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Side chain organometallic polymers containing cyclopalladated potentially second order nonlinear optical active fragments as pendants

U. Caruso[a], A. Di Matola[a], B. Panunzi[b], A. Roviello[a,*], A. Sirigu[a]

[a]*Dipartimento di Chimica, Università degli Studi di Napoli "Federico II", Complesso Universitario di Monte S.Angelo, Via Cinthia, 80126, Naples, Italy*
[b]*Dipartimento di Scienza degli Alimenti, Università degli Studi di Napoli "Federico II", Via Università 100, 80055, Portici, Naples, Italy*

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Abstract

Three new organometallic homopolymers and a copolymer have been obtained by radical polymerization of acrylic monomers. The monomers were obtained by bridge splitting reaction from cyclopalladated dinuclear species and the appropriate imines. The polymers exhibit good thermal and chemical stability and are soluble in common organic solvents. Their potential ability to display second order nonlinear optical activity was tested by solvatochromic effect measurements on the corresponding monomers. In particular, the copolymer appears to be the most versatile in consideration of its thermal behaviour, solubility and inherent viscosity. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It is well known that many acentric organic molecules exhibit large second order nonlinear optical (NLO) response, due to the high polarizability of a π-electron system apt to couple an electron-donor and an electron-acceptor group [1]. The adjunct of a transition metal to an asymmetric conjugated organic structure significantly influences the π-electron behaviour of the organic ligand. Thus, coordination compounds offer, in addition to a larger variety of structures, a much greater span of electronic properties than simply organic structures. These effects mainly derive from the abundance of the excited states pertaining to the low lying d–d transitions potentially relevant to optical nonlinearity [1,2]. In particular, the tailorability of these effects by variation of metal–ligand interactions was enlightened both by experimental and by theoretical quantum-mechanical results in the case of organometallic transition derivatives [3]. Evidence could be also afforded of an extension of the π-electron conjugation to the metal, contributing to second order polarizability [4,5].

In the field of organometallic reactivity palladium (II) holds a remarkable role as a typical electrophile for the facile activation of C–H bonds in hetero-substituted organic molecules to give cyclometallated products [6]. In particular, Schiff bases can behave as easily cyclopalladating moieties or simply as ancillary ligands [7,8].

The chemistry of cyclopalladated compounds is very rich. They find application in several areas, recently including nonlinear optics for the very good electron donating ability of the square-planar Pd(II) fragment in donor/acceptor π-electron complexes [9,10].

In this article we report the synthesis of complexes of acrylated Schiff bases by reaction of the corresponding acetato-bridged binuclear cyclopalladated complexes with chelating Schiff bases containing azobenzene chromophores. The mononuclear cyclopalladated acrylic complexes are stable enough in solution to undergo radical polymerization without decomposition. Thus, it was possible to obtain three homopolymers and one copolymer (with methyl methacrylate), bearing organometallic chromophores in side-chain. Preliminary 'blue-shift' tests on two monomeric complexes, which are precursors of two of the polymers, indicate that these are expected to display second order optical nonlinearities.

2. Experimental section

2.1. Materials

Phase transition temperatures and enthalpies were measured with a Perkin–Elmer DSC-7 apparatus, at

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* Corresponding author. Dipartimento di Chimica, Università di Napoli "Federico II" Complesso Universitario di Monte S. Angelo, Via Cinthia, 80126 Napoli, Italy. Tel.: + 39-081674371; fax: + 39-081674090.
E-mail address: roviello@chemistry.unina.it (A. Roviello).

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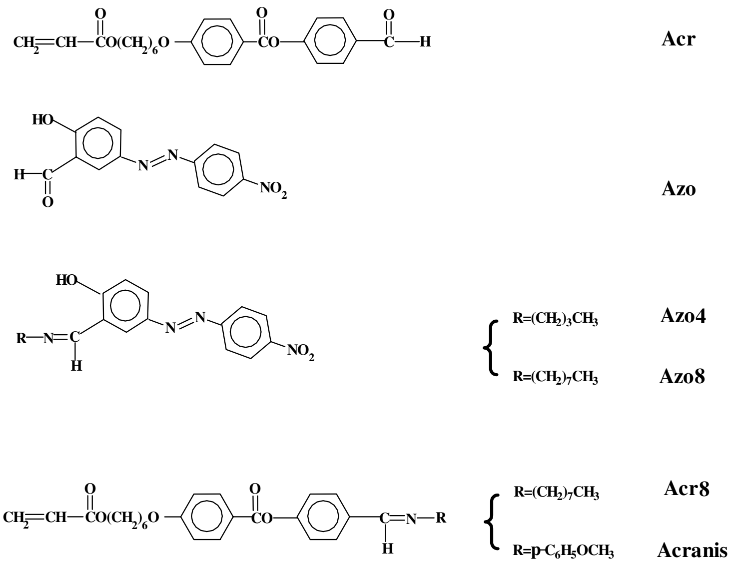


Scheme 1.

scanning rate of $10\,\mathrm{K\,min^{-1}}$, under a dry nitrogen flow. Optical observations on monomers, their precursors and polymers were performed by use of a Zeiss polarizing microscope equipped with a Mettler FP5 microfurnace. A Mettler TG50 apparatus was employed for thermogravimetric analysis to evaluate the palladium content of monomers and polymers and the decomposition temperature of the polymers. X-ray diffraction patterns were recorded at room temperature by flat film camera using Ni-filtered CuKα radiation. ^{1}H NMR spectra were recorded in $CDCl_3$ or Me_2SO-d_6 at 200 MHz using a Varian Gemini 200 spectrometer. Inherent viscosities (η_{inh}) of one homopolymer and of the copolymer were measured in chloroform solution at 25°C using an Ubbelohde viscometer. Molecular weights of the homopolymers in chloroform at 37°C were measured by means of a Knauer vapour pressure osmometer. UV–VIS absorption spectra were recorded at room temperature utilizing a Perkin–Elmer Lambda 7 spectometer. Reactions requiring nitrogen atmosphere were carried out by using Schlenk techniques. Solvents for polymerizations were dried before use. Reagents *n*-butylamine, *n*-octylamine, anisidine, anisaldehyde, 4-nitroaniline, 2-hydroxybenzaldehyde, 4-hydroxybenzaldehyde were commercially available (Aldrich). Palladium diacetate by Aldrich was recrystallized from benzene/acetic acid.

Aldehyde Acr (see formula in Scheme 1; formulas of organic ligands and precursors) was obtained by standard methods, starting from $CH_2{=}CHCOO(CH_2)_6O$–*p*-C_6H_4–*p*-COCl [11] and 4-hydroxybenzaldehyde.

Aldehyde Azo (Scheme 1) [12] was synthetized according to literature methods [13] by addition of sodium nitrite to a cold solution of 4-nitroaniline in hydrochloridric acid (6 M) and coupling of the diazonium salt with 2-hydroxybenzaldehyde in presence of sodium hydroxide. After recrystallization in ethanol/water the aldehyde melts at 191–193°C [13]. Yield = 81%. ^{1}H NMR is consistent with the expected formula.

2.2. Synthesis of imines

Imines Azo4 and Azo8 (Scheme 1) were prepared by adding under magnetic stirring an equimolar amount of Azo to *n*-butylamine or, respectively, to *n*-octylamine in boiling ethanol. After 10 min the solution was cooled at room temperature and crystallization of the imines ensued. By recrystallization from tetrahydrofurane/ethanol (1:3) red crystals were obtained.

Azo8: yield = 80%, mp = 129°C, $\Delta H_{\mathrm{m}} = 88.4$ J/g; Azo4: yield = 83%, mp = 172°C, $\Delta H_{\mathrm{m}} = 104.4$ J/g. Imine Acranis (Scheme 1) was prepared in ethanol at room temperature and recovered as a yellow solid by keeping in a freezer the mother liquor after evaporation of one third of the solvent. Recrystallization could be attained from tetrahydrofurane/ethanol (1:5). Acr8 was obtained in a similar way as a dark yellow liquid. It has to be noted that Acr8 and Acranis were not isolated during the preparation of the corresponding dinuclear complexes.

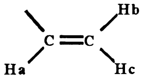
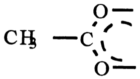
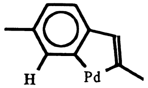
The most significant ^{1}H NMR resonances pertaining to the imines are reported in Table 1.

2.3. Synthesis of dinuclear complexes

The two dinuclear cyclopalladated complexes (Scheme 2; formulas of organometallic complexes and polymers) were obtained by the same general procedures. As an example, the preparation of $Pd_2Ac_2(Acr8)_2$ is described.

To a stirred solution of 0.396 g (1 mmol) of Acr in 8 ml of acetic acid 0.165 ml (1 mmol, $d = 0.782$ g/ml) of *n*-octylamine was added at room temperature. After 30 min, 0.224 g (1 mmol) of palladium diacetate was added and the stirring was continued at 25°C for three days. A little amount of dark

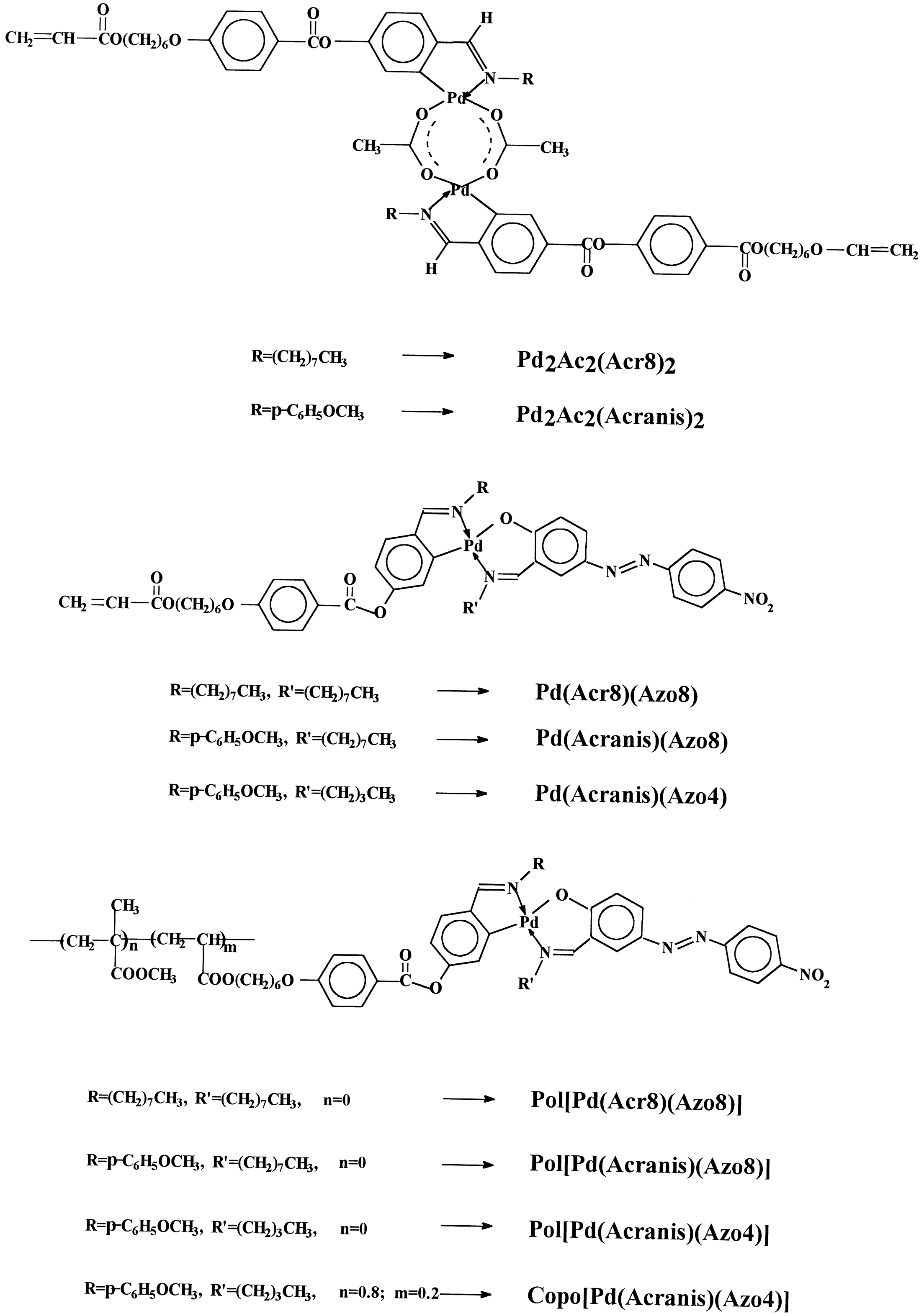
Table 1
^{1}H NMR more relevant data for the imines and the dimeric and monomeric complexes (s = singlet; d = doublet; dd = double doublet; t = triplet)

Fragment	Compound								
	Acr8	Acranis	Azo8	Azo4	Pd_2Ac_2 $(Acr8)_2$	Pd_2Ac_2 $(Acranis)_2$	Pd(Acr8) (Azo8)	Pd(Acranis) (Azo8)	Pd(Acranis) (Azo4)
	6.12 dd	6.14 dd	–	–	6.23 dd	6.12 dd	6.15 dd	6.15 dd	6.16 dd
ϕ-OH	–	–	14.35 s	14.34 s	–	–	–	–	–
ϕ-OCH_3	–	3.84 s	–	–	–	3.57 s	–	3.90[a]	3.88[a]
= N–CH_2–	4.06 t	–	3.65 t	3.68 t	4.16 t	–	4.10 t	4.05 t	4.05 t
	–	–	–	–	2.19 d[b]	1.80 d[b]	–	–	–
	–	–	–	–	6.65 d	6.46 d	6.82 d	6.64 d	6.68 d
–CH=N–in free ligands	8.17 s	8.49 s	8.18 s	8.16 s	–	–	–	–	–
–CH=N–in palladated imines	–	–	–	–	7.36 s	7.63 s	[c]	[c]	[c]

[a] Two very narrow singlets.

[b] Two isomers, *cis* and *trans* on Pd.

[c] Not assignable.



R=$(CH_2)_7CH_3$ → Pd2Ac2(Acr8)2

R=p-$C_6H_5OCH_3$ → Pd2Ac2(Acranis)2

R=$(CH_2)_7CH_3$, R'=$(CH_2)_7CH_3$ → Pd(Acr8)(Azo8)

R=p-$C_6H_5OCH_3$, R'=$(CH_2)_7CH_3$ → Pd(Acranis)(Azo8)

R=p-$C_6H_5OCH_3$, R'=$(CH_2)_3CH_3$ → Pd(Acranis)(Azo4)

R=$(CH_2)_7CH_3$, R'=$(CH_2)_7CH_3$, n=0 → Pol[Pd(Acr8)(Azo8)]

R=p-$C_6H_5OCH_3$, R'=$(CH_2)_7CH_3$, n=0 → Pol[Pd(Acranis)(Azo8)]

R=p-$C_6H_5OCH_3$, R'=$(CH_2)_3CH_3$, n=0 → Pol[Pd(Acranis)(Azo4)]

R=p-$C_6H_5OCH_3$, R'=$(CH_2)_3CH_3$, n=0.8; m=0.2 → Copo[Pd(Acranis)(Azo4)]

Scheme 2.

Table 2
Thermodynamic data and Pd content (%) of the dimeric and monomeric complexes

	T_{m} (°C)[a]	ΔH_{m}.(J/g)	T_{i}.(°C)	ΔH_{i}.(J/g)	%Pd calc[b]	%Pd exp[c]
$Pd_2Ac_2(Acr8)_2$	117	16.7	–	–	15.80	16.08
$Pd_2Ac_2(Acranis)_2$	170	14.8	204	0.42	16.80	15.97
Pd(Acr8)(Azo8)	133	22.3	–	–	10.07	10.08
Pd(Acranis)(Azo8)	136	23.0	–	–	10.76	10.84
Pd(Acranis)(Azo4)	117	21.7	–	–	11.78	11.43

[a] Peak temperature.
[b] Calculated palladium content.
[c] Experimental palladium content estimated by TGA measurements in air.

precipitate was eliminated by filtration; the solution was concentrated in vacuo and methanol was added to produce (in freezer) a yellow precipitate.

In the synthesis of $Pd_2Ac_2(Acranis)_2$ the reaction solution was gently boiled for about 10 min until precipitation of a little amount of dark solid ensued. This was eliminated by filtration and the solution was cooled to produce a dark-yellow precipitate. The solid was recovered by filtration, washed with methanol and dried in air.

Yield: $Pd_2Ac_2(Acr8)_2 = 70\%$; $Pd_2Ac_2(Acranis)_2 = 78\%$.

Both compounds were employed as crude products in the further reactions. Palladium content calculated by TGA measurements and some crucial ^1H NMR resonances (Table 1) gave evidence of fairly high purity (≥95%).

Palladium contents and thermodynamic data are reported in Table 2.

2.4. Synthesis of mononuclear complexes

The reactions between the appropriate dinuclear species and the appropriate imine were carried out by the same general procedure to afford the mononuclear complexes (see formulae in Scheme 2). As an example, the synthesis of Pd(Acr8)(Azo8) is reported.

1.61 g (4.2 mmol) of Azo8 were dissolved in a mixture of 180 ml absolute ethanol and 120 ml dichloromethane. To this solution were added under stirring 1.94 g (1.4 mmol) of potassium carbonate, 1.23 g (1.5 mmol) of sodium acetate, and finally 2.90 g (2.1 mmol) of $Pd_2Ac_2(Acr8)_2$. After stirring for 1 h at room temperature, the suspension was filtered, and the filtrate concentrated in vacuo to ca. 100 ml. The solution was diluted with 100 ml of dry ethanol. On cooling, the product was obtained as a red precipitate which was recovered by filtration.

The mononuclear complexes were purified by crystallization. Pd(Acr8)(Azo8) was crystallized from chloroform/petroleum benzin (bp = 80–110°C) (1:10), Pd(Acranis)-(Azo8) from the same mixture (1:3) and Pd(Acranis)(Azo4) from tetrahydrofurane/ethanol (1:3).

Yield: 71% for Pd(Acr8)(Azo8); 73% for Pd(Acranis)-(Azo8); 90% for Pd(Acranis)(Azo4).

According to ^1H NMR data (Table 1) and TGA analyses (Table 2) of the palladium content the purity of the monomeric complexes was satisfactory (≥95%).

2.5. Synthesis of polymers

Three homopolymers and one copolymer were obtained by similar procedures. Polymerization was carried out in chlorobenzene for Pd(Acr8)(Azo8) and Pd(Acranis)(Azo8) and in dry *N*,*N*-dimethylformamide for Pd(Acranis)(Azo4) and for the copolymer. To obtain the latter, methyl methacrylate and Pd(Acranis)(Azo4) were employed in the ratio 3:7 by weight.

Table 3
Thermodynamic data and Pd content (%) of the polymers

	T_{g}(°C)	T_{m}(°C)[a]	ΔH_{m} (J/g)	%Pd calc[b]	%Pd exp[c]	Molecular mass[d]	η_{inh} (dl/g)[e]	$\lambda_{\max}$ (nm)[f]
Pol[Pd(Acr8)(Azo8)]	65	106	6.43	10.07	10.06	≥ 20,000		480
Pol[Pd(Acranis)(Azo8)]	112	[g]	–	10.76	10.84	13,000		492
Pol[Pd(Acranis)(Azo4)]	129	–	–	11.43	11.78	11,000	0.12	484
Copo[Pd(Acranis)(Azo4)]	120	–	–	8.75	8.86	[h]	0.74	484

[a] Onset temperature.
[b] Calculated palladium content.
[c] Experimenthal palladium content estimated by TGA measurements in air.
[d] ± 1000.
[e] Measured using $CHCl_3$ solutions at 25.0°C at 0.50 g/dl concentration.
[f] Maximum UV–VIS absorption on film samples.
[g] Decomposition goes before isotropization.
[h] The solutions for the osmometric determination are too viscous, so we have determined inherent viscosity as an indication of the polymerization degree if compared with the analogous homopolymer.

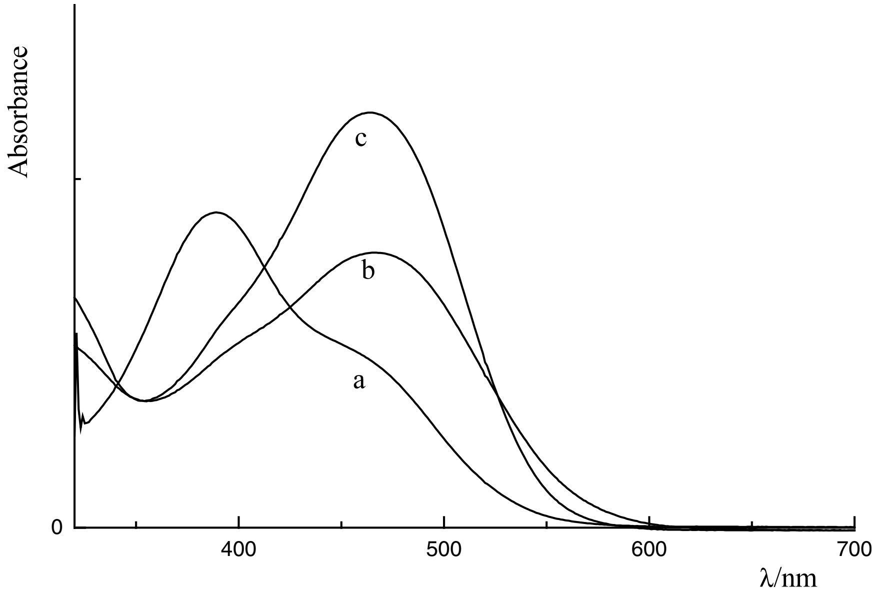


Fig. 1. UV–VIS spectra of: (a) Azo4;, (b) Pd(Acranis)(Azo4); and (c) Pol[Pd(Acranis)(Azo4)].

In a typical preparation, 1 g of monomer was dissolved in 2 ml of solvent with 50 mg (5% by weight) of initiator (AIBN). The vial containing the suspension of the monomer and the initiator was sealed under nitrogen atmosphere after several freeze–thaw cycles [11]. The vial was kept for 72 h at 70°C. After cooling, the solution was poured in hexane, in case chlorobenzene was the solvent, while, when *N*,*N*-dimethylformamide was used, the solution was added to methanol. The precipitated polymers were recovered by filtration, dissolved in chloroform and re-precipitated by addition of ethanol. The polymers were dried at 50–60°C for 12 h.

Yield: 62% for Pol[Pd(Acr8)(Azo8)], 54% for Pol[Pd(Acranis)(Azo8)], 50% for Pol[Pd(Acranis)(Azo4)], 59% for Copo[Pd(Acranis)(Azo4)].

Thermodynamic data, the average molecular mass and palladium content for the polymers are reported in Table 3.

3. Results and discussion

This article reports a preliminary study on acrylic polymers, containing cyclopalladated Schiff bases, directly attainable from the corresponding monomers. In fact, these can undergo a clean radicalic polymerization, due to their remarkable chemical stability. Three stable side-chain homopolymers and one copolymer were obtained. The polymers show satisfactory chemical and thermal (far above glass transition) stability and good solubility in common solvents. Indication of potential second order NLO activity of the monomeric precursors was obtained by measurement of the solvatochromic effect. On increasing solvent polarity, a negative solvatochromism (blue-shift) was observed. Although the solvatochromic shift is only of 7 nm, it is not incompatible with a significant change of the dipole moment, related to the second order NLO response [14,15].

The chemical and the chemical–physical properties of polymers, monomers, and of their precursors will be presented and discussed below.

3.1. Imines

Two types of imines, one suitable for cyclometallation and the other simply apt to chelation, have been employed. Imines Acr8 and Acranis were synthetized in order to obtain the dimeric species by cyclopalladation, while the salicylaldimine derivatives Azo8 and Azo4 were designed to complete the coordination sphere of the palladium (II) as chelating ligands, affording the formation of the stable monomeric complexes.

Upon consideration of the limited stability and of the difficult purification of Acr8, the preparation of the related Acranis was attempted, which proved to be more easily processable and purificable. Besides, the introduction of another aromatic ring increases rigidity. Acranis is liquid-crystalline with a very wide range of stability (more then 100°C). The nematic nature of the mesophase was ascertained by the optical observation of a very mobile schlieren texture.

Salicylaldimines Azo8 and Azo4 are chelating Schiff bases including a π-electron conjugated system with a strong electron-acceptor substituent. These compounds are themselves potentially NLO-active as they also show 'blue-shift' effect. Moreover, the formation of a six terms cycle by palladium coordination is expected to increase the conjugation. In fact, forcing the metalated ring and the iminic bond to be coplanar increases the transfer of electron density from the metal-iminic bond region to the nitro group, thus enhancing polarization [10]. Indication of a substantial

Table 4
UV–VIS absorption maxima for Pd(Acr8)(Azo8) and Pd(Acranis)(Azo4) in solvents at different polarities

Complex	$\lambda_{\max}$.(nm)			
	Acetonitrile	Acetone	Ethyl acetate	Benzene
Pd(Acr8)(Azo8)	459	462	464	466
Pd(Acranis)(Azo4)	454	462	466	468

change in π-electron coniugation upon coordination is given by the shift of the maximum UV–VIS absorption of the imines compared to the corresponding monomeric complexes (see Fig. 1).

3.2. Dinuclear complexes

The easiness of the cyclopalladation and of the successive splitting reaction in presence of bridging acetate groups justifies the choice of the adopted synthetic approach. Two dinuclear acetato-bridged species were obtained from Acr8 and Acranis. By comparison of the behaviour of the complexes with that of the precursor imines it was found, as expected [15], that metal coordination gives a substantial increase of T_m. In fact $Pd_2Ac_2(Acr8)_2$ is a solid which melts at 114.5°C (Acr8 is a liquid), and $Pd_2Ac_2(Acranis)_2$ melts about 80°C above the melting point of Acranis. Coordination also causes a little decrease of T_i. It has been found that $Pd_2Ac_2(Acranis)_2$ also shows a nematic mesophase (optically detectable) stable over a range of about 65°C.

3.3. Mononuclear complexes

The monomeric species were obtained by reaction of the appropriate dinuclear acetato complexes with imines. The products are soluble in common organic solvents (such as chloroform, acetone, tetrahydrofuran) and no trace of decomposition is observed after standing in solution for several days. The three complexes show good thermal stability till about 200°C, as confirmed by TGA data.

Preliminary X-ray analysis [16] on a model complex related to Pd(Acranis)(Azo4) has shown the two iminic nitrogens to be in *trans* positions. In fact, the ^{1}H NMR data show that the three monomers are all *trans* isomers, unlike $Pd_2Ac_2(Acr8)_2$, which is obtained as a mixture of *cis* and *trans* isomers.

The monomer with $R = R' = p\text{-}C_6H_5OCH_3$ (Scheme 2) was synthetized but it was not employed in polymerization because of its very poor solubility in common solvents and of the partial decomposition accompanying fusion (mp about 180°C).

The optical absorption spectra of the monomers, registered in the region between 200 and 700 nm, present a strong single band centred at ca. 460 nm. (Table 4). This band exhibits a negative solvatochromism, i.e. a hypsochromic shift, with increasing solvent polarity. This feature appears to be common occurrence for a number of salicylaldiminate complexes examined so far [14,17].

As for the phase behaviour, it has to be noted that none of the monomers displays liquid-crystalline behaviour. Melting points are reported in Table 2.

3.4. Polymers

The three homopolymers and the copolymer are thermally stable, as shown by TGA measuraments, and remain substantially unaltered below about 250°C. They are also stable in solution of common solvents (such as chloroform, *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone). Some of their thermodynamic properties are reported in Table 3.

The glass transition temperature of Pol[Pd(Acr8)(Azo8)] is very near room temperature. This may cause a poorly stable *poling*, due to the difficulty in retaining dipole alignment in the direction of the field owing to the relevant

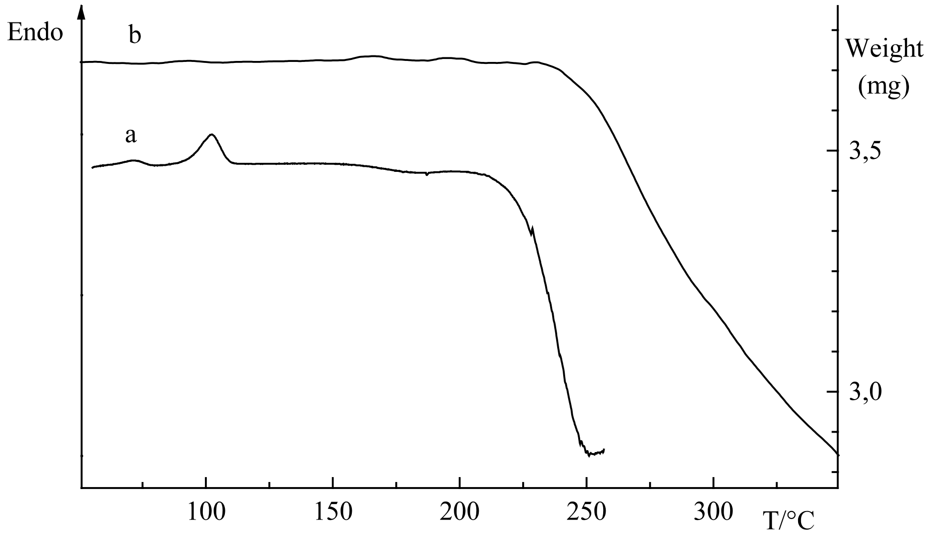


Fig. 2. First heating run DSC (a) and TGA (b) curves of polymer Pol[Pd(Acr8)(Azo8)].

thermal fluctuations of the system at room temperature. In order to obtain higher glass transitions and a more rigid structure, we attempted the synthesis of Pol[Pd(Acranis)(Azo8)], where a *p*-$C_6H_5OCH_3$ group is present instead of the *n*-octyl group $(CH_2)_7CH_3$. Actually, the glass transition of Pol[Pd(Acranis)(Azo8)] is nearly 50°C higher than that of Pol[Pd(Acr8)(Azo8)]. The glass transition temperature also grows by shortening of the alkylic chain in the chelating imines, as in Pol[Pd(Acranis)(Azo4)]. Thus, variation of substituents on the imines can promote fairly relevant changes of the glass transition temperature, as reported in Table 3.

Optical microscope observations were performed on thin films obtained by evaporation at room temperature of chloroform solutions or at 120°C of *o*-dichlorobenzene solutions. Thin films of Pol[Pd(Acr8)(Azo8)] appear to be amorphous not only at room temperature but also after annealing 20°C above glass transition for 10 min. On the contrary, optical observations on a powder sample indicate the anisotropic nature of the polymer up to about 110°C (i.e. after melting). The DSC thermogram of the first heating run shows an endothermic signal peaked at 106°C, corresponding to the melting of a crystal phase (Fig. 2). The semicristallinity is confirmed by the X-ray diffraction pattern of the prepared samples. The pattern is characterized by three Bragg lines at 10.40, 8.50 and 3.73 Å, which are more sharp for a sample previously annealed at 85°C for 1 h. A diffuse halo peaked at $\sin\theta/\lambda = 0.118$ Å^{-1} and a strong halo at $\sin\theta/\lambda = 0.032$ Å^{-1}, the latter possibly related to the average distance between the organometallic pendants, are also observed.

The amorphous thin film obtained by evaporation at room temperature of a Pol[Pd(Acranis)(Azo8)] solution develops very quickly a mosaic texture, consistent with a smectic phase, on annealing for 10 min at 20°C above the glass transition. The X-ray diffraction pattern displays a Bragg line at 15.5 Å, and a halo peaked at $\sin\theta/\lambda = 0.109$ Å^{-1}. A sample annealed at 130°C for 1 h shows two more weak lines at 6.61 and 9.82 Å. No isotropization signal was observed in the DSC curve, probably owing to decomposition. Optical observation on a powder sample indicate that decomposition occurs up to about 220°C (the sample grows dark).

Thin films of Pol[Pd(Acranis)(Azo4)] and powder samples are amorphous on microscopic observation also after annealing for 10 min at 20°C above the glass transition. The X-ray diffraction pattern recorded at room temperature for untreated samples and for samples previously annealed at 150°C for 1 h, gives evidence for an amorphous phase. In both cases they are characterized only by two diffuse haloes peaked at $\sin\theta/\lambda = 0.035$ Å^{-1} and at $\sin\theta/\lambda = 0.115$ Å^{-1}. The only signal detectable in the DSC thermogram is related to the glass transition.

Finally, we synthetized Copo[Pd(Acranis)(Azo4)] from CH_2=CMeCOOMe and Pd(Acranis)(Azo4) (3:7 by weight). Both optical observation on thin films and X-ray diffraction patterns show that the copolymer is amorphous (as Pol-[Pd(Acranis)(Azo4)]) and therefore suited to poling. Moreover, the solubility in common solvents, the inherent viscosity (which must be high to obtain good *spin-coated* films) and the thermal stability of the copolymer are much greater than for the homopolymer. The glass transition (120°C) is not much lower than for the homopolymer and lower than the decomposition threshold (ca. 200°C). Moreover, a further desirable increase of the glass transition could be obtained by shortening, in the mononuclear complex, R' (see Scheme 2) and/or the aliphatic spacer.

In conclusion, the cyclometallation reaction represents a suitable synthetic tool for the obtainment of organometallic acrylic monomers directly employable in a radical polymerization to afford potentially second order NLO active materials. Besides, it seems that copolymerization represents a way of tuning the organometallic monomer content in the polymers in order to improve relevant chemical–physical properties of the materials.

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