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Reactions Occurring during the Melt Mixing of Nylon 6 and Oxazoline−Cyclophosphazene Units

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ABSTRACT: Specific reactions of amino and carboxyl end groups of Nylon 6 with the reactive oxazoline groups belonging to a cyclophosphazene compound (referred as CP2OXA) were carried out at 240 °C for different times, under inert atmosphere. Ny6 polymers terminated with one specific reactive chain end (−COOH or NH_2) were reacted with different amounts of CP2OXA to study the kinetic order of the reactions. All Ny6−CP2OXA reacted products soluble in trifluoroethanol (TFE) were well characterized by MALDI−TOF MS, FT-IR and (^{1}H and ^{13}C) NMR techniques. The MALDI−TOF results show that the oxazoline rings react with the carboxyl chain ends of Ny6 following second-order kinetics. The reactions with amino chain ends are very fast and high amounts of gels are produced in just 5 min heating, whereas traces of gel are formed when Ny6COOH and CP-2OXA are reacted for 60 min. The gels were characterized by FTIR analyses, and also by MALDI−TOF MS after partial acid hydrolysis. MALDI−TOF mass spectra reveal also that oxazoline rings can react with −NH amide groups along the Ny6 chains, and with secondary amino groups formed by a condensation reaction involving the elimination of ammonia from two amino chain ends. These side reactions could be responsible of the formation of the gels. The polymerization of CP2OXA was also observed, and the oligomers formed could also react with Ny6 samples during the melt mixing.

1. Introduction

The reaction in the molten state between coupling agents or chain extenders with hydroxyl (HO), carboxyl (COOH), or amine (NH_2) terminated polymers is an important and attractive route for the synthesis of functionalized polymers, high molar mass polymers and copolymers. In particular, copolymers produced in *situ* during the melt processing of incompatible polymer blends often act as compatibilizers, leading to a system with a significantly improved compatibility and morphology. Generally, compatibilized polymer blends show better mechanical properties than the initial incompatible blends. Several low molar mass mono- or multifunctional compounds such as oxazolines,[1−11] oxazines,[5] imidazolines,[12] oxazolinones,[13,14] isocyanates,[9,15] epoxy,[9] and cyclic anhydrides[9] have been used as chain extenders or as coupling agents to favor the formation of copolymers. Over the past decade, the utilization of cyclophosphazenes (CPs) as polymer modifiers has attracted considerable attention, with a particular interest toward their exploitation as versatile chain extenders possibly for recycle issues, cross-linkers, to enhance mechanical properties of polymeric materials, to introduce specific branching in linear polymers, and also as compatibilizers to favor the formation of compatible blends between originally incompatible organic polymers. CPs find applications in several fields such as biomaterials,[16,17] photochemistry,[18−23] sol−gel precursors,[24,25] cores for dendrimers or star polymers,[27−31] preparation of linear organic macromolecules with CP moieties,[32] fire retardant additives.[33] CPs substituted with azide or 2-oxazoline groups have been used in the selective cross-linking of polyolefins and in the chain extension of poly(ethylene terephthalate) (PET) and PA6.[34−39] Recently, cyclophosphazene (CP) compounds having two reactive epoxy groups (CP2EPOX) have been used in the preparation of compatibilized poly(butylene terephthalate)/polyamide blends.[40,41] The authors observed the formation of Ny6-PBT block copolymers with the blocks linked by cyclophosphazene units, and suggested that these should act as compatibilizers of the initial biphasic blends improving their morphology and mechanical properties, especially the impact resistance.[41] The authors of the present paper, in another preliminary and unpublished study have also observed the formation of Ny6-PBT block copolymers in the Ny6/PBT (50/50 w/w) melt blended in a glass reactor at 240 °C for 5 min, under nitrogen flow, in the presence of a cyclophosphazene having two oxazoline groups (CP2OXA). Therefore, we believe that epoxy and oxazoline groups of the CP compound may react with both amino and carboxyl end groups of the Ny6 chains and also with aromatic carboxyl end groups of the PBT polymer. The reactivity in the molten state (240 °C) of CP2EPOX and CP2OXA compounds toward carboxyl and amine Ny6 end chains was previously investigated by calorimetric and rheological measurements.[38,39] In these works the authors have observed that the molecular weight of a Ny6 sample slightly increases by adding CP compounds,[38−40] and assumed that both −COOH and NH_2 end groups of Ny6 chains react with the specific functions of the CP compounds. However, reliable information about the mechanism of the reactions that occur between CP compounds and Ny6 can not be unequivocally inferred by these methods. Therefore, we have decided to perform the reaction of CP2OXA with Nylon 6 specifically terminated with $-NH_2$

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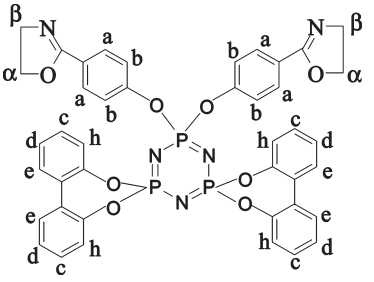


Figure 1. Chemical structure of CP2OXA and proton assignments.

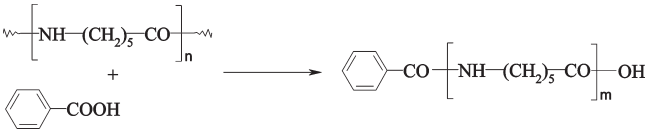
or −COOH groups, to highlight the specific reactivity of these typical Ny6 end groups with oxazoline reactive groups of the CP samples. The reactions were performed homogeneously by blending different Ny6/CP molar ratios (2:1, 1:1, and 1:2 with respect to the Ny6 end group concentrations), in a glass reactor at 240 °C for different times under stirring and nitrogen flow. The reaction products were characterized by MALDI−TOF mass spectrometry, ^{1}H and ^{13}C NMR, and FT-IR techniques. The reactions were also monitored by end group titrations, UV analysis, SEC, and viscosity measurements.

2. Experimental Section

2.1. Materials. Aldrich Chemical Co. (Italy) supplied the high molar mass analytical-grade Ny6 commercial samples, reagents and solvents used. The reagents were purified before use. The MALDI matrices 2-(4-hydroxyphenylazo)benzoic acid (HABA) and 1,8-dihydroxy-10*H*-anthracen-9-one (dithranol) were analytical-grade materials (Sigma Aldrich Chemical Co.), used as supplied. The 2,2-bis(4-oxazolinophenoxy)-4,4,6,6-bis-[spiro(2,2′-dioxy-1,1′-biphenyl)]cyclophosphazene (CP2OXA) used in this work was prepared by functionalization of the commercially available hexachlorocyclotriphosphazene (6Cl-CP) (Aldrich). Details on the preparation and characterization of CP2OXA were reported elsewhere,[24−26] and its chemical formula is depicted in Figure 1. Its structure and chemical composition was here studied by (^{1}H, ^{13}C and ^{31}P)-NMR, MALDI−TOF MS and FT-IR analyses. ^{1}H, ^{13}C, and ^{31}P NMR spectra of CP2OXA, previously dried under vacuum at 60 °C overnight, are reported in Figures 1SA, 2SA, and 3SA, respectively. The ^{1}H NMR spectrum reveals the presence of about 2% mol of hydrolyzed CP2OXA formed by hydrolysis of one oxazoline ring during the synthesis. In fact the ^{1}H NMR spectrum, beside the expected triplet at 4.87 ppm and 4.02 ppm due to the methylene protons (−CH_2−) of the oxazoline ring, shows another two triplet signals at 3.78 ppm and 1.88 ppm that were assigned to the methylene in α and in *β* to the hydroxyl (−OH) of the *N*-hydroxyethyl-oxamide group (−CO−NH−CH_2−CH_2−OH) of hydrolyzed CP2OXA (see assignment reported in Figure 1SA). The presence of hydrolyzed CP2OXA molecules was also confirmed by MALDI−TOF mass spectrum (Figures 4SA). It shows one intense peak at 849.5 Da due to the sodiated ions of the CP2OXA molecules, and also a less intense peak at 867.6 Da corresponding to the sodiated ions of the hydrolyzed molecules.

2.2. Polymer Syntheses. *a. Carboxy-Terminated Ny6.* Ny6 with one carboxylic acid end group per chain (Ny6COOH) was prepared by acidolysis at 240 °C (Scheme 1) of high molar mass (MM) Ny6 (MM = 45 000 Da) with benzoic acid (BA), using a Ny6/BA molar ratio 1:0.2 (calculated with respect to the Ny6 repeat units) in diphenyl sulfone (DPSO) under inert atmosphere. Typically, 10.00 g (90 mmol) of Ny6 and 10.00 g of DPSO were placed in a three-necked flask, with a mechanical stirrer, under nitrogen flow. When the temperature was raised to 240 °C, 2.20 g (29 mmol) of benzoic acid was added to the liquid reaction mixture, and the reaction was carried out for 15 min. DPSO was extracted by refluxing with acetone overnight. The

Scheme 1



solid residue was filtered and dried at 60 °C in a vacuum oven for 24 h.

b. Monoamino Ended Ny6. Ny6 with one amino end group per chain, namely $Ny6NH_2$ (polymer 2, Table 1), and a MM of about 5800 Da, was prepared by partial aminolysis of high MM Ny6 with decylamine (Scheme 2), in a molar ratio 1:0.2 at 240 °C, under N_2 flow and in the presence of DPSO. The reaction was carried out for 10 min; then the DPSO was extracted with acetone under reflux for 12 h. The solid residue was filtered and dried at 60 °C in a vacuum oven for 24 h before use.

c. Bulk Reaction between Ny6COOH and CP2OXA Samples. The reaction between Ny6COOH and CP2OXA samples was carried out in a glass reactor having a magnetic stirrer, at 240 °C for different times, 2, 5, 15, 30, and 60 min, under anhydrous nitrogen flow (100 mL/min). The initial compounds have been carefully dried prior to processing in order to avoid hydrolytic scission during the reactions in the molten state. In order to follow the kinetics of this reaction, different amounts of CP2OXA were used. These amounts were calculated in order to obtain a COOH/CP2OXA molar ratio of about 2:1, 1:1, and 1:2. The reacted mixtures were treated with $CHCl_3$ to eliminate unreacted CP2OXA, and then with trifluoroethanol (TFE) to verify the formation of insoluble components. Only the mixtures reacted for 60 min gave small amounts of insoluble fractions, as it can be observed in Table 1. The same results were obtained using other typical solvents for Ny6 polymer such as hexafluoroisopropanol (HFIP), formic acid (HCOOH), trifluoroacetic acid (CF_3COOH, TFA) and $CHCl_3$/TFA 70/30 v/v. We have indicated the insoluble fractions as Ny6COOH−CP2OXA gels, and their percentages were reported in Table 1. All soluble fractions were characterized by MALDI−TOF MS, ^{1}H and ^{13}C NMR, FT-IR, SEC, and UV−visible techniques, whereas the gels were analyzed by FT-IR.

In a typical procedure, 100 mg of Ny6COOH was mixed for 5 min at 240 °C with 15.70 mg of CP2OXA in order obtain a COOH/CP2OXA molar ratio of 1:1. The mixture was then cooled and treated with $CHCl_3$ at room temperature for 2 h, filtered, and treated with TFE at 25 °C for 4 h. After that it was filtered and dried at 60 °C for 24 h under vacuum.

d. Bulk Reaction between Ny6NH$_2$ and CP2OXA Samples. The reactions between $Ny6NH_2$ and CP2OXA were carried out in a glass reactor having a magnetic stirrer, at 240 °C for 2, 5 10, and 15 min, using the same procedure described before, using NH_2/CP2OXA molar ratios of 2:1 and 1:1. In this case, the bulk reactions had a shorter duration than Ny6COOH−CP2OXA systems, since 97−98% gel was obtained after 5 min heating for both mixtures, as reported in Table 1.

e. Partial Hydrolysis of Ny6NH$_2$−CP2OXA Gels. All $Ny6NH_2$−CP2OXA gels were partially hydrolyzed by treatment with a mixture of H_2O/HCOOH/$ClSO_3H$ (40/30/30 v/v) at reflux for 2 h, under N_2 flow. The mixtures were precipitated with a large excess of water and the insoluble residues were recovered by centrifugation, and then washed several times with water until neutrality. The recovered hydrolyzed residues were dried at 50 °C under vacuum for 24 h, dissolved in HFIP (5 mg/mL) and then characterized by MALDI−TOF MS analysis

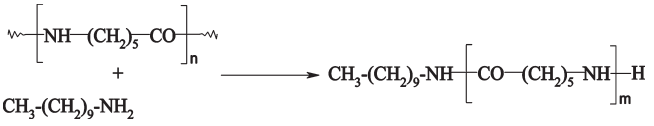
2.3. Analyses. *a. NMR Analysis.* The ^{1}H and ^{13}C NMR analyses were performed by a Bruker A-CF200 spectrometer (operating at 200 MHz for ^{1}H and at 50 MHz for ^{13}C) at room temperature, using deuterated solvent and tetramethylsilane (TMS) as an internal standard. A solvent mixture of $CDCl_3$/$(CF_3CO)_2O$ (80:20 v/v) was used to analyze the PA6

Table 1. Some Properties of the Materials Studied

sample	material	reaction time (min)	η_{inh}	M_v[a]	gel (%)	[COOH] (mmol/kg)	[NH_2] (mmol/kg)	T_g[b]	T_m[b]
1	Ny6COOH		0.25	7700		190	2.5	56	218
2	Ny6NH_2		0.265	8400		15.1	175	57	216
			Ny6COOH/CP2OXA reacted at 240 °C						
3	Ny6COOH/CP2OXA (2:1)	2	0.26	8000	–	55	–	57	217
4	Ny6COOH/CP2OXA (2:1)	5	0.27	8600	–	35	–	56	217
5	Ny6COOH/CP2OXA (2:1)	15	0.29	9450	–	12	–	58	216
6	Ny6COOH/CP2OXA (2:1)	30	0.33	11200	–	n.d.	–	58	215
7	Ny6COOH/CP2OXA (2:1)	60	0.41	14960	2	–	–	59[c]	216[c]
8	Ny6COOH/CP2OXA (1:1)	2	0.28	9000	–	31	–	57	217
9	Ny6COOH/CP2OXA (1:1)	5	0.30	9900	–	15	–	57	216
10	Ny6COOH/CP2OXA (1:1)	15	0.36	12600	–	6	–	59	217
11	Ny6COOH/CP2OXA (1:1)	30	0.39	14000	–	n.d.	–	59	216
12	Ny6COOH/CP2OXA (1:1)	60	0.44	16450	8	–	–	59[c]	215[c]
13	Ny6COOH/CP2OXA (1:2)	2	0.29	9450	–	21	–	56	218
14	Ny6COOH/CP2OXA (1:2)	5	0.31	10300	–	5	–	57	216
15	Ny6COOH/CP2OXA (1:2)	15	0.39	14000	–	n.d.	–	57	216
16	Ny6COOH/CP2OXA (1:2)	30	0.41	14960	–	–	–	59	215
17	Ny6COOH/CP2OXA (1:2)	60	0.46	17450	18	–	–	59[c]	214[c]
			Ny6NH_2/CP2OXA reacted at 240 °C						
18	Ny6NH_2/CP2OXA (2:1)	2			15	–	–	58[d]	–
19	Ny6NH_2/CP2OXA (2:1)	5			90	–	–	58[d]	–
20	Ny6NH_2/CP2OXA (2:1)	10			97	–	–	60[d]	–
21	Ny6NH_2/CP2OXA (2:1)	15			98	–	–	59[d]	–
22	Ny6NH_2/CP2OXA (1:1)	2			28	–	–	57[d]	–
23	Ny6NH_2/CP2OXA (1:1)	5			97	–	–	58[d]	–
24	Ny6NH_2/CP2OXA (1:1)	10			97	–	–	58[d]	–
25	Ny6NH_2/CP2OXA (1:1)	15			99	–	–	59[d]	–

[a] Determined by viscosity method using the Mark–Houwink equation: $[\eta] = KM_v^a$ with $K = 30.3 \times 10^{-3}$ mL/g and $a = 0.75$. [b] T_g is the glass transition temperature; T_m is the melting temperature, ΔH_m is the enthalpy of melting; [c] Determined on the TFE soluble fraction. [d] Determined on the gel.

Scheme 2



samples and all Ny6/CP2OXA reacted products. $CDCl_3$ was used to analyze the CP2OXA compound. ^{13}C NMR spectra were recorded using the following acquisition parameters: sweep width, 11111 Hz; 32 000 data points, giving a digital resolution of 0.42 Hz per point and an acquisition time of 1.5 s. A pulse width of 4 μs and delay of 3 s were used for about 15 000 accumulations.

^{31}P NMR spectra have been recorded in solution of $CDCl_3$ (sample concentration of about 30 mg/mL) at 25 °C by a Varian-Inova instrument operating at 200 MHz using H_3PO_4 (85%) as external reference. All ^{13}C and ^{31}P NMR spectra have been recorded decoupling from the proton. All the chemical shifts are reported in ppm with respect to the used reference. The data were elaborated with 1D Win-NMR software applying the Lorentz–Gauss enhance function using appropriate Line broadening and Gaussian broadening parameters in order to improve the peaks resolution.

b. MALDI–TOF Mass Spectrometry. MALDI–TOF mass spectra were recorded both in linear mode and in reflectron mode, using a Voyager-DE STR (Perseptive Biosystem) mass spectrometer instrument, equipped with a nitrogen laser emitting at 337 nm, with a 3 ns pulse width, and working in positive ion mode. The accelerating voltage was 25 kV, the grid voltage and delay time (delayed extraction, time lag), were optimized for each sample to achieve the higher mass resolution, expressed as the molar mass of a given ion divided by the full width at half-maximum (fwhm). The laser irradiance was maintained slightly above the threshold. 2-(4-hydroxylphenylazo)-benzoic acid (HABA) 0.1 M in hexafluoro-2-propanol (HFIP) solvent, was used as matrix. The concentration of tailored Ny6 polymers and Ny6–CP2OXA bulk reacted products was 5–6 mg/mL in HFIP. Here, 10 μL of polymer solution was mixed with 10 or 30 μL of HABA solution. Then 1 μL of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallization. The MALDI–TOF MS analyses of the CP2OXA samples were performed using Dithranol as a matrix with a concentration 0.1 M in THF. In this case 2–3 mg of CP2OXA were dissolved in $CHCl_3$ and 10 μL of the solution were then mixed with 30 μL of the Dithranol solution. The best MALDI spectra reported here were recorded in reflectron mode, and present a mass resolution of 3000–4000 fwhm. The accuracy of mass determination was about 120 ppm in the mass range 1000–2300 Da and 190 ppm in the mass range 2300–3200 Da.

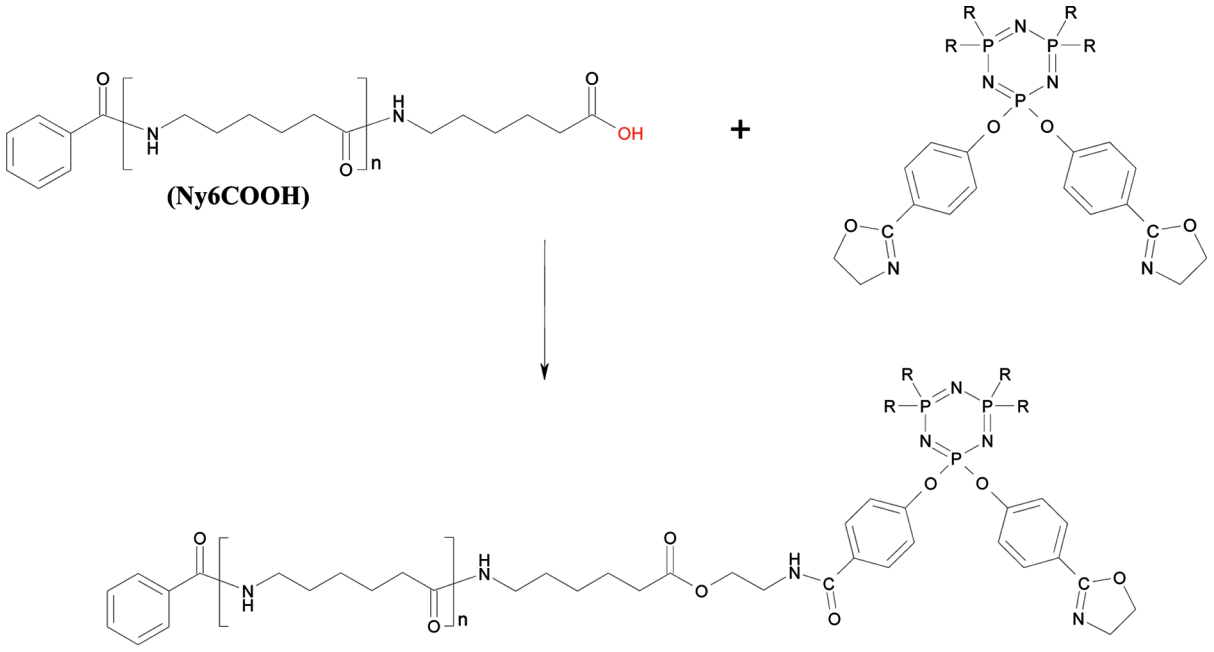
c. FT-IR. FT-IR spectra of all samples were recorded on a Perkin-Elmer Instruments, Spectrum One FT-IR Spectrometer. KBr pellets with a sample concentration of 0.5% w/w were prepared by a mechanical press operating at 10 atm.

d. Viscosimetry. The inherent viscosity ($\eta_{inh} = \ln\eta_{rel}/C$; $C = 0.5$ g/dl) of each soluble sample was determined by viscosimetry using a Ubbelohde suspended-level viscometer at 30 °C, in trifluoroethanol (TFE) solvent. The M_v values reported in Table 1 were calculated using the published Mark–Houwink coefficients for Ny6 in TFE: $K = 30.3 \times 10^{-3}$ mL/g and $a = 0.75$,[42] using the equation $[\eta] = KM_v^a$, and assuming that for Ny6–CP2OXA reacted products that the K and a values do not change.

e. UV. UV–visible spectra were recorded on a Shimadzu Model 1601 spectrophotometer, using a solution of polymeric materials in freshly distilled and anhydrous TFE (1 mg/mL).

f. SEC. SEC analyses were performed on a Waters 515 apparatus, equipped with four Ultrastyragel HR columns (7.8–300 mm) (in the order HR-4, HR-3, HR-2 and HR-1) connected in series, and a Waters R401 differential refractometer. The SEC curves were recorded and processed using a

Scheme 3. End Functionalization



PC Caliber software provided by Polymer Laboratories. In a typical analysis, 100 μL of analyte in $CHCl_3$ solutions (10 mg/mL) were injected and eluted at a flow rate of 1 mL/min using $CHCl_3$ as eluent and *o*-dichlorobenzene (1 μL) as flow marker. Ny6 samples and the Ny6−CP2OXA reacted products soluble in TFE, were first trifluorocetylated by reaction with $(CF_3CO)_2O$ in $CHCl_3$ to dissolve in this solvent. Generally 10 mg of each sample was treated with a mixture of $CHCl_3/(CF_3CO)_2O$ 80/20 v/v for 15 min at room temperature, then the solvent and the excess of $(CF_3CO)_2O$ were removed by rotavapor. Each residues was dissolved in the $CHCl_3$ used as eluent and then analyzed by SEC.

2.4. DSC (Differential Scanning Calorimetry). The thermal properties of monomer and polymer samples synthesized were determined by a Mettler DSC 20 calorimeter coupled with a Mettler TC 10A processor as control and evaluation unit. Both heat flow and temperature calibrations of calorimeter were performed following the procedures suggested by the supplier and reported in the operating instructions of the equipment. The reported T_g values were taken at the midpoint of the glass transition in all DSC thermograms. Samples of about 6−7 mg, held in sealed aluminum crucibles, the scanning rate of 10 °C·min^{-1} and an inert atmosphere due to N_2 flow (60 mL/min) were used for determinations. Pertinent data were reported in Table 1

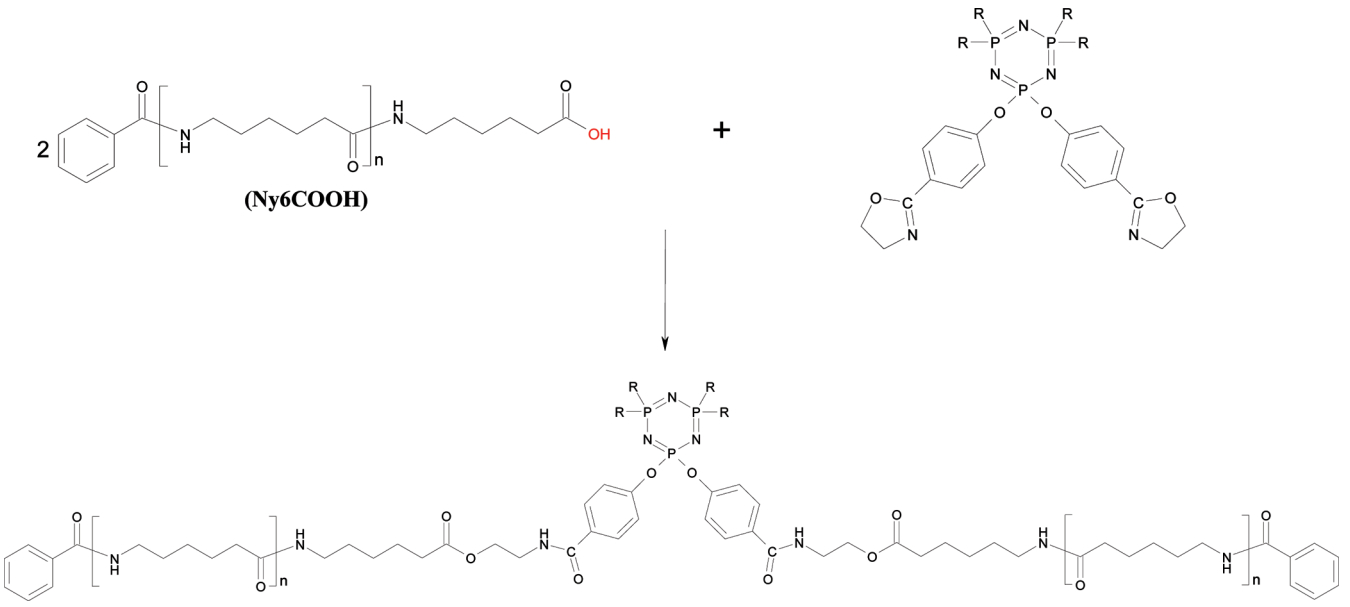
a. Detection of Amino and Carboxylic End Groups. The amount of amino and carboxylic end groups in Ny6 samples and in the Ny6COOH/CP2OXA reacted samples was determined as described in literature.[43,44] Specific values (mmol/kg of polymer) are reported in Table 1. The content of carboxyl groups in the Ny6 samples was determined by conductometric titration in TFE with an aqueous 0.05 N solution of sodium hydroxide.[45]

3. Results and Discussion

In order to get information on the reaction mechanism and on the reactivity of each typical end group of Ny6 chains (i.e., NH_2 and −COOH) with the oxazoline rings of CP2OXA, reactions between $Ny6NH_2$ and Ny6COOH tailored polymers with different amount of CP2OXA were carried out at 240 °C under nitrogen flow for different times. The amount of CP2OXA was calculated in order to obtain a [COOH]/CP2OXA molar ratio of about 2:1, 1:1, and 1:2 in the case of Ny6COOH/CP2OXA mixture and a [NH_2]/CP2OXA molar ratio of about 2:1 and 1:1 for $Ny6NH_2$/CP2OXA system. The initial concentration of the NH_2 and COOH ends present in the Ny6COOH and $Ny6NH_2$ polymers are reported in Table 1. The reaction products were characterized by means of MALDI−TOF MS, ^{1}H and ^{13}C NMR, and FT-IR spectroscopy, UV spectroscopy, SEC analysis and also by viscosimetry measurements. Both telechelic Ny6 polymers and CP2OXA sample were also preliminarily treated at 240 °C for different times, under N_2 flow, in order to investigate their behavior, and the results were discussed in the Supporting Information. We have found that at 240 °C some reactions occur which lead to a decrease in the amount of carboxyl end groups after 60 min of heating the Ny6COOH sample, while the amount of amino ends decreases already after 15 min of heating the $Ny6NH_2$ polymer (see Supporting Information). ^{1}H and ^{31}P NMR spectra of CP2OXA heated at 240 °C for 30 min (Figure 1SB and 3SB) show that the cyclophosphazene groups are stable in the experimental condition used for reactive blending of all Ny6/CP2OXA systems in Table 1, and therefore the ring-opening polymerization of the cyclophosphazene units[46,47] does not occur (see support information).

In order to avoid the side reactions discussed before, the Ny6COOH−CP2OXA reactions were carried out in the bulk for 2, 5, 15, 30, 45, and 60 min, under N_2 flow, whereas the $Ny6NH_2$−CP2OXA mixtures were bulk reacted under the same experimental conditions for 2, 5, 10, and 15 min. All Ny6−CP2OXA bulk reacted materials were treated with $CHCl_3$ to eliminate unreacted CP2OXA, and then with TFE to verify the formation of insoluble components, as this is the best solvent for Ny6 polymer. Ny6COOH−CP2OXA reacted samples gave small amounts of gel after 60 min of heating, whereas $Ny6NH_2$−CP2OXA reacted systems formed high amounts of gel already after 2 min of heating at 240 °C (see Table 1). All TFE soluble Ny6COOH−CP2OXA reacted samples were analyzed by SEC, viscosimetric analysis and also by end-groups titration, and some data are summarized in Table 1. All gel fractions obtained from both $Ny6NH_2$−CP2OXA reacted systems were characterized by FTIR analysis, and after hydrolysis with a mixture of H_2O/HCOOH/$ClSO_3H$ (40/30/30 v/v) by MALDI−TOF MS.

Scheme 4. Chain Coupling



1. Ny6COOH−CP2OXA Bulk Reacted Systems. Viscosimetric data reported in Table 1 indicate that the viscosimetric average molar mass (M_v) of the soluble Ny6COOH−CP2OXA products slightly increases with increasing the reaction time and the initial amount of the CP2OXA compound. This suggests that both oxazoline rings can react with Ny6 chain ends and, therefore that the CP2OXA sample can act both as an end functionalizing agent and as a coupling agent (Schemes 3 and 4). The increase of average molar masses was also confirmed by SEC analysis, as we can see in Figure 8S that report the SEC traces of Ny6-COOH−CP2OXA (1:1 molmol) reacted samples for 5, 15, and 60 min.

The formation of different amounts of gel (between 3 and 18% w/w) when the different Ny6COOH/CP2OXA mixtures were reacted for 60 min at 240 °C (samples 7, 12, and 17 in Table 1) indicate that some side reactions may also occur, leading to branched or even cross-linked Ny6 polymers. The amount of the Ny6COOH−CP2OXA gel increases as the amount of CP2OXA sample in the feed is raised. However, the viscosimetric and SEC data give qualitative information on the reactions occurring during the bulk reactions of Ny6COOH and CP2OXA. Therefore, in order to get better information about the reaction mechanisms and to fully elucidate the structure of the Ny6COOH−CPOXA reacted systems, we have analyzed them by spectrometric and spectroscopic techniques such as MALDI−TOF MS, ^{1}H and ^{13}C NMR, and FT-IR. First, the Ny6COOH−CP2OXA products were characterized by MALDI−TOF MS, which enables the measurement of the mass of single molecules in a mixture of homologues and therefore the structural identification of the single macromolecules.[48−51] In fact, the literature reports that this powerful technique provides mass-resolved spectra up to 50−70 kDa, allowing the identification of repeat units, chain ends, cyclic oligomers and also of species present in a smaller amount in polymer samples.[48−52] MALDI−TOF mass spectra of all Ny6-COOH−CP2OXA products, recorded in reflectron mode, show well resolved mass peaks in the mass range 700−9000 Da permitting their pertinent assignments and the identification of the reaction mechanisms that could lead to their formation. The mass spectra recorded in the linear mode

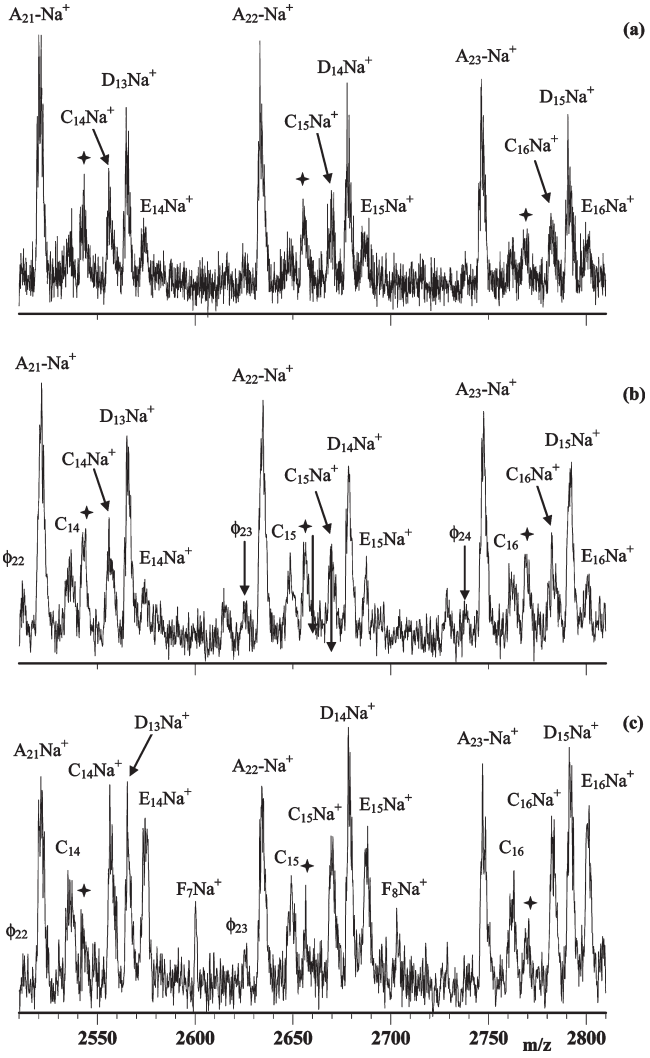


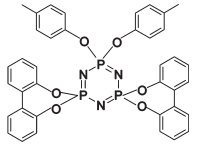
Figure 2. Enlarged section of mass spectra of Ny6COOH−CP2OXA (1:1) products obtained after (a) 5, (b) 15, and (c) 30 min of heating at 240 °C.

Table 2. Structural Assignments of the Mass Peak Series Displayed in the MALDI Spectra Reported in Figures 2, 3, 4, 8, 9, 4S, 6S, and 7S[a]

Species	Structures[b]	$[M+Na^+]$ (n)[c]
A	Ph-CO-[NH-$(CH_2)_5$-CO]$_n$-OH M_{An} = n·113.15+122.20	2521.30 (21); 2634.45 (22); 2747.60 (23); 3879.15 (33); 3992.30 (34); 4105.45 (35)
B	H-[NH-$(CH_2)_5$-CO]$_n$-OH M_{Bn} = n·113.15+18	2530.30 (22); 2643.45 (23); 2756.60 (24)
C	Ph-CO-[NH-$(CH_2)_5$-CO]$_n$-**OCH_2-CH_2NH-CO**-CP M_{Cn} = n·113.15+949.70	2556.80 (14); 2669.95 (15); 2783.10 (16); 3914.60 (26); 4027.75 (27); 4140.90 (28)
D	Ph-CO-[NH-$(CH_2)_5$-CO]$_x$-**O-$(CH_2)_2$-NH-CO**-CP-**CO-NH-$(CH_2)_2$-O**-[CO-$(CH_2)_5$-NH]$_y$-CO-Ph M_{Dn} =(x +y)·113.15+1071.90	2565.85 (13); 2679.00 (14); 2792.15 (15); 3923.65 (25); 4036.80 (26); 4149.95 (27)
E	Ph-CO-[NH-$(CH_2)_5$-CO]$_n$-**O-$(CH_2)_2$-NH-CO**-CP-**CO-NH-$(CH_2)_2$-OH** M_{En} = n·113.15+967.70	2574.80 (14); 2687.95 (15); 2791.10 (16); 3932.60 (26); 4045.75 (27); 4158.90 (28)
F	Ph-CO-[NH-$(CH_2)_5$-CO]$_x$-N-$(CH_2)_5$-CO-[NH-$(CH_2)_5$-CO]$_y$-**OCH_2-CH_2NH-CO**-CP **CH_2-CH_2NH-CO**-CP M_{Fn} =(x +y)·113.15+1890.35	2592.25 (6)[d]; 2705.40 (7)[d]; 3836.90 (17)[d]; 3950.05 (18)[d] 4063.20 (19)[d]
G	Ph-CO-[NH-$(CH_2)_5$-CO]$_x$-N-$(CH_2)_5$-CO-[NH-$(CH_2)_5$-CO]$_y$-N-$(CH_2)_5$-CO-[NH-$(CH_2)_5$-CO]$_z$-**OCH_2-CH_2NH-CO**-CP **CH_2-CH_2NH-CO**-CP **CH_2-CH_2NH-CO**-CP M_{Gn} =(x+y+z)·113.15+2831.00	3872.35 (9)[d]; 3985.50 (10)[d]; 4098.65 (11)[d]
H	CH_3-$(CH_2)_9$NH-[CO-$(CH_2)_5$-NH]$_n$-CO-Ph M_{Mn} = n·113.15+261.2	1868.30 (14); 1981.45 (15); 2094.60 (16); 2547.20 (20); 2660.35 (21); 2773.50 (22)
I	HO-[CO-$(CH_2)_5$-NH]$_n$-**CH_2-CH_2NH-CO**-CP M_{In} =n·113.15+845.5	1547.40 (6); 1660.55 (7)
N	CH_3-$(CH_2)_9$NH-[CO-$(CH_2)_5$-NH]$_n$-H M_{Nn} = n·113.15+157.2	1538.00 (12); 1651.15 (13); 1764.30 (14); 2556.35 (21); 2669.50 (22); 2782.65 (23)
Δ	CH_3-$(CH_2)_9$NH-[CO-$(CH_2)_5$-NH]$_n$-$(CH_2)_5$-CO-[NH-$(CH_2)_5$-CO]$_n$-NH-$(CH_2)_9CH_3$ $M_{\Delta n}$ = n·113.15+410.5	1565.00 (10); 1904.45 (13); 2016.60 (14); 2583.35 (19); 2696.50 (20)
ω	CH_3-$(CH_2)_9$NH-[CO-$(CH_2)_5$-NH]$_n$-CO-$(CH_2)_3$-CH=CH_2 $M_{\omega n}$ =n·113.15+253.2	2539.20 (20); 2652.35 (21); 2765.50 (22)
ϕ	-[NH-$(CH_2)_5$-CO]$_n$- $M_{\phi n}$ =n·113.15	1833.40 (16); 1946.55 (17); 2059.70 (18); 2512.30 (22); 2625.45 (23); 2738.60 (24)
γ	H-[N(C=O)-CH_2-CH_2-O-CH_2-CH_2-N(H)-C(=O)-CP]$_n$-CP *$M_{\gamma n}$ =n·827.50+845.50*	1696.00 (1); 2523.50 (2); 3351.00 (3); 4178.50 (4); 5008.00 (5 ; 5835.50 (6); 6663.00 (7); 7490.50 (8);

[a] For each structure is also reported the respective pertinent equation to calculate the corresponding molecular mass (M), considering that the mass of Ny6 repeat units is 113.15 Da and the molecular mass of CP2OXA is 827.5 Da.

[b] CP =



[c] *n* indicates the Ny6 repeat units along the macromolecular chains; [d] Corresponding to the sum of the Ny6 repetitive units

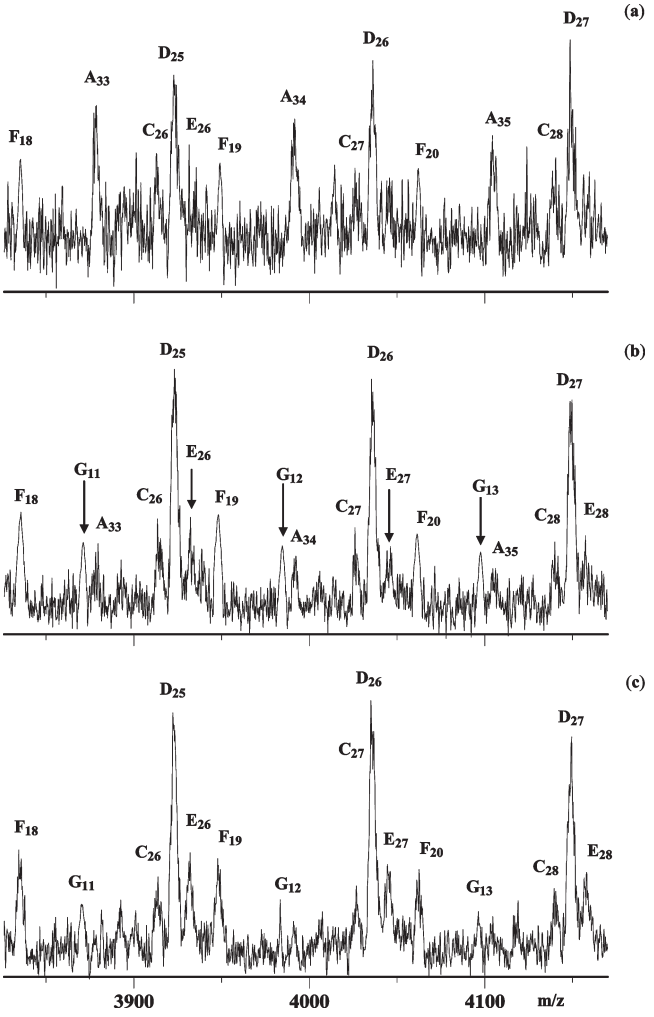


Figure 3. Enlarged section of MALDI spectra of Ny6COOH−CP2OXA (1:1) products obtained after (a)15 min, (b) 30 min, and (c) 60 min of heating at 240 °C.

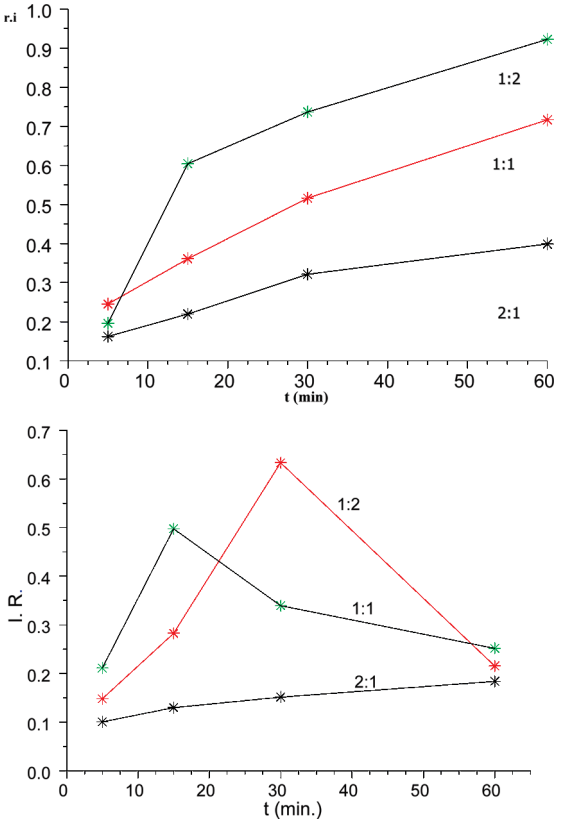
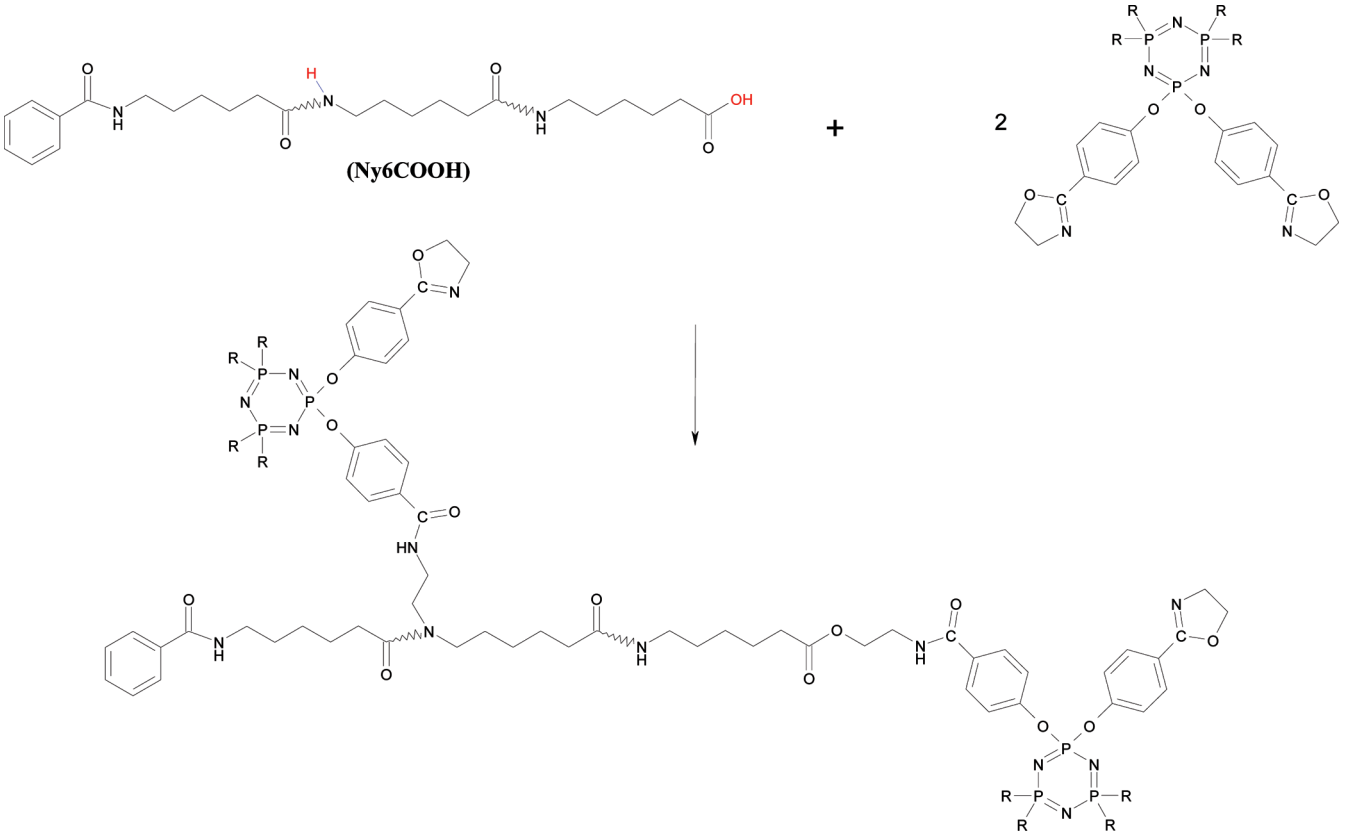


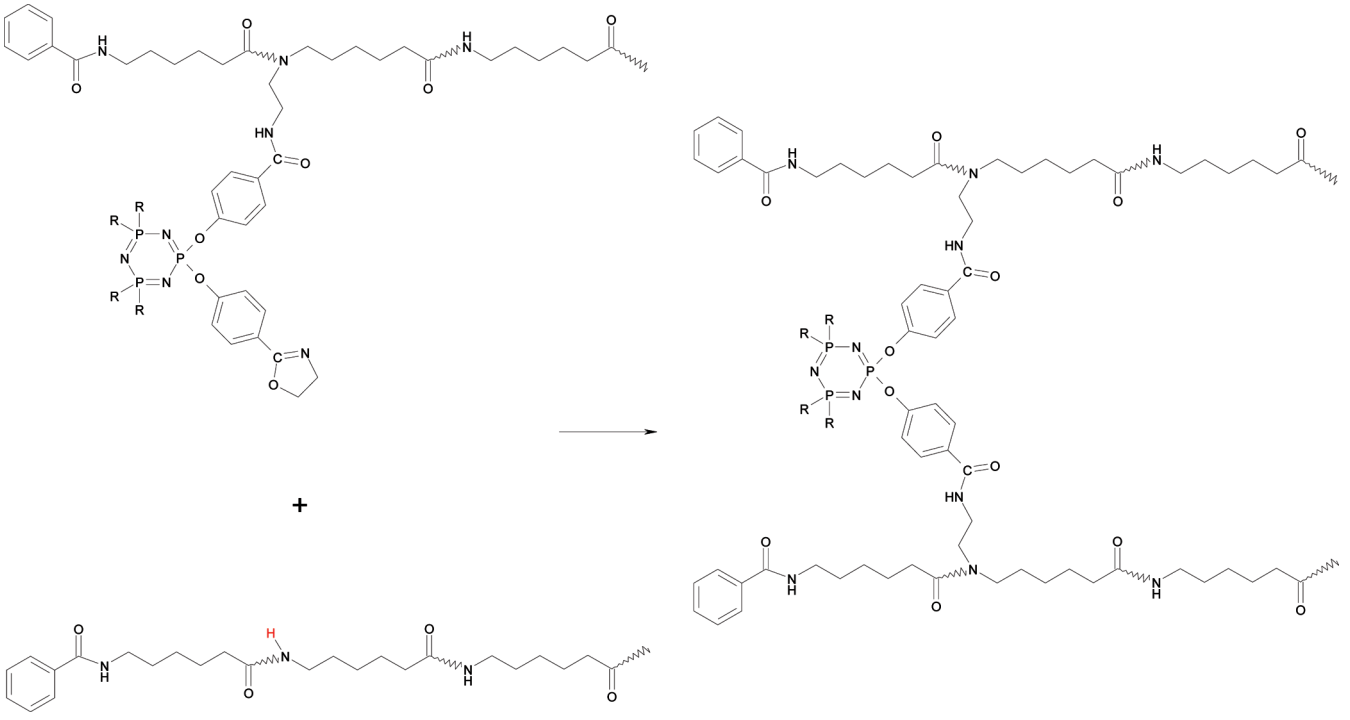
Figure 4. Relative intensities of (a) oligomer species D with respect to oligomers A (I_{Dn}/I_{An}) having n = 14 Ny6 repeat units and (b) oligomer species C with respect to oligomers A (I_{Cn}/I_{An}) having n = 14 Ny6 repeat units, as a function of the reaction time. The intensities relative to these oligomers were taken from MALDI−TOF mass spectra of Ny6COOH−CP2OXA products obtained by bulk reaction of different Ny6COOH/CP2OXA mixtures (2:1, 1:1 and 1:2 mol/mol) at 240 °C.

show peaks up to 12 000−15 000 Da, but with a lower mass resolution (800−1000 Da) with respect to those recorded in reflectron mode (3000−5000 Da). Figure 2 reports the enlargement, in the mass range 2510−2810 Da, of the mass spectra of the products obtained by reaction of the mixture Ny6COOH/CP20XA with a 1:1 molar ratio for 5, 15, and 30 min. It reveals four different families of homologous peaks that can be assigned to the sodiated ions of four families of Ny6 macromolecular chains (labeled as A, C, D, and E). The structures of the corresponding macromolecular species are summarized in Table 2. The peak series A belong to the unreacted Ny6COOH oligomers, whereas the families of peaks C and E correspond to the Ny6 oligomers formed by the reaction of only one oxazoline ring with the −COOH ends of the Ny6COOH sample (Scheme 3). The oligomers family C presents one unreacted oxazoline group linked to the CP unity, whereas the oligomers E present a *N*-hydroxy ethyl oxamide end group (−CO−NH−CH_2−CH_2−OH) linked to the CP moiety. The last groups, as reported in the experimental part, are present as about 2% mol in the CP2OXA compound, being formed by the hydrolysis reaction that occurs during its synthesis. The intense peak series D was assigned to the Ny6 oligomers having one CP2OXA group incorporated in the Ny6 polymer chains. These macromolecules were formed by reaction of both oxazoline groups of CP2OXA with two carboxylic acid end groups belonging to two different Ny6COOH chains (Scheme 4). The presence of these oligomers indicates that both oxazoline groups of the CP2OXA sample may react independently with two Ny6COOH chains, and then the CP2OXA sample can also act as a coupling agent yielding the increased average molar mass of the Ny6COOH−CP2OXA reacted samples. In the mass range 4000−9000 Da, the intensities of the peak series D increases with respect to those of the oligomer species C (see Figure 3) with the reaction time, while the peaks belonging to the Ny6COOH oligomers (mass series A) do not appear in the MALDI spectra of the products obtained after 15, 30, and 60 min heating (Figure 3). Therefore the very low amount of unreacted Ny6COOH oligomers, not detectable by titration method, can be detected only by MALDI−TOF mass spectra in the mass range 800−4000 Da (see Figure 2). The oxazoline rings present in Ny6−CP2OXA chains belonging to the species C are allowed to react with the carboxyl end groups of another Ny6COOH chain as the reaction time increases, leading to their total disappearance. In the MALDI mass spectrum of the Ny6COOH−CP2OXA products obtained after 30 min of reaction (Figure 4c), another family of peaks (labeled as F) also appears, which we have assigned to the oligomers formed by reaction of one Ny6COOH chain with two CP2OXA molecules (Scheme 5). We believe that these unexpected macromolecules are formed by reaction of one CP2OXA molecule with the carboxyl end of one Ny6COOH chain in accord to the Scheme 3, while another one CP2OXA molecule reacts with one −NH amide group along the same Ny6COOH chain,

Scheme 5



Scheme 6



leading therefore to a branched Ny6COOH−CP2OXA species (Scheme 5). Observing the MALDI spectra of the Ny6-COOH−CP2OXA products obtained after 30 and 60 min of heating (Figure 3, parts c and d, respectively), in the range 3825−4150 Da we can also observe weak peaks (labeled as G) corresponding to the Ny6 oligomers formed by reaction of one Ny6COOH chain with three CP2OXA molecules. Therefore these oligomers G contain two CP2OXA branched groups. The oxazoline groups of the branched groups present in the Ny6 oligomers F and G may react successively with a −NH amide group belonging to another Ny6 chain producing cross-linked polyamides (Scheme 6). The presence of the oligomer species

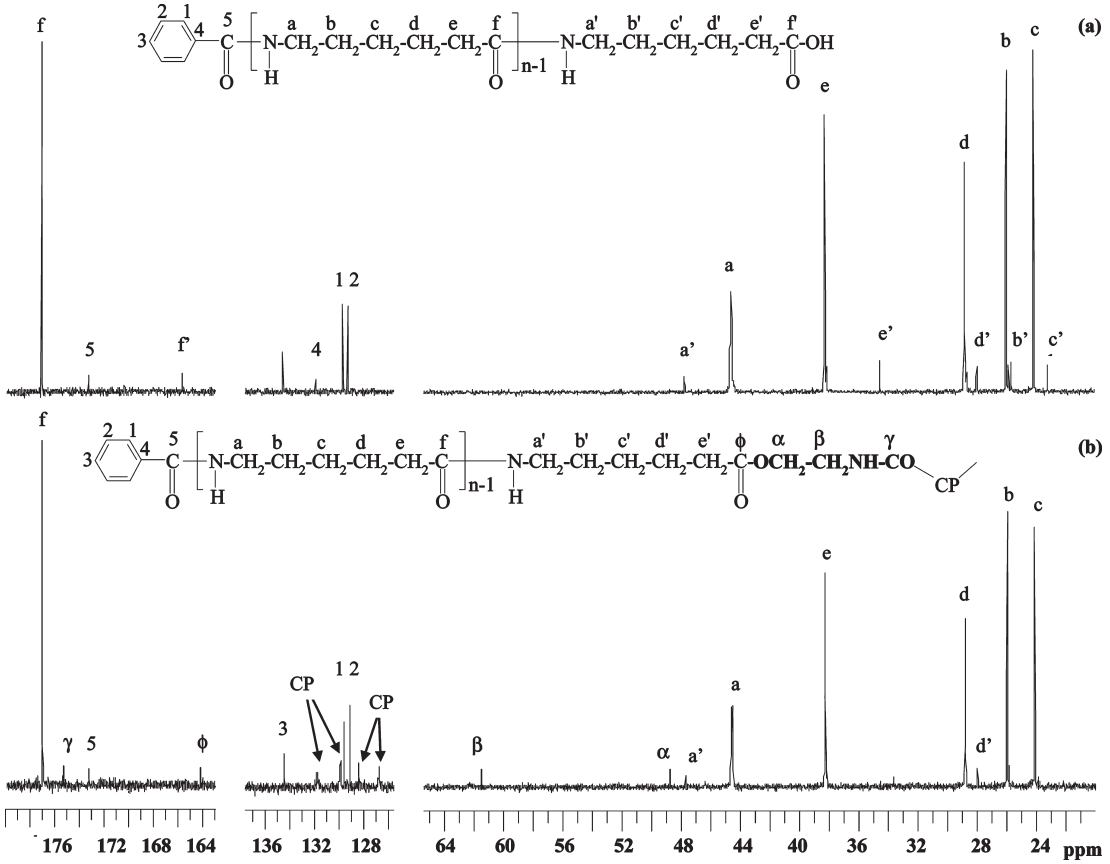


Figure 5. ^{13}C NMR spectra of (a) Ny6COOH sample and (b) of Ny6COOH−CP2OXA (1:1) products obtained after 15 min of heating at 240 °C.

F and G could explain the formation of the gel formed when Ny6COOH and CP2OXA were reacted for longer times (60 min). In accord with the data in Table 1, the cross-linking side reactions are favored as the CP2OXA amount in the feed increases. Since the MALDI−TOF mass spectra gives unambiguous information on the chemical structure of the Ny6COOH−CP2OXA products and on the reaction mechanisms that lead to their formation, we have followed the kinetic of the Ny6COOH−CP2OXA reactions using the relative intensities of the peak families observed in their MALDI spectra. For this purpose we have assumed that the oligomers with the same number of Ny6 repeat units (n) and having different end groups show similar ionization efficiency; thus, the relative intensities of the corresponding mass peaks reflect their molar fractions in the analyzed mixture. We have measured the intensity ratio, as a function of reaction time, of peak species D (referred as I_{Dn}) and of peak series C (referred as I_{Cn}) with respect to that of the Ny6COOH oligomers (referred as I_{An}) having the same number of Ny6 repeat units (n). For each Ny6COOH−CP2OXA product the average intensities I_{Dn}, I_{Cn}, and I_{An} were measured from seven corresponding MALDI−TOF mass spectra. Figure 4a reports the intensity ratio I_{Dn}/I_{An} of the oligomers with $n = 14$ belonging to the soluble Ny6COOH−CP2OXA products obtained at 240 °C, versus the reaction time. It shows that the intensity ratio I_{Dn}/I_{An} doubles as the moles of CP2OXA are doubled in the feed. Very similar results were obtained using the intensity ratio (I_{Dn}/I_{An}) of the oligomers D and A with 16, 20, and 24 Ny6 repeat units. Similar behavior was observed at lower reaction times (max 15 min) using the intensity of the peak species C (I_{Cn}), as it can be observed in Figure 4b. It shows also that the ratio I_{Cn}/I_{An} reaches a maximum when the Ny6COOH−CP2OXA 1:1 mol/mol and 1:2 mol/mol moieties have reacted for 30 and 15 min, respectively, and then decreases as the reaction time increases. These last data confirm the progress of the reaction between Ny6COOH and CP2OXA with time, and therefore that CP2OXA acts more efficiently as a coupling agent with increasing its concentration in the feed and the heating time at 240 °C. Very similar results were obtained using the intensities I_{Dn}, I_{Cn}, and I_{An} of the oligomers having 14, 16, 20, and 24 Ny6 repeat units along the chains. Therefore, in accord with the I_{Dn}/I_{An} data depicted in Figure 4a, we believe that the Ny6COOH−CP2OXA coupling reaction (Scheme 4) follows second order kinetics, and that all oxazoline rings linked to the CP moiety are most probably equireactive.

This hypothesis and the data discussed above are in accord with the literature.[2,3] Indeed, Fradet et al.[2,3] came to the same conclusions studying the bulk reactions of the arylene-bis-oxazoline with dodecanoic acid to 140 °C[2] and of the pyridylene bis(oxazoline) with carboxyl terminated Ny12 at 200 or 240 °C.[3] At variance with our results, the authors do not observe any side reaction studying the Ny12-COOH-bisoxazoline products by ^1H and ^{13}C NMR. However, in accord with our MALDI data, the side reactions between NH−amide and oxazoline groups were observed from Sano et al.[53] studying the kinetics of benzoic acid−bis(oxazoline) reaction.

The reactions between Ny6COOH and the oxazoline groups of CP2OXA were also studied by ^1H and ^{13}C NMR spectroscopy. The NMR spectra of all Ny6COOH−CP2OXA soluble products were recorded in a mixture of $CDCl_3$ and trifluoroacetic anhydride ($CDCl_3$/TFA) 80/20 v/v, because they are insoluble in the mixtures of HFIP and $CDCl_3$ used from several researchers for the NMR analysis of aliphatic polyamides such as Ny12.[3,4] Very similar ^{13}C and ^1H NMR spectra were recorded for all

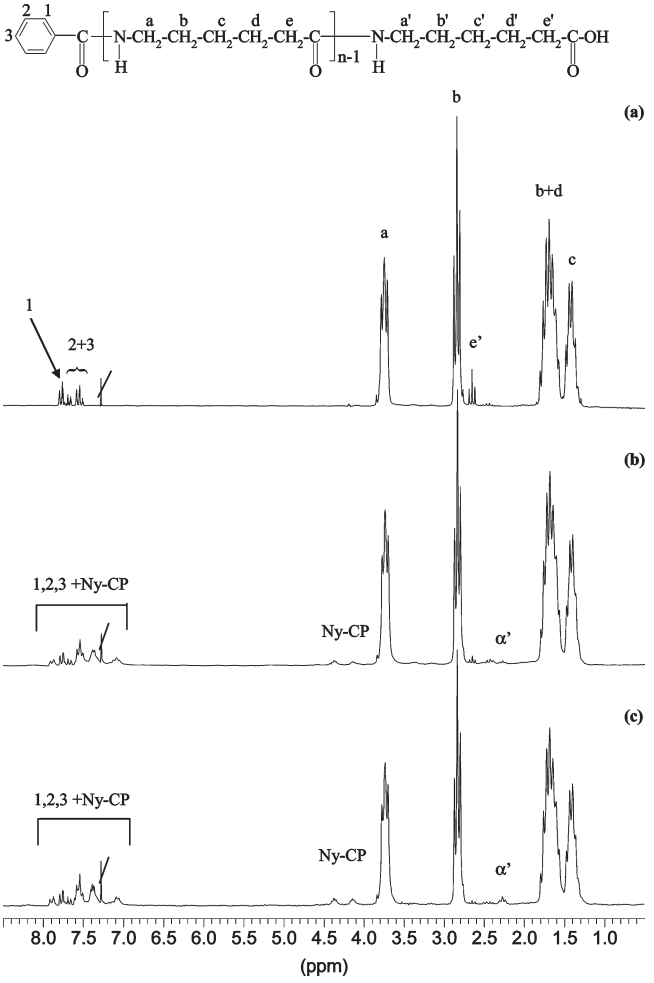


Figure 6. ^{1}H NMR spectra of Ny6COOH prepolymer (a) and of Ny6COOH−CP2OXA (1:1) products obtained after 15 min (b) and 30 min (c) of heating at 240 °C.

Ny6COOH−CP2OXA products confirming that the reactions between Ny6COOH and CP2OXA are fast and that they can take place according to Schemes 3 and 4. As an example, the ^{13}C NMR spectra of the starting Ny6COOH polymer and of the Ny6COOH−CP2OXA (1:1 mol/mol) products obtained after 15 min at 240 °C (sample 10 in Table 1) are reported in Figure 5 together with the pertinent assignments. Comparing the ^{13}C NMR spectra of all Ny6COOH−CP2OXA samples with that of the Ny6COOH (Figure 5a), one observes in the spectra of the Ny6COOH−CP2OXA reacted products the disappearance of the signal at 165.71 ppm (labeled as f′ in Figure 7a), due to the Ny6 carboxyl end groups. In the ^{13}C NMR spectra of Ny6COOH−CP2OXA products, the signal due to the initial −COOH ends is replaced by two new peaks at 175.2 ppm (carbons γ in Figure 5b) and at 164.05 ppm (carbons ϕ in Figure 5b) due to the resonance of the ester and amide groups formed by reaction of COOH and oxazoline moieties (Schemes 3 and 4), while one can still observe the signal at 173.38 ppm due to the carbonyl of the benzamide end groups of the initial Ny6 chains (carbons 5, Figure 5a). In Figure 5, the comparison of the aliphatic region of the starting polyamide and of its reaction product with CP2OXA shows two new signals β and α at 62.68 and 48.65 ppm, respectively, corresponding to methylene (−CH_2−) carbons of the ester-amide formed in the reaction between COOH and oxazoline groups. Signals corresponding to the methylene (−CH_2−) of

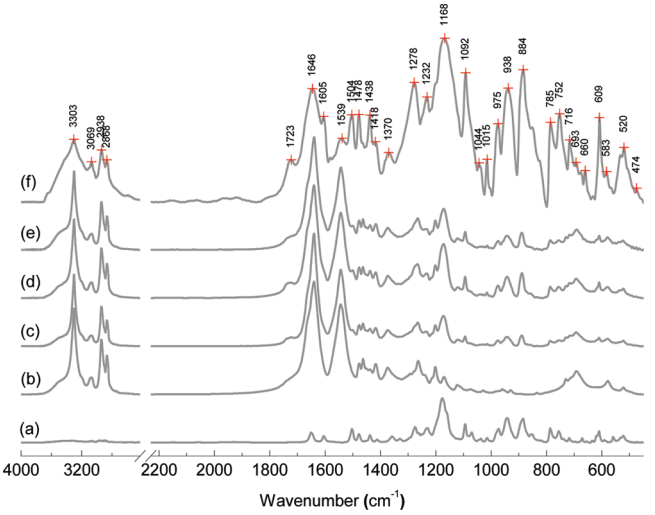


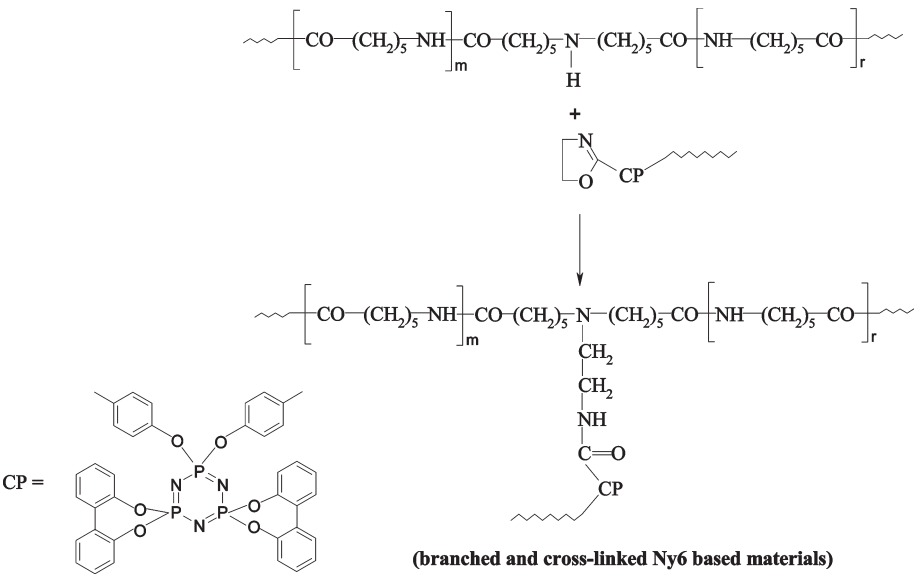
Figure 7. FT-IR spectra of samples (a) CP2OXA, (b) Ny6COOH, (c) Ny6COOH−CP2OXA (1:1) 5 min at 240 °C, (d) Ny6COOH−CP2OXA (1:1) 30 min at 240 °C, (e) Ny6COOH−CP2OXA (1:1) 60 min at 240 °C (TFE soluble fraction), and (f) Ny6COOH−CP2OXA (1:1) gel obtained after 60 min heating at 240 °C.

unreacted oxazoline end groups, present in some Ny6COOH−CP2OXA chains (species C in Table 2), were not observed in the ^{13}C NMR spectra because the oxazoline groups react with CF_3COOH present in the $CDCl_3$/TFA mixture and the corresponding product gives two weak peaks at 72.98 and 65.01 ppm. The lower field part of the spectrum of the Ny6COOH−CP2OXA reaction products (Figure 5b) shows four new aromatic peaks at 124.54, 126.94, 130.08, and 132.15 ppm (labeled as CP) due to the aromatic carbons of the CP units.

Contrary to the MALDI−TOF spectra, peaks coming from branched products (species F and G in Table 2) were not observed in the ^{13}C NMR spectra. This may be due to the low concentration of the branched or partially cross-linked Ny6COOH−CP2OXA macromolecules in the reacted products, and also because NMR is an averaging technique that generally possesses lower sensitivity with respect to the MALDI−TOF MS, which is able to detect individual and intact polymer molecules even in a complex mixture, including species present in smaller amounts in a polymer sample.[48−52]

All samples were also studied by ^{1}H NMR spectroscopy, and as an example, the proton spectra of neat Ny6COOH sample and of the Ny6COOH−CP2OXA (1:1) products obtained after 15 and 30 min of reaction at 240 °C, are reported in Figure 6. Comparing the spectra of the Ny6COOH polymer with those of the Ny6COOH−CP2OXA (1:1) products, some peculiar differences arise. In the spectra of the Ny6COOH−CP2OXA products the resonance peaks (triplet) at 2.53 ppm (protons e′ in Figure 6a), due to the methylene in α at the −COOH end groups of starting Ny6COOH polymer, were replaced by a new signal at 2.27 ppm (protons α′ in Figure 6b,c). The ^{1}H NMR spectra in Figures 6b,c show also new signals centered at 4.15 and 4.37 ppm due to the methylene groups of the oxamide functions formed in the −COOH-oxazoline reactions (Schemes 3 and 4). Peaks related to the CP moiety are overlapped in the range 7.0−8.0 ppm, where also the aromatic protons of the benzamide end groups of the Ny6COOH−CP2OXA chains resonate. Since the ^{1}H NMR spectra of all Ny6COOH−CP2OXA products are very similar, as well as the ^{13}C NMR spectra, only

Scheme 7



partial information about the structure and chemical composition of the Ny6COOH−CP2OXA products can be obtained.

Further characterization of the Ny6COOH−CP2OXA reacted samples were carried out by FT-IR analysis both of soluble Ny6COOH−CP2OXA products and of the gel fractions obtained at 60 min reaction (see Table 1). Very similar FTIR spectra were recorded for all soluble Ny6-COOH−CP2OXA reacted products and also for each gel fraction. An inspection of the Ny6COOH−CP2OXA products was carried out with FTIR in the spectral regions 3600−3150 and 1850−1420 cm^{-1}, in order to obtain information about their chemical structures. As an example, the FTIR spectra of the Ny6COOH polymer, of the CP2OXA compound, of the Ny6COOH−CP2OXA (1:1) soluble products obtained at 5, 30, and 60 min of reaction, and of the gel obtained at 60 min heating, are given in Figure 7a−f. The FTIR spectrum of the Ny6COOH sample (Figure 7a) shows typical broad absorption bands at 3061 and 3300 cm^{-1} due to the asymmetric stretching of amide NH groups, and the adsorption band at 1640 cm^{-1} due to asymmetric stretching of amide C=O groups. The aliphatic −C−H stretching modes are observable at 2869 and 2944 cm^{-1}. These peaks are also present in the spectra of all Ny6COOH−CP2OXA products (Figure 7c−f). FT-IR spectrum of the CP2OXA sample (Figure 7b) shows a strong signal at 1176 cm^{-1} due to the asymmetric vibration of −*P*=N− groups, another band at 940 cm^{-1} assigned to the vibration of P−O−Ph groups, and also a band at 1650 cm^{-1} assigned to the asymmetric stretching of the −C=N− groups in the oxazoline units. FT-IR spectra of the Ny6COOH−CP2OXA soluble products and of the gel (Figure 7c−f), besides the typical adsorption bands due to the Ny6 units and CP moieties discussed above, present a signal at about 1665 cm^{-1} that we have assigned to the asymmetric stretching of the −C=O ester groups formed in the reactions between the carboxyl end chains of Ny6COOH and the oxazoline rings of CP2OXA (Schemes 3 and 4). The FTIR spectrum of the Ny6COOH−CP2OXA gel (Figure 7f) shows also a broad absorption band between 1880 and 2040 cm^{-1} that we have tentatively assigned to the N substituted amide groups formed by branching and cross-linking reactions between ozaxoline rings and amide −NH−C=O− groups along Ny6 chains (Schemes 5 and 6).

The progress of the Ny6COOH−CP2OXA reactions was followed also by visible ultraviolet analysis, which shows two maxima of absorbance at about 204 and 243 nm. The UV spectra of initial Ny6COOH and CP2OXA, and that of the Ny6COOH−CP2OXA (1:1) soluble products obtained at 5, 15, 30, and 60 min of reaction at 240 °C, are reported in Figure 9S. The absorbance peaks at 204 and 243 nm increase with reaction time and also as with the amount of CP2OXA reagent.

DSC data (T_g and T_m) given in Table 1 reveal that all TFE-soluble Ny6COOH−CP2OXA products show T_g and T_m values very similar to those of initial Ny6COOH polymer and, therefore, indicate that the composition and, above all, the different end groups have negligible effect on the crystallization of Ny6 chains.

2. Ny6NH$_2$−CP2OXA Bulk Reacted Systems. The data reported in Table 1 indicate that about 95−98% of gel were obtained when Ny6NH$_2$ polymer and CP2OXA were reacted at 240 °C for a time higher than 5 min. As discussed in the Supporting Information, secondary amino (−NH−) groups along the Ny6 chains can be formed when Ny6NH$_2$ sample is heated at 240 °C (Scheme 2S). We believe that these species can react with oxazoline groups of the CP2OXA sample leading to the formation of branched and cross-linked Ny6 oligomers (Scheme 7). Therefore, these side reactions and the concomitant reactions involving inner amide (−NHCO−) groups and oxazoline moieties (Schemes 5 and 6) may have led to gel formation when Ny6NH$_2$ and CP2OXA were bulk reacted for a time higher than 5 min, at 240 °C. MALDI−TOF mass spectra of the small amount of Ny6NH$_2$−CP2OXA fraction soluble in TFE show peaks due to the unreacted Ny6 oligomers, as it can be observed in Figure 8. It reports the MALDI−TOF mass spectrum of the Ny6NH$_2$−CP2OXA (1:1) soluble fractions obtained at 5 min of heating at 240 °C. In the range 1000−4000 Da there is a series of peaks corresponding to three families of Ny6 oligomers, which appear as mass resolved peaks in the inset reported in Figure 8. One can observe peaks belonging to Ny6 cyclic oligomers (mass peak series ϕ), to Ny6 oligomers terminated with a decylamide group at one end and with a benzamide group at the other (species H in Figure 8 and in Table 2), and to Ny6 oligomers containing one secondary amino group along the chain (oligomers Δ in Figure 8 and in Table 2). This mass spectrum

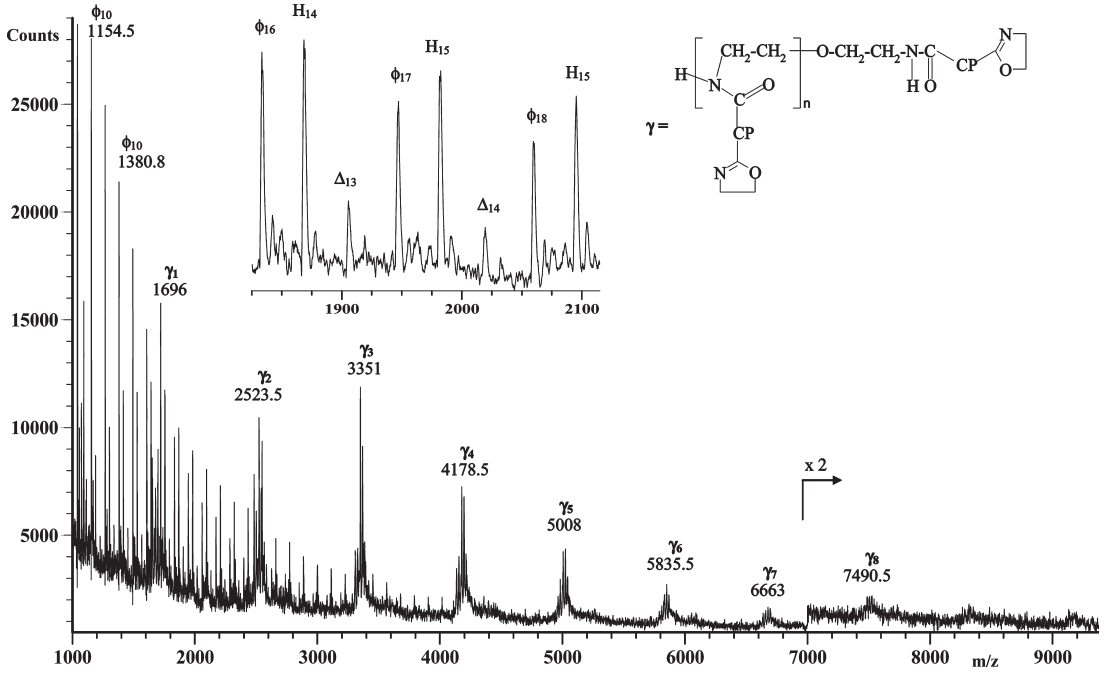


Figure 8. MALDI−TOF mass spectrum of the soluble fraction from Ny6NH_2−CP2OXA bulk reacted mixture (1.1) at 240 °C for 5 min.

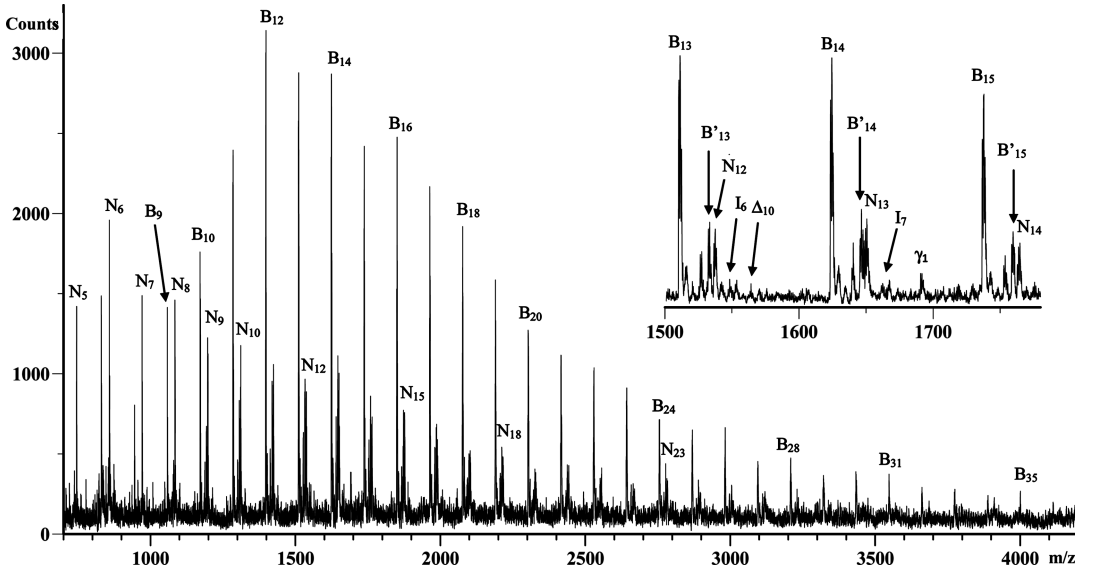


Figure 9. MALDI−TOF mass spectrum of the hydrolyzed gel obtained from Ny6NH_2−CP2OXA mixture reacted at 240 °C for 5 min.

shows also another distribution of peaks from *m*/*z* 1650 to 9000 Da with an interval between two principal peaks of 827.5 Da, corresponding to the molecular mass of the CP2OXA monomeric unit. These unexpected peaks were assigned to the oligomers formed by polymerization of CP2OXA at 240 °C (Scheme 1S). Such oligomers were also observed in the soluble fractions of the Ny6NH_2−CP2OXA mixture reacted for 10 min, while they are absent in those obtained from the mixture reacted for 15 min, indicating that these CP2OXA oligomers can react with Ny6 chains. The formation of the CP2OXA oligomers was also confirmed by MALDI−TOF MS and SEC analyses of the CP2OXA heated at 240 °C for different times (from 5 min up to 30 min), and the results are discussed in the Supporting Materials (see Figures 4S and 5S). Probably the CP2OXA oligomers were not observed in the MALDI spectra of the Ny6COOH−CP2OXA reacted samples because of the high intensity of the mass peaks due to the Ny6COOH and Ny6COOH−CP2OXA functionalized compounds, which may overlap those due to traces of CP2OXA oligomers.

In further studies, in order to investigate the composition and chemical structure of the Ny6NH_2−CP2OXA gels, we have performed their partial hydrolysis with a mixture of H_2O/HCOOH/$ClSO_3H$ (40/30/30 v/v) at reflux for 2 h under N_2 flow. The TFE soluble materials obtained were then analyzed by MALDI−TOF MS. Figure 9 reports the mass spectrum of the materials obtained by partial hydrolysis of the Ny6COOH−CP2OXA (1:1) gel formed after 5 min of heating at 240 °C. It shows several well resolved mass peaks in the mass range 100−4200 Da, as it can be observed in the inset of Figure 9. All peaks appear as sodiated ions and their assignment are reported in Table 2. The most intense peaks (labeled as B) correspond to the expected Ny6 oligomers

terminated with amino and carboxyl groups formed by hydrolysis of Ny6COOH−CP2OXA chains. Peaks B′ correspond to sodium salts of species B, whereas peaks N correspond to the expected Ny6 oligomers terminated with decylamine groups. The peaks I and γ (see Table 2) have particular relevance, as they confirm that CP2OXA oligomers are linked to the Ny6 chains. The presence of Ny6 oligomers containing secondary amino groups along the chains (species Δ, in Figure 9 and in Table 2) confirms that these groups can react with CP2OXA to yield branched and also cross-linked Ny6.

4. Conclusions

Our studies show that the oxazoline ring groups of CP2OXA sample react with carboxyl and amino end groups of Ny6 at a different rate. The structural characterization of the Ny6−CP2OXA bulk reacted products provided especially by MALDI−TOF MS analysis allowed the identification of the reaction products from the reaction between Ny6 and CP2OXA. The oxazoline rings linked to the cyclophosphazene groups of the CP2OXA compound are most probably equireactive and react with carboxyl-Ny6 end chains according to second order kinetics. The reactions with amino ends are very fast yielding high amounts of gels when Ny6NH_2 and CP2OXA are heated at 240 °C for a short time (5 min), whereas trace of gels are produced when Ny6COOH and CP2OXA are bulk reacted for 60 min. MALDI-MS data show that oxazoline rings can also react with −NH− amide groups along the Ny6 chains and with secondary amino groups that might be formed by a condensation reaction involving the elimination of ammonia from two amino end chains (Scheme 2S). Our data also reveal that CP2OXA can be polymerized at 240 °C, and then the formed oligomers can react with the Ny6 chains leading to branched and cross-linked materials. Therefore, we believe that the reactions of the oxazoline rings of the CP2OXA species (monomer and oligomers) with amido inner groups and with secondary amino groups, are mainly responsible for the gel formed during the heating of Ny6 with CP2OXA at 240 °C.

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Supporting Information Available: Text giving data obtained from studies on the thermal stability of CP2OXA and both Ny6 tailored prepolymers, their characterization, and also either SEC and UV−visible analyses of Ny6−CP2OXA reacted samples soluble in TFE, schemes showing the reactions and figures showing NMR spectra, MALDI−TOF mass spectra, SEC curves,and UV spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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