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THERMAL BEHAVIOUR AND STRUCTURE OF CYANOPHENOXY COPOLYMERS OF POLY(BIS-PHENOXYPHOSPHAZENE)

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Abstract—The effect of an increasing amount of cyanophenoxy groups on the thermal behaviour and structure of poly(bis-phenoxyphosphazene) was studied by differential scanning calorimetry, X-ray diffraction and thermo-optical analysis. The thermotropic behaviour was preserved in the copolymers, but the crystallinity and the crystal–liquid crystal transition temperatures were considerably lowered as the content in cyano groups increased. Polymorphic forms existed in the copolymer with 6% of cyano groups, as was the case in poly(bis-phenoxyphosphazene). The obtained mesophases had the same structure as that observed in the homopolymer. The kinetics of crystallization from the mesophase were analysed and Avrami exponents of $n = 3$ and 4 have been found. The temperature at which the mesophase is held prior to crystallization was found to have an important influence on the crystallization process. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Polyphosphazenes are of interest among the inorganic polymers because of the broad spectrum of properties that can be attained depending on the substituents attached to the main chain. A large number of chemical structures, and studies concerning the understanding of their solid-state properties, have appeared in the literature during the last few years [1–6].

Poly(aryloxyphosphazenes) are usually semicrystalline polymers that exhibit a thermotropic transition from the crystal to mesophase denoted as $T(1)$, prior to reaching the isotropic melt, T_i. It has also been reported [7, 8] that some of these polyphosphazenes have multiple crystalline forms depending on the crystallization conditions. Extensive structural and morphological investigations [7, 9–11] have been carried out on poly(bis-phenoxyphosphazene), PBPP, in order to understand the formation of several crystalline forms with different thermal histories. It has been observed [7] that the α-monoclinic form is obtained from solution, and when it is heated above the $T(1)$ transition, and then cooled to room temperature, it undergoes a change to an orthorhombic γ-form from the mesophase which exists above $T(1)$.

The effect of different types of substituents in poly(bis-phenoxyphosphazene) has also been studied [8, 12–16]. The size and polarity of these substituents have been found to have a significant influence on the thermal transitions as well as on the mesophase formation of these polymers. Most of the physical properties could be related to the location of the thermotropic transition, which can be expressed as a linear function of the substituent size. Some of these polyphosphazenes also exhibited polymorphic forms depending on the thermal history.

In this work, we report on the effect of the introduction of different amounts of cyano groups in poly(bis-phenoxyphosphazene) and how this will affect the formation of polymorphs and the thermotropic behaviour. A characterization of the phase transitions of the random copolymers was carried out by differential scanning calorimetry (DSC), X-ray diffraction, optical microscopy, and thermo-optical analysis, and the results compared with those reported for the homopolymer. The kinetics of crystallization from the mesophase were analysed for the copolymers. The synthesis of a random copolymer with cyano groups, $[NP(OC_6H_5)_{1.33}(OC_6H_5CN_{0.66}]_n$, has been described in the literature [17], although its properties were not reported.

EXPERIMENTAL PROCEDURES

Synthesis and characterization

The reactions were carried out under nitrogen. Infrared (IR) spectra were recorded with a Perkin-Elmer FT 1720-X spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AC-200 and AC-300 instruments. ^1H and ^{13}C-NMR are given in δ relative to TMS. ^{31}P-NMR are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hz. C, H, N analysis was performed with a Perkin-Elmer 240 microanalyser. P and Cl analyses were performed by Gailbraith Laboratories. Gel permeation chromatography (GPC) was measured with a Perkin-Elmer equipment with a Model LC 250 pump, a Model LC 290 UV, and a Model LC 30 refractive index

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detector. The samples were eluted with a 0.1 wt% solution of tetra-*n*-butylammonium bromide in THF through Perkin-Elmer PLGel (Guard, Mixed Bed 10^4, 10^3 A) at 30°C. Approximate molecular weight calibration was obtained using narrow molecular weight distribution polystyrene standards.

Petroleum ether refers to that fraction distilling in the range 60–65°C. Phenol was purified by distillation in a vacuum followed by dissolution in CH_2Cl_2, filtering through Na_2Co_3 and evaporation *in vacuo*. The other phenols were used as purchased or recrystallized from CH_2Cl_2/petroleum ether. The hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Strem Chemicals) was purified from hot petroleum ether and dried *in vacuo*.

Polydichlorophosphazene was prepared by thermal polymerization of $[N_3P_3Cl_6]$ in solution [18].

Preparation of $[NP(OC_6H_5)_{1.72}(OC_6H_4\text{–}CN)_{0.28}]_n$, *PBPPCN-28*

To a solution of $[NPCl_2]_n$ (5.27 g, 45.5 mmol) in THF (400 ml), HOC_6H_5 (9.41 g, 100 mmol) and K_2CO_3 (27.6 g, 200 mmol) were added, and the mixture was refluxed with vigorous magnetic stirring for 465 hr. More phenol (1.5 g, 16 mmol) and K_2CO_3 (4.45 g, 32.2 mmol) were added, and the refluxing was continued for 150 hr. Another addition of phenol and potassium carbonate in the same amounts, 175 hr at reflux gave a solution of $[NP(OC_6H_5)_{1.69}(Cl)_{0.31}]_n$. To this, HOC_6H_4–CN (5.5 g, 4.6 mmol) and more K_2CO_3 (6.35 g, 46 mmol) were added, and the refluxing was maintained until the signals at −16 ppm in the ^{31}P-NMR spectrum of the solution were no longer observed (*ca.* 275 hr), plus another 50 hr to ensure total substitution.

The mixture was poured into water (1.5 l), and the precipitate was redissolved in THF, concentrated under reduced pressure, and reprecipitated into water (1.5 l). The product was reprecipitated once into isopropanol, and once into petroleum ether. The resulting material was dried first under vacuum at room temperature, and then at 1 mbar at 70°C for 6 days, to give the polymer PBPPCN-28 as a white solid. Yield: 6.1 g, 56.3%.

The ratio of OC_6H_5 and OC_6H_4–CN groups was confirmed by ^{13}C-NMR. The molecular weight (M_w) (GPC) = 800,000 ($M_w/M_n = 1.8$).

^{1}H-NMR: δ 6.8 (m 24 H, aromatic rings); ^{31}P-NMR: δ −20.7 (m, P(OPh)(OC_6H_4–CN)), −19.3 (m, $P(OPh)_2$); ^{13}C-NMR: δ 108 s, 121 s, 122 s, 125 s, 130 s, 134 s, 152 s, 155 s (aromatic rings). Analysis calculated for $C_{12.28}H_{9.72}O_2N_{1.28}P$: C, 61.9; H, 4.1; N, 7.5; found: C, 60.1, H, 4.0; N, 7.2. Chlorine content 0.24%.

Preparation of $[NP(OC_6H_5)_{1.94}(OC_6H_4\text{–}CN)_{0.06}]_n$, *PBPPCN*-6

This polymer was similarly prepared allowing the reaction of $[NPCl_2]_n$ with phenol to a degree of substitution of $[NP(OC_6H_5)_{1.9}(Cl)_{0.1}]_n$ (*ca.* 600 hr), adding the 4-cyanophenol with more K_2CO_3, and refluxing for *ca.* 100 hr. The work-up was the same and the yield was 58%. The ratio of OC_6H_5 and OC_6H_4–CN groups was confirmed by ^{13}C-NMR. The M_w (GPC) = 750,000 ($M_w/M_n = 1.7$).

^{1}H-NMR: δ 6.8 (m, aromatic rings); ^{31}P-NMR: δ −19.3; (THF/D_2O): δ −18.7 (s, $P(OPh_2)$; ^{13}C-NMR: δ 122 s, 123 sh, 124 s, 129 s, 134 s, 152 s, 152 sh (aromatic rings). Analysis calculated for $C_{12.06}H_{9.94}O_2N_{1.06}P$: C, 62.2; H, 4.3; N, 6.4; P, 13.3; found: C, 61.1; H, 4.3; N, 6.4; P, 14.0. Chlorine content 0.61%.

Physical properties

Thermogravimetric analysis (TGA) was performed on a Mettler TG50 using nitrogen as the purge gas. The thermal transitions were measured in a Mettler TA4000 differential scanning calorimeter with a DSC30 furnace and a TA72 software. The heating rate was 10°C min^{-1} and all cycles were from −150 to 200°C.

Crystallization kinetics studies were carried out from the mesophase in a Perkin-Elmer DSC7/Unix. The samples were cooled at 32°C min^{-1} until the desired crystallization temperature was reached, and the corresponding crystallization exotherms were scanned as a function of time. The partial areas corresponding to a given transformation percentage were determined on a PE 7700 computer with Perkin-Elmer DSC-7 kinetic software.

Wide-angle X-ray diffractograms were obtained using a Rigaku GeigerflexD/max diffractometer with a Rigaku RU-200 rotating anode generator and a high-temperature attachment. The diffractograms were recorded at 1° min^{-1} in the 2θ range between 2° and 35° using Ni filtered CuK$_\alpha$ radiation.

Microscopy studies and thermo-optical analysis were carried out using a Reichert Zetopan Pol polarizing microscope, equipped with a Mettler FP80 hot stage and a Nikon FX35A camera. Samples were observed between crossed polars and the transmitted intensity was measured simultaneously during the heating and cooling processes.

RESULTS AND DISCUSSION

The preparation of the random copolymers $[NP(OC_6H_5)_{2\text{-}x}(OC_6H_4\text{–}CN)_x]_n$, $x = 0.06$ (PBPPCN-6) and 0.28 (PBPPCN-28), from $[NPCl_2]$ obtained by the solution method [18], using directly the phenols and K_2CO_3 in THF [19] (see Experimental Procedures), gave lower molecular weights and, in particular, more narrow molecular weight distributions than those reported by poly(bis-phenoxyphosphazene) [7, 12] and other polyphosphazenes, which will affect considerably their properties.

The thermal stability of the cyano copolymers of PBPP was studied by thermogravimetry under dynamic conditions, using a heating rate of 10°C min^{-1} and nitrogen as the purge gas. Both polymers showed a small loss at 260–300°C and a very important loss (~50%) at 400°C, forming a residue that was stable up to 700–800°C (Fig. 1). The degradation of polyphosphazenes has been found [20, 21, 16] to consist of a variety of mechanisms such as main-chain scission and depolymerization to monomer or small cyclic oligomers, as well as side-chain cleavage–condensation reactions leading to networks, depending on the substituents attached to the main chain. In our case, the copolymers undergo main chain scission below 300°C, and above 300°C depolymerization to cyclic trimers, some producing crosslinking reactions that are responsible for the high-temperature residue.

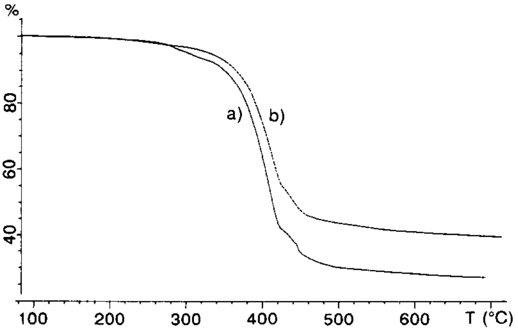

Fig. 1. Thermal stability of (a) PBPPCN-6; (b) PBPPCN-28. Heating rate 10°C min^{-1}.

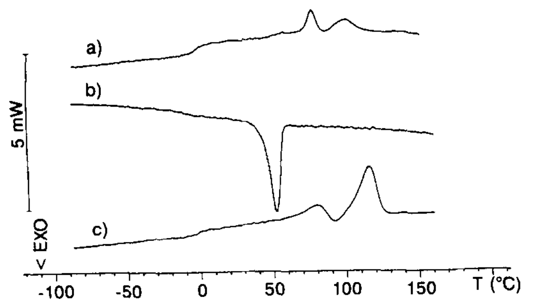

Fig. 2. DSC curves of PBPPCN-6: (a) sample as obtained from the synthesis, heated to 200°C at 10°C min^{-1}; (b) subsequent cooling cycle to room temperature; (c) sample reheated to 200°C.

The phase transitions of the copolymers were studied by DSC, TOA and X-ray diffraction, using several thermal treatments. Figure 2a shows the heating run of a sample precipitated from the synthesis of PBPPCN with 6% of cyanophenoxy groups, PBPPCN-6. It displayed a glass transition temperature at -2°C with a ΔC_p of 0.16 J g^{-1} °C^{-1}, an endotherm at 77°C with an enthalpy of 6.5 J g^{-1} and an endotherm at 100°C with an enthalpy of 5.5 J g^{-1}. In a subsequent cooling cycle (Fig. 2b), an exotherm at 53°C with an enthalpy of 19.8 J g^{-1} and a glass transition temperature at -9°C with a ΔC_p of 0.06 J g^{-1} °C^{-1} were observed. When the sample was heated again, a glass transition temperature at -5°C with a ΔC_p of 0.09 J g^{-1} °C^{-1}, an endotherm at 78°C with ΔH of 7.9 J g^{-1} and an endotherm at 116°C with an enthalpy of 15.6 J g^{-1} were observed (Fig. 2c).

Several polymorphic forms have been reported for poly(bis-phenoxyphosphazene) and a great deal of work has been done [7, 9–11] in order to understand the influence of the sample history on the phase transitions and structure changes of this polymer. It has been established that the monoclinic α-form can be obtained from solution, and the orthorhombic γ-form by rapid cooling from the mesophase. In a film cast from solution, the α-form transforms at 133°C to a pseudohexagonal δ-form, and in a sample containing both forms, the transition $\gamma \rightarrow \alpha$ takes place at 126°C and $\alpha \rightarrow \delta$ at 146°C [7].

The existence of two endotherms in our copolymer may be assigned to the existence of two crystalline forms as in PBPP. The endotherm at higher temperatures can be associated with the transformation of an α-monoclinic form to a mesomorphic state, and the one observed at lower temperatures to the transformation of the γ-form to the α. The two endotherms can also be assigned to the presence of different crystallite sizes which cause the process of melting and further recrystallization and melting. However, as the polydispersity is the lowest reported in polyphosphazenes, it seems more plausible that two crystalline forms exist.

In order to characterize these transitions further, samples with different preparative methods and thermal histories were studied. Figure 3b shows the heating run of a film of PBPPCN-6 cast from THF solution. An endotherm at 101°C with an enthalpy of 16.5 J g^{-1} was observed. This behaviour will corroborate the assignment of the high-temperature endotherm to the $\alpha \rightarrow \delta$ transition that is favoured when the sample is prepared from solution. When the sample PBPPCN-6 was heated to 200°C and quenched into liquid nitrogen, the thermogram obtained in a heating run corresponded to that shown in Fig. 3a. An endotherm at 76°C with an enthalpy of 7.3 J g^{-1} and a second endotherm at 115°C with an enthalpy of 20.4 J g^{-1} were observed. The existence of an endotherm at low temperatures will be consistent with the formation of the γ-form by rapid cooling from the mesophase reported in PBPP [7] and an increasing amount of mesophase.

Figure 4a shows the heating run of a sample of PBPPCN-28 obtained from the synthesis. It displayed a glass transition temperature at 6.5°C with a ΔC_p of 0.25 J g^{-1}°C^{-1}, and an endotherm at 45°C with an enthalpy of 3.2 J g^{-1}. In a cooling cycle (Fig. 4b), only a glass transition temperature at -5°C with ΔC_p of 0.25 J g^{-1}°C^{-1} was observed. When the sample was heated again up to 200°C, a glass transition temperature at 9°C with ΔC_p of 0.21 J g^{-1}°C^{-1}, an exotherm at 21°C with an enthalpy of 1.8 J g^{-1} and an endotherm at 42°C with an enthalpy of 2.3 J g^{-1} were observed (Fig. 4c). The increase in cyano groups makes the crystallization of the copolymer more difficult as is reflected in a higher T_g and ΔC_p. The crystallization takes place during the second heating cycle.

The transitions were also observed by thermo-optical analysis between room temperature and 300°C at a heating rate of 10°C min^{-1} for samples slowly cooled from 200°C to room temperature. Figure 5a

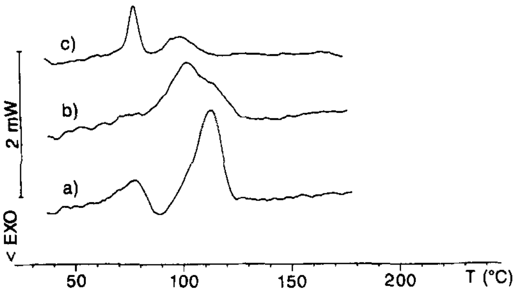

Fig. 3. DSC curves of PBPPCN-6: (a) sample quenched from 200°C into liquid nitrogen and heated at 10°C min^{-1}; (b) film cast from THF solution heated to 200°C at 10°C min^{-1}; (c) sample as obtained from the synthesis.

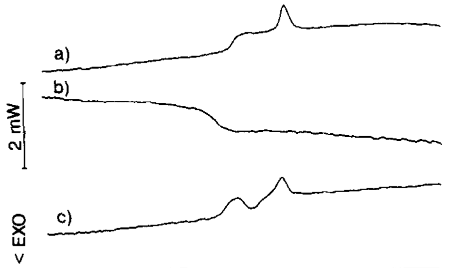

Fig. 4. DSC curves of PBPPCN-28: (a) sample as obtained from the synthesis heated at 10°C min^{-1}; (b) subsequent cooling cycle at room temperature; (c) sample reheated to 200°C.

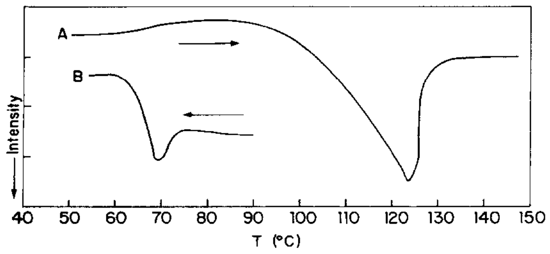

Fig. 5. Thermooptical analysis of PBPPCN: (a) heating; (b) cooling.

shows a gain in light intensity in PBPPCN-6 at 120°C with an important increase in birefringence typical of a transformation from the crystalline to the liquid crystalline state. This birefringence was maintained up to 300°C, when the sample started to degrade. When a new sample of PBPPCN-6 prepared in the same manner was cooled from 200°C at 10°C min^{-1}, a loss in light intensity was found at 69°C corresponding to the crystallization of the polymer (Fig. 5b). The copolymer PBPPCN-28 also showed thermotropic behaviour as observed by TOA, with a birefringence typical of a mesophase at 80°C that was maintained until degradation took place.

Figure 6 shows the wide-angle X-ray diffractograms of PBPPCN-6 at room temperature for samples with different histories. Although all the diffractograms were very poor and showed very little crystallinity, some differences could be observed. The sample cast from solution showed the higher crystallinity (Fig. 6b), and the one quenched from the mesophase (Fig. 6c) showed an intense peak in the low-angle region, indicating an increase in the amount of mesophase, compared with the one obtained from the synthesis (Fig. 6a).

Figure 7 (a–f) shows the X-ray diffractograms recorded at different temperatures, between room temperature and 180°C, for a sample of PBPPCN-6 obtained from the synthesis. At room temperature several weak reflections were observed in the high-angle region, indicating three-dimensional ordering. The reflections remained up to 120°C, where only a broad halo was observed. In the low-angle region, the broad peak observed became sharper, especially at 120°C when the crystal–liquid transition takes place, and remained up to 300°C. This reflection at $2\theta = 7.75°$ corresponds to an interplanar distance d $(100)_\delta$ of 11.4 Å assigned to the mesophase. This value is coincident with the one reported for PBPP [7].

Figure 8 shows the diffractogram at room temperature of a sample of PBPPCN-28 as obtained from the synthesis. As detected by DSC, the sample showed very little crystallinity, although a reflection at low angle was observed, indicating the existence of mesomorphic order.

The isothermal crystallization from the mesophase was studied in PBPPCN-6 in the crystallization temperature range 80–90°C, in which the rate of the process could be measured on a reasonable time scale by DSC. Two conditioning temperatures, T_a $[T(1) < T_a < T_i]$, temperature from which the undercooling was considered, were used: 140 and 170°C. In polyphosphazenes [15] and thermotropic polyesters [22, 23] a strong dependence has been observed of the rate of transformation on the conditions of the mesophase, in particular, the temperature at which the mesophase was held before crystallization.

The shape of the isothermal curves and their dependence on the crystallization temperature indicated that the transformation was similar to the crystallization of polymers from the melt, and involved a nucleation and growth mechanism.

The time taken to reach 50% of the total transformation was found to be very dependent on both the crystallization temperature, T_c, and the conditioning temperature, T_a. As shown in Fig. 9, $\tau_{0.5}$ increased exponentially with T_c, and at a given T_c increased with T_a being more pronounced at the lower undercoolings.

Analysis of the isotherms was carried out by the Avrami approximation [24]. Values of n were obtained from the slope of the double logarithmic plot of the degree of transformation versus time. Figure 10 shows an Avrami exponent $n = 3$ for PBPPCN-6 at

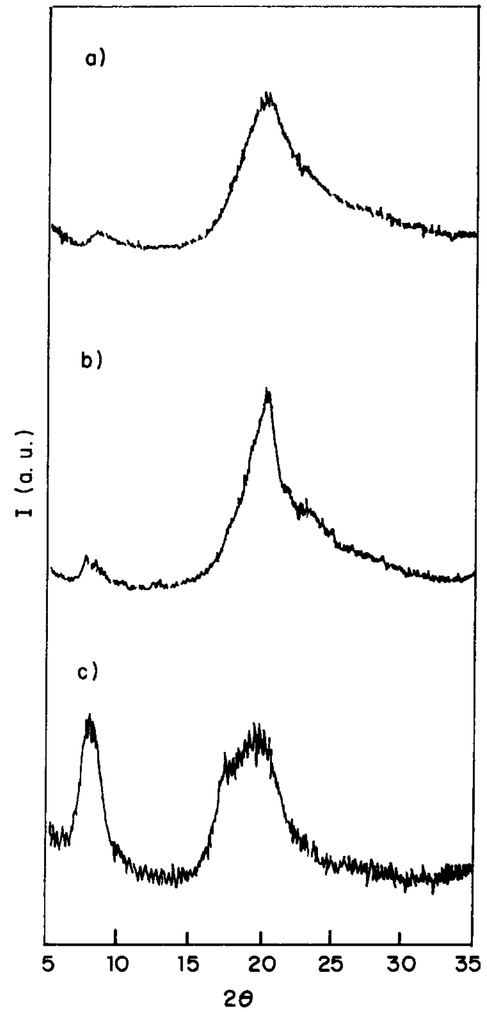

Fig. 6. X-ray diffractograms of PBPPCN-6: (a) sample as obtained from the synthesis; (b) sample cast from THF solution; (c) sample quenched from the mesophase.

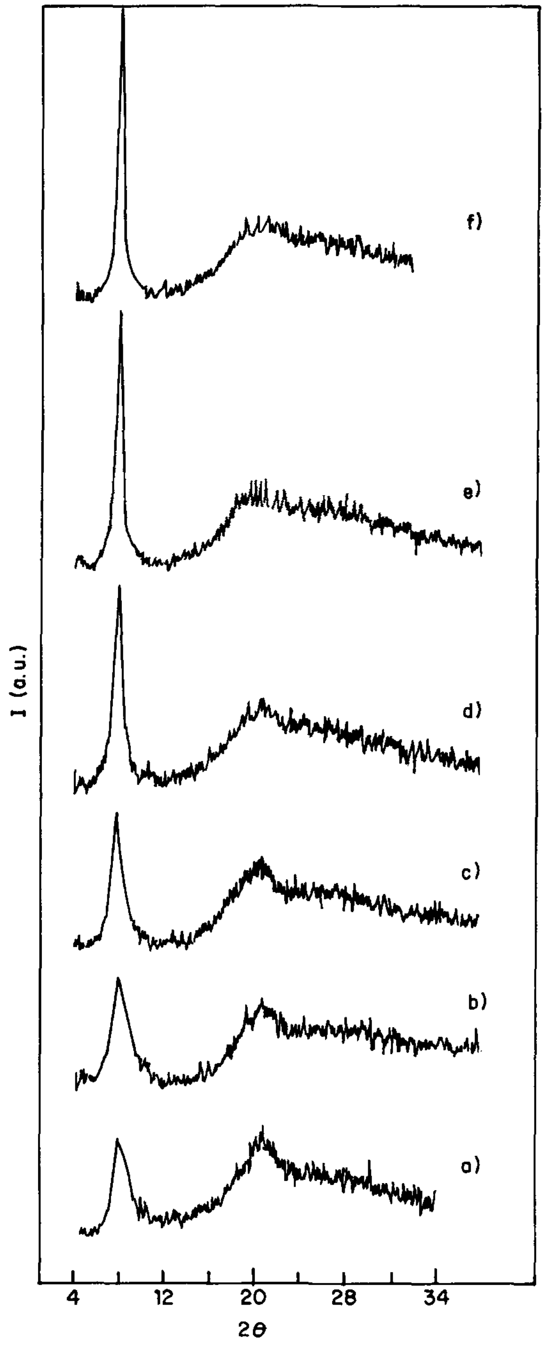

Fig. 7. X-ray diffractograms of PBPPCN-6 at different temperatures: (a) 25°C; (b) 70°C; (c) 90°C; (d) 110°C; (e) 130°C; (f) 160°C.

$T_a = 140°C$ and $n = 4$ at $T_a = 170°C$. The integral value $n = 3$ is related to homogeneous nucleation and two-dimensional growth, and $n = 4$ to three-dimensional growth [25]. The conversion of the mesophase into the crystalline state was studied for some polyphosphazenes by Magill and co-workers [26–29] using different experimental techniques. They found an Avrami exponent $n = 2$ for the mesophase–crystalline transformation [26–29]. In another study carried out by our group [15] in substituted poly (bis(4-R-phenoxy)phosphazenes), values of $n = 4$ and $n = 3$ were found.

Additionally, the crystallization temperature coefficient was analysed by incorporating the expression for the nucleation rate given by Turnbull and Fischer, for condensed systems and all types of nuclei [30], into the expression for the overall rate of crystallization for semicrystalline polymers [31]. This expression is given by the equation:

$$\ln\,(\tau_{0.5})^{-1} = \ln\,(\tau_{0.5})_0^{-1} - (K_n/R)\,(T(1)/\Delta T)^n/T_c \quad (1)$$

in which $\tau_{0.5}^0$ and K_n are constants, and ΔT is the undercooling given by $(T(1) - T_c)$. The exponent n depends on the mode of nucleation and growth and has a value of 2 for three-dimensional homogeneous nucleation [32] and 1 for coherent two-dimensional nucleation [32]. In the first case:

$$K_2 = 8\pi\sigma_u^2\sigma_e/\Delta H_{100}^2$$

and in the second case

$$K_1 = 4\sigma_e\sigma_u/\Delta H_{100}$$

in which σ_e is the interfacial free energy per sequence as it emerges from the basal plane and σ_u is the lateral free energy.

In our analysis, a value of $\Delta H_{100}(T(1)) = 35\ \mathrm{J\,g^{-1}}$ reported for PBPP [33] was used. From the slopes of the plot of $\ln(\tau_{0.5})^{-1}$ versus $(T(1)/\Delta T)^n/T_c$ values of $\sigma_e\sigma_u$ and $\sigma_e\sigma_u^2$ were obtained. These values are $\sigma_e\sigma_u = 1.9 \times 10^6\ (\mathrm{J\,mol^{-1}})^2$ for PBPPCN-6 ($T_a = 140°C$) and $\sigma_e\sigma_u^2 = 9.9 \times 10^7\ (\mathrm{J\,mol^{-1}})^3$ for PBPPCN-6 ($T_a = 170°C$). These values are similar to those reported for other poly(aryloxyphosphazenes) [15] and other thermotropic polyesters [22, 23].

In summary, the DSC, TOA and X-ray results confirmed the thermotropic behaviour of the copolymers, in spite of the introduction of cyano groups, and the enormous influence of the thermal history on the formation of the crystalline forms, as has been observed as a general feature in poly(oxyphosphazenes) [1].

The copolymer with 6% of cyano groups has the same T_g as PBPP, but the one with 28% of cyano has a T_g 10° higher, owing to the increase in dipole–dipole interactions with the increasing amount of CN. The existence of single T_g confirmed the random nature of the copolymers.

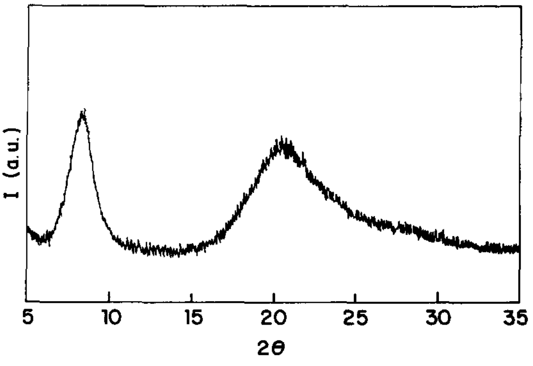

Fig. 8. X-ray diffractogram of PBPPCN-28 at room temperature.

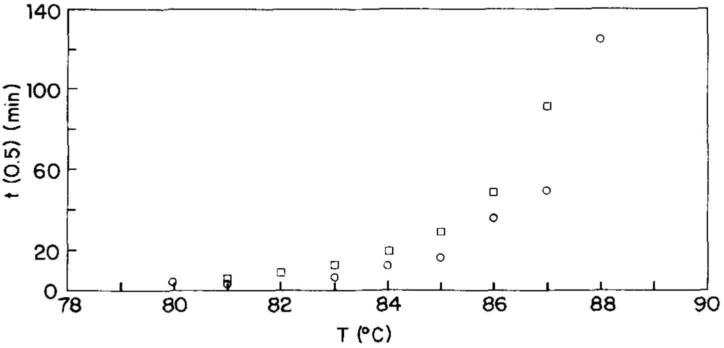

Fig. 9. Plot of $\tau_{0.5}$ against crystallization temperature for PBPPCN-6 at conditioning temperatures: (○) $T_a = 140°C$; (□) $T_a = 170°C$.

The crystal–liquid crystal transition temperature and the crystallinity are considerably lowered with the increase in cyano groups with respect to PBPP. However, the copolymer with 6% of CN presents polymorphic transformations prior to the formation of the smectic mesophase, as has been reported in PBPP, and successive heating cycles produced an increase in the $T(1)$ temperature (crystal–liquid crystal temperature), and in the enthalpy associated to it, as has also been observed in PBPP. The interplanar spacing of the smectic mesophase is the same as that reported for PBPP.

Both copolymers degraded before reaching the isotropic melt, as was the case for PBPP. However, it is possible to calculate the T_m for the copolymers using the equation proposed by Magill *et al.* [8]. The values obtained are 343°C for PBPPCN-6 and 290°C for PBPPCN-28.

Finally, the kinetics of formation of three-dimensional order from the mesophase were studied in the copolymers. The crystallization isotherms had similar behaviour to that found in the crystallization of homopolymers, and Avrami exponents of $n = 3$ and $n = 4$ were found. The rate of transformation was found to be influenced by the temperature at which the mesophase was held.

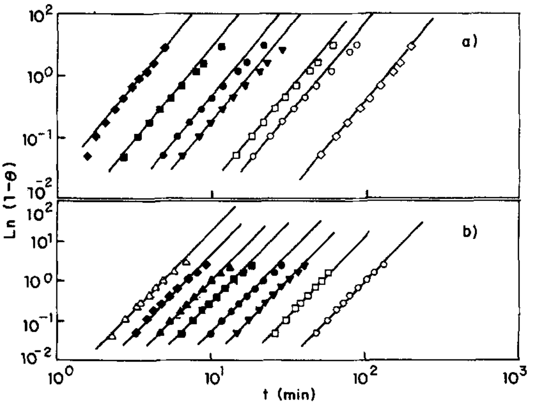

Fig. 10. Double logarithmic plot of $\ln(1-\theta)$ against time for PBPPCN-6: (a) from $T_a = 140°C$ at the indicated temperatures: T_c = (◆) 81°C; (■) 83°C; (●) 84°C; (▼) 85°C; (□) 86°C; (○) 87°C; (◇) 88°C; (b) from $T_a = 170°C$ at the indicated temperatures: T_c = (△) 80°C; (◆) 81°C; (▲) 82°C; (■) 83°C; (●) 84°C; (▼) 85°C; (□) 86°C; (○) 87°C.

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