1 g., 0.1 FD mmol of COOH) and ϵ-caprolactam (0.0113 FD R g, 0.1 FD R mmol) was placed on a Carius Tube that was closed in vacuo and heated at 230 °C for 15 h (at ∼200 °C, the mixture melted to a clean solution). The resulting products were taken out of the tube and stirred with THF (150 mL) for 7 days, filtered, washed with hot THF, then washed for 7 days with THF at room temperature and dried to give the polyamides **4**, **5**, and **6** as a white or slightly colored material (70−92% of the total mass of the reactants). Analytical data are given in Table 3. TGA and DSC data for the selected polyamide-branched polyphosphazenes (see text) are given in Tables 4 and 5.

Table 3. Analytical Data[a] for the Polyamide-polyphosphazenes 4, 5, and 6

product	*x*	*R*[b]	yield [c]	% C	% H	% N	unaltered P[d]
4a	0.2	10	76	52.4	6.21	8.36	48
4b	0.2	56	77	58.0	9.38	10.8	2.0
4c	0.5	5.0	75	57.8	7.58	10.1	65
4d	0.5	10	86	58.0	8.18	10.8	55
4e	0.7	5.0	82	58.6	7.80	10.3	79
4f	0.7	10	91	59.6	8.66	10.8	64
5a	1.0	5.0	85	58.6	8.65	11.7	61
5b	1.0	10	92	59.1	8.47	11.3	51
6a	0.45	6.3	61	58.5	7.57	10.1	59[e]
6b	0.7	5	74	57.0	8.68	10.7	53[e]

[a] The calculated values for a pure Nylon-6 are, 63.7% C, 9,77 H, 12.4 N. [b] *R* is the ratio mmol $-\epsilon$ caprolactam/mmol-COOH. [c] Mass of the insoluble product in % of the total mass of the reactants. [d] It is the % of the Phosphorus atoms in the product that are in [$NP(O_2C_{12}H_8)$], [$NP(O_2C_{20}H_{10})$], or [$NP(OC_6H_4-CO-)_2$] units (see text), measured by ^{31}P NMR in CF_3CH_2OH/CH_2Cl_2 (3:1) solution. [e] Because of the broadness of the phosphazene signals, those signals are estimated values.

Table 4. TGA Data[a] for the Polyamide Branched Polyphosphazenes

product	drying 50−200 (°C)	main T_{max} (°C)	loss (%)	loss after 1/2 h at 800 °C	residue (%)
4c	3.6	372	85.2	1.6	9.6
4e	1.5	350	90	2.0	6.5
4f	3.0	390	91	2.0	4.0
Nylon−6	0	440	99.8	0	0.2

[a] Only those products approaching the ideal composition in 65% or more are shown.

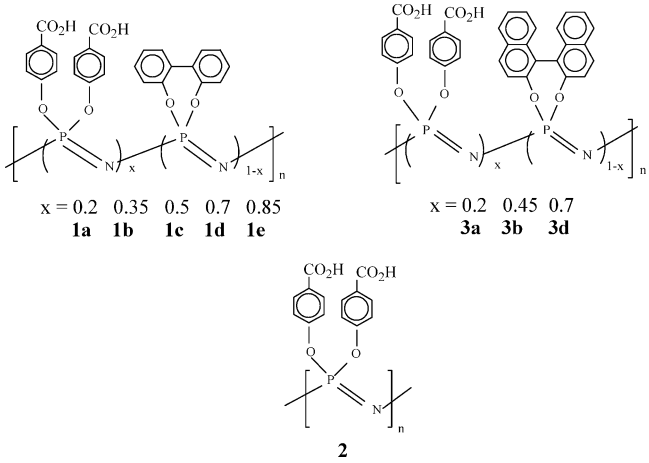
IR (KBr, cm^{-1}). Main bands: 3450 sh, 3003 s, 3084 w, 2940 s, 2866 w (ν-CH polyamide); 1641 vs (ν-CO); 1544 (δ-NH); 1249, 1209−1201, 1169 (ν-PN); 1096 int increasing as *x* decreases (ν-P−OC); 930−940 (δ-POC); 788 int decreasing as *x* increases (δ-PNP, δ-CaromH). Other bands: 1500 w, 1463 w, 1417 w, 1372 w, 1264 w, 1213 w, 1016 vw, 853 w, 691 w, 611 w, 520−540w, br.

^{31}P NMR (3:1 mixture of $CF_3CH_2OH-CH_2Cl_2$): −4 br ([$NP(O_2C_{12}H_8)$]) or −3 br ([$NP(O_2C_{20}H_{12})$]); −23 br shifting to −20 br as *x* increases ([$NP(O-C_6H_4-CONH-Nylon\text{-}6)_2$]). Other peaks (only the most conspicuous) from the chain imperfections: 1.5−0.7, (increasing with *x* from 7 to 31%); 6.0 br (not observed in the cases of $x = 1$ with an intensity that increased with *R* and decreased with *x*, varying from 8% for $x = 0.7$, $R = 5-91\%$ for $x = 0.2$, $R = 50$).

Results and Discussion

The 2,2′-dioxybiphenylphosphazene random copolymers carrying carboxylic acids $\{[NP(O_2C_{12}H_8)]_{1-x}-[NP(OC_6H_4COOH)_2]_x\}_n$ [$x = 0.2$ (**1a**), 0.35 (**1b**), 0.5 (**1c**), 0.7 (**1d**), 0.85 (**1e**)] and the chiral binaphthoxy analogues $\{[NP(O_2C_{20}H_{12})]_{1-x}\ [NP(OC_6H_4COOH)_2]_x\}_n$ [$x = 0.2$ (**3a**), 0.45 (**3b**), 0.7 (**3c**)] (Chart 1) were prepared by hydrolysis of the propylcarboxylate precursors[2] using potassium *tert*-butoxide in THF as described in the literature for analogous phosphazene polymers.[3]

Chart 1. The Phosphazene Random Copolymers Carrying Carboxylic Acids



For comparative purposes, the well-known[3,5] homopolymer **2** ($x = 1$) was also prepared following the same method. Because of their low solubility in THF that decreased with the content of OC_6H_4COOH units (from $x = 0.35$ they were almost insoluble), it was not possible for the accurate measurement of all the Mw by GPC, but it is reasonable to suppose that they are close to those of the starting materials.[2] In fact, for **1a**, it was found that Mw = 0.7 10^6 (PDI = 1.8) and for the precursor Mw = 0.85 10^6 (PDI = 3.3)[2].

The isolated products (see experimental section) were white solids, and the SEM micrographs (Figure 1) revealed that their physical characteristics changed with the composition, ranging from very porous materials (some of them, as **1c**, consisting of fused regular spheres of about 1 μm) to highly compacted particles with very wrinkly surfaces (**1d**).

The X-ray diffraction disclosed the typical halo around $2\theta = 22°$ and the wide angle reflection of a mesomorphic phase (2θ below 7°), the intensity of which was not incremented on raising the temperature to 120 °C. As expected, the interplanar distances (Table 1) increased with *x*, but much less than in the case of the related CO_2Pr^n derivatives.[2]

All the analytical (Table 1) and spectroscopic data (experimental section) were in accord with their chemical composition.

The IR spectra showed the very broad absorption extending from 3100 to 3500 cm^{-1} [HO−C(O)] and the very strong one near 1692 cm^{-1} [C=O(OH)] also observed in the spectrum of the homopolymer [$NP(O-C_6H_4-CO_2H)_2]_n$ (**2**). Interestingly, two distinct absorptions at 2600−2500 cm^{-1} were noticed in all cases, strongly supporting the presence of H-bonded HOCO−HOOC dimers in the solid structure.[19] Other important frequencies, such as those in the regions 1250−1160

Table 5. DSC Data[a] for the Polyamide Branched Polyphosphazenes

	melting[b]		crystallization[c]			
product	T_{max} (°C)	ΔH_F (Jg^{-1})1	T_{max} (°C)	ΔH_C (Jg^{-1})	$\Delta H_C(4)/\Delta H_C(2)$[d]	% polyamide[e]
4c	170, 180	25	135	24	1.1	56
4e	175, 185	37	135	37	1.0	67
4f	200, 210	42	170	49	1.1	83
Nylon−6[f]	225	47	170	57	1.0	100

[a] Only those products approaching the ideal composition in 65% or more are shown. [b] Measured in the second heating (run number 3). [c] Measured in the second cooling (run number 4). [d] Ratio of the ΔH_C of the 2nd and 1st cooling processes (i.e., the 4th and 2nd runs). [e] Maximum (%) of polyamide calculated, taking into account the degree of conversion. [f] Those values were measured in this work under the same experimental conditions and with the same equipment as the rest of the products.

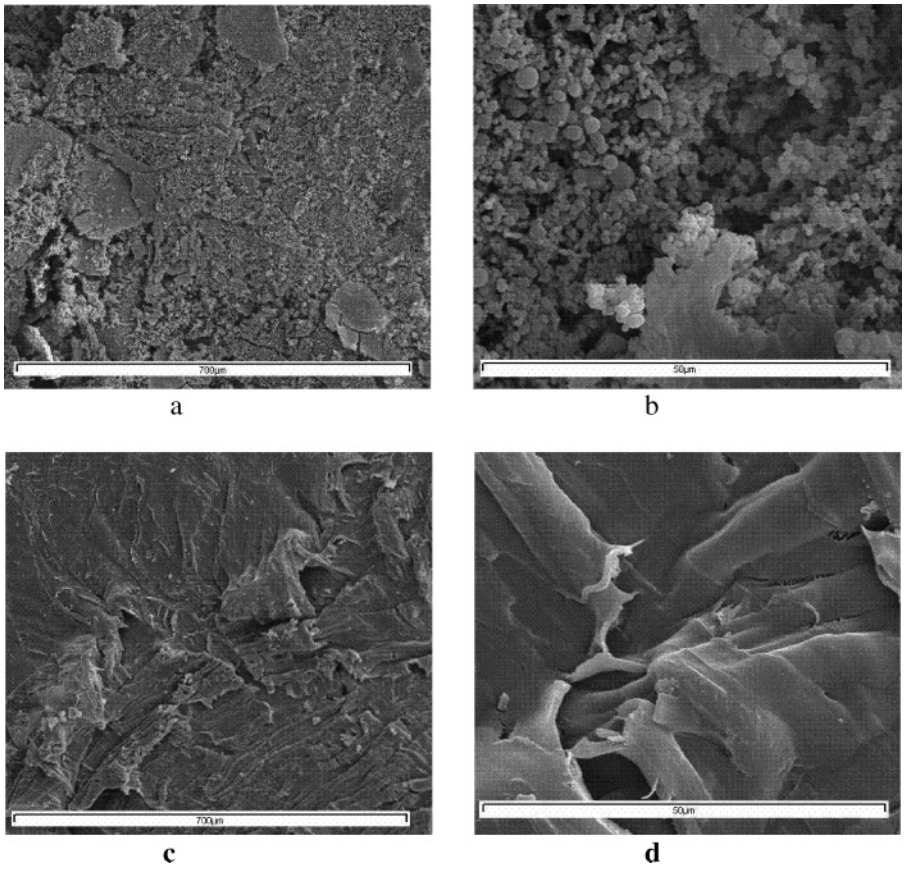


Figure 1. SEM micrographs of (a) polymer **1c** (70×), (b) polymer **1c** (1000×), (c) polymer **1d** (70×), and (d) polymer **1d** (1000×).

cm^{-1} (ν-PN), 1600−1500 cm^{-1} (ν-C=C), 1100 cm^{-1} (ν-P−OC), 950 cm^{-1} (δ-POC), and 800 cm^{-1} (δ-PNP), were assigned according to the literature.[20] The relative intensities of several of the bands (see experimental section) varied consistently with the proportion of both polymeric units.

The ^{1}H spectra, measured in DMSO-d_6 (where they were soluble), demonstrated the total absence of *n*-propyl groups and the presence of only tiny amounts of retained solvents. Significantly, no polytetrahydrofuran (PTHF) that might have been formed during the precipitation of the THF solution in hydrochloric acid was present. The ^{1}H NMR also showed the H atoms of the COOH groups as a broad singlet at 12.7 ppm. The ^{31}P NMR spectra (also in DMSO-d_6) displayed two broad multiplets with the same relative intensities found in the spectra of the starting CO_2Pr derivatives.[2]

As observed[3] with the homopolymer $\{[NP(O-C_6H_4-CO_2H)_2]_n$ (**2**), the members of the series **1** ($x > 0.5$) were very soluble in water at basic pH (0.5 M aqueous sodium carbonate) and could be reprecipitated as white gels by adding hydrochloric acid. The ^{31}P NMR spectra of the basic aqueous solutions also exhibited the expected two broad multiplets (the chemical shifts were only slightly higher than in DMSO). The polymers **3** are chiral (their specific rotations are given in Table 1), and **3d**, which is soluble in basic aqueous media, yields optically active water solutions {−9° in 0.5 M aqueous sodium carbonate (0.5 c)}.

The TGA analysis of the polymers **1**, **2**, and **3** (Table 2) indicated that their thermal stability was moderate. The first decomposition began in the vicinity of 200 °C, and in many of the cases, it occurred overlapped with other decomposition processes, resulting in a continuous loss of weight. The final residue left at 800 °C was, however, high, ranging from 15 to 40%.

The DSC thermograms (measured from 0 to +250 °C and also from −100 to 250 °C) showed that only in the case of **1a** ($x = 0.2$) a distinctive and reproducible heat capacity jump could be observed. The glass transition temperature ($Tg = 96$ °C) was, as expected, intermediate between those of **2** (−4.7 °C)[3] and the homopolymer $[NP(O_2C_{12}H_8)]_n$ (161 °C).[21] Assuming that the *T*g's of the random copolymers **1** decrease linearly with x as found for their carboxylate precursors,[2] all the other values should be well under 100 °C, sufficiently far from the decomposition temperatures. Therefore, the fact that no glass transitions were detected in the other cases is probably connected with the occurrence of the hydrogen bonding in the solids (see the IR discussion above).

Considering the ring-opening polymerization of ϵ-caprolactam promoted by the cyclic trimer $\{[N_3P_3(O-C_6H_4-COOH)_6]_n$,[6] we extended the reaction to the high molecular weight polymers **1**, **2**, and **3** that could generate phosphazene copolymers branched with Nylon-6 polyamides. Thus, all the members of the series were heated at 230 °C in a sealed tube in vacuo with ϵ-caprolactam in ratios R (mmol ϵ-caprolactam/mmol COOH) of ∼5, 10, or 60. We observed that at the beginning, the mixture melted to a clear and mobile liquid, indicating that the polyphosphazenes carrying the carboxylic acid terminal groups were soluble in melted ϵ-caprolactam. We also checked that the heating of ϵ-caprolactam with the nonfunctionalized parent homolpolymer $[NP(O_2C_{12}H_8)]_n$ gave less than 5% yield of a polyamide (probably due to traces of water in the reagents).

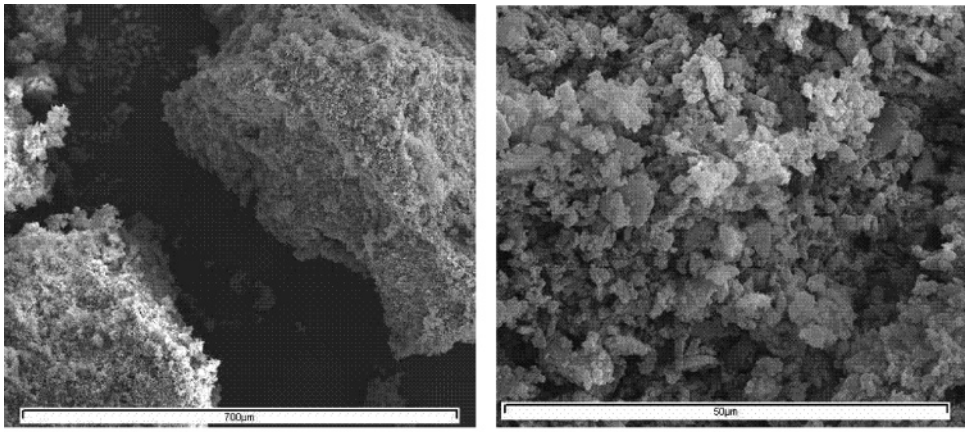


Figure 2. SEM micrographs of the polyamide-phosphazene product **4c** at 70× (a) and 1000× (b).

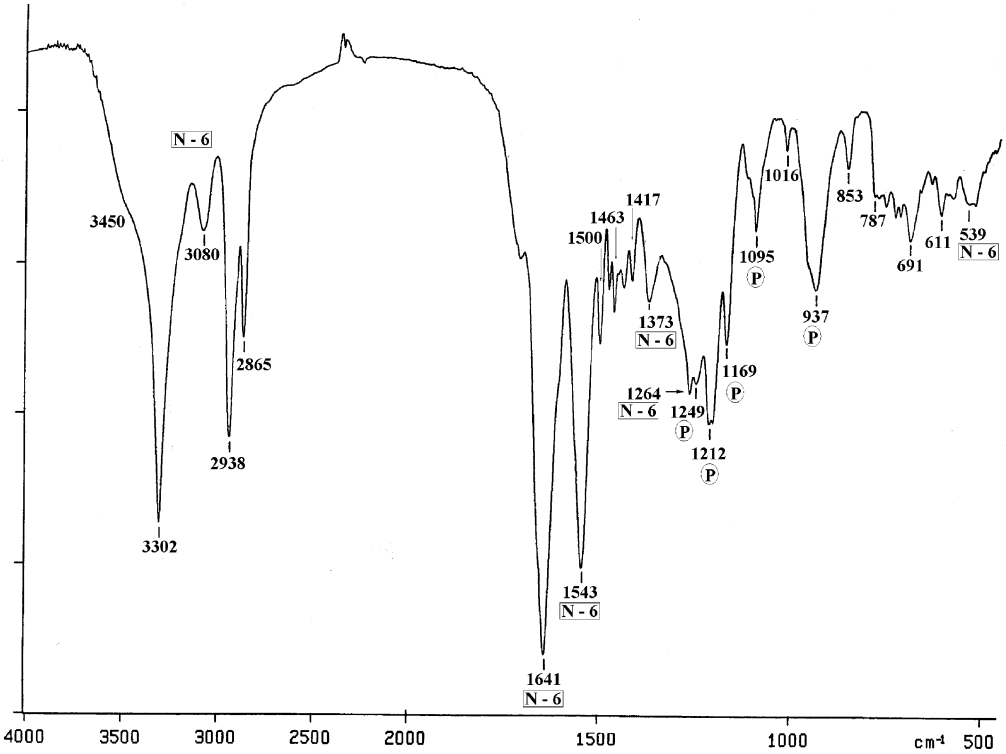


Figure 3. IR spectrum (KBr pellet) of **4e**.

The products obtained by reacting **1**, **2**, and **3** with ϵ-caprolactam (**4, 5,** and **6,** respectively) were white or slightly creamy, hard, brittle, and homogeneous solids (the SEM micrographs shown in Figure 2 were taken from the products formed by cooling the melt). The yields (Table 3) ranged from ~60 to 92% of the total weight of the reactants, tending to be higher as x and R were increased. However, the actual values were not always reproducible. In general, the yields were lower with the dioxybinaphthyl derivatives **3**, particularly in the case of $x = 0.2$ (only 11%), probably due to the higher steric hindrance of the active COOH in those polymers.

All the analytical and spectroscopic data and the thermal properties (experimental section and tables 3, 4, and 5) confirmed that the products were nylon-polyamides attached to linear un-cross-linked polyphosphazene chains (the latter being probably shorter than those of the starting polymers because it is known[22,23] that the average Mw of the related species $[NP(O_2C_{12}H_8)]_n$ and $[NP(O_2C_{20}H_{12})]_n$ are significantly reduced near 250 °C).

Thus, similarly to all polyamides,[24] **4**, **5**, and **6** were insoluble in THF (see experimental section) but very soluble in a 3:1 mixture of $CF_3CH_2OH-CH_2Cl_2$ (in which the COOH precursors were quite insoluble).

The IR spectra (Figure 3) showed the typical pattern of a Nylon-6 crystallized in the H-bonded α-phase,[25] with the strong NH stretching band at 3300 cm^{-1} having a broad shoulder at ~3450 cm^{-1} and a weak absorption at 3084 cm^{-1}. The CH stretching consisted of two main absorptions at 2940 and 2866 cm^{-1}; the CO stretching appeared at 1641 cm^{-1} and the NH bending at 1544 cm^{-1}. Also very significant were the IR absorptions that could be unambiguously attributed to the polyphosphazene vibrations, especially those corresponding to the PN stretchings (near 1200 cm^{-1}) that were consistently more intense in the derivatives made with lower R.

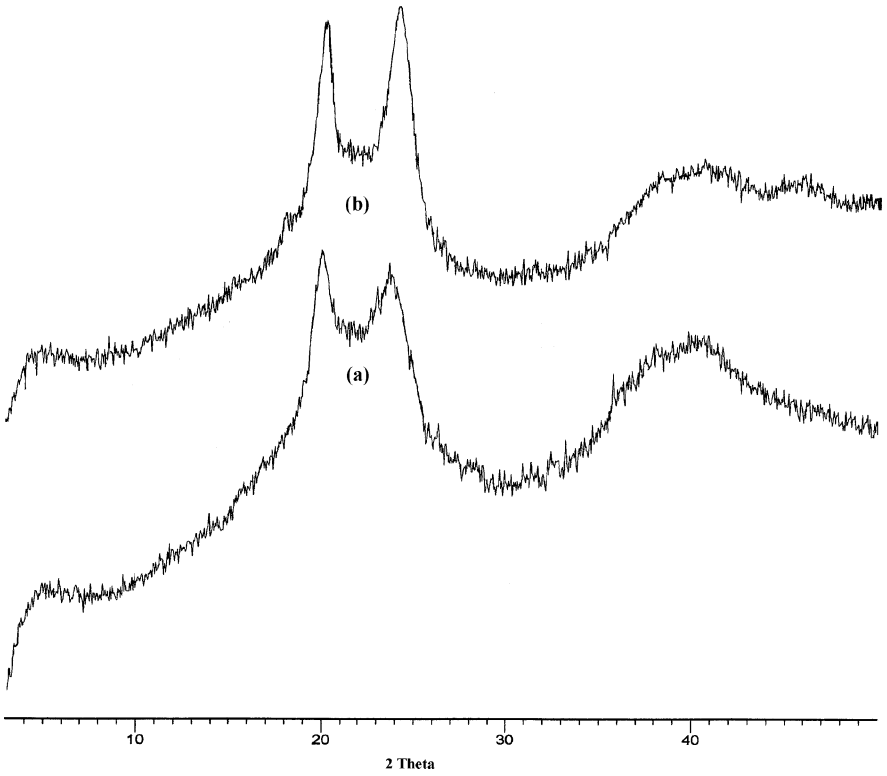


Figure 4. X-ray diffractograms of **4e** (a) and **4f** (b).

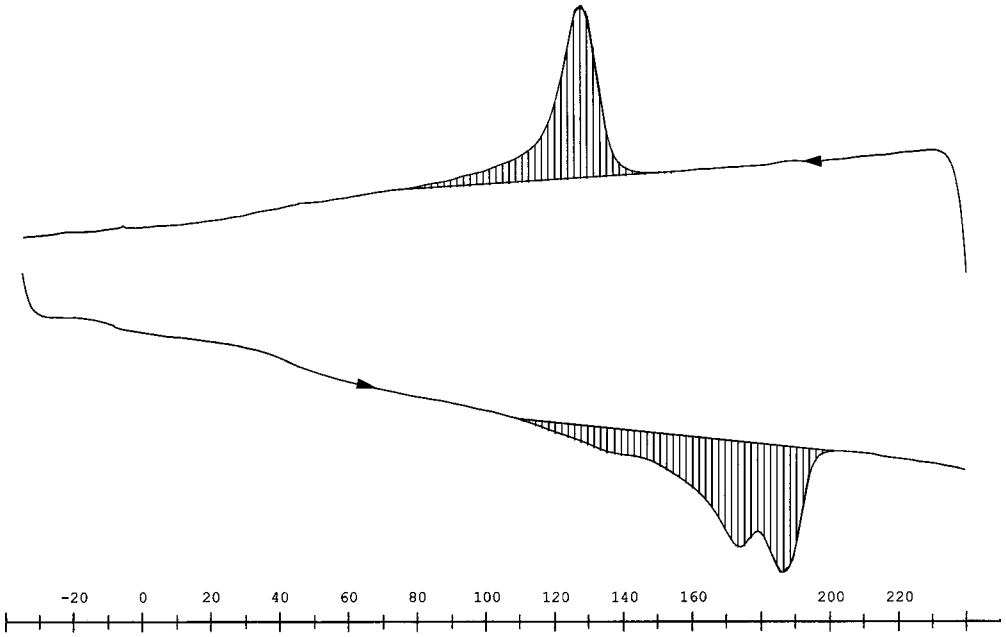


Figure 5. DSC thermogram for the product **4e**.

The presence of the α-phase polyamide was also confirmed by the X-ray diffractograms (Figure 4) that exhibited the two intense sharp reflections at $2\theta = 20°$ and 24°, typical of the (200) and (002) H-bonded planes.[25] The diffractograms also showed that the relative intensities of the broad halo centered near 22° (normally encountered in the polyphosphazenes[26]) were consistent with the phosphazene contents.

The TGA thermograms of **4**, **5**, and **6** (in Table 4 are presented selected data as explained below) showed a fast decomposition centered in the range 350−390 °C with a weight loss of ∼90%. The final residues left at 800 °C (of the order of 4−10%) increased with the phosphazene content, indicating that the main process is the depolymerization of the polyamide to give volatile ϵ-caprolactam and a degraded phosphazene residue.

The DSC thermograms (Table 5 and Figure 5) exhibited in the heating runs a strong, irregularly shaped endothermic peak near 200 °C and a sharper exothermic signal in the cooling runs around 160 °C that were unambiguously assigned to the fusion and crystallization of the polyamide. As might have been expected, the ΔH of the crystallization increased regularly with the proportion of polyamide present in the material approaching that of the commercial Nylon-6 (Table 5).

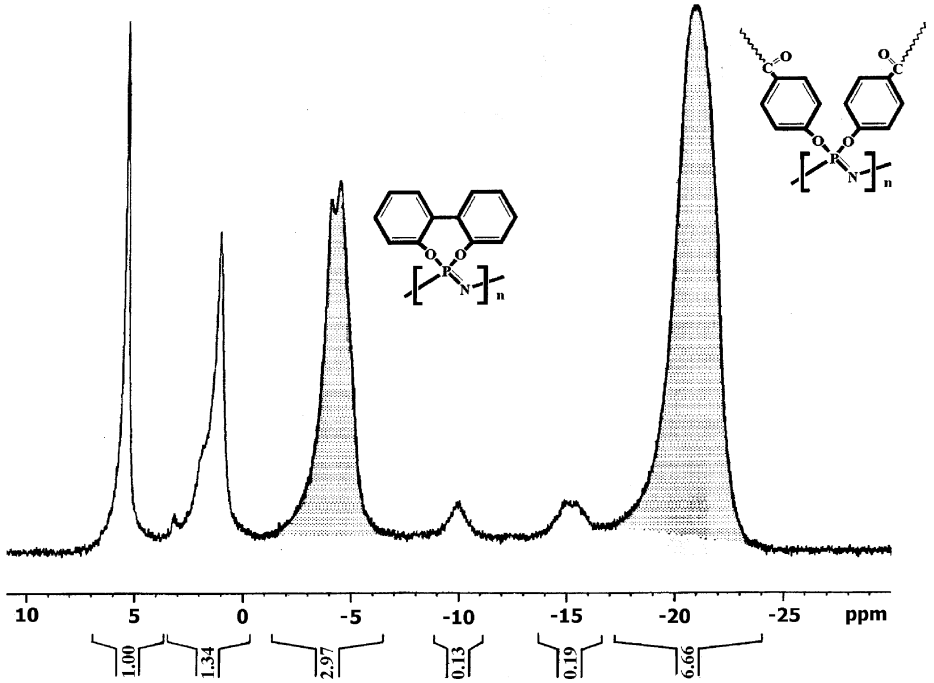


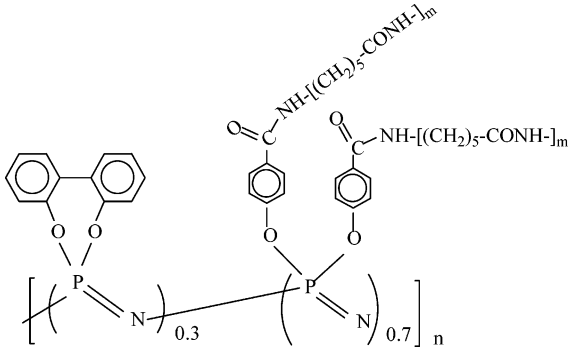
Figure 6. ^{31}P NMR spectrum of **4e** in CF_3CH_2OH/CH_2Cl_2 (3:1).

The solubility of the phosphazene-polyamides **4**, **5**, and **6** in the 3:1 mixture of $CF_3CH_2OH-CH_2Cl_2$ allowed a more detailed characterization by ^{31}P NMR spectroscopy (experimental section and Figure 6).

Thus, the spectra clearly showed the expected two broad signals of the phosphazene units, one at ~−20 ppm ([$NP(OC_6H_4CO-NY\text{-}6)_2$]), and other near −4 ([$NP(O_2C_{12}H_8)$]) (or −3 br in the case of the [$NP(O_2C_{20}H_{12})$] derivatives), with the same relative intensities found in the starting copolymers. It is noteworthy that those values were very close to those of the propyl-ester copolymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(OC_6H_4CO_2Pr)_2]_x\}_n$ in the same solvent mixture. However, all the spectra contained other signals (see experimental section), the relative intensities of which were unchanged after a reprecipitation by pouring the solutions into THF. The corresponding chemical shifts resembled those of some of the compounds formed in the thermal degradation of polyphenoxyphosphazene[27] at temperatures well above 230 °C, and therefore, it is possible that similar or related derivatives, arising from the less-stable carboxylatophenoxyphosphazenes, are present in the materials **4**, **5**, and **6**. In the cases of the polyamides with $x < 1$, the spectra showed a conspicuous peak at +6 ppm with an intensity that increased with R and decreased with x, varying from 8% ($x = 0.7$, $R = 5$) to 91% ($x = 0.2$, $R = 56$) and that did not appear in the cases of **5** (i.e., $x = 1$). Those observations indicated that the ring-opening polymerization of the caprolactam on the COOH groups attached to the polyphosphazenes was accompanied by collateral reactions affecting the composition of several of the phosphazene units.

The measurement of the relative intensities of the signals made it possible for a quantitative determination of the fraction of phosphorus atoms that remained unaffected by the collateral reaction (Table 3). The results showed that only the materials containing [$NP(O_2C_{12}H_8)$] units with $x > 0.5$ and made with $R < 10$ consisted mainly (i.e., more than 65%) of the expected polyamide-branched phosphazenes. Thus, **4e** approached the idealized composition in ~80% (see Chart 2, where

Chart 2. Idealized Formula for Polymer 4e that Corresponds to 80% of the Solid Material



the linking of the Nylon-6 branches to the phosphazene chains by $-OC_6H_4-CONH-$ links was proposed, taking into account the probable mechanism of this polymerization).[28]

Conclusions

New phosphazene copolymers having [$NP(O_2C_{12}H_8)$] or chiral [$NP(O_2C_{20}H_{12})$] units and $O-C_6H_4-COOH$ pendant groups, some of them soluble in basic water, have been synthesized. The use of those polymers as initiators for the ring-opening polymerization of ϵ-caprolactam, in molar ratios ϵ-caprolactam/COOH $R < 10$, gave new polymeric materials, consisting essentially (80−65%) of linear un-cross-linked polyphosphazenes branched with short Nylon-6 chains but having a fraction of the PN units modified by collateral secondary reactions.

Acknowledgment. We are grateful to the FYCIT (project PB-EXPO1-15), the DGICYT (project BQU2001-3676), the CSIC, and the CONYCYT (project 2003CL0027) and the FONDECYT (project 1030515) for financial support.

References and Notes

(1) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992. Allcock, H. R.

Chemistry and Applications of Polyphosphazenes; Wiley and Sons: New York, 2002. Gleria, M., De Jaeger, R. Eds. *Phosphazenes: a Worldwide Insight*; Nova Science Publishers: New York, 2004.
(2) Carriedo, G. A.; Fidalgo, J. I.; García Alonso, F. J.; Presa Soto. A.; Díaz Valenzuela, C.; Valenzuela, M. L. *Macromolecules* **2004**, *37*, 9431−9437.
(3) Allcock, H. R.; Kwon, S. *Macromolecules* **1989**, *22*, 75−79.
(4) Allcock, H. R.; Morrissey, C. T.; Way, W. K.; Winograd, N. *Chem. Mater.* **1996**, *8*, 2730−2738.
(5) Andrianov, A. K.; Chen, J.; LeGolvan, M. P. *Macromolecules* **2004**, *37*, 414−420.
(6) Miyata, K.; Watanabe, Y.; Itaya, T.; Tanigaki, T.; Inoue, K. *Macromolecules* **1996**, *29*, 3694−3700.
(7) Tada, Y.; Sato, M.; Takeno, N.; Nakacho, Y.; Shigehara, K. *Chem. Mater*. **1994**, *6*, 27−30. Lee, B. H.; Lee, Y. M.; Sohn, Y. S.; Song, S.-C.; *Bull. Kor. Chem. Soc.* **2002**, *23*, 549−554. See also, Inoue, K. In *Phosphazenes: a Worldwide Insight*. Gleria, M., De Jaeger, J., Eds.; Nova Science Publishers: New York, 2004. Chapter 22, p 543.
(8) Wisian-Neilson, P.; Schaefer, M. A. *Macromolecules* **1989**, *22*, 2003−2007.
(9) Wisian-Neilson, P.; Safiqul Islam, M. *Macromolecules* **1989**, *22*, 2026−2028.
(10) Cambre, J. N.; Wisian-Neilson, P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **2003**, *44*, 919−920.
(11) Minto, F.; Scoponi, M.; Fambri, L.; Gleria M.; Bortolus, P.; Pradella, F. *Eur. Polym. J.* **1992**, *28*, 167−173.
(12) Young Chang, J.; Jeung Park, P.; Jung Han, M. *Macromolecules* **2000**, *33*, 321−325.
(13) Leung, L. M.; Liu, C. M.; Wong, C. K.; Kwong, C. F. *Polymer* **2002**, *43*, 233−237.
(14) Allcock, H. R.; Young Chang, J. *Macromolecules* **1991**, *24*, 993−999.
(15) Minto, F.; Gleria M.; Bortolus, P.; Fambri, L.; Pegoretti, A. *J. Appl. Polym. Sci.* **1995**, *56*, 747−766. Minto, F.; Gleria M.; Favero G. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *34*, 2177−2203.
(16) See: Allcock, H. R.; Nelson, C. J.; Coggio, W. D. *Chem. Mater.* **1994**, *6*, 516−524. Pemberton, L.; De Jaeger, R.; Gengembre. L. *Polymer* **1998**, *39*, 1299−1307. Lora, S.; Carenza, M.; Palma, G.; Pezzin, G.; Caliceti, P.; Battaglia, P.; Lora, A. *Biomaterials* **1991**, *12*, 275−280. Minto, F.; Borzatta, V.; Gleria, M. *J. Inorg. Organomet. Polym.* **1996**, *6*, 171−193. Fambri, L.; Minto, F.; Gleria, M. *J. Inorg. Organomet. Polym.* **1996**, *6*, 195−220.
(17) Allcock, H. R.; Powell, E. S.; Maher, A. E.; Berda, E. B. *Macromolecules* **2004**, *37*, 5824−5829. Allcok, H. R.; Powell, E. S.; Maher, A. E.; Prange, R. L.; de Denus, C. R. *Macromolecules* **2004**, *37*, 3635−3641.
(18) Pemberton, L.; De Jaeger, R. *Chem. Mater.* **1996**, *8*, 1391−1395.
(19) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman-Hall: London, 1975; Vol. 1, p 188.
(20) Carriedo, G. A.; García Alonso, F. J.; González, P. A.; Menéndez, J. R. *J. Raman Spectrosc.* **1998**, 29, 327−330.
(21) Carriedo, G. A.; Fernández Catuxo, L.; García Alonso F. J.; Gómez Elipe, P.; González P. A. *Macromolecules* **1996**, 29, 5320−5325.
(22) Laguna, M. T. R.; Tarazona, M. P.; Carriedo, G. A.; García Alonso F. J.; Fidalgo J. I.; Saiz. E. *Macromolecules* **2002**, *35*, 7505−7515.
(23) Carriedo, G. A.; García Alvarez, J. L.; García Alonso F. J.; Presa Soto, A.; Tarazona, M. P.; Mendicuti F., Marcelo, G. *Macromolecules* **2004**, *37*, 5437−5443.
(24) Weber, J. N. In *Kirk-Othmer Encyclopedia of Chemical Thechnology*, 4th ed.; Wiley & Sons: New York, 1996; Vol. 19, p 467.
(25) Loo, L. S.; Gleason, K. *Macromolecules* **2003**, *36*, 6114−6126.
(26) Magill, J. H.; Kojima, M. In *Phosphazenes: a Worldwide Insight*; Gleria M., De Jaeger, R., Eds. Nova Science Publishers: New York, 2004; Chapter 13, p 305.
(27) Maynard, S. J.; Sharp, T. R.; Haw, J. F. *Macromolecules* **1991**, *24*, 2794−2799.
(28) Puffr, R.; Sebenda, J. *Makromol. Chem., Makromol. Symp*. **1986**, *3*, 249−264.

MA047514T