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NLO active Pd(II)-based organometallic side-chain polymers with C,N or N,O-chelating chromophoric ligands

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Abstract

Three organometallic homopolymers and three copolymers have been obtained, by reacting, respectively, cyclopalladated dinuclear complexes with a polymeric backbone, and by radical copolymerization of cyclopalladated acrylic monomers and methyl methacrylate. Taking into account thermal behaviour and solubility, the copolymers, which display good second order nonlinear optical activity, seem to be the most promising for applications within the new metallated macromolecules. Macroscopic nonlinear optical coefficients d_{33} have been determined on spin-coated corona-poled thin films by means of Second Harmonic Generation (SHG) measurements at the wavelength of 1064 nm.

Keywords: Organometallic; Polymers; Nonlinear optics

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1. Introduction

The second order NLO properties of organometallic complexes which display metal-to-ligand or ligand-to-metal charge-transfer bands in the UV-visible region of the spectrum have been investigated in recent years, the metal centre often resulting to be an extremely strong electron donor or acceptor [1,2].

The basic reason for the growing interest in organometallic compounds is that variation in metal, oxidation state, coordination geometry and ligand environment allows to tune NLO responses in ways unattainable for purely organic molecules. To date, systematic studies of related organometallic chromophores allowed a satisfactory understanding of significant relationships between structure and NLO properties [3,4].

In particular, chelation of the chromophoric ligands to a metal centre should be responsible for improvement of their NLO activity. In fact, this coordination, forcing the chelating atoms into fairly rigid cycles can favour the π-electron push–pull effect of the chromophores. Moreover, it is noted that the metal centre has an intrinsic role in the charge-transfer in various bis(salicylaldiminato)metal Schiff base complexes: it favours the conjugation of the chromophore acting as a donor, and hence allows a larger charge transfer in excited states [5].

In this field, one of the most promising approaches to the development of new materials for second order nonlinear optical activity is claimed to be that dealing with polymers containing organometallic NLO active fragments [6].

A series of Schiff bases-cyclopalladated compounds with second order NLO properties, which was employed to obtain side-chain polyacrylates, has been previously examined in our laboratory [7,8]. The present work is a further contribution to this field.

We have synthesised two groups of polymers which include square-planar cyclopalladated complexes as pendants. The first group is made up by three metallated polymers, obtained by reacting acetato-bridged cyclopalladated dinuclear complexes with a suitable functionalised polyacrylate as polymeric support, according to the next

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sequence:

chromophoric C, N-ligand—(+Pd acetate)

→ dinuclear complex → —(+polyacrylate)

→ acrylate polymer with mononuclear pendants

Three copolymers with methyl methacrylate were obtained from acrylic mononuclear complexes, as schematized below.

chromophoric N, O-ligand—(+dinuclear acrylic complex)→

→acrylic mononuclear complex − (+methyl methacrylate)

→ copolymer

The two groups of polymers contain both C,N- and N,O-chelate chromophores; variation in design aiming to introduce changes in the properties of the final materials.

2. Experimental section

2.1. Materials

Optical observations on low molecular weight species and polymers were performed by use of a Zeiss polarizing microscope equipped with a Mettler FP5 microfurnace. Phase transition temperatures and enthalpies were measured with a Perkin–Elmer DSC-7 apparatus, adopting a scanning rate of 10 K min^{-1}, under a dry nitrogen flow. Thermogravimetric analysis was employed using a Mettler TG50 apparatus to evaluate the palladium content of complexes and polymers and decomposition temperatures. X-ray diffraction patterns were recorded at room temperature by a flat film camera using Ni-filtered Cu Kα radiation. ^1H NMR spectra were recorded in $CDCl_3$, Me_2SO-d_6 or 1,1,2,2,-tetrachloroethane-d_2 at 200 MHz using a Varian Gemini spectrometer. Inherent viscosities (η_{inh}) were measured in 1,1,2,2-tetrachloroethane or in dichloromethane solutions at 25 °C using an Ubbelohde viscosimeter. Reactions requiring inert atmosphere were carried out by using Schlenk techniques in nitrogen. Solvents for polymerisations were dried before use by keeping them on molecular sieves after distillation.

The reagents 4-(dimethylamino)benzaldehyde, 4-nitroaniline, *N,N*-dimethylaniline, 2-amino-5-nitrophenol, 2-methyl-5-nitrophenol, *N,N*-dimethyl-4-nitrosoaniline, sodium hydrosulfite, *N*-bromosuccinimide, 4-(diethylamino)salicylaldehyde, 3-(diethylamino) phenol and AIBN were commercially available (Aldrich). Palladium diacetate was obtained from palladium sponge by standard methods [9] and recrystallized from benzene/acetic acid.

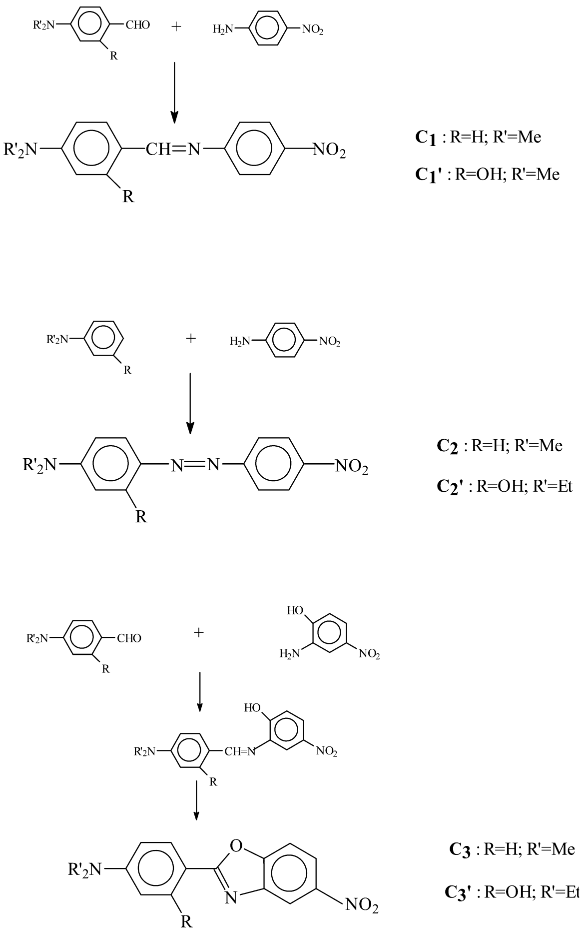
The imine $\mathbf{C}_1$ (for the formulas of the six chromophoric ligands, see Scheme 1) is commercially available (Supelco). For this work, it was obtained from stoichiometric amounts of 4-nitroaniline and 4-(dimethylamino)-benzaldehyde in boiling *o*-dichlorobenzene as orange crystals which melt at 106–107 °C. Yield = 79%.

The compounds $\mathbf{C}_2$ [10] and $\mathbf{C}_2'$ [11] were synthesised according to literature methods by addition of sodium nitrite to a cold solution of 4-nitroaniline in 6 M hydrochloridric acid and coupling of the diazonium salt with *N,N*-dimethylaniline or, respectively, 3-(diethylamino)phenol in presence of sodium acetate. After crystallization in chloroform/hexane $\mathbf{C}_2$ (yield = 76%) melts at 238–239 °C and $\mathbf{C}_2'$ (yield = 80%) melts at 222–225 °C.

The imine 2-[[4-(dimethylamino)phenyl]methylene]amino-5-nitrophenol (*dibenp*), precursor of $\mathbf{C}_3$ [12], was obtained from 4-(dimethylamino)benzaldehyde and 2-amino-5-nitrophenol by the same procedure followed for $\mathbf{C}_1$. Yield = 91%, mp = 230 °C.

The preparation of the functionalised chelating Schiff base $CH_2{=}CHCOO(CH_2)_6O$-*p*-C_6H_4O-*p*-COO-*p*-C_6H_3–(*m*-OH)–*p*-CH=N-*p*-C_6H_4-*p*-$O(CH_2)_6CH_3$ ($\mathbf{I}_{Acr\text{-}OH}$) was already described [7].

The Schiff base $CH_2{=}CHCOO(CH_2)_3O$-*p*-C_6H_4O-*p*-



Scheme 1. Formulas of the organic ligands.

COO-*p*-C_6H_4-*p*-CH=N-*p*-C_6H_4-*p*-OCH_3 ($\mathbf{I}_{acr}$) was obtained as already described [13] from the appropriate aldehyde.

The polymer $\mathbf{P}_0$ (see Scheme 2) was synthetised according to literature methods [7] from $\mathbf{I}_{Acr\text{-}OH}$.

2.2. Synthesis of the chromophoric ligands

Scheme 1 summarizes the sequence of the synthetic steps followed for all the ligands.

2.2.1. Synthesis of 4-nitrosalicylaldehyde

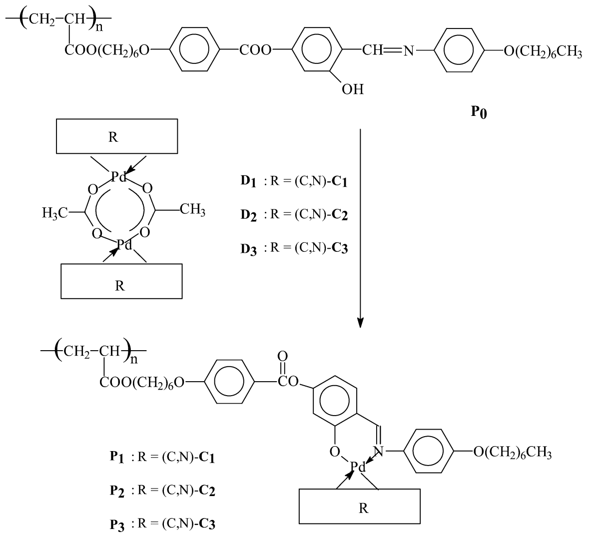
The synthesis of 4-nitrosalicylaldehyde, a precursor of the chromophoric ligand $\mathbf{C}'_1$, was attained in steps by adapting a literature method [14].

Synthesis of 2-methyl-5-nitrophenol. The compound was obtained following a literature method [15] from 2-methyl-5-nitroaniline suspended in sulphuric acid (10% aqueous solution) at 0 °C and sodium nitrite. By crystallization from benzene/petroleum ether (bp = 80–110 °C) dark yellow crystals were obtained which melt at 118–119 °C. Yield 64%.

Synthesis of 4-nitro-2-acetoxytoluene. Standard methods [16] were used in the acetylation of 2-methyl-5-nitrophenol in pyridine and acetic anhydride. The compound was crystallised from ethanol/water obtaining amber crystals melting at 72–73 °C. Yield 82%.

Synthesis of 4-nitro-2-acetoxybenzyl bromide. Standard methods [17] were also employed in this step, by reacting 4-nitro-2-acetoxytoluene with *N*-bromosuccinimide in carbon tetrachloride, with benzoyl peroxide as initiator. The brown crystals (two polymorphic crystalline phases) melt in part at 56–58 °C and in part at 75–76 °C. Yield = 55%

Synthesis of N-(4-nitro-2-acetoxybenzyl)pyridinium bromide. [17] A mixture of 17.98 g (0.066 mol) of 4-nitro-2-acetoxybenzyl bromide in 55 mL of absolute ethanol and 6 mL of pyridine dry was refluxed for 45 min. On cooling, the white solid precipitate was recovered and dried at 100 °C. It was employed as a crude product. Yield = 46%. Decomposition occurs before melting.



Scheme 2. Formulas of the dinuclear complexes $\mathbf{D}_{1-3}$, of $\mathbf{P}_0$ and of the homopolymers.

Synthesis of the 4-nitrosalicylaldehyde. [17] To a stirred suspension of 1.90 g (5 mmol) of the pyridinium salt and 0.95 g (6 mmol) of *N,N*-dimethyl-4-nitrosoaniline in 18 mL of ethanol at 4 °C were added slowly 0.81 g of sodium hydroxide in 10 mL of water. The solution colour turned to dark red. After stirring 1 h at 2–4 °C, the solution was poured into about 200 mL of cold water and acetic acid (pH = 4–5). The solid was recovered by filtration and dissolved in a solution of ethanol and hydrochloridric acid in water (pH = 2 ca.). The solution was filtered and the filtrate concentrated to attain a brown precipitate. This was obtained by crystallization from acetone/water as dark pink crystals which melted at 136–137 °C [16]. Yield = 42%. ^{1}H NMR ($CDCl_3$): δ 7.4 (1H, d, $J = 8.5$ Hz); δ 7.5 (1H, s); δ 7.7 (1H, d, $J = 8.5$ Hz); δ 10.0 (1H, s); δ 10.6 (1H, s).

2.2.2. Synthesis of C'_1

To a solution of 1.50 g (10 mmol) of *N,N*-dimethyl-4-nitrosoaniline in 20 mL of ethanol/water (3:1) was added a large excess (about 7 g) of sodium hydrosulfite, the colour turning from brown to yellow. To this suspension, 1.67 g (10 mmol) of 2-hydroxy-4-nitrobenzaldehyde was added and, after about 1 h stirring, a dark red solid precipitated. This solid was recovered by filtration and recrystallised from chloroform as red crystals. Yield = 60%. UV–Vis spectrum: $\lambda_{max} = 459$ nm.

^{1}H NMR ($CDCl_3$): δ 3.1 (6H, s); δ 6.7 (2H, d, $J = 7.0$ Hz); δ 7.4 (2H, d, 7.0 Hz); δ 7.5 (1H, d, $J = 8.0$ Hz); δ 7.8 (2H, dd, $J = 8.0$, 2.0 Hz); δ 8.7 (1H, s); δ 14.3 (1H, s).

2.2.3. Synthesis of C_3

Compound $\mathbf{C}_3$ was reported in a patent [18]. The synthesis was performed from the corresponding imine *dibenp*. To a suspension of 3.60 g (13 mmol) of the imine in 100 mL of dry chloroform, 6.30 g (14 mmol) of lead (IV) acetate were added slowly. The suspension turned from brown to dark red. After stirring 2 h, the mixture was filtered and the solution concentrated. Brick red crystals precipitated by addition of cold ethanol. Yield = 91%. UV–Vis spectrum: $\lambda_{max} = 409$ nm.

^{1}H NMR ($CDCl_3$): δ 3.1 (6H, s); δ 6.8 (2H, d, $J = 7.0$ Hz); δ 7.7 (1H, d, $J = 9.0$ Hz); δ 8.1 (2H, d, $J = 7.0$ Hz); δ 8.3 (1H, d, $J = 9.0$ Hz); δ 8.4 (1H, s).

2.2.4. Synthesis of C'_3

The synthesis was performed in two steps.

Synthesis of 2-[[[4-(diethylamino)-2-(hydroxy)]phenyl]-methylene]amino-5-nitro-phenol. In about 80 mL of hot acetic acid 5.00 g (32 mmol) of 2-amino-5-nitrophenol were dissolved, and 6.00 g (31 mmol) of 4-(diethylamino)salicylaldehyde were dissolved in about 60 mL of hot acetic acid. The two solutions were mixed with stirring. After few minutes an orange solid precipitated, which was recovered by filtration, washed with ethanol, and dried at 80 °C for 2 h. Yield = 90%.

^{1}H NMR ($CDCl_3$): δ 1.2 (6H, t, $J = 7.0$ Hz); δ 3.4 (4H, q, $J = 7.0$ Hz); δ 6.0 (1H, s); δ 6.4 (1H, d, $J = 9.0$ Hz); δ 7.3 (1H, d, $J = 9.0$ Hz); δ 7.5 (1H, d, $J = 9.0$ Hz); δ 7.8 (2H, d, $J = 9.0$ Hz); δ 8.8 (1H, s); δ 10.5 (1H, s); δ 14.0 (1H, s).

Synthesis of the ligand. To a suspension of 9.34 g (28 mmol) of the iminic precursor in 140 mL of dry dioxane/acetic acid (10:4) 13.20 g (29 mmol) of lead (IV) acetate were added and the temperature was kept at 5–7 °C during the addition. After this time, the suspension was stirred for 4 h at 8–10 °C, and finally for 1 h at room temperature. The suspension was poured in about 400 mL of water. A brown solid precipitate was formed, which was recovered by filtration, washed in water, then dried at 80 °C for 4–5 h. It was purified by chromatography in dichloromethane on a florisil 100–200 mesh column. From the concentrated solution bright orange crystals precipitated. Yield = 20%. UV–Vis spectrum: $\lambda_{max} = 422$ nm.

^{1}H NMR ($CDCl_3$): δ 1.2 (6H, t, $J = 7.0$ Hz); δ 3.4 (4H, q, $J = 7.0$ Hz); δ 6.3 (1H, s); δ 6.4 (1H, d, $J = 9.0$ Hz); δ 7.6 (1H, d, $J = 9.0$ Hz); δ 7.8 (1H, d, $J = 9.0$ Hz); δ 8.2 (1H, d, $J = 9.0$ Hz); δ 8.4 (1H, s); δ 11.1 (1H, s).

2.3. Synthesis of the dinuclear complexes

The dinuclear complexes $\mathbf{D}_{1-3}$ (see Scheme 2 for the formulas) and $\mathbf{D}_{acr}$ (see Scheme 3) were obtained by reaction of palladium(II) acetate with the appropriate ligands following the same general procedure [19].

The complexes $\mathbf{D}_{1-3}$ were obtained, respectively, from $\mathbf{C}_{1-3}$. As an example, the preparation of $\mathbf{D}_1$ is described.

A mixture of 3.00 (11.2 mmol) of $\mathbf{C}_1$ and 2.50 g of palladium (II) acetate (11.2 mmol) in 40 mL of acetic acid was gently boiled for ca. 10 min. On cooling at room temperature an orange microcrystalline solid precipitated. The solid was recovered by filtration and washed with ethanol.

In the case of $\mathbf{D}_2$ the reaction mixture was kept at 60 °C for 4 h. Yields: $\mathbf{D}_1 = 37\%$; $\mathbf{D}_2 = 40\%$; $\mathbf{D}_3 = 43\%$. UV–Vis absorption spectra give, respectively: $\lambda_{max} = 467$ nm for $\mathbf{D}_1$; $\lambda_{max} = 546$ nm for $\mathbf{D}_2$; $\lambda_{max} = 413$ nm for $\mathbf{D}_3$.

The preparation in acetic acid, of $\mathbf{D}_{acr}$, from stoichiometric amounts of palladium(II) acetate and $\mathbf{I}_{acr}$, is quite similar. Yield = 38%.

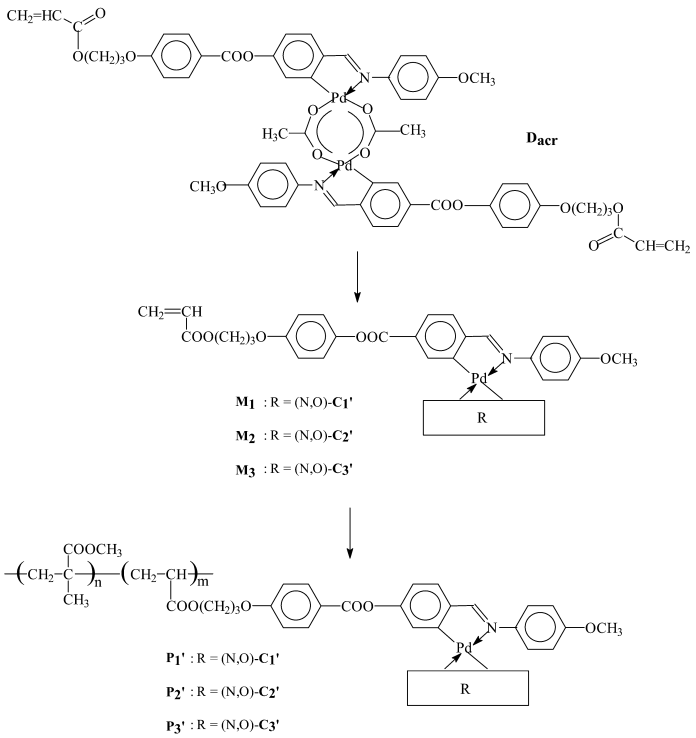
Palladium contents calculated by TGA measurements and thermodynamic data are reported in Table 1. All the dinuclear species were employed as crude products in the further reactions.

C, H, N analysis data for the dimeric complexes $\mathbf{D}_{1-3}$ are reported below.

$\mathbf{D}_1$: calculated: C 46.96, H 4.17, N 9.66%; found: C 46.82, H 4.06, N 9.46%.

$\mathbf{D}_2$: calculated: C 44.10, H 3.93, N 12.86%; found: C 43.91, H 3.70, N 12.65%.

$\mathbf{D}_3$: calculated: C 45.50, H 3.59, N 9.36%; found: C 45.56, H 3.78, N 9.45%.



Scheme 3. Formulas of $\mathbf{D}_{acr}$, of the monomeric complexes and of the copolymers.

Table 1
Thermodynamic data and Pd content (%) of $\mathbf{D}_{1-3}$ and the monomeric complexes

	T_{m} (°C)[a]	ΔH_{m} (J/g)	T_{d} (°C)[b]	$\mathrm{Pd}_{\mathrm{calc}}$[c] (%)	$\mathrm{Pd}_{\mathrm{exp}}$[d] (%)
$\mathbf{D}_1$	–	–	229	24.53	26.95
$\mathbf{D}_2$	–	–	270	24.47	25.51
$\mathbf{D}_3$	–	–	210	23.79	24.01
$\mathbf{D}_{\mathrm{acr}}$	192.2[e]	–[f]	235	17.05	17.11
$\mathbf{M}_1$	191.3	20.4	257	12.53	13.08
$\mathbf{M}_2$	–	–	255	12.12	13.47
$\mathbf{M}_3$	179.2	12.0	290	11.94	11.54

[a] Onset value.
[b] Decomposition temperature calculated at 5% by weight loss.
[c] Calculated palladium content.
[d] Experimental palladium content estimated by TGA measurements in air.
[e] Peak value.
[f] Signal not integrable.

^{1}H NMR data, reported below, gave evidence of fairly high purity of the products.

^{1}H NMR (CDCl$_3$) for $\mathbf{D}_1$: δ 2.0 (3H, s); δ 2.9 (6H, s); δ 5.4 (1H, d, $J = 2.0$ Hz); δ 6.3 (1H, dd, $J = 10.0, 2.0$ Hz); δ 6.8 (2H, d, $J = 9.5$ Hz); δ 7.3 (1H, d, $J = 10.0$ Hz); δ 7.7 (1H, s); δ 7.9 (2H, d, $J = 9.5$ Hz).

^{1}H NMR (CDCl$_3$) for $\mathbf{D}_2$: δ 2.1 (3H, s); δ 2.9 (6H, s); δ 5.4 (1H, d, $J = 2.0$ Hz); δ 6.4 (1H, dd, $J = 9.0, 2.0$ Hz); δ 7.5 (3H, m); δ 7.9 (2H, d, $J = 9.0$ Hz).

^{1}H NMR (CDCl$_3$) for $\mathbf{D}_3$: δ 2.1 (3H, s); δ 3.0 (6H, s); δ 5.7 (1H, d, $J = 2.0$ Hz); δ 5.8 (1H, s); δ 7.0 (1H, d, $J = 10.0$ Hz); δ 7.1 (1H, d, $J = 10.0$ Hz); δ 8.2 (2H, m).

^{1}H NMR (CDCl$_3$) for $\mathbf{D}_{\mathrm{acr}}$: δ 1.7 (2H, m); δ 1.9 (3H, s); δ 3.6 (2H, t, $J = 7.0$ Hz); δ 3.8 (3H, s); δ 4.2 (2H, t, $J = 7.0$ Hz); δ 5.8 (1H, dd, $J = 10.5, 1.5$ Hz); δ 6.0 (1H, d, $J = 2.0$ Hz); δ 6.1 (1H, q, $J = 10.5$ Hz); δ 6.4 (1H, dd, $J = 17.0, 1.5$ Hz); δ 6.6 (8H, m); δ 7.2 (2H, d, $J = 8.5$ Hz); δ 7.5 (1H, s).

2.4. Synthesis of the mononuclear complexes

The preparation of the mononuclear complexes $\mathbf{M}_{1-3}$ (formulas in Scheme 3) was attained from the corresponding ligands $\mathbf{C}_{1'-3'}$ and the dinuclear complex $\mathbf{D}_{\mathrm{acr}}$ with the same general procedure. In a typical preparation of $\mathbf{M}_1$ 0.230 g (0.8 mmol) of $\mathbf{C}'_1$ were suspended in 8 mL of absolute ethanol and 20 mL of dichloromethane and to the suspension were added 0.200 g of sodium acetate, 0.300 g of potassium carbonate and finally 0.500 g of $\mathbf{D}_{\mathrm{acr}}$ (0.4 mmol). The suspension was stirred for about 1 h at room temperature, while the colour faded. After this time the mixture was filtered and concentrated in vacuo to ca.15 mL. On cooling, it was obtained a light brick red precipitate, which was recrystallized from dichloromethane/ethanol and dried in air. Yield = 80%. For $\mathbf{M}_2$ and $\mathbf{M}_3$ yields were, respectively, 90 and 92%.

Thermodynamic data and Pd contents (%) are reported in Table 1. UV–Vis absorption spectra give, respectively, $\lambda_{\mathrm{max}} = 489$ nm for $\mathbf{M}_1$; $\lambda_{\mathrm{max}} = 553$ nm for $\mathbf{M}_2$; $\lambda_{\mathrm{max}} = 460$ nm for $\mathbf{M}_3$.

C, H, N analysis data for the mononuclear complexes are reported.

$\mathbf{M}_1$: calculated: C 59.40, H 4.51, N 6.59%; found: C 59.25, H 4.65, N 6.70%.
$\mathbf{M}_2$: calculated: C 58.81, H 4.70, N 7.97%; found: C 58.02, H 4.44, N 8.11%.
$\mathbf{M}_3$: calculated: C 59.29, H 4.52, N 6.28%; found: C 59.25, H 4.63, N 6.41%.

^{1}H NMR data (reported below) gave evidence of high purity of the products.

^{1}H NMR (CDCl$_3$) for $\mathbf{M}_1$: δ 1.6 (2H, m); δ 2.7 (6H, s); δ 3.9 (3H, s); δ 4.1 (2H, t, $J = 6.5$ Hz); δ 4.4 (2H, t, $J = 6.5$ Hz); δ 5.3 (1H, d, $J = 2.0$ Hz); δ 5.9 (1H, dd, $J = 10.5, 1.5$ Hz); δ 6.2 (1H, q, $J = 10.5$ Hz); δ 6.5 (1H, d, $J = 1.5$ Hz); δ 6.6 (3H, m); δ 6.8 (2H, dd, $J = 9.5, 2.0$ Hz); δ 7.0 (4H, m); δ 7.3 (6H, m); δ 8.1 (4H, m).

^{1}H NMR (CDCl$_3$) for $\mathbf{M}_2$: δ 1.4 (6H, t, $J = 7.0$ Hz); δ 2.2 (2H, m); δ 3.5 (4H, q, $J = 7.0$ Hz); δ 3.9 (3H, s); δ 4.2 (2H, t, $J = 6.5$ Hz); δ 4.5 (2H, t, $J = 6.5$ Hz); δ 5.8 (3H, m); δ 6.1 (1H, q, $J = 10.5$ Hz); δ 6.3 (1H, dd, $J = 10.5, 2.0$ Hz); δ 6.5 (1H, d, $J = 17.0$ Hz); δ 6.9 (1H, dd, $J = 8.0, 1.5$ Hz); δ 7.0 (4H, m); δ 7.4 (4H, m); δ 7.9 (2H, d, $J = 9.0$ Hz); δ 8.1 (5H, m).

^{1}H NMR (CDCl$_3$) for $\mathbf{M}_3$: δ 1.4 (6H, t, $J = 7.0$ Hz); δ 2.2 (2H, m); δ 3.4 (4H, q, $J = 7.0$ Hz); δ 3.7 (3H, s); δ 4.2 (2H, t, $J = 6.5$ Hz); δ 4.5 (2H, t, $J = 6.5$ Hz); δ 5.8 (1H, d, $J = 2.0$ Hz); δ 5.9 (1H, dd, $J = 10.5, 1.5$ Hz); δ 6.4 (5H, m); δ 7.1 (4H, m); δ 7.5 (3H, m); δ 8.1 (1H, d, $J = 9.0$ Hz); δ 8.3 (3H, m).

2.5. Synthesis of metallated homopolymers

By reacting by similar procedures [7] the polymeric ligand $\mathbf{P}_0$ with $\mathbf{D}_{1-3}$ the three homopolymers $\mathbf{P}_{1-3}$ (see formulas in Scheme 2) were obtained. As an example the synthesis of $\mathbf{P}_1$ is described. To a stirred solution of 1.00 g (1.6 mmol) of $\mathbf{P}_0$ in 90 mL of 1,1,2,2-tetrachloroethane were added 0.786 g (0.90 mmol) of $\mathbf{D}_1$ and a solution of 0.064 g of sodium hydroxide in 10 mL of ethanol. After stirring 15 min at room temperature, the mixture was filtered and the filtrate washed three times with 20 mL of water. The organic layer was dried with sodium sulfate and kept in freezer till characterization was performed. Thermal data and Pd contents (collected on precipitated samples) and inherent viscosity values (measured on the mother solutions) of the homopolymers are reported in Table 2.

2.6. Synthesis of metallated copolymers

The polymerization of $\mathbf{M}_{1-3}$ was attempted, following the same general procedure, from the methylmethacrylate metallorganic monomers (80% by weight) and co-monomer

Table 2
Thermodynamic data and Pd content (%) of the polymers

	T_g (°C)	T_d (°C)^a	η_{inh} (dL/g)^b	Pd_{calc}^{c} (%)	Pd_{exp}^{d} (%)
$\mathbf{P}_0$	98^e	320	1.06*	–	–
$\mathbf{P}_1$	119	255	1.10*	10.91	10.80
$\mathbf{P}_2$	111	258	0.68*	10.90	11.26
$\mathbf{P}_3$	112	271	0.85*	10.75	10.70
$\mathbf{P}'_1$	129	265	0.11**	9.93	9.00
$\mathbf{P}'_2$	175	250	0.18***	9.60	9.21
$\mathbf{P}'_3$	152	276	0.21**	9.56	9.06

[a] Decomposition temperature calculated at 5% by weight loss.

[b] Inherent viscosity measured at 25.0 °C at 0.50 g/dL concentration using: *, 1, 1, 2, 2-tetrachlorethane; **, dichloromethane; ***, *N,N*-dimethylformamide solutions.

[c] Calculated palladium content.

[d] Experimental palladium content extimated by TGA measurements in air.

[e] The polymer shows a smectic phase with isotropization at 280 °C.

(20% by weight). The obtained products were the three copolymers $\mathbf{P}_{1'-3'}$ (see formulas in Scheme 3).

As an example, in a typical synthesis of $\mathbf{P}'_1$ 0.500 g (0.59 mmol) of $\mathbf{M}_1$, 0.14 mL (1.3 mmol) of fresh distilled methylmethacrylate, 1.4 mL of dry *N,N*-dimethylformamide and 0.025 g of AIBN were poured into a vial. After three freeze and thaw cycles the vial was sealed in vacuum and kept at 75 °C for 3 days. After this time, the content of the vial was added to about 50 mL of methanol. The precipitated polymer was recovered by filtration, dissolved in dichloromethane, and the solution was filtered on a glass filter funnel. The product was re-precipitated in about 100 mL of hexane. Finally, the polymer was washed in absolute ethanol/dichloromethane (9:1), and dried at 60 °C for 5 h.

The three copolymers appear, respectively, red, brown and orange in colour. Their characterization data are reported in Table 2. For all copolymers yields range from 80 to 90% by weight.

2.7. NLO characterization

The NLO characterization was carried out by performing SHG measurements on 0.5–1 μm thick films deposited by spin coating on glass slides. The SHG experimental set-up, described in detail elsewhere [20] involved a Quantel Brilliant Q-switched Nd:YAG laser (frequency up to 10 Hz, 400 mJ/pulse) providing the fundamental-beam output at $\lambda = 1064$ nm. The nonlinear coefficient d_{33} of samples were measured by performing a Maker fringes reference experiment [21,22] with a quartz crystal slab (110) ($d_{11} = 0.335$ pm/V) [23]. A high-temperature high-voltage corona poling set-up was used to orient the dipoles [24] by using a gold wire biased with +7.0 kV across a 1 cm gap normal to the film. The HV generator was grounded to heating stage and the poling current was carefully monitored to control the efficiency of the procedure and allow the comparison of measurements for different samples. Moreover, the SH signal was corrected for the different thickness of the samples. The poling experiments were performed by measuring the SHG growth while the samples were heated for 30 min at a temperature near the T_g of the samples, with the electric field on. The films were then cooled down to room temperature at about 1 °C/min and the electric field was switched off. Intensity of Second Harmonic signal allowed an estimate of second order NLO coefficient d_{33}. In addition, absorption spectra measurements of the films were performed before and immediately after the poling procedure, to estimate independently the orientational order of the dipoles through the decrease of the absorption coefficients [25].

3. Results and discussion

3.1. Ligands and complexes

New ligands, three ($\mathbf{C}_{1-3}$) suitable for C,N-cyclometallation and three other ones ($\mathbf{C}_{1'-3'}$) apt to N,O-chelation were synthetised. All the ligands possess a π-electron system able to couple an electron-donor and an electron-acceptor group (Scheme 1). So, they are themselves second order nonlinear optical active [26].

Chromophores $\mathbf{C}_{1-3}$ are the precursors of the dinuclear species $\mathbf{D}_{1-3}$ (Scheme 2) which have been reacted with the polymeric ligand $\mathbf{P}_0$ (Scheme 2) in order to obtain the homopolymers $\mathbf{P}_{1-3}$. This procedure has been exploited on account of the poor result of preliminary experiments aiming to obtain direct polymerisation of complexes containing the C,N-chelate chromophores $\mathbf{C}_{1-3}$ and N,O-ligands of the type $\mathbf{C}_{1'-3'}$ bearing an acrylic function. These experiments gave evidence of various degree of decomposition in standard polymerization conditions. Therefore, no details are here reported for the monomers, obtained by procedures similar to those adopted for $\mathbf{M}_{1-3}$ and characterized by NMR.

The poor solubility of the homopolymers prompted to focus attention on copolymers. It was found that the ligands $\mathbf{C}_{1'-3'}$, whose structures are substantially the same of chromophores $\mathbf{C}_{1-3}$, can be satisfactorily used as N,O-chelating moieties in the reaction with the cyclopalladated specie $\mathbf{D}_{acr}$ (Scheme 3) to give the acrylic monomers $\mathbf{M}_{1-3}$ (Scheme 3). The synthesis of $\mathbf{C}_{1'-3'}$ is more difficult than the synthesis of $\mathbf{C}_{1-3}$, but the derived monomers $\mathbf{M}_{1-3}$, where the acrylic group is on the C,N-binding moiety, do not suffer decomposition during polymerization. Of course also homopolymers could be obtained from $\mathbf{M}_{1-3}$, but, due to the requirement of good solubility these monomers were used only in copolymerization.

The purity of all the ligands was confirmed by the sharp endothermic DSC signal, related to the melting, and by the ^{1}H NMR spectra, which are in good agreement with the expected patterns.

The dinuclear palladium acetato-bridged complexes $\mathbf{D}_{1-3}$

(Scheme 2) were prepared by reaction of the corresponding chromophores with palladium acetate. $\mathbf{D}_{1-3}$ decompose on heating and no melting signal was observed by DSC analysis.

For the compound $\mathbf{D}_{\mathrm{acr}}$, parent of the three monomers $\mathbf{M}_{1-3}$, the DSC analysis shows a broad endothermic signal at 192 °C, overlapping a polymerization signal.

Thermodynamic data and Pd content of the dinuclear species are reported in Table 3. The complexes, as shown by TGA analysis of Pd content (Table 1), by ^{1}H NMR data and by C, H, N analysis, are pure enough for use in the successive bridge-splitting reaction.

Mononuclear complexes $\mathbf{M}_{1-3}$ (in Scheme 3) were obtained by reaction of the functionalised dinuclear specie $\mathbf{D}_{\mathrm{acr}}$ with the appropriate ancillary ligand $\mathbf{C}_{1'-3'}$.

As detected by optical observation, they are microcrystalline solids, respectively, red, brown and orange. The monomers $\mathbf{M}_1$ and $\mathbf{M}_3$ melt with polymerization, their DSC curves showing broad irregular endothermic signals peaked at the values reported in Table 1, while for $\mathbf{M}_2$ no melting signal was detected. Their decomposition temperatures, reported in the same table, are quite high. They are soluble ($\mathbf{M}_2$ very soluble) in common organic solvents, such as chloroform, *o*-dichlorobenzene, *N,N*-dimethylformamide and stable in solution under the attempted polymerization conditions. The palladium content, as determined by TGA analysis, is reported in Table 1. Also elemental analyses (Section 2) confirm the expected formulas.

The ^{1}H NMR spectra show the good purity of the synthesized products. Shifts of some diagnostic resonances are observed if the signals for either the free N,O-chelating ligands or the dinuclear species are compared with those of the mononuclear complexes. In particular, the signal related to the aromatic hydrogen *orto* to Pd–C is found at 6.0 ppm in $\mathbf{D}_{\mathrm{acr}}$ and in the range 5.3–5.8 ppm in the mononuclear complexes.

3.2. Metallated homopolymers

The synthesis of the metallated homopolymers $\mathbf{P}_{1-3}$ (Scheme 2) was performed by reacting the appropriate dinuclear acetato-bridged complexes $\mathbf{D}_{1-3}$ with the polymeric ligand $\mathbf{P}_0$ in 1,1,2,2-tetrachlorethane solution. The mother solutions containing the products were immediately stored at 4 °C, to avoid precipitation. In fact, in case the product was isolated by precipitation in *n*-hexane, crystallization preventing re-dissolution of the polymers could easily ensue. RX diffraction patterns obtained at room temperature from specimens not thermally treated confirm the presence of structurated phases. Bragg diffractions are observed at 8.12 and 6.28 Å for $\mathbf{P}_1$, at 3.39 and 2.53 Å, with an halo peaked at $\sin\theta/\lambda = 0.110$ Å for $\mathbf{P}_2$, and as a complex group of lines at 7.79, 6.28, 3.72, 2.94, 2.73 and 2.58 Å, with an halo peaked at $\sin\theta/\lambda = 0.11$ Å for $\mathbf{P}_3$. Thin films of the three polymers obtained by evaporation of the 1,1,2,2-tetrachloroethane solutions on glass slides at about 80 °C are amorphous. After annealing at 150 °C for 30 min while $\mathbf{P}_1$ appeared substantially unaltered, polymer $\mathbf{P}_2$ locally crystallized and $\mathbf{P}_3$ exhibited textures typical of a smectic phase.

Table 3
Nonlinear d_{33} coefficients measured for the copolymers

	T_p (°C)[a]	V_p (kV)[b]	Φ[c]	L (μ)[d]	d_{33} (pm/V)
$\mathbf{P}'_1$	120	7	0.12	1.1	20
$\mathbf{P}'_2$	160	7	0.42	0.4	25
$\mathbf{P}'_3$	140	7	0.08	1.0	10

[a] Poling temperature.
[b] Poling electric field.
[c] Order parameter.
[d] Thin film sample thickness.

Thermodynamic properties of the three polymers are reported in Table 3. TGA data of palladium content allowed to assess that grafting of the organometallic fragments is substantially complete. Their glass transition temperatures range just up to 110 °C, but decomposition occurs above ca. 250 °C.

Their inherent viscosity, measured on the 1,1,2,2-tetrachloroethane solutions, is slightly lower then that of the parent polymer $\mathbf{P}_0$ (see thermodynamic data in Table 2). UV–Vis spectra were recorded on transparent parts of the thin films. UV–Vis absorption spectra give, respectively, maximum transmittance at ca. 460 nm for $\mathbf{P}_1$, at 400 nm for $\mathbf{P}_3$ and at ca. 550 nm for $\mathbf{P}_2$. So, it is detectable a range absorption-free up to 560 nm for $\mathbf{P}_1$ and $\mathbf{P}_3$ and between 420 and 480 nm and up to 650 nm for $\mathbf{P}_2$.

^{1}H NMR spectra were recorded on samples synthetised in 1,1,2,2-tetrachloroethane-d$_2$ solutions. They show the broad bands of the polymeric precursor $\mathbf{P}_0$ overlapped to the signals due to the organometallic fragments. In particular, it was detectable a signal at about 6.2 ppm, due to the aromatic hydrogen in *orto* position with respect to the Pd–C bond, that was not observed in the free polymeric precursor. Also the singlet at about 2.6–3.0 ppm (6H) related to the methyl groups on the nitrogen, is not observed in the polymeric precursor. By comparing the integration of this signal with the alifatic signals (due to the polymeric chain) it can be evaluated that metallation of the polymeric precursor is not less than 90% in mole.

Despite favourable features of the homopolymers, i.e. the wide stability range (as indicated by glass transition temperatures), the low viscosity and the high content of organometallic chromophore, a major drawback in their NLO application is given by their structuring and insolubility. Thus, the polymers $\mathbf{P}_{1'-3'}$ were designed with the purpose of overcoming this hindrance without prominent structural changes in the metallorganic chromophores.

3.3. Metallated copolymers

The random copolymers $\mathbf{P}_{1'-3'}$ (Scheme 3) were synthesised from monomers $\mathbf{M}_{1-3}$ and methyl methacrylate. Their structure was chosen in order to possibly obtain amorphous materials more soluble than the analogous homopolymers. The molar ratio metallorganic monomer/comonomer (M/C) was arranged at 0.45 (i.e. 80% by weight of metallorganic monomer) in order to keep high content of NLO-active fragment and high glass transition temperatures.

In fact, the three copolymers show good solubility in common solvents, such as chloroform, dichlorometane, *N,N*-dimethylformamide, *o*-dichlorobenzene, tetrachloroethane. Their glass transition temperatures range from 129 °C, for $\mathbf{P}'_1$, to 152 °C for $\mathbf{P}'_3$, and 175 °C for $\mathbf{P}'_2$ (see Table 2), the last value being particularly favourable to the stability of poling. For all the polymers the decomposition temperature are quite higher than the glass transition temperature, i.e. above 260 °C (see also Table 2). For example, in Fig. 1 the DSC and the TGA curves for a sample of $\mathbf{P}'_2$ are presented.

Optical observation, DSC analysis (only the glass transition signal is detectable in the DSC curves) and RX spectra (they show only one halo at about $\sin\theta/\lambda = 0.104$ Å^{-1}) confirmed that all the polymers are amorphous. As expected, thin films obtained by evaporation of *N,N*-dimethylformamide or tetrachloroethane solutions at about 100 °C appear homogeneous and transparent by optical observation. UV–Vis spectra were recorded on these films. Maximum transmittance is observed at ca. 550 nm for $\mathbf{P}'_1$ and $\mathbf{P}'_3$ and at ca. 600 nm for $\mathbf{P}'_2$ and a fairly wide absorption-free range can be employed in the SHG measurements.

In Table 2 are reported the values of inherent viscosity in dichlorometane solutions at 0.500 g/dL for all the copolymers and the amount of palladium content from TGA data. This is always a little less than the nominal content, calculated on the base of the employed molar ratios. These data are confirmed by the ^{1}H NMR spectra. By comparing the integration of the signal at about 3.6 ppm (due to the methyl group of the co-monomer) with the integral of the aromatic signals (due to the metallorganic monomer) the molar ratio M/C 0.41, 0.44 and 0.40, respectively, is obtained for the three copolymers. For $\mathbf{P}'_1$ and $\mathbf{P}'_3$ is also detectable a signal at about 5.3 ppm due to the aromatic hydrogen *orto* to the Pd–C bond.

Their chemical stability, good solubility and amorphism make them promising for use in NLO measurements. In the following section we report the preparation of the thin film samples and the SHG measurements for the three copolymers.

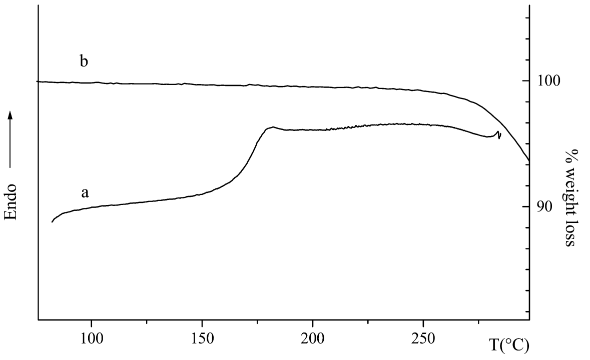


Fig. 1. DSC (a) and TGA (b) curves for a sample of $\mathbf{P}'_2$.

3.4. NLO measurements

Because of the relationship between NLO properties and solvatochromism [26] we note that this was observed both in the chromophoric ligands and in the derived complexes.

As for EFISH measurements, we report first, as an example, the absorption spectrum of a corona-poled $\mathbf{P}'_2$ sample, shown in Fig. 2. The solid curve refers to as-prepared films, i.e. before poling, while the dashed one was recorded immediately after poling. In the spectrum after poling a decrease of absorbance can be observed. A similar behaviour has been observed for the other copolymers and it could be ascribed to two different mechanisms: (a) partial alignment of molecules along the direction of the poling field (i.e. perpendicular to the plane of the film) which decreases the absorption cross section for light at normal incidence [27], (b) a possible partial degradation of the chromophores during the poling process [28]. However, for our copolymers the decomposition temperatures are well above the poling one, and the second mechanism can be ruled out. Moreover, a partial recover of absorbance has been observed with time, in parallel with SHG intensity decrease, this indicating the partial disorientation of chromophores. Measured nonlinear d_{33} coefficients are reported in Table 3. The observed NLO responses are in the range for other metal containing polymers [29,30].

The table shows, in particular, that d_{33} coefficient for $\mathbf{P}'_2$ copolymer is greater than $\mathbf{P}'_1$ and $\mathbf{P}'_3$. This is in agreement with the different structure of conjugation chain in the chromophoric part. In fact, we can expect [31] that the conjugation increase in the ligand $\mathbf{C}'_2$ by the presence of the N=N bridge, respect to $\mathbf{C}'_1$ (with iminic N=CH bridge) and

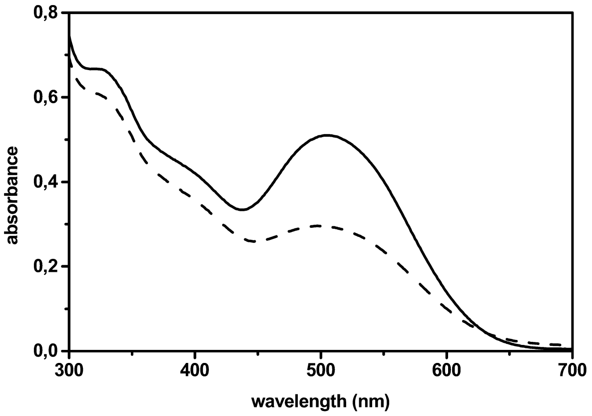


Fig. 2. Absorbance before poling (solid line) and after poling (dashed line) of a $\mathbf{P}'_2$ sample.

C'_3 (where conjugation occurs through a phenylazo group). So, this behaviour is reflected both in the organometallic monomers and in the polymers.

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