On the Presence of Polytetrahydrofuran in the Polyspirophosphazenes $[NP(O_2C_{12}H_8)]_n$ Prepared from $[NPCl_2]_n$ and 2,2′-Dihydroxybiphenyl in THF as Solvent

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ABSTRACT: Polydichlorophosphazene $[NPCl_2]_n$ reacts with the diphenol 2,2′-$(HO)C_6H_4$-$C_6H_4(OH)$ in THF in the presence of K_2CO_3 to give the polymers $[NP(O_2C_{12}H_8) \cdot x(OC_4H_8)]_n$ (**1**) that contain variable ammouts of polytetrahydrofuran (PTHF) with x ranging from 0.05 to 0.8. This PTHF content (x) depends on the method followed to prepare the THF solutions of $[NPCl_2]_n$ used for the reactions with the biphenol and can be made negligibly small, forming these solutions in the presence of K_2CO_3. This reveals the presence in the $[NPCl_2]_n$ of acidic species capable of catalyzing the ring opening polymerization of THF. Polyphosphazene $[NP(O_2C_{12}H_8)]_n$ (**2**) was prepared completely free of PTHF using dioxane as solvent. A comparison of the thermal behavior and morphological data of the polymers **1**, **2**, PTHF (**5**), and mixtures of $[NP(O_2C_{12}H_8)]_n + x(OC_4H_8)_m$ (**4**) revealed that the products **1** are strongly interacting polymer blends and ruled out the possibility of block copolymers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 568–576, 2000

Key words: phosphazene polymers; thermal polymerization; crystalline phase

INTRODUCTION

We previously reported[1] that diphenol 2,2′-$(HO)C_6H_4$-$C_6H_4(OH)$ reacts in tetrahydrofuran (THF) with $[NPCl_2]_n$ and K_2CO_3 to give the uncrosslinked phosphazene polymers shown in

Scheme 1. However, the products of the reactions contained variable amounts of polytetrahydrofuran (PTHF) and respond to the general formula $[NP(O_2C_{12}H_8) \cdot x(OC_4H_8)]_n$ (**1**) with $x = 0$ to 0.5.

Considering that the starting material $[NPCl_2]_n$ was obtained by the thermal polymerization of the trimer $[N_3P_3Cl_6]$ in 1,2,4-trichlorobenzene solution in the presence of sulphamic acid,[2] we initially believed that the formation of PTHF occurred, induced by traces of this acid, when $[NPCl_2]_n$ was dissolved in THF before its reaction with biphenol. However, the fact that the PTHF could not be removed even after several reprecipitation steps in isopropanol, in which PTHF is soluble,[3] led us to suspect that the materials obtained in these reactions were not simply blends of the polyphosphazenes with PTHF,
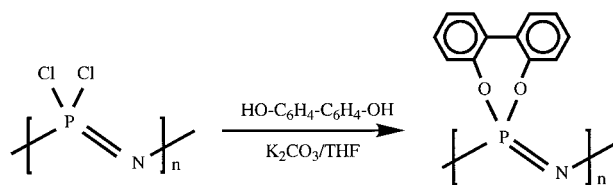
Scheme 1

and therefore we decided to study these products in more detail.

On the other hand, the ring opening polymerization of THF is catalyzed, not only by protonic acids, but also by other acidic species present in some phosphazene compounds. Thus, it is known that short linear polyphosphazenes having terminal $-PCl_3^+$ groups are able to polymerize the THF[4] and other alkylene oxides.[5] In addition, it has recently been reported that THF oligomers are formed in the reactions of $[NPCl_2]_n$ with $NaOCH_2CH_2NMe_2$ in THF.[6] Furthermore, according to the proposed polymerization mechanism of $[N_3P_3Cl_6]$,[7] there is a terminal $-N = PCl_2^+$ group at the end of each polydichorophosphazene chain, and such groups could be capable of initiating the cationic polymerization process depicted in Scheme 2, as occurs with many other Lewis acids.[8] Therefore, the formation of diblock copolymers during the synthesis of polyphosphazenes from $[NPCl_2]_n$ in THF as solvent cannot be ruled out. Similar sequential polymerizations leading to different types of diblock copolymers involving THF have been described,[9] and poly(phosphazene ethylene oxide) block copolymers have been recently prepared,[10] although by condensation re-

actions. Therefore, we also considered it to be of interest to study the origin of the PTHF present in **1**.

In this article we describe the preparation of $[NP(O_2C_{12}H_8)]_n$ free of PTHF and several experimental results that prove that the polyspirophosphazenes **1** are strongly interacting blends of $[NP(O_2C_{12}H_8)]_n$ with PTHF. This PTHF is formed when the $[NPCl_2]_n$ is dissolved in THF, and it can be almost completely avoided by making this solution in the presence of K_2CO_3, suggesting the presence in the dichlorophosphazenes of some acidic species able to catalyze the ring opening polymerization of THF.

EXPERIMENTAL

K_2CO_3 was dried at 140°C prior to use. 1,4-Dioxane was distilled from Na in the presence of benzophenone. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Petroleum ether refers to that fraction with boiling point in the range 60–65°C. The diphenol was used as purchased (Aldrich, Milwaukee, WI). Phenol was purified by vacuum sublimation followed by dissolution in CH_2Cl_2, filtration through Na_2CO_3, and evaporation of the solvent in vacuum. The hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Fluka, Ronkonkoma, NY) was purified from hot petroleum ether and dried in vacuum. The starting polymer $[NPCl_2]_n$ was prepared as described by Magill et al.[2] or by Allcock et al.[11] The polymers $[NP(O_2C_{12}H_8) \cdot x(OC_4H_8)]_n$ were prepared as described earlier.[1] All the reac-
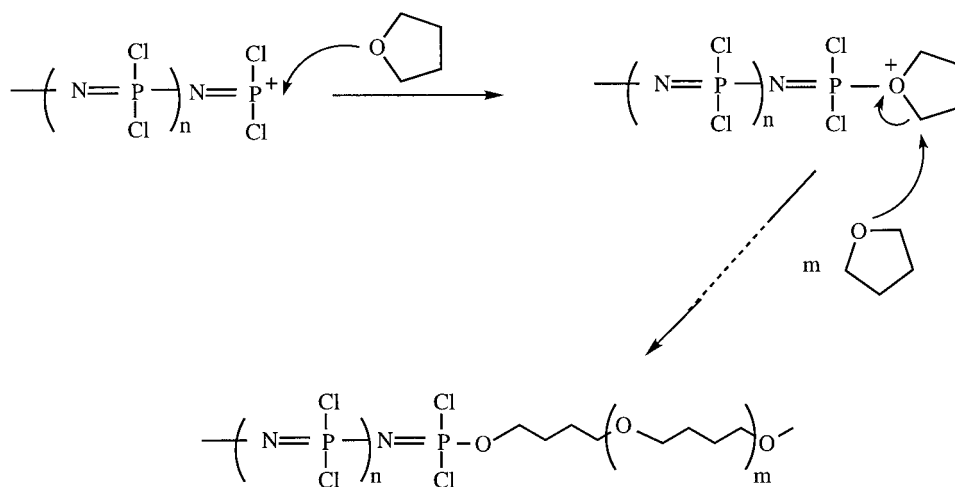
Scheme 2

tions were carried out under dry nitrogen. The white solid PTHF (M_w = 3000) was supplied by Polysciences (Warrington, PA) or prepared[12] by polymerization of THF with methyl-trifluoromethanesulphonate as described below (M_w = 10,000 or 20,000). The blend **4** was prepared by dissolving **2** and PTHF in CH_2Cl_2 and reprecipitating into hexane or by evaporating the solvent and drying in vacuum for 24 h.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker (Billerica, MA) AC-200 and AC-300 instruments, using $CDCl_3$ as the solvent unless otherwise stated. ^{1}H- and ^{13}C{^{1}H}-NMR spectra are given in δ relative to TMS. ^{31}P{^{1}H}-NMR spectra are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hertz. C, H, N analyses were performed with a Perkin Elmer (Norwalk, CT) 240 microanalyzer. The chlorine analyses were performed by Galbraith Laboratories.

Molecular weights were measured by gel permeation chromatography (GPC) with a Perkin Elmer equipment with a Model LC 250 pump, a Model LC 290 UV spectrophotometer, 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. An approximate molecular weight (MW) calibration was obtained using narrow MW distribution polystyrene standards.

Thermogravimetric analysis (TGA) was performed on a Mettler (Highstown, NJ) TGA-4000/TG-50 thermobalance, using nitrogen as the purge gas. The TGA under dynamic conditions was carried out at a heating rate of 10°C/min, recording the percent weight loss against temperature.

The thermal transitions were measured using a Mettler TA-4000 differential scanning calorimeter (DSC) with a DSC-30 furnace under an inert nitrogen atmosphere, using Mettler TA-72 thermal analysis software. The heating rate was 10°C/min and all cycles were performed over the range from −50 to 300°C. The inflexion point in the change of the specific heat was used to determine the glass transition temperature, and the temperatures corresponding with the minimum and maximum were used to define the melting and crystallization transitions.

Wide-angle X-ray diffractograms were obtained using a Rigaku (Danvers, MA) Geiger-flexD/max diffractometer with a Rigaku RU-200 rotating anode generator. The diffractograms were recorded at 1°/min, in the range between 2Θ = 2 and 35°, using Ni-filtered CuKα radiation.

Fourier transform infrared (FTIR) and FT-Raman spectra were recorded using a Perkin-Elmer System 2000. In the FTIR mode, samples were introduced as KBr disks, and 50 scans were collected over a period of 2 min, at a resolution of 4 cm^{-1}. In the FT-Raman mode, a Spectron SL-301 Nd^{3+} : YAG laser ($λ_0$ = 1.064 nm) with a sample power of between 20 and 100 mW was used to excite the Raman scatter, which was collected at 180°, processed by the interferometer and registered on a room temperature InGaAs detector, accumulating 400 scans at a resolution of 4 cm^{-1}. A CIC Photonics microscope hot-stage, with temperature control modified to record Raman spectra, was used to measure the Raman spectrum of PTHF as a function of temperature. All Raman spectra were corrected for the transmission characteristics of the instrument optics.

Synthesis of [NP($O_2C_{12}H_8$)]$_n$ (2)

In Dioxane

To a solution of [NPCl$_2$]$_n$ (2.37 g, 20.45 mmol) (prepared by the Magill′s method[2]) in 1,4-dioxane (200 mL) 2,2′-HO-C_6H_4-C_6H_4-OH (5.71 g, 30.66 mmol) and K_2CO_3 (11.29 g, 81.69 mmol) were added and the mixture was refluxed for 51 h with vigorous mechanical stirring. The mixture was concentrated in a vacuum and poured into water (1.5 L) to give a white precipitate that was washed twice with water (1.5 L) and dissolved in THF (200 mL). The solution was filtered and concentrated to a viscous liquid that was poured into water (1.5 L). The product was similarly reprecipitated once from THF/isopropanol and once from THF/petroleum ether. The resulting solid was predried first in vacuum at room temperature and then at 70°C for 7 days. The product was [NP($O_2C_{12}H_8$)]$_n$. Yield: 3.2 g, 68%.

^{1}H-NMR: 6.6–7.4 (m, 8 H, arom. rings). ^{31}P{^{1}H}-NMR: −5.80 (−5.7 in dioxane/D_2O). ^{13}C{^{1}H}-NMR: 124, 126, 129, 130, 149 ($C_{12}H_8O_2$).

Anal: Calcd. for $C_{12}H_8O_2NP$: C, 62.9%; H, 3.5%; N, 6.1%.

Found: C, 62.8%; H, 3.6%; N, 5.8%. Chlorine content 0.04%.

M_w (GPC) = 370,000. M_w/M_n = 4.7. TGA. −85% (470°C). T_g (DSC) = 156°C.

The products from different preparations had MWs ranging from 400,000 to 500,000 with polidispersities of 5–6.

In THF

The $[NPCl_2]_n$ was prepared by the Magill's method[2] and extracted with THF in the presence of K_2CO_3 (1 g). To a solution containing the $[NPCl_2]_n$ (1.85 g, 16 mmol in 300 mL), $2,2'$-HO-C_6H_4-C_6H_4-OH (4.5 g, 24 mmol) and K_2CO_3 (8.8 g, 63.8 mmol) were added and the mixture was refluxed for 20 h with vigorous mechanical stirring. The mixture was concentrated in vacuum and poured into water (1.5 L) to give a white precipitate that was washed twice with water (1.5 L) and dissolved in THF (200 mL). The solution was filtered and concentrated to a viscous liquid that was poured into water (1.5 L). The product was similarly reprecipitated once from THF/isopropanol and once from THF/petroleum ether. The resulting solid was predried first in vacuum at room temperature and then at 70°C for 3 days. The product was $[NP(O_2C_{12}H_8)]_n$. Yield (averaged) 2.4 g, 68%. The products obtained contained a very small amount of PTHF, as measured by ^{1}H-NMR, corresponding to the formulation $[NP(O_2C_{12}H_8) \cdot x(OC_4H_8)]_n$, with x varying from 0 to 0.05.

M_w (GPC) = 600,000–800,000. M_w/M_n = 3–4.

Synthesis of $[NP(O_2C_{12}H_8)]_n$ (3)

To a solution of $[NPCl_2]_n$, prepared by the Allcock's method,[11] (0.5 g, 4.31 mmol) in THF (130 mL), $2,2'$-HO-C_6H_4-C_6H_4-OH (1.2 g, 6.44 mmol) and K_2CO_3 (2.38 g, 17.22 mmol) were added, and the mixture was refluxed for 37 h with vigorous mechanical stirring. The polymer **3** was isolated and purified following the same procedure as for **2**. Yield: 0.55 g, 50%. The product contained a very small amount of PTHF, as measured by ^{1}H-NMR, corresponding to the formulation $[NP(O_2C_{12}H_8). 0.05 (OC_4H_8)]_n$.

ANAL: Calcd. for $C_{12}H_8O_2NP$: C, 62.9%; H, 3.5%; N, 6.1%.

Found: C, 62.5%; H, 3.4%; N, 5.9%. Chlorine content 0.04%.

M_w (GPC) = 900,000. M_w/M_n = 7.7. TGA: -2.17% (360°C), -88% (500°C).

Preparation of PTHF (5)

To THF (50 mL) methyltrifluoromethanesulphonate (0.20 mL) was added, and the mixture was stirred at room temperature for 10 min, concentrated in vacuum to 20 mL, and poured into water (200 mL). The white precipitate was dissolved in CH_2Cl_2, dried over magnesium sulphate, filtered, and evaporated to dryness. Yield: 7 g, 16%.

ANAL: Calcd. for C_4H_8O: C, 66.6%; H, 11.2%.

Found: C, 66.1%; H, 11.1%.

^{1}H-NMR: 3.4 m, 1.6 m.^{13}C-NMR: 71.2, 27.1.

M_w (GPC) = 11,000. M_w/M_n = 1.2.

The PTHF with M_w 20,000 was prepared in a similar manner, with 1.5 h stirring. Yield: 4 g, 15%.

ANAL: Calcd. for C_4H_8O: C, 66.6%; H, 11.2%.

Found: C, 65.4%; H, 11.1%.

RESULTS AND DISCUSSION

As described earlier[1] the reaction of $[NPCl_2]_n$, prepared after Magill et al.,[2] and the biphenol $2,2'$-$(HO)C_6H_4$-$C_6H_4(OH)$ in THF, in the presence of K_2CO_3, gave the materials that may be represented by the following formula: $[NP(O_2C_{12}H_8) \cdot x(OC_4H_8)]_n$ (**1**). The products from 12 independent preparations, isolated in an identical manner, contained different amounts of PTHF ranging from x = 0.05 to 0.8. The M_w of these polymers depends on the reaction time, decreasing from 800,000 (12 h) to 500,000 (20 h) and to 350,000 (35 h), as does the residual unreacted chlorine, which falls below 0.1% after 35 h. The M_w also decreases slowly with the drying time at 70°C (3–7 days). The GPC chromatograms are similarly, but not equally, bimodal and the polydispersity index (M_w/M_n) varies from 4 to 7.

The PTHF content of each product could not be susbtantially reduced after several reprecipitation steps. Only when x was higher than 0.5 was a significant decrease observed, for example, from x = 0.8 to x = 0.35. Although the prolonged stirring of the THF solutions of the $[NPCl_2]_n$, before its reaction with the biphenol, did not consistently increase or decrease the PTHF content on the products **1**, the use of $[NPCl_2]_n$ purified once by reprecipitation from THF/hexane gave products with lower PTHF contents (x near 0.1).

These observations suggest that PTHF is formed when the $[NPCl_2]_n$ is dissolved in THF and that the amounts are very sensitive to the experimental conditions. It is also apparent that at least part of this PTHF can be removed from the $[NPCl_2]_n$, but the separation from the polymer $[NP(O_2C_{12}H_8)]_n$ is much more difficult.

In principle, the formation of the PTHF could be attributed to some acidic residues present in the $[NPCl_2]_n$ obtained by the polymerization method of Magill, which are promoted by sulpha-

mic acid.[2] However, when the phosphazene polymer $[NP(O_2C_{12}H_8)]_n$ was prepared using polydichlorophosphazene obtained by the method described by Allcock et al.[11] (based on the heating of pure melted $[N_3P_3Cl_6]$ without the addition of acidic promoters), we obtained a product **3** also with PTHF, although the amounts were practically negligible ($x = 0.05$). Additionally, we observed that, in this case, the chlorine substitution was slower, and the M_w of the product was almost double than that of **1**, which is consistent with the published M_w values of polyphosphazenes prepared from $[NPCl_2]_n$ obtained by solution polymerization[2] or by melting polymerization[11,13] of $[N_3P_3Cl_6]$.

The formation of traces of PTHF in the THF solutions of the polydichlorophosphazene made by the melting method may suggest that also in this case there are some acidic species, such as small oligomers with $-PCl_3^+$ groups, that are known to catalyze the polymerization of THF,[4,5] but it is also possible that it comes from the action of the relatively few cationic $NPCl_2^+$ ends of the polyphosphazene chains. In fact, it is interesting to note that the formation of THF oligomers has been detected in the reactions of $[NPCl_2]_n$ with $NaOCH_2CH_2NMe_2$ in THF.[6] However, when we carried out the preparation of the polyspirophosphazene $[NP(O_2C_{12}H_8)]_n$ in THF as solvent, starting from $[NPCl_2]_n$ formed by the method described by Magill and colleagues,[2] but dissolving it in THF in the presence of K_2CO_3 to neutralize any acid present, the products contained only traces of PTHF, never exceeding $x = 0.05$. Therefore, it can be concluded that the PTHF in **1** comes mostly from the presence of acidic species, but that it is possible that a very small amount is due to a few unidentified cationic groups in the polydichlorophosphazene.

In fact, the polymer $[NP(O_2C_{12}H_8)]_n$ (**2**) completely free of PTHF could only be obtained by reacting $[NPCl_2]_n$ with the biphenol 2,2'-$(HO)C_6H_4$-$C_6H_4(OH)$ and K_2CO_3 in dioxane as solvent. This reaction was slower than in THF (51 h), and the M_w (400,000–500,000) and the polydispersity index (5–6) were slightly lower than those of the products obtained in THF using $[NPCl_2]_n$ also made by the solution polymerization method.

As noted above, the PTHF can be partly separated from the $[NPCl_2]_n$ but not from $[NP(O_2C_{12}H_8)]_n$. However, we have detected the presence of PTHF in other polyphosphazenes prepared in THF, for example, $[NP(OC_6H_5)_2 \cdot 0.6(OC_4H_8)]_n$ ($M_w = 500,000$),[14] and in this case, the PTHF could be almost completely separated by reprecipitation from THF/isopropanol, giving a product with $x = 0.07$. Consistently, we found that a mixture formed with the homopolymer $[NP(OC_6H_5)_2]_n$ and PTHF could also be separated efficiently.

All these observations prove the polymer $[NP(OC_6H_5)_2 \cdot 0.6\ (OC_4H_8)]_n$ and, therefore, the products **1** are mostly phosphazene–PTHF blends, although in the latter case very difficult to separate, suggesting strong interactions between the two components. In fact, we checked that, similarly to the products **1**, various authentic blends (**5**) obtained by mixing in solution the homopolymer **2** (MW of ca. 500,000) and PTHF (MW 3,000, 10,000, or 20,000) could not be well separated by reprecipitation from THF/petroleum ether. The best separations were achieved from CH_2Cl_2/isopropanol, but the PTHF content of the mixtures, initially having $x = 0.6$ to 0.8, could never be reduced below 0.35. The results also indicated that the separations were more effective the larger the difference in the Mw of the two polymers.

The comparison of the GPC chromatograms (refractive index detector) of the products **1** with those of **2**, PTHF and the mixtures **2** + PTHF (**5**) did not give reliable information about the nature and M_w of the PTHF present in **1**, because the signals that could be attributed to the PTHF were broad, weak, and too near to those of the phosphazene to be unambiguously assigned. Therefore, the M_w distribution of the PTHF present in **1** could not be determined. However, the data suggested values above 10,000.

In order to further study the nature of the products **1**, we compared the thermal behavior (TGA and DSC curves) and structural data of the materials $[NP(O_2C_{12}H_8) \cdot x(OC_4H_8)]_n$ (**1**), $[NP(O_2C_{12}H_8)]_n$ (**2**), and blends made from **2** and the appropriate amount of PTHF $\{[NP(O_2C_{12}H_8)]_n + x(OC_4H_8)_m\}$(**4**) formed with phosphazenes of comparable MW, and PTHF of different MWs. The comparisons were made using samples as obtained by precipitation from THF/petroleum ether or by slowly evaporating from solutions in dichloromethane.

Figure 1 shows the degradation curves for the materials **1** ($M_w = 400,000$, $x = 0.4$), **2** ($M_w = 500,000$), **4** (11.2% PTHF of $M_w = 20,000$, $x = 0.4$), and **5**, PTHF ($M_w = 20,000$), all obtained by precipitation. In the TGA curve of **1** a step is observed at 350°C that corresponds to a weight loss of between 10 and 14% and arises from the degradation of PTHF in the sample. As expected, this
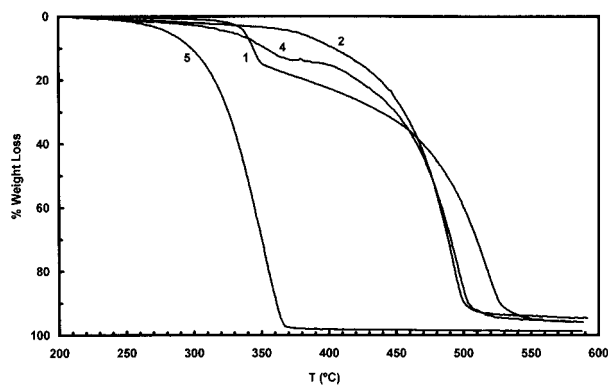
**Figure 1** Thermal stability of materials **1**, **2**, **4**, and **5**.

step is absent in the TGA curve of **2** and present in that of **4**. The comparison of the TGA curves shows that the degradation of **1** and **4** occurs at a slightly different rate, suggesting that the level of interaction in each product is not exactly the same.[15,16]

On the other hand, the analysis by differential scanning calorimetry corresponding to materials **1** and **2** shows a series of important differences, which can be observed by comparing the thermograms in Figures 2 and 3. In each case, the following thermal cycles were used at a rate of 10°C/min: first heating cycle from −50 to 300°C, cooling cycle from 300 to −50°C, and second heating cycle from −50 to 300°C.

The first heating curve of **1** [Fig. 2(a)] shows a well-developed glass transition at 80°C , followed by a second complex exothermic transition between 145 and 190°C, which is probably associated with a reorganization of the mesophase (see
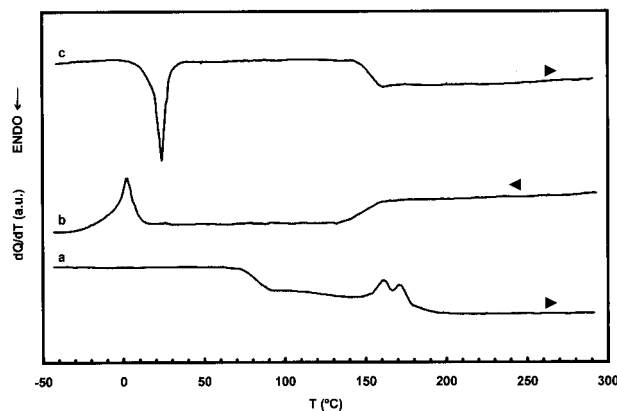
Figure 2 DSC thermograms for **1**. (a) First heating cycle, (b) cooling cycle, and (c) second heating cycle, as described in the text.
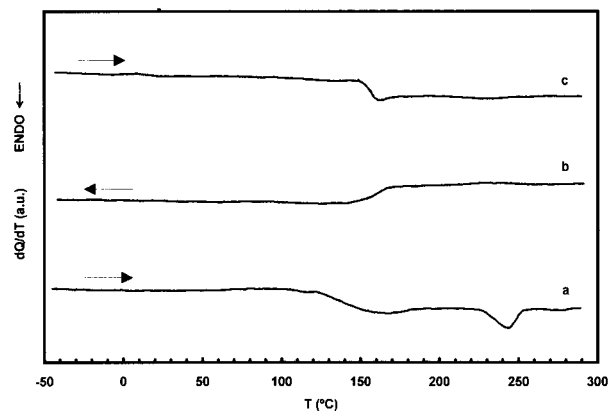

Figure 3 DSC thermograms for **2**. (a) First heating cycle, (b) cooling cycle, and (c) second heating cycle, as described in the text.

below). In the subsequent cooling cycle, a change in the specific heat at 148°C was observed, followed at lower temperature by an exothermic transition at 2°C, which could be attributed to the crystallization of PTHF[17,18] [Fig. 2(b)]. The second heating cycle [Fig. 2(c)] shows a sharp endothermic peak at 24°C corresponding to the melting of PTHF.[17,18] Only a clearly defined glass transition is observed at 150°C, with no evidence for the exothermic transition previously observed in the first heating cycle. From these results, a series of fundamental observations can be made. There is an important shift in the glass transition temperature that depends on the thermal history, that is, on whether the sample is precipitated from solution or cooled from the mesophase. Correspondingly, the thermal history also conditions the crystallization behavior of PTHF in the sample, whereby crystalline order is only observed when the sample is cooled from 300°C.

In the case of **2**, the glass transition temperature in the first heating cycle [Fig. 3(a)] appears at 140°C, followed by a small endotherm at 243°C. A narrower glass transition is observed at 156°C in the second heating cycle [Fig. 3(c)].

The most obvious difference between **1** and **2** is the expected absence of transitions associated with PTHF in **2**. The presence of PTHF in **1** is confirmed by the IR and Raman data. As an example, Figure 4 shows the Raman spectra of **1**, **2** and pure PTHF ($M_w = 20,000$) **5**, at room temperature [Fig. 4(c)] and in the molten state [Fig. 4(d)]. In PTHF, the aliphatic CH stretching vibrations are the most prominent bands in the spectrum and can be clearly observed in **1**. Raman spectra of the polyphosphazenes are dominated
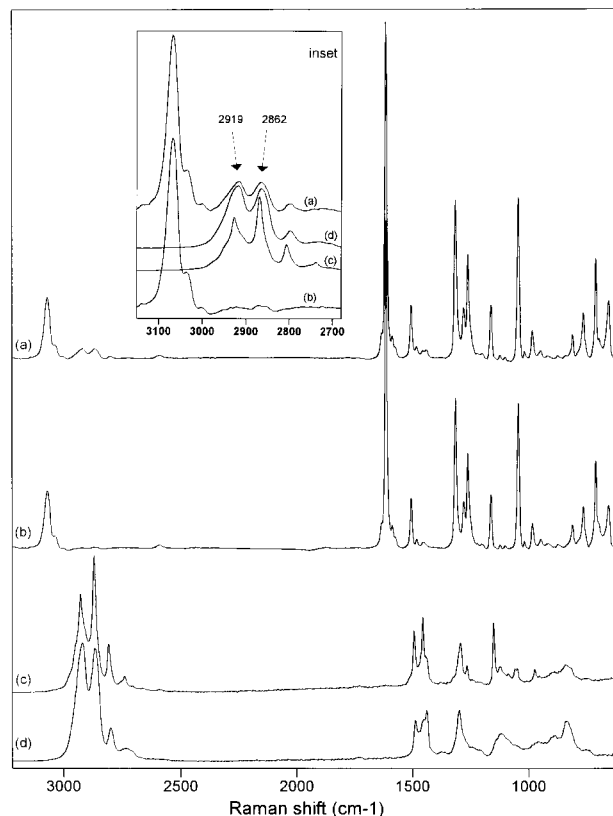
Figure 4 FT-Raman spectra of (a) **1**, (b) **2**, (c) **5** at room temperature, and (d) **5** at 70°C. Inset: comparison of aliphatic CH stretching region.

by the bands arising from the aromatic substituents. This is a general rule previously reported for Raman spectra of this type of material,[19] since the skeletal vibrations of the PN chain are very weak in comparison. The nature of the polyphosphazene in samples **1** and **2** appears to be identical in both the IR and Raman spectra. However, when we examine the nature of the aliphatic CH stretching zone of **1** in more detail (see inset), we observe that the band structures centred at around 2919 and 2862 cm^{-1} are more similar to the spectrum of molten PTHF than to the semicrystalline sample. It is evident that this spectral region is comprised of different conformational structures associated with the amorphous and crystalline phase, and although the degree of crystallinity in the PTHF sample at room temperature is relatively low since it is close to its melting range, the difference between the spectra of the molten and semicrystalline sample is considerable. This allows us to use a simple band ratio correlation, the ratio 2919/2862 cm^{-1}, which gives values of 0.71 for semicrystalline PTHF and

1.05 for the molten sample. The value of the ratio observed for **1** is 1.03, which implies that the PTHF present in **1** is mostly amorphous in nature. This result correlates with the absence of a melting transition for PTHF in the first heating cycle of the DSC data and with the complete absence of crystalline PTHF reflections in the X-ray diffractograms (Fig. 5). It is important to note that the ratio measured from the Raman spectra, recorded from a sample of **1** contained in a DSC pan after the thermal analysis described above, is between 0.70 and 0.79, which indicates an important increase in the crystallinity of PTHF after the thermal treatment, as observed in the DSC data [Fig. 2(c)].

Figure 5 shows the wide-angle X-ray diffractograms recorded at room temperature for **1**, **2**, and **5**. The diffractogram of pure PTHF shows two reflections at 2Θ = 19.2 and 23.8°, which correspond to the monoclinic crystal structure reported for this polymer.[17,20] Materials **1** and **2** show a reflection at 2Θ = 7.3° that corresponds to an
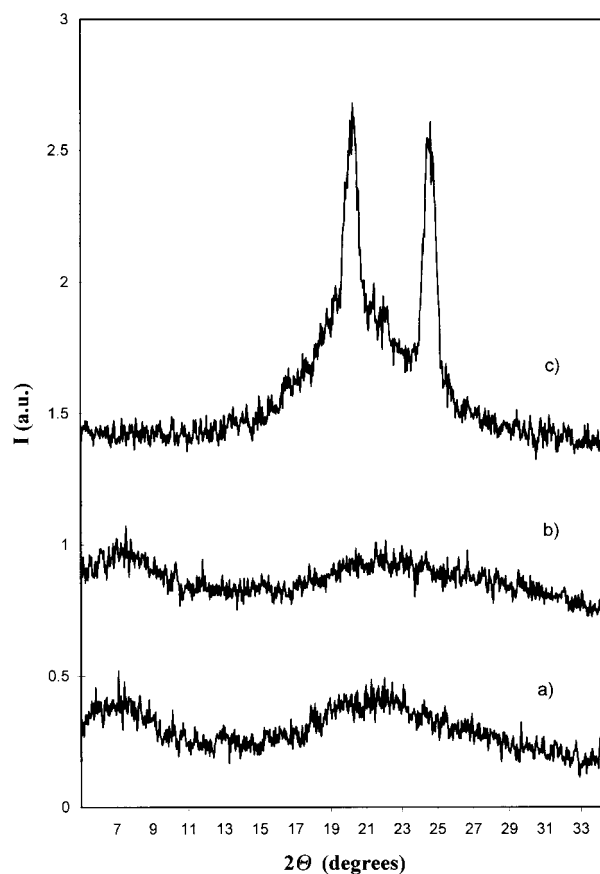
Figure 5 X-ray diffractograms of (a) **1**, (b) **2**, (c) **5**, at room temperature.
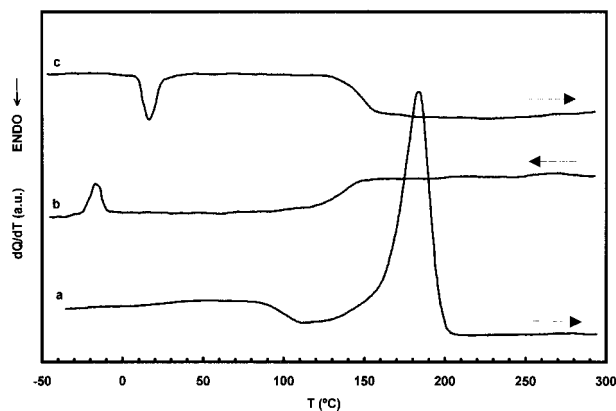
Figure 6 DSC thermograms for **4**. (a) First heating cycle, (b) cooling cycle, and (c) second heating cycle, as described in the text.

interplane distance of 12.1Å, attributed to the mesophase in other polyphosphazenes,[21–24] and a broad halo centred at $2\Theta = 22°$. The diffractograms of **1** and **2** appear identical, indicating the absence of crystalline PTHF in **1**, as previously mentioned.

It is important to reiterate here the large difference in the DSC data between the position of the glass transition temperature observed in the first heating cycle for **1**, which is considerably lower than that observed for **2**. This specific point will be discussed later; however, in an attempt to clarify these differences, the same analysis was applied to the physical blend **4**, described above.

In the first heating cycle [Fig. 6(a)] a variation in the specific heat is observed at around 98°C, which is similar to the case for **1** [cf. Fig. 2(a)]. However, in **4** a considerably larger exothermic transition at 183°C is observed. In the cooling cycle, the glass transition appears at 137°C, and a small exothermic transition is observed at around −17°C, corresponding to the crystallization of PTHF [Fig. 6(b)]. In the subsequent heating cycle, both the melting of PTHF at 17°C and the glass transition at 142°C can be clearly distinguished [Fig. 6(c)]. Comparison of the IR and Raman spectra of **1** and **4**, are essentially identical, showing only slight differences in intensity of the PTHF component, which are probably due to a small variation in the relative composition. In the same respect, the X-ray diffractograms of **1** and **4** are identical, with the corresponding absence in **4** of reflections due to crystalline PTHF.

From this evidence we can observe an important analogy between the nature of **1** and **4**. Given that the glass transition of the polyphosphazene

without PTHF, **2**, is located at 140°C, the lowering to 80°C can be associated with the existence of interactions between the chains of PTHF and **2**, considered as components of a miscible blend.[25] Under this premise, a reduction of 60°C in the value of T_g is approximately that corresponding with the expected value based on the Fox equation[26] for a blend with a concentration of around 10% ww in PTHF, considering a value of −84°C for the T_g of PTHF[27,28] in excellent agreement with the NMR data.

These interactions, generated by precipitation from solution prevent, on the one hand, the crystallization of PTHF, as is observed for other blended systems,[29] and on the other, the stabilization of the mesophase, as can be deduced from Figures 2(a–c). The fact that the T_g is displaced to around 150°C when the samples are cooled from the mesophase can be associated with the loss of these interactions, during heating. The nature of these specfic interactions is the subject of further spectroscopic investigation.

The dependence of the interactions on the preparative history of the material was amply demonstrated when the physical blend **4** was prepared by evaporating from methylene dichloride. In this case, as can be deduced from the thermogram in Figure 7, the interactions between **2** and **5** are weaker. The existence of the melting endotherm at 28°C indicates the crystallization of PTHF during the process of evaporation. On the other hand, the splitting of the T_g is clearly indicative of the existence of a segregated phase of **2**, with a T_g of 150°C and the existence of another phase, with a T_g of 116°C. The higher value of T_g in this second phase, compared with that of **4**, is expected since there is a lower PTHF content,
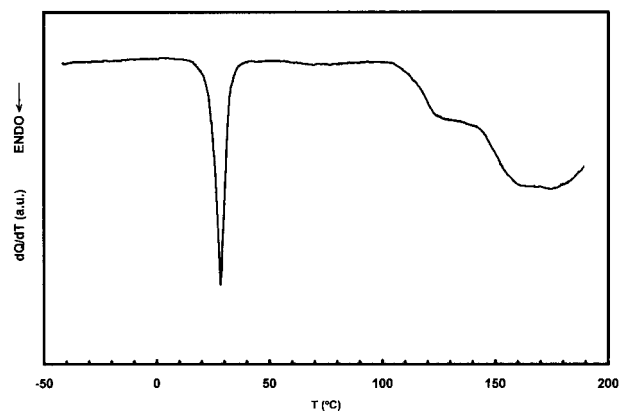
Figure 7 DSC thermogram for **4** evaporated from methylene dichloride solution; first heating cycle.

because of the crystalline segregation of PTHF and clearly confirms that miscibility exists between **2** and **5**.

CONCLUSIONS

The PTHF present in the poly-(2,2′-dioxybiphenyl)phosphazenes $[NP(O_2C_{12}H_8) \cdot x(OC_4H_8)]_n$ obtained in THF is mainly due to the presence of acidic residues in the starting $[NPCl_2]_n$ and can be avoided by neutralization with K_2CO_3 or by carrying out the reaction in dioxane.

However, the traces that always remain in the reactions in THF suggest that the $[NPCl_2]_n$ may carry a few cationic ends able to catalyze the ring opening polymerization of THF.

The PTHF is present in (**1**) as a component of a blend. The nature of the interactions between PTHF and the polyphosphazene in this material and in blends of similar composition is strongly conditioned by the preparative history of the products. The significant depression of the glass transition temperature in the precipitated samples rules out the possibility that **1** is a polyphosphazene/PTHF block copolymer. Furthermore, the existence of the crystalline phase in PTHF is indicative of phase separation, which contrasts with the absence of crystalline transitions when the system consists of a single miscible phase.

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