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Synthesis and Matrix-Assisted Laser Desorption Ionization−Time of Flight Characterization of an Exactly Alternating Copolycarbonate and Two Random Copolyethers Containing Schiff Base Copper(II) Complex Nonlinear Optical Units in the Main Chain

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ABSTRACT: Copolymers containing second-order nonlinear optical (NLO) active transition metal complexes into the main chain were synthesized and characterized by matrix-assisted laser desorption ionization−time of flight mass spectrometry (MALDI−TOF MS), TG, and DSC analyses for the first time. The Cu(II) complex **Ia** of the *N,N′*-bis(2,4-dihydroxybenzylidene)-1,2-phenylenediamine ligand was synthesized and used as the NLO unit. The polycondensation between the copper(II) complex **Ia** (NLO unit) and butanediol bischloroformate was performed to obtain the exactly alternating copolycarbonate **II**. Two copolyethers, **III** and **IV**, containing different amounts of NLO units in the main chain (10% and 47%, respectively), were obtained by reaction of dibromomethane and suitable mixtures of the Cu(II) diimine complex **Ia** and bisphenol A in different molar ratios. The resulting copolymers **II**−**IV** were characterized by MALDI−TOF MS. The structure of low molecular weight oligomers contained in each polymeric sample inferred by MALDI spectra was found diagnostic of their composition and microstructure. Copolymers **II**−**IV** exhibit very good thermal stability and are promising candidates for second-order NLO materials.

Introduction

The synthesis of new polymeric materials with nonlinear optical (NLO) properties is currently attracting large interest due to the possibility of large nonresonant susceptibilities, high damage thresholds, and the inherent tailorability of their molecular structures.[1−3] Poled polymer films[4,5] with second-order optical nonlinearity consist of NLO chromophores embedded in polymeric matrices. Depending on how the NLO chromophores are incorporated in the polymer, several classes of NLO materials can be distinguished as follows: guest−host systems, side-chain and main-chain polymers, and cross-linked polymers.[4,5] Poling involves the application of an electric field to the polymer, near to the glass transition temperature (T_g), which causes partial alignment of the NLO active chromophores and induces an acentric microstructure. It is well established that the temporal NLO characteristics of such poled systems depend upon T_g values.[4] Therefore, besides their good chemical stability, higher T_g values are required for practical device applications.

Metal complexes are attractive candidates as potential high-T_g poled polymers due to their generally higher (compared to organic chromophores) thermal stability (e.g., metallophthalocyanines). To date, however, investigations have been limited to organotransition ferrocene-based[6−10] and tungsten-carbonyl[11] NLO-functionalized polymers.

We have recently reported[12,13] the second-order NLO properties of a series of robust *N,N′*-bis(disalicylidene-1,2-phenylenediaminato)M(II) Schiff base complexes [M(salophen); M = Co, Ni, Cu], whose NLO response is “switched on” by the metal complexation. The good NLO response and the excellent thermal stability of these compounds prompted us the attempt to incorporate these NLO units into polymeric systems.

In the last few years, the synthesis of polymeric systems containing transition metal complexes has attracted our interest, and in previous papers, we have reported the synthesis and characterization of some polyethers and copolyethers containing units of porphyrin-based metal complexes in the main chain.[14,15]

In this contribution we report on the synthesis and characterization of the first copolymers containing *N,N′*-bis(2,4-dihydroxybenzylidene)-1,2-phenylenediaminato]-copper(II) (**Ia**) NLO units into the main chain.[16] The exactly alternating copolycarbonate **II** has been prepared by interfacial condensation between **Ia** and 1,4-butanediol bischloroformate. In addition, two random copolyethers (**III** and **IV**), containing different amounts of the NLO unit **Ia** in the main chain, have also been synthesized by reaction of **Ia** and bisphenol A (BPA), in different molar ratios, and dibromomethane (Table 1).

These copolymers are very low soluble materials, and their structural characterization has been made possible using the MALDI−TOF MS.[17−21] This very powerful, recently acquired technique has allowed to establish the exactly alternating[22] structure of copolymer **II** and the composition of copolymers **III** and **IV** by detecting the

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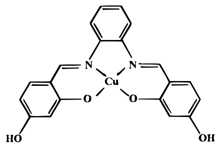
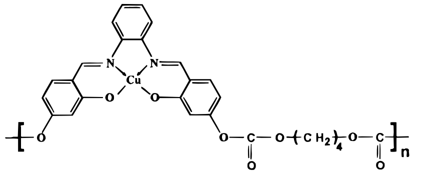
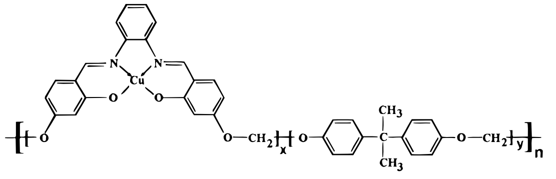


Ia



II



III, $x = 0, 10; y = 0, 90$
IV, $x = 0, 47; y = 0, 53$

low molecular weight oligomers contained in the polymeric samples.

Experimental Section

Materials. All solvent and basic materials were commercial products appropriately purified before use.

***N*,*N*′-Bis(2,4-dihydroxybenzylidene)-1,2-phenylenediamine (Ib).** The Schiff base free ligand was prepared as follows: To a solution of 9.5 g (88 mmol) of 1,2-phenylenediamine in 200 mL of CH_3OH, under stirring and N_2 atmosphere was added slowly 25 g (180 mmol) of 2,4-dihydroxybenzenaldehyde in 300 mL of CH_3OH. The solution was then refluxed for 5 h, and after cooling, the yellow product formed was filtered and crystallized from THF/CH_3OH (yield 80%). The compound was characterized by FAB-MS, TG, and ^1H-NMR analyses. The positive FAB mass spectrum shows a molecular ion detected as MH^+ at *m*/*z* 349. A temperature of 220 °C, at which 2% of weight loss occurs, and a residue at 800 °C of about 50% (experiment under N_2) were determined. By comparison with the spectrum of a nickel complex derivative (**Ic**), the signals present in the proton NMR spectrum of compound **Ib** were so assigned (see formula **Ic**): 13.399 (s, $2H_h$) and 10.263 (s, $2H_f$) hydroxyl protons, 8.739 (s, $2H_c$), 7.277−7.451 (m, $2H_a + 2H_b + 2H_d$), 6.297−6.425 (m, $2H_e + 2H_g$) ppm.[23]

[*N*,*N*′-Bis(2,4-dihydroxybenzylidene)-1,2-phenylenediaminato]copper(II) (Ia) and -nickel(II) (Ic) Complexes. To a stirring solution of 2 g (5.75 mmol) of *N*,*N*′-bis(2,4-dihydroxybenzylidene)-1,2-phenylenediamine in 100 mL of THF was slowly added a solution of 1.2 g (6 mmol) of copper(II) acetate monohydrate in 100 mL of CH_3OH. As soon as the copper complex was formed, a yellow-red solid precipitated, and it was then filtered. Recrystallization from DMF/CH_3OH yielded a brown-red compound, mp 310 °C dec. FAB-MS analysis of this compound showed two peaks at *m*/*z* 410 and 412, corresponding to molecular ions (as MH^+) of the complex containing the two copper isotopes. To confirm the total metalation of the Schiff base, TG experiments under air flow were made. The black residue obtained at 800 °C, constituted from CuO, amounted to 19.2% of the initial weight of the diimine complex **Ia**, corresponding to the theoretical value for a complete metalation. The compound was also characterized by elemental analysis: C, 58.1; H, 3.6; N, 6.6. Correct C, H, and N amounts for $C_{20}H_{14}N_2O_4Cu$ are 58.5, 3.4, and 6.8, respectively.

The Ni(II) complex **Ic** was prepared in the same way as compound **Ia** using nickel(II) acetate tetrahydrate.

Copolycarbonate II Synthesis. The copolycarbonate **II** was obtained by interfacial condensation reaction between 1,4-butanediol bischloroformate and the copper(II) derivative **Ia** in the presence of tetrabutylammonium bromide (TBAB) as phase transfer catalyst. In a typical synthesis, 500 mg (1.22 mmol) of compound **Ia** was placed in a 10 mL vial together with 98 mg (2.44 mmol) of NaOH, 393 mg (1.22 mmol) of TBAB, and 6 mL of a 1:1 toluene/water solution. The mixture was heated at 50 °C under stirring and N_2 atmosphere; then 262 mg (1.22 mmol) of 1,4-butanediol bischloroformate in 2 mL of toluene was added. After 1 h, the formed polymer insoluble in toluene was filtered, dissolved in *N*-methylpyrrolidone (NMP), and precipitated in water. After washing with water (two times) and CH_3OH (two times), the copolymer was dried under vacuum at 60 °C ($\eta_{inh} = 0.16$). Elemental analysis: C, 56.1; H, 4.1; N, 5.3. Correct C, H, and N amounts for an exactly alternating structure, $C_{26}H_{20}N_2O_8Cu$, are 56.6, 3.63, and 5.08, respectively.

Table 1. Composition, Viscosity, Glass Transition Temperature, and Thermal Stability of Copolymers II−IV

sample	NLO[a] (%)	η_{inh}[b]	T_g[c]	PDT[d]
copolycarbonate **II**	50 (50)	0.16		270 (200)
copolyether **III**	10 (8)	0.19	88	400 (400)
copolyether **IV**	47 (44)	0.17		420 (350)

[a] The amount of NLO units in each copolymeric material was deduced by considering the residue at 800 °C in TG experiments under air flow. In parentheses are reported the values deduced by elemental analysis. [b] Inherent viscosity measurements were performed in *N*-methylpyrrolidone at 50 °C. [c] Glass transition temperature determined by DSC experiment. [d] Temperatures of maximum rate of polymer degradation (PDT) from TG experiments under N_2 flow. The temperatures at which 2% of weight loss of material is observed, are also reported in parentheses.

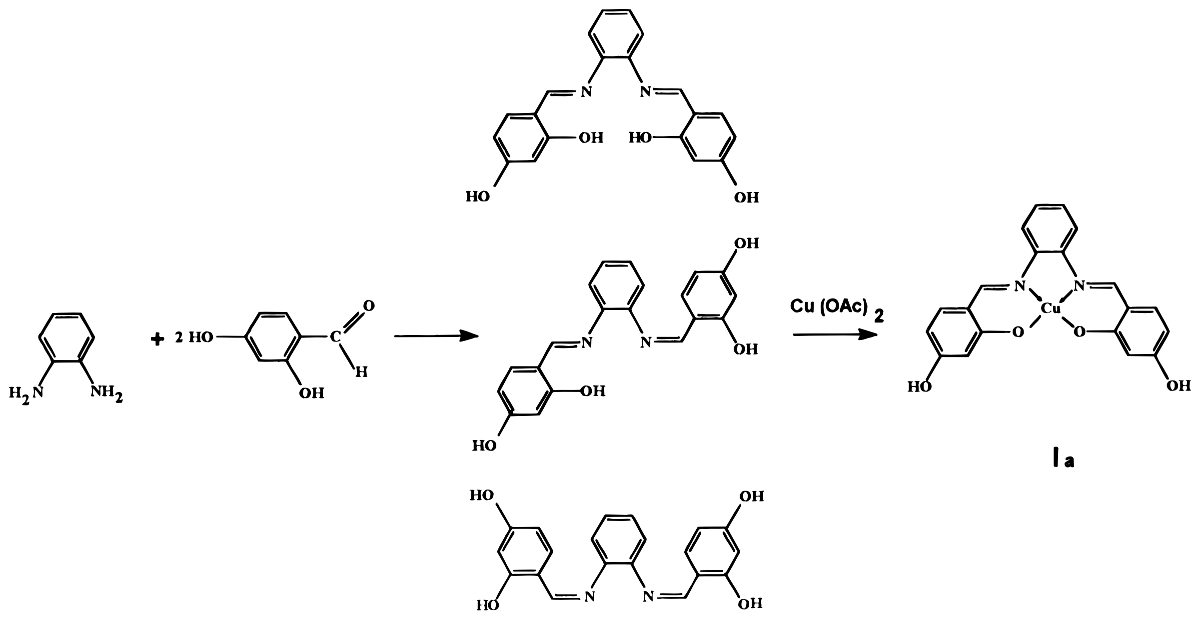
Copolyethers III and IV Synthesis. Copolyethers **III** and **IV** were prepared according to the method previously described.[14,15] We report, as an example, the synthesis of copolymer **III**: In a 10 mL vial with a magnetic stirrer, a mixture of 21 mg (0.05 mmol) of Cu(II) diimine complex **Ia** and 103 mg (0.45 mmol) of BPA was placed together with 100 mg (2.5 mmol) of NaOH, 161 mg (0.5 mmol) of TBAB, used as phase transfer catalyst, and 5 mL of a toluene/water (2:1) mixture. The mixture was heated at 80 °C under stirring; then 1 mL of CH_2Br_2 (a large excess) was added and the vial closed hermetically under N_2. After a few hours, a yellow insoluble material was formed; it was widely washed with ethanol containing 5% acetic acid and then with hot water and dried under vacuum. The yield was about 100%. Elemental analysis for compound **III**: C, 77.9; H, 5.9; N, 0.8 (fitting with a 8% diimine abundance in the copolymer). Elemental analysis compound **IV**: C, 68.7; H, 4.5; N, 3.9 (fitting with a 44% diimine abundance in the copolymer). The inherent viscosities of the NMP soluble fractions of copolymers and the molar percent of NLO units (see also TG analysis) contained in the copolyethers **III** and **IV** are reported in Table 1.

Thermal Measurements. Thermogravimetric analyses (TG) were performed with a Perkin-Elmer TGS-2 apparatus under an N_2 or air atmosphere with a flow rate of 60 mL/min and a heating rate of 10 °C/min. The amount of thermal stable residue at 800 °C (under air flow), constituted from CuO, was used to calculate the molar percent of Cu NLO units in the copolymers **II**−**IV**, assuming that each CuO molecule corresponds to one NLO unit (see Table 1). Differential scanning calorimetry (DSC) to determine the melting point of the synthesized samples and the glass transition temperature of the copolymers was performed by using a Mettler DSC-20 instrument equipped with a subambient system. The starting temperature was −30 °C with a heating rate of 10 °C/min, under an N_2 or air atmosphere.

Elemental Analysis. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer.

^{1}H- and ^{13}C-NMR Analyses. ^1H and ^{13}C-NMR spectra were obtained on a AC 200 F Bruker spectrometer interfaced with an Aspect 3000 computer using the Bruker DISR 90 acquisition software. Samples were solubilized in DMSO-d_6, and the chemical shifts are expressed in ppm by comparison

Scheme 1



with the signals (2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C) of the non-deuterated 0.1% DMSO. The DEPT 135° ^{13}C-NMR spectra were acquired with the Bruker microprogram DEPT.AU. The ^{1}H−^{13}C chemical shift-correlated experiment (HETCOR) data were acquired with the Bruker microprogram XHCOR-R.AU. Data points were zero-filled in F_1 and multiplied by an unshifted sine-bell function in F_1 and by an exponential function in F_2 before Fourier transformation. The NOEDIFF experiments were performed using the Bruker microprogram NOEDIFF.AU.

Viscometry. Inherent viscosities of the copolymers **II**−**IV** ($\eta_{inh} = \ln \eta_r/c$, $c = 0.5$ g dL^{-1}) were measured in a Desreux-Bishoff suspended level viscometer. The measurements were performed on the NMP soluble fractions of copolymers **II**−**IV** at 50 °C, and pertinent values are reported in Table 1.

FAB-MS Analysis. FAB analysis was performed on a double-focusing Kratos MS 50S mass spectrometer equipped with the standard FAB source. The FAB gun (Ion Tech) was operated with a 7−8 keV xenon beam. The instrument was scanned from *m*/*z* 4000 to 90, with a scan rate of 30 s/decade. The accelerating voltage was 8 kV. The mass resolution was ca. 4000. Mass spectra were obtained by using a UV recorder and 3-nitrobenzyl alcohol as a matrix.

MALDI−TOF MS Analysis. The MALDI−TOF mass spectra were performed by a Bruker reflex mass spectrometer equipped with a nitrogen laser (emission at 337 nm, for 3 ns), a flash ADC (time base 8 ns), and a double-plate microchannel detector. Accelerating voltage was 30 kV. The laser irradiance was slightly above threshold (ca. 10^6 W/cm^2). The detection was in the reflection mode (31.4 kV). Ions below *m*/*z* 500 were removed with pulsed deflection, and 50 transients were summed. The resolution was about 370 (fwhh) at *m*/*z* 3000. MALDI spectra were obtained by using 2-(4-hydroxyphenylazo)benzoic acid (HABA) as a matrix. In each MALDI experiment the sample was prepared loading on the probe tip about 0.1 nmol of polymer and 40 μmol of matrix, using THF as a solvent; 0.05 nmol of 4-*tert*-butylcalix(4)arene tetraethyl ester ($C_{60}H_{80}O_{12}$; Janssen) and tetra(*p*-dodecanoxyphenyl)porphyrin ($C_{92}H_{126}N_4O_4$; our preparation) as internal standards for *m*/*z* calibration were also added.

Results and Discussion

In order to introduce the NLO metal complex units into the main chain of copolymers, the structure of the previously investigated Cu(salophen) complex ($\mu\beta = 350 \times 10^{-48}$ esu; $\hbar\omega = 0.92$ eV)[13] was appropriately functionalized with two −OH groups. The synthesis of *N*,*N*′-bis(2,4-dihydroxybenzylidene)-1,2-phenylenediamine Schiff base free ligand was made by reaction of 1,2-phenylenediamine and 2,4-dihydroxybenzaldehyde. According to the Scheme 1, a mixture of three diastereoisomers, each containing four −OH groups in the molecule, is formed in the reaction. In order to obtain polymers with a linear structure, with only one kind of diimine unit along the chain, and to avoid cross-linking reactions, the NLO metal unit was synthesized before the polymerization.

The Cu(II) complex **Ia** was prepared by reaction of a THF solution of *N*,*N*′-bis(2,4-dihydroxybenzylidene)-1,2-phenylenediamines mixture with a methanolic solution of copper acetate. A pure diastereoisomer with both trans-imine linkages (Scheme 1) was rapidly and efficiently separated from the mixture, since the Cu diimine complex **Ia** is insoluble in THF/CH_3OH (yield about 70%). Its structure was established by FAB-MS and thermogravimetric analysis (see the experimental part). Similarly to the unsubstituted Cu(salophen) complex,[13] compound **Ia** exhibits a good thermal stability, with a temperature at which 2% weight loss occurs of 310 °C in air (370 °C under N_2).

Only the chemical structure of the diimimato Ni(II) complex **Ic** was determined by NMR analysis (^{1}H-NMR, ^{13}C-NMR, DEPT, NOEDIFF, and HETCOR spectra) because of the paramagnetic characteristic of copper. In Figure 1 the ^{1}H-NMR (trace a in which the signal at 9.957 ppm assigned to the free hydroxyl group, H_f, has been cut off for lack of space) and relative NOEDIFF (traces b−f) spectra of compound **Ic** are reported.

The negative signal in each NOEDIFF (b−f) spectrum is due to the irradiated hydrogen atom, whereas those positive indicate the protons to it correlated (distance from it of <3 Å). On the basis of these data, the proton atoms contained in **Ic** were so identified as H_f, 9.957 (s); H_c, 8.481 (s); H_b, 7.956 (m); H_d, 7.392 (m); H_a, 7.190 (m), H_e and H_g, 6.217 (m) ppm.

The ^{1}H−^{13}C chemical shift correlation map (HETCOR) of Figure 2 shows that the six tertiary ^{13}C peaks reported in the DEPT spectrum inset in the figure correspond to 103.269 and 107.371 ppm, C_g and C_e; 114.972 ppm, C_b; 125.935 ppm, C_a; 135.362 ppm, C_d; 153.668 ppm, C_c. The four signals at 114.253, 142.175, 164.005, and 167.212 ppm, present in the ^{13}C-NMR

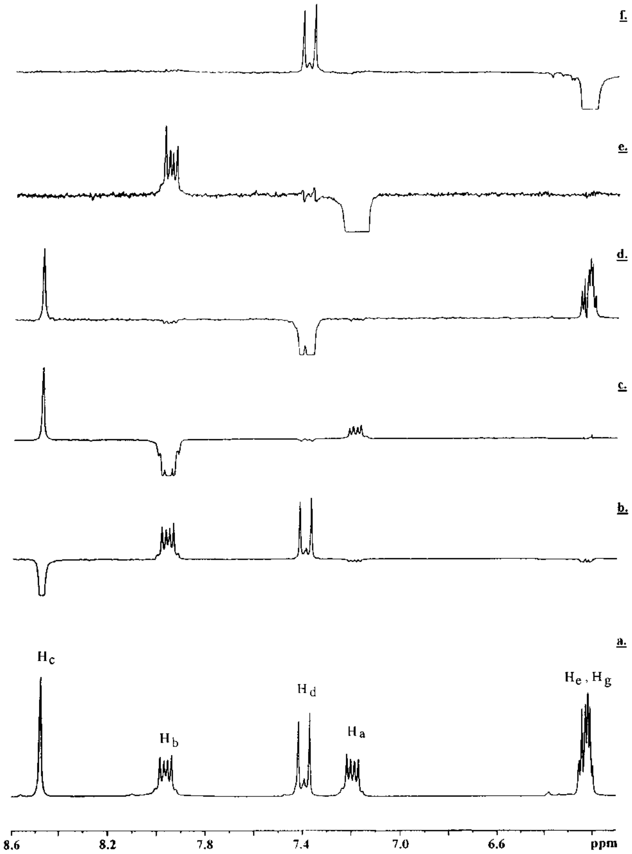


Figure 1. ^{1}H-NMR spectrum (a) and NOEDIFF spectra obtained by irradiation of (b) H_c, (c) H_b, (d) H_d, (e) H_a, and (f) H_e and H_g, in DMSO-d_6 at 30 °C, of [*N,N′*-bis(2,4-dihydroxybenzylidene)-1,2-phenylenediaminato]Ni(II), **Ic**.

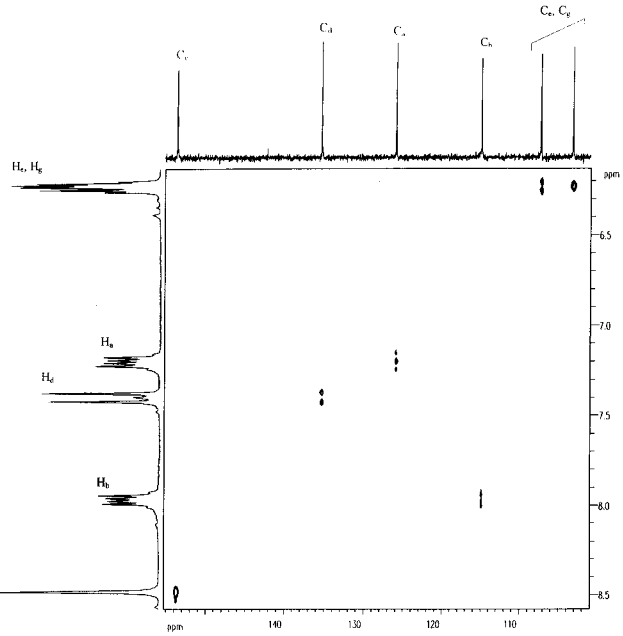
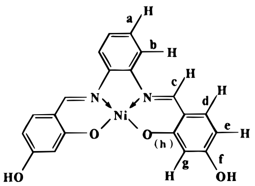


Figure 2. ^{1}H−^{13}C-NMR correlation spectrum of compound **Ic** in DMSO-d_6. The ^{1}H and ^{13}C-NMR (DEPT) spectra are shown along the F_1 and F_2 axes, respectively.

spectrum (omitted for brevity) and absent in the DEPT spectrum, are due to the remaining quaternary carbons.

An exactly alternating copolycarbonate, **II** (some characteristic parameters of which are reported in Table 1), having Cu NLO units separated by aliphatic linkages along the polymer chain, was prepared by interfacial polycondensation between compound **Ia** and 1,4-butanediol bischloroformate in the presence of TBAB as phase transfer catalyst.



Ic

The presence of paramagnetic Cu ions in the sample precluded the NMR analysis, and also FAB-MS spectra gave no useful information about the polymeric structure. However, the MALDI−TOF MS technique was successfully used to identify the low molecular weight oligomers present in the copolymer material.

The MALDI−TOF spectrum of copolycarbonate **II,** obtained using HABA as a matrix and two pure compounds as internal standards for *m*/*z* calibration (see the experimental part), is reported in Figure 3. The structures corresponding to the peaks appearing in the spectrum are reported in Table 2. Although no Na or K salts were added to the sample, the molecular ions in the MALDI spectrum appear as MNa^+ and MK^+.[20−25] The two series of intense peaks at *m*/*z* 1534, 2085, 2636 and 1550, 2101, 2652 correspond to molecular ions (detected as MNa^+ and MK^+, respectively) associated to dimer, trimer, and tetramer open-chain oligomers having two Cu NLO units as end groups. Two other series of peaks at *m*/*z* 1650, 2201, 2752 and 1666, 2217, 2752 are due to molecular ions (either MNa^+ or MK^+) of linear oligomers with a Cu NLO and a butanol unit as end groups (Table 2). Peaks corresponding to cyclic oligomers also appear in the MALDI spectrum at *m*/*z* 1676, 1692, and 2227. The low-intensity peaks at *m*/*z* 1766, 1782, and 2317 are due to open-chain compounds having two butanol units as end groups. All these spectral features find counterparts in the four expected families of oligomers (Table 2). It can also be noticed that the structures of all these compounds are consistent with an alternating sequence of Cu NLO and butanediol units in the molecules.[22,26]

The copolymer **II,** in spite of the relatively low T_g values (about 0 °C) commonly observed in aliphatic polycarbonate materials,[27]does not exhibit any T_g in the temperature range between −30 °C and the decomposition temperature (about 200 °C). Probably, the presence of rigid NLO units (50 mol %) into macromolecules increases the T_g value, even though the thermal decomposition behavior of this material remains unchanged.[28]

In order to obtain more thermal stable polymeric materials containing different amounts of metal NLO complex units into the main chain, copolyethers **III** and **IV** were synthesized by interfacial condensation reaction between mixtures of the Cu(II) diimine complex **Ia** and BPA in the molar ratio of 1:10 and 1:1, respectively, and dibromomethane (in Table 1 are reported some of their characteristic parameters). The Cu(II) diimine molar percent contained in each copolymer (10% for copolymer **III** and 47% for copolymer **IV**) was evaluated by considering the amount of CuO residue found in thermogravimetric experiments (see Experimental Section) and confirmed by elemental analysis (see Table 1).

The structural characterization of these materials was performed by MALDI−TOF MS analysis. Also in these cases the molecular ions of the low molecular weight oligomers contained in the polymer samples were detected as MNa^+ and, with lower abundance, MK^+.

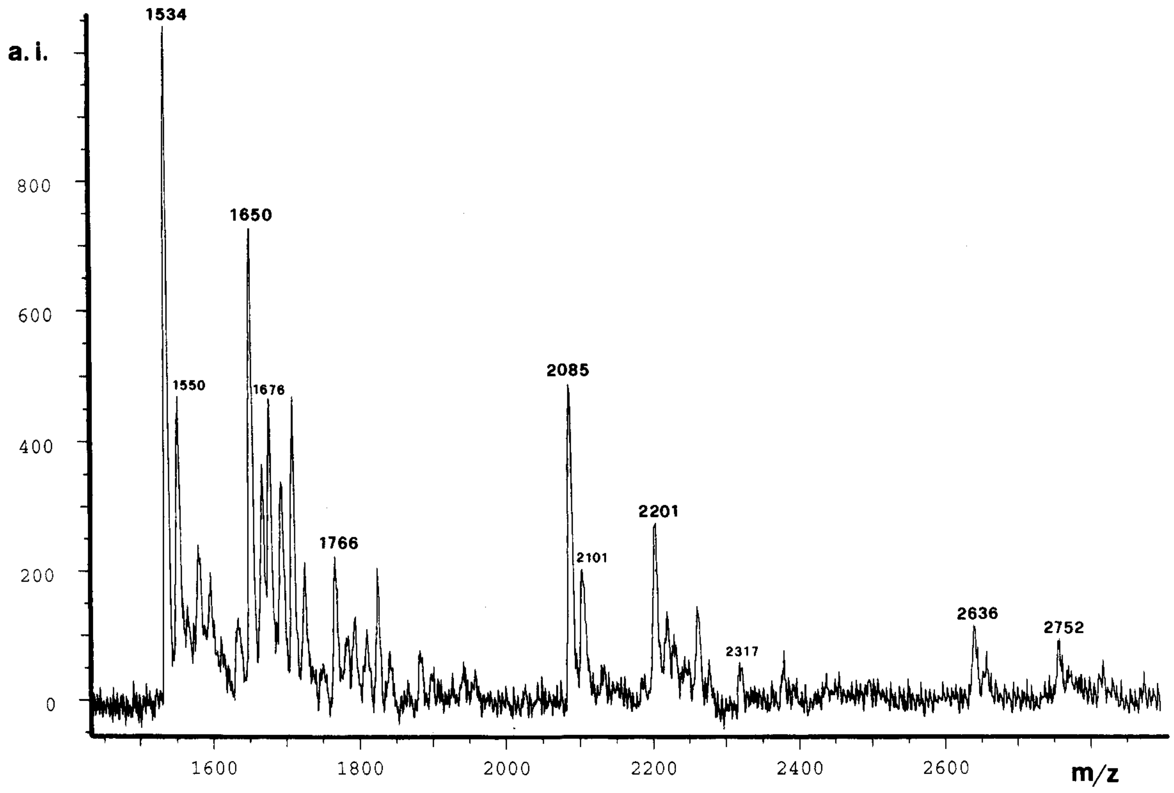
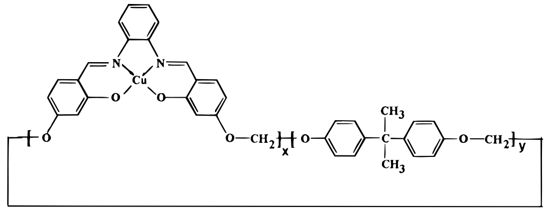


Figure 3. MALDI–TOF mass spectrum of the exactly alternating copolycarbonate **II**.

Nevertheless, only peaks due to MNa^+ ions are discussed here, to simplify the following discussion, and their *m*/*z* values marked in the spectra.

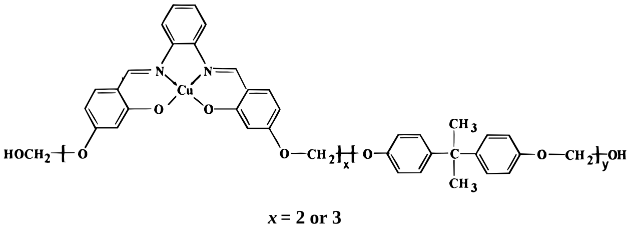
The MALDI–TOF spectrum of copolyether **III** is reported in Figure 4. The spectrum is essentially constituted by a family of intense peaks at *m*/*z* 1644 + *n*240 with $n = 0-8$, corresponding to the molecular ions (as MNa^+) of cyclic oligomers containing a Cu NLO unit ($x = 1$) and up to 13 BPA units ($y = 13$), having the following formula (see also Table 3):



Two series of peaks due to cyclic oligomers with only BPA units ($x = 0$) or BPA and two Cu NLO units ($x = 2$) in the molecule are also present with low intensities either at *m*/*z* 1703 + *n*240 or at *m*/*z* 1585 + *n*240 ($n = 0-6$, Table 3).

The MALDI spectrum of copolyether **IV** is shown in Figure 5. The structural assignment of the compounds corresponding to the observed spectral peaks is reported in Table 3. The comparison with the spectrum of copolymer **III** (Figure 4) suggests that the higher molar content of Cu NLO units in the sample (47%) is associated to a larger number of peaks in the spectrum (Figure 5). Analogously to copolymer **III,** two series of peaks, due to molecular ions of cyclic oligomers containing one or two Cu NLO units ($x = 1$ or 2) in each molecule, appear in the spectrum of copolymer **IV** (Figure 5) at *m*/*z* 1644 + *n*240 and 1585 + *n*240 (with $n = 0-9$). Moreover, peaks due to cyclic oligomers with three Cu NLO units ($x = 3$) are also present with low intensities at *m*/*z* 2486 + *n*240 (Table 3).

Inspection of Figure 5 reveals also the presence in the spectrum of two new series of intense peaks at *m*/*z* 1633 + *n*240 and 1814 + *n*240 (with $n = 0-8$) (Table 3), corresponding to molecular ions of open-chain oligomers containing two or three Cu NLO units ($x = 2$ or 3) and having $-CH_2OH$ end groups, as indicated in the following structure:



$x = 2$ or 3
$y =$ up to 9

The formation of cyclic oligomers in the synthesis of polyformals is well known.[26,29–31] On the other hand, it has been also reported that open-chain oligomers are produced in the presence of low reactive comonomeric units.[14,15] The presence of open-chain oligomers only in the case of the copolymer **IV** (Figure 5, Table 3) is certainly due to the higher amount of NLO monomer in the reaction mixture. As a matter of fact, only one kind of open-chain compound (with two methanol end groups, Table 3) is found among the oligomers. It can be therefore argued that both the methanol groups are attached to NLO units in these molecules. The rigidity of both terminals (due to the NLO units) of the growing chain favor their deactivation, hence the formation of open-chain compounds rather than cyclic oligomers.[14,15]

It can be also observed that, in spite of the high molar content of bisphenol units in the copolymer **III** (90%), only some peaks due to oligomers containing only BPA

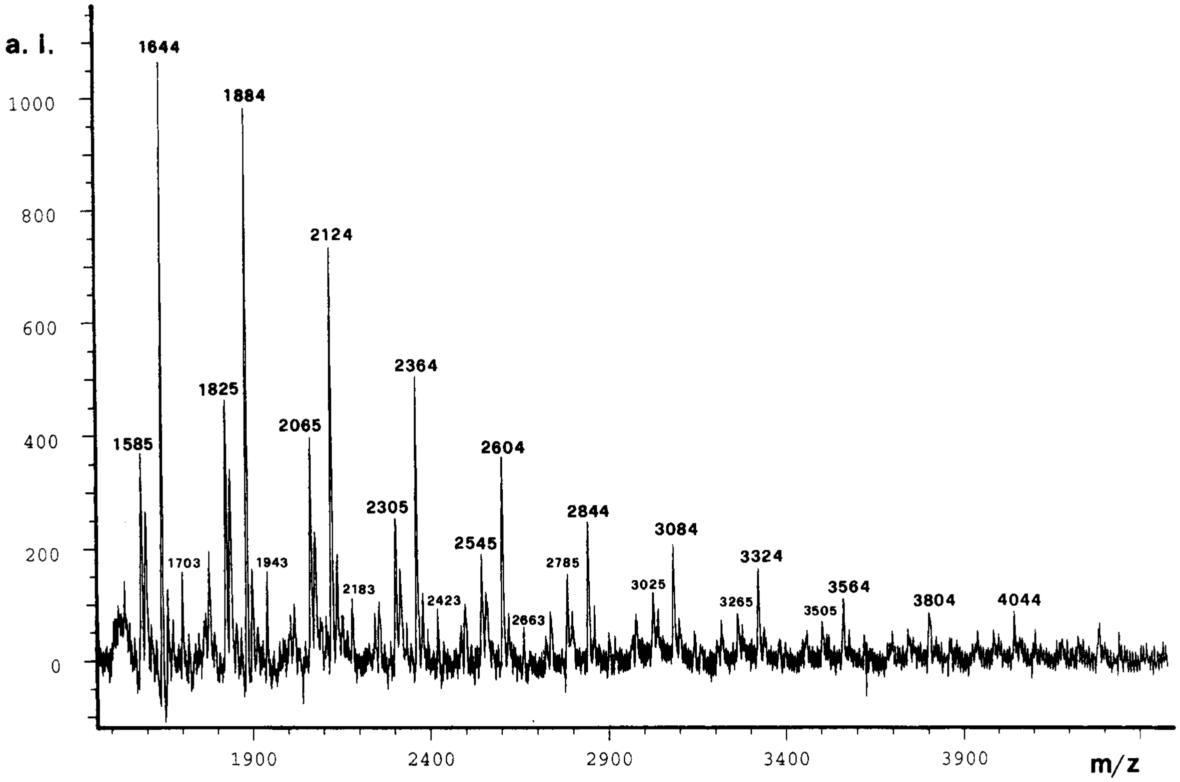
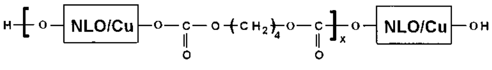
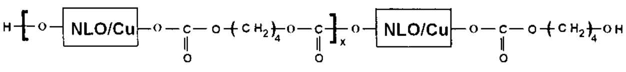
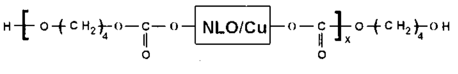
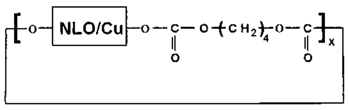


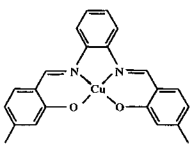
Figure 4. MALDI–TOF mass spectrum of the random copolyether **III**.

Table 2. Compounds Present in the Copolymer II and Detected as MNa$^+$ or MK$^+$ Ions in the MALDI–TOF MS

Structure [a]	molecular ions (m/z) as MNa$^+$ and (MK$^+$) for x=		
	2	3	4
	1534 (1550)	2085 (2101)	2636 (2652)
	1650 (1666)	2201 (2217)	2752 (2768)
	1766 (1782)	2317	
	1676 (1692)	2227	

a) Abbreviation in the reported structures:

NLO/Cu =



units are found in the MALDI spectrum of Figure 4, whereas they are absent in the spectrum of Figure 5. A possible explanation of this behaviour is that the presence of the Cu diimine complex units in the molecules (as observed in other analogous cases)[15] renders easier their detection in the mass spectrometric experiments. The composition of low molecular weight oligomers inferred by MALDI spectra is however diagnostic of the random copolymer structures of **III** and **IV**.

The copolymer **III** exhibits a distinct glass transition temperature (88 °C, Figure 6), slightly higher than that of bisphenolic polyformals (about 80 °C).[27] In contrast, copolymer **IV** does not show any T_g. Moreover, both copolymers **III** and **IV** exhibit a high decomposition

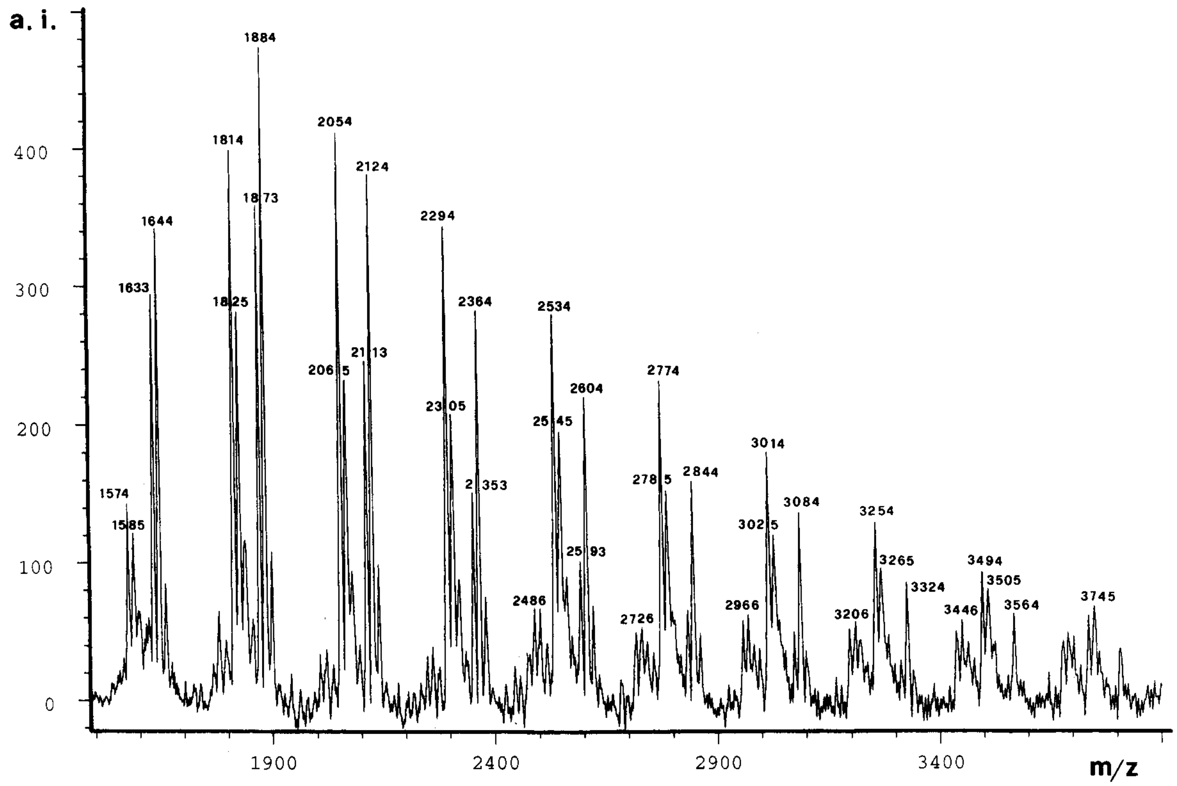
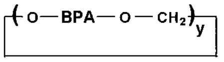
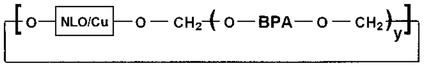
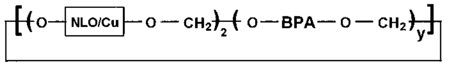
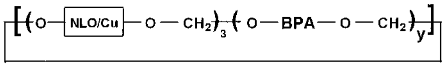
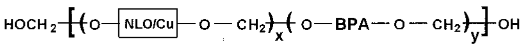


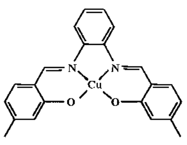
Figure 5. MALDI−TOF mass spectrum of the random copolyether **IV**.

Table 3. Compounds Present in the Copolymers III and IV, Detected as MNa$^+$ Ions in their MALDI−TOF MS

Structure[a]		molecular ions (m/z) as MNa$^+$ for y =											
		2	3	4	5	6	7	8	9	10	11	12	13
							1703	1943	2183	2423	2663	2903	3143
					1644	1884	2124	2364	2604	2844	3084	3324	3564
			1585	1825	2065	2305	2545	2785	3025	3265	3505	3745	
					2486	2726	2966	3206	3446	3686			
	x=2		1633	1873	2113	2353	2593	2823					
	x=3	1814	2054	2294	2534	2774	3014	3254	3494				

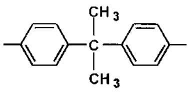
a) Abbreviations in the reported structures:

NLO/Cu =



and

BPA =



temperature (above 400 °C under N_2 atmosphere), as commonly encountered in polyethers.[14,15,32] The absence of any T_g in the case of copolymers **II** and **IV** until a temperature of 200 and 400 °C, respectively, (where a continuous and rapid weight loss begins to occur) is indicative of a tendency toward higher T_g values as the molar ratio of the Cu(II) complex (NLO unit **Ia**) in the copolymer increases.

In summary, this work demonstrates that transition metal complexes exhibiting second-order NLO response can be easily incorporated into polymeric matrices as main-chain units. The obtained copolymers **III** and **IV** are robust, exhibit very good thermal stability, and are promising candidates for second-order NLO applications. The synthesis of other copolymeric NLO systems with higher molecular weight, higher glass transition temperature, and larger solubility and the investigation of their second-order NLO properties are currently in progress.

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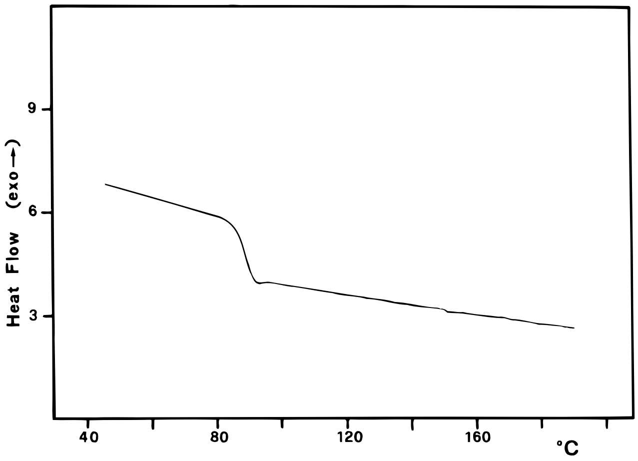

Figure 6. DSC thermogram of copolyether **III**.

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