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Metallorganic side group liquid crystalline polymers containing π-allylpalladium(II) groups

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The preparation and phase properties of some LC π-allyl and π-crotyl Pd(II) side group metallorganic polymers and some related salicylaldiminates are described. The LC acrylate functionalized monomers are easily prepared, but their use to obtain the corresponding polymers by radical reaction failed because extensive decomposition of the complexes occurs with the formation of Pd metal. The synthesis of the metallated polymers was therefore performed by reacting the dimeric chloro-bridged organometallic π-allyl or π-crotyl Pd(II) complexes with the appropriate ligand polymer which is prepared without difficulties. The organometallic polymers show a nematic mesophase, while the ligand polymer exhibits a smectic A or C phase. Both metallated low molecular mass model compounds and the polymers give stable mesophases, although at lower temperatures compared with the parent ligand compounds.

1. Introduction

The development of useful chemical and physical properties in macromolecules by appropriate introduction of metal atoms is one of the central issues of contemporary polymer chemistry [1]. The metal centres, of various nature, oxidation number, coordination environment and geometry, can strongly influence or determine molecular properties (e.g. homogeneous catalytic activity) [2] and bulk properties (e.g. conductivity) [3].

The more common metallated polymers involve the coordination of the metal ions to donor atoms (N, O, S, Cl) within the main chain or in pendant groups, and are more easily obtained by the anchoring of complex fragments to a preformed polymer [4]. The real organometallic polymers, i.e. compounds involving at least one carbon–metal bond, when compared with the more common metallated polymers just mentioned, display two differences. They are usually less easily obtained and manifest a poorer general stability. The latter observation does not hold in the case of derivatives of a ferrocenyl fragment; these are of exceptional thermal stability, chemical versatility and wide applicability [5].

Despite the two above drawbacks, organometallic polymers deserve interest even in cases where they display only a moderate stability. In fact, one should note that an appropriate choice of the ancillary ligands can sensibly increase the general stability of the complex moiety and that of the entire molecule. (As expected, in the case of d8 ions, coordinative saturation of the metal centre increases the general stability of the polymers [6].) Moreover, some uses of metallated polymers, e.g. possible involvement in catalytic processes, do not necessarily require high thermal stability, as illustrated by the case of polymer anchored enzyme catalysts operating under mild conditions in food processing [7].

This work deals with imine derived polymers including a π-allylpalladium(II) fragment as the organometallic

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moiety. The new polymers have been designed with the aim of obtaining mesogenic products, considering that metallomesogens attract substantial interest in relation to their potential use in new materials [8]. It is noted that the organometallic macromolecules investigated have a side group structure, of which only a few examples are known among those showing liquid crystalline (LC) phases [9, 10].

2. Experimental

^{1}H NMR spectra were recorded at 200 MHz using a Varian Gemini 200 spectrometer. $CDCl_3$ was used as solvent and TMS as an internal standard. Reactions requiring a nitrogen atmosphere were carried out by using Schlenk techniques. Phase transition temperatures and enthalpies were measured using a Perkin Elmer DSC-7 apparatus, adopting a scanning rate of 10 K min^{-1}, under a dry nitrogen flow. Optical observations on monomer and polymer samples were performed using a Zeiss polarizing microscope equipped with a Mettler FP5 microfurnace. A Mettler TG50 apparatus was employed for thermogravimetric analysis. X-ray diffraction patterns were recorded by the photographic method utilizing a flat-film camera and Ni-filtered CuK$_\alpha$ radiation. Inherent viscosities (η_{inh}) of polymer solutions were measured using $CHCl_3$ solutions at 25°C and an Ubbelohde viscometer. The molecular mass of one polymer in $CHCl_3$ solution at 37°C was obtained by means of a Knauer vapour pressure osmometer.

Solvents were dried before use. The reagents 4-nitrophenol, 1-bromoheptane and *n*-octylamine were commercially available (Aldrich). By reaction of 1-bromoheptane with 4-nitrophenol, 4-heptyloxynitrobenzene was obtained [11]. The aniline **C7NH2** (see scheme 1) was prepared by reduction of 4-heptyloxynitrobenzene in ethanol/water (10:1) with a large excess of sodium hydrosulphate, following standard reduction methods [12]. The aldheyde **C8CHO** (see scheme 1) was obtained as reported in the literature [13]. The compounds $[(\eta^3\text{-}R\text{CH:CHCH}_2)\text{PdCl}]_2$ were prepared according to literature methods (R = H [14] or Me [15]). Selected ^{1}H NMR data for all the new compounds are reported in table 1.

2.1. *Synthesis of* ***Acr-C6CHO***

The method reported here for the synthesis of **Acr-C6CHO** is a modification of a known procedure [16]. To a solution of 4-(6-propenoyloxyhexyloxy)benzoic acid [17] (5·20 g, 17·8 mmol), 2,4-dihydroxybenzaldehyde (2·95 g, 21·4 mmol), 4-pyrrolidinopyridine (0·26 g, 1·75 mmol) in 25 ml of tetrahydrofuran, and 1,3-dicyclohexylcarbodiimide (4·04 g, 19·6 mmol) dissolved in 6 ml of the same solvent was added with stirring at room temperature. After 2 h the solid was filtered off, and to the resulting solution 1·91 g (9·57 mmol) of copper(II) acetate monohydrate dissolved in 40 ml of absolute ethanol and 3·43 g (41·8 mmol) of sodium acetate dissolved in 90 ml of water were added. The resulting solid Cu(II)-complex was recovered by filtration, washed with ethanol and recrystallized from ethanol/$CHCl_3$ (5:1). The product recovered by filtration was redissolved in $CHCl_3$ (55 ml) and 150 ml of HCl (about 2% by weight) was added with stirring to the solution. The organic phase was separated, washed with water, dried over sodium sulphate, concentrated to about 10 ml and the product precipitated with heptane. Recrystallization from heptane gave 2·20 g (5·33 mmol) of fairly pure aldheyde (30% yield, m.p. (T_m) = 78°C, ΔH = 120 J mol^{-1}).

2.2. *Synthesis of* ***Im1-4***

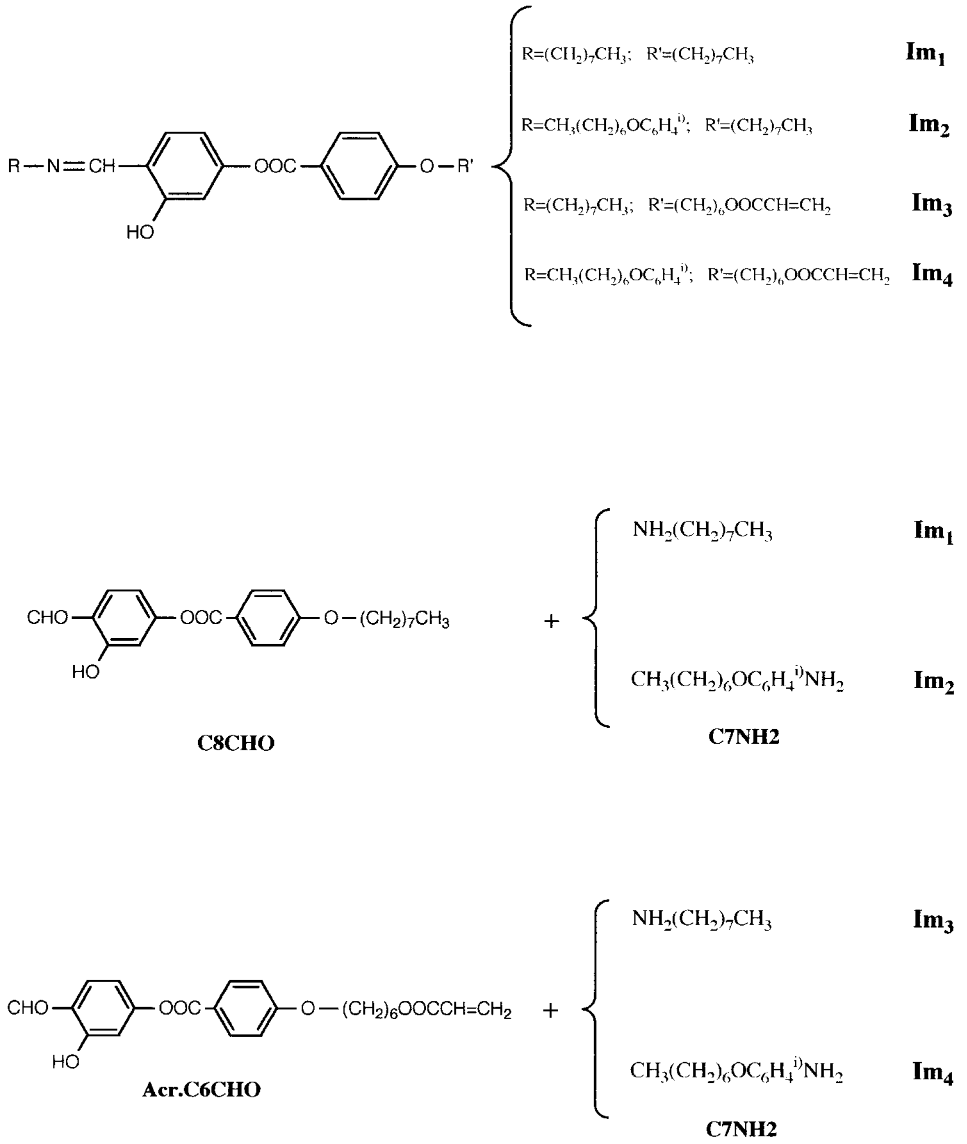
Stoichiometric amounts of the appropriate aniline and aldheyde were dissolved in dry ethanol and the solution (0·05M in both compounds) was gently boiled for 15 min. The crude imines were obtained as yellow precipitates, except for **Im3**, which was obtained as an oil and required removal of the solvent and cooling in a refrigerator for crystallization. All the crude imines could be crystallized from absolute ethanol/tetrahydrofuran (9:1) for further purification.

2.3. *Synthesis of complexes* ***PdIm1-4*** *and* ***PdMeIm1-4***

The same general procedure (scheme 2) was adopted for the reaction between the appropriate imine and $[(\eta^3\text{-}R\text{CH:CHCH}_2)\text{PdCl}]_2$ (R = H or Me). As an example, the preparation of **PdMeIm4** is described. To a stirred solution of 0·70 g (1·16 mmol) of **Im4** in 20 ml of absolute ethanol was added 0·230 g of K_2CO_3 (1·67 mmol), 0·138 g of $NaOOCCH_3$ (1·68 mmol), and finally $[(\eta^3\text{-CH}_3\text{CH:CHCH}_2)\text{PdCl}]_2$ (0·230 g, 0·58 mmol). After stirring for 15 min at room temperature, the resultant yellow precipitate was recovered by filtration. This material was dissolved in a minimum amount of methylene chloride and the solution filtered through a bed of Florisil (60–100 mesh). Addition of hexane resulted in crystallization of the product.

2.4. *Synthesis of* ***P(Im4)***

Under a nitrogen atmosphere, **Im4** (0·586 g, 0·975 mmol) was dissolved in 1 ml of a 0·137M methylene chloride solution of butyl peroxybenzoate. The solution was transferred to a vial, the solvent removed *in vacuo*, and the sealed vial kept for 5 min at 105°C. The resulting polymer was recovered by dissolving in chloroform, filtering through a sintered glass filter, and precipiting by addition of hexane.



i) 1, 4-phenylene

Scheme 1.

2.5. *Synthesis of* **P(PdIm4)** *and* **P(PdMeIm4)**

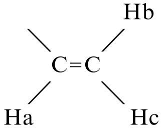
The two polymers were obtained by similar procedures (scheme 3). As an example, the synthesis of **P(PdMeIm4)** is described. To a stirred solution of 0·209 g (0·348 mmol) of **P(Im4)** in 40 ml of chloroform/ethanol (3:1) was added 0·100 g (0·725 mmol) of K_2CO_3, 0·238 g (2·90 mmol) of $NaOOCCH_3$, and finally $[(\eta^3\text{-}CH_3CH{:}CHCH_2)PdCl]_2$ (0·069 g, 0·174 mmol). After stirring for 1 h at room temperature, ethanol was added to produce a yellow precipitate, which was recovered by filtration. This material was dissolved in a minimum amount of chloroform and reprecipitated by addition of ethanol; the product was recovered by filtration and dried *in vacuo* at 35°C.

3. Results and discussion

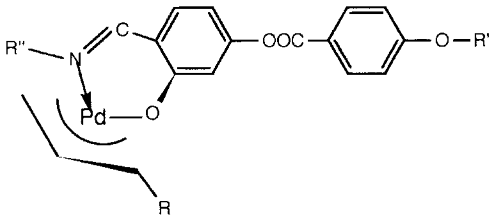
3.1. *Imines*

It is well known that a chelating Schiff's base derived from a salicylaldehyde imine derivative can complete the coordination sphere of a (η^3-allyl) palladium(II) moiety affording fairly stable complexes [18]. In this work, four imines (three of which give liquid crystalline melts) have been prepared, in order to obtain stable liquid crystalline (LC) π-allyl Pd(II) complexes and

Table 1. Some ^{1}H NMR resonances of the most important compounds: s = singlet; d = doublet; dd = double doublet; t = triplet; m = multiplet.

	Compound									
Fragment	**Acr-C6CHO**	**Im$_2$**	**Im$_4$**	**PdIm$_2$**	**PdIm$_4$**	**PdMeIm$_2$**	**PdMeIm$_4$**	**P(Im$_4$)**	**P(PdIm$_4$)**	**P(PdMeIm$_4$)**
–O(R)CH$_3$		0·91t	0·89t	0·83t	0·89t	0·90t	0·88t	0·84t	0·88t	0·89t
=N–CH$_2$–		3·51t		3·65t		3·71t				
–CH$_2$O-ϕ	4·05t	4·07t	4·05t	4·02t	4·03t	4·05t	4·04t	[a]	[a]	[a]
–COOCH$_2$-ϕ	4·20t	4·21t	4·19t	4·16t	4·18t	4·18t	4·17t	[a]	[a]	[a]
	Ha = 6·13dd	6·17dd	6·17dd	6·15dd	6·12dd	6·13dd	6·12dd			
	Hb = 6·40d	6·43d	6·42d	6·38d	6·38d	6·37d	6·38d			
	Hc = 5·81d	5·85d	5·85d	5·80d	5·81d	5·81d	5·83d			
ϕ-CH=N		8·35s	8·61s	7·91	8·05s	7·29s	8·07s	8·42s	[a]	[a]
ϕ-CHO	9·88s									
ϕ-OH	11·24s	14·10s	14·11s							
CH$_2$ allylic or crotylic				*anti*: 2·70d 3·12d *syn*: 2·83d a	*anti*: 2·75d 3·10d *syn*: 2·80d a	*anti*: 2·50d *syn*: 2·72d	*anti*: 2·50d *syn*: 2·71d		[a]	[a]
CH allylic or crotylic				5·59m	5·58m	5·31m	5·30m		5·50m	5·22m
CH$_3$ crotylic						1·45d	1·42d			[a]
CH-Me crotylic						3·81m	3·80m			[a]

[a] Not assignable.



R=H	R'=$(CH_2)_7CH_3$; R''=$(CH_2)_7CH_3$	**PdIm$_1$**
	R'=$(CH_2)_7CH_3$; R''=$CH_3(CH_2)_6OC_6H_4$$^{i)}$	**PdIm$_2$**
	R'=$(CH_2)_6OOCCH{=}CH_2$; R''=$(CH_2)_7CH_3$	**PdIm$_3$**
	R'=$(CH_2)_6OOCCH{=}CH_2$; R''=$CH_3(CH_2)_6OC_6H_4$$^{i)}$	**PdIm$_4$**
R=CH_3	R'=$(CH_2)_7CH_3$; R''=$(CH_2)_7CH_3$	**PdMeIm$_1$**
	R'=$(CH_2)_7CH_3$; R''=$CH_3(CH_2)_6OC_6H_4$$^{i)}$	**PdMeIm$_2$**
	R'=$(CH_2)_6OOCCH{=}CH_2$; R''=$(CH_2)_7CH_3$	**PdMeIm$_3$**
	R'=$(CH_2)_6OOCCH{=}CH_2$; R''=$CH_3(CH_2)_6OC_6H_4$$^{i)}$	**PdMeIm$_4$**

i) 1, 4-phenylene

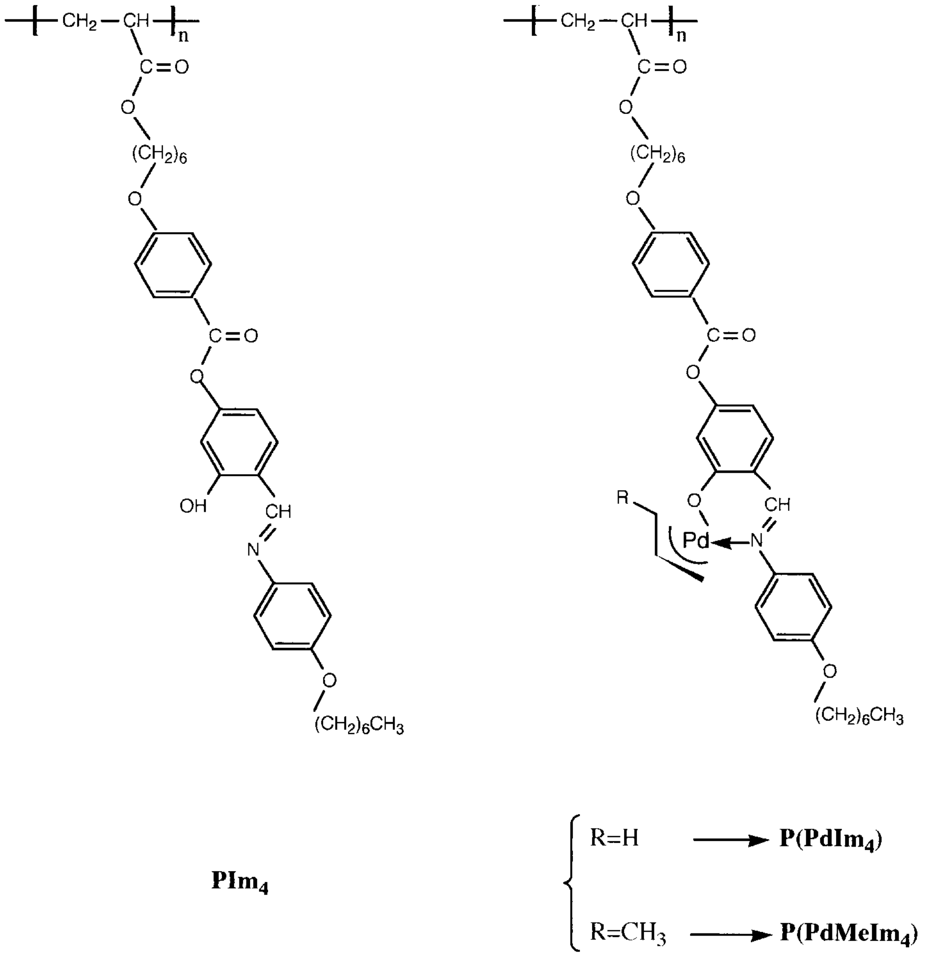
Scheme 2.

polymers. A sketch of the synthetic path to the imines has been shown in scheme 1. In table 2 thermodynamic data concerning the phase behaviour of the imines are reported.

The first compound, prepared with the purpose of acquiring a simple mesogen containing the chelating function was **Im1**. However, the mesophase of this compound has a very narrow range of instability. With the purpose of obtaining a better mesogen, the introduction of a phenoxy group into the ligand was accomplished in **Im2**, which has a satisfactory mesophase stability, as shown by the increased isotropization temperature (T_i). In order to evaluate the influence of the acrylic function on the stability of the mesophase and to obtain more simple molecules for testing the coordination behaviour expected for the polymers, the preparation of **Im3** and **Im4** was also carried out. It was found that the stability range of the two acrylate derivatives is narrower than that of the corresponding non-acrylated imines, with a decrease of T_m and T_i.

It was also observed that **Im1** has a nematic phase (N) stable over a range of about 8°C, while the analogous acrylate, **Im3**, is a liquid at room temperature and does not display any LC behaviour above 0°C.

Due to the presence of a better mesogenic core, the thermal stability range of the mesophase increases in both **Im2** and **Im4**, which also show a DSC signal due to a reversible smectic C–nematic phase transition (see



Scheme 3.

Table 2. Thermodynamic data for the imines and complexes and Pd content (%) of the complexes.

Compound	T_{m}/°C[a]	ΔH_{m}/J g^{-1}	$T_{\mathrm{SmC-N}}$/°C[a]	$\Delta H_{\mathrm{SmC-N}}$/J g^{-1}	$T_{\mathrm{N-I}}$/°C[a]	$\Delta H_{\mathrm{N-I}}$/J g^{-1}	%Pd (calc)[f]	%Pd (exp)[g]
Im1	67·9	72			76·8	2·5		
Im2	99·9	71·7	162·6	3·4	220·4	2·7		
Im3	[b]							
Im4	89·0	95·0	123·6	1·4	198·1	1·4		
PdIm1	89·5	79·6					16·91	16·40
PdIm2	127·5; 138·0[c]	59·8; 19·7			(114·5)[d]	0·45	15·00	14·95
PdIm3	73·0	55·0					15·88	15·45
PdIm4	124·08	65·9			(97·3)[d]	0·80	14·22	14·34
PdMeIm1	94·0	56·5			(35 → 40)[e]		16·54	16·14
PdMeIm2	147·6	27·2			(142·5)[e]		14·76	15·05
PdMeIm3	70·6; 84·5[c]	53·9; 22·5			(35 → 40)[e]		15·55	15·44
PdMeIm4	83·6	64·5			120·3	0·94	13·94	13·28

[a] Onset temperatures.

[b] Isotropic liquid at room temperature.

[c] Two solid phases.

[d] Monotropic.

[e] Monotropic, detectable by optical observations, not by DSC.

[f] Calculated palladium content.

[g] Experimental palladium content estimated by thermogravimetric measurements in air.

figure 1). The nature of the LC phases was ascertained by optical observation, since the isotropic melts of **Im2** and **Im4** generate on cooling a very mobile schlieren texture (nematic phase). On further cooling, coexisting broken fan and schlieren textures, typical of the smectic C phase, are observed.

3.2. *Imine monomeric complexes*

Allyl and crotyl palladium derivatives were obtained for all the four imines **Im1-4**. The complexes have the general formulae and labels shown in scheme 2. They were obtained by reaction of the binuclear species $[(\eta^3\text{-}R\mathrm{CH{:}CHCH_2})\mathrm{PdCl}]_2$ with the appropriate imine in ethanol solution, in the presence of a base. The products display various shades of yellow and are soluble in common organic solvents, such as chloroform, ethanol and acetone. After dissolution of the crude products in chloroform, filtering the solution through a bed of Florisil, and partial removal of the solvent, crystallization was effected from ethanol. The crystalline complexes are thermally stable enough to give reversible melting and isotropization transitions. In table 2 the thermodynamic data concerning the phase behaviour of the complexes are reported.

By comparison with the behaviour of the precursor imines, it is found that metal coordination gives a decrease of T_i, which accounts for the absence of mesophases for some of the complexes. This effect is more significant for the molecules including the simple allyl moiety. In fact, **PdIm1** and **PdIm3** are not LC, while **PdMeIm1** and **PdMeIm3** have a monotropic nematic phase (mobile schlieren textures are observed). Also **PdIm2**, **PdIm4** and **PdMeIm2** produce monotropic nematic phases. On cooling the isotropic liquid, schlieren textures are observed and a low intensity DSC signal is detected, except in the case of the crotyl complex. It is noted that the range of stability of the mesophase for **PdMeIm4** is ~60°C.

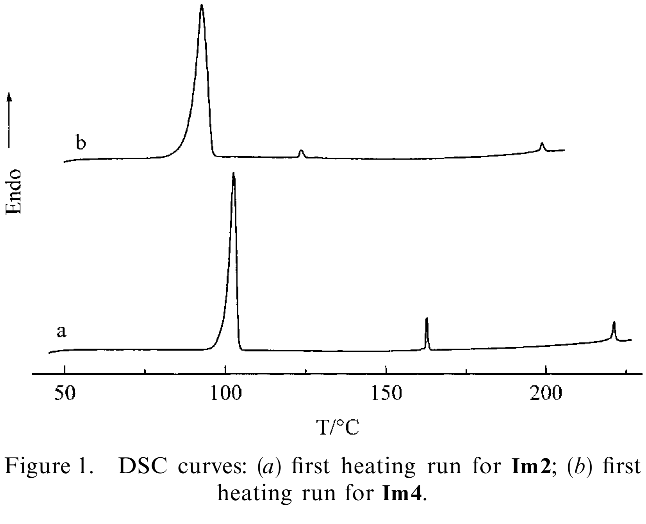


Figure 1. DSC curves: (*a*) first heating run for **Im2**; (*b*) first heating run for **Im4**.

In particular, in figure 2 are shown the DSC traces for the first heating run for the allyl complex **PdIm4** (the inset shows the monotropic nematic transition) and the crotyl complex **PdMeIm4**†. The two complexes show good thermal stability, provided they are not warmed above 140°C. On the basis of these results, complexes **PdIm4** and **PdMeIm4** were chosen as precursors of the new acrylate LC polymers.

^{1}H NMR data and analysis of the Pd content by TGA measurements (see for example figure 3) confirm the high purity of the monomeric complexes and the substantially complete metallation of **PIm4** (calculated and experimental TGA data are reported respectively in tables 2 and 3). In the ^{1}H NMR spectra, the chemical

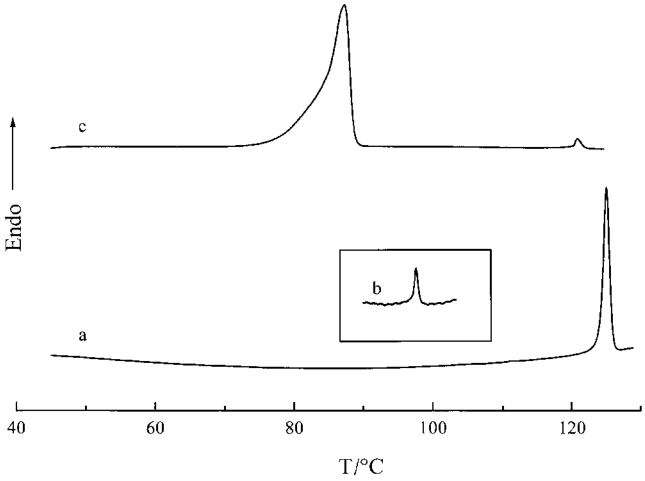


Figure 2. DSC curves: (*a*) first heating run for **PdIm4**; (*b*) monotropic isotropic–nematic transition; (*c*) first heating run for **PdMeIm4**.

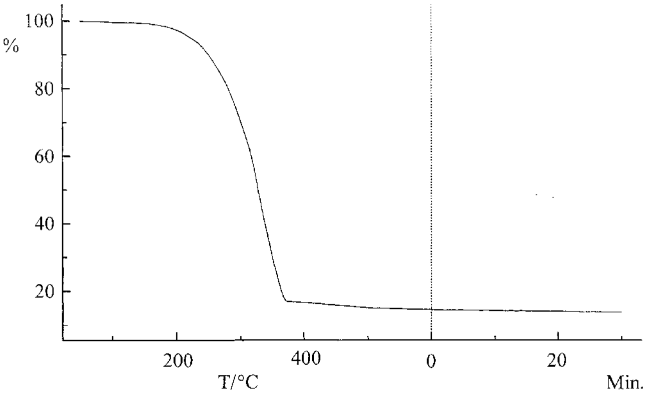


Figure 3. Thermogravimetric curve for a sample (10·116 mg) of **P(PdIm4)**: run from 50°C to 600°C at 10°C min^{-1}, followed by an isotherm at 600°C for 30 min in air.

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†The crotyl derivatives are a mixture of the two possible isomers (*syn* and *anti*).

Table 3. Thermodynamic data, the inherent viscosity of **P(Im$_4$)**, Pd % and molecular masses of the polymers.

Polymer	T_g/°C	η_{inh}/dL g^{-1} [a]	Molecular mass	T_{dec}/°C [b]	Phase [c]	%Pd (calc) [e]	%Pd (exp) [f]
P(Im$_4$)	69	1·08	15000	330	Sm		
P(PdIm$_4$)	70	1·25	[d]	210	N	14·22	14·00
P(PdMeIm$_4$)	72	1·03	[d]	260	N	13·94	14·11

[a] Measured using $CHCl_3$ solutions at 25·0°C at a 0·20 g dl concentration.
[b] Temperature of initial decomposition (5%), evaluated by TGA, under N_2 flow, at 10°C min^{-1}.
[c] Checked by X-ray diffraction.
[d] Measurements were performed only on polymeric ligand.
[e] Calculated palladium content.
[f] Experimental palladium content estimated by thermogravimetric measurements in air.

shift of the iminic proton is a diagnostic test of complexation. In fact, the iminic proton singlet in the complexes is shifted closer to the other aromatic signals, compared with the same signal in the free ligands (see table 1).

3.3. *Polymeric ligand **P(Im$_4$)***

Some preliminary experiments, aimed at obtaining direct polymerization of the acrylate monomeric complexes, gave evidence that decomposition accompanies polymerization under the attempted reaction conditions. Thus, the preparation of a polymer containing type **Im$_4$** units, suitable for use as a ligand system, was attempted. The synthesis of **P(Im$_4$)** was accomplished by radical polymerization of **Im$_4$** promoted by *t*-butyl peroxybenzoate.

In table 3, thermodynamic data, the inherent viscosity and the average molecular mass of the polymer are reported. This polymer, as shown by TGA measurements, is notably stable and substantially unaltered up to about 300°C. The polymer has LC behaviour as confirmed by optical observation. The X-ray spectrum recorded at room temperature on a sample (glassy state), as prepared, is in agreement with a smectic structure. In fact, beside the high angle halo, five Bragg reflections are clearly observed, corresponding, respectively, to a spacing of 52 Å and its sub-multiples. The layer periodicity of 52 Å is greater than the length of **Im$_4$** in its most extended conformation (39 Å) and agrees with a bilayer intercalated structure (Smectic A or C). The type assignment of the smectic phase was not possible owing to the lack of macroscopic orientation of the sample. On the DSC diagram, the glass transition signal is detectable at 69°C and isotropization, followed by thermal decomposition, is observed at 280°C.

3.4. *Metallated polymers*

The general formulae of the polymers and their labels are shown in scheme 3. The polymeric ligand **P(Im$_4$)** was reacted with $[(\eta^3\text{-}CH_2{:}CHCH_2)PdCl]_2$ or $[(\eta^3\text{-}CH_3CH{:}CHCH_2)PdCl]_2$ to give, respectively, **P(PdIm$_4$)** and **P(PdMeIm$_4$)**. Similarly to the polymeric ligand, the metallated polymers are soluble in common organic solvents. Furthermore, their inherent viscosity is nearly equal to that of the parent polymer. The different polymer–solvent interactions clearly balance the effect of the increase in molecular mass due to metallation.

Thermodynamic properties of the two organometallic polymers are reported in table 3. It is noted that the glass transition (T_g) is in both cases only slightly greater than that of the parent **P(Im$_4$)**. Instead, a substantial decrease of the T_i from 280°C is afforded by the metal coordination. This effect, similar to that observed for the monomeric complexes, is more substantial for **P(PdIm$_4$)**. A similar trend has been observed for previously described side group polymers [10].

For both metallated polymers the isotropization can be observed by polarized light microscope. Isotropization is complete above 130°C for **P(PdIm$_4$)** and 150°C for **P(PdMeIm$_4$)** and appears to some extent—more significantly in the case of **P(PdIm$_4$)**—to be reversible. In fact, a little decomposition, with formation of palladium metal, begins just above T_i, but is marked only at higher temperature (see TGA data in table 3). However, isotropization can be clearly observed by DSC only for **P(PdMeIm$_4$)** (see figure 4).

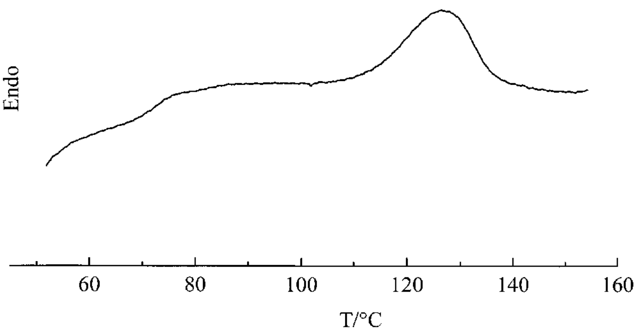

Figure 4. DSC trace for a **P(PdMeIm4)** sample: first heating run.

X-ray diffraction patterns, obtained at room temperature from specimens not thermally treated or from specimens annealed for 10 min at ≈40°C below T_i, confirm in both cases the presence of a nematic mesophase (unlike the polymeric ligand, which shows a smectic phase).

4. Conclusions

In this paper we have described the preparation and some properties of organometallic polymers which display LC properties and enclose palladium(II) in the pendant groups. The polymers could not be obtained by radical polymerization of the corresponding organometallic acrylate monomers, due to their poor stability under the attempted reaction conditions. However, the synthesis was carried out easily by anchoring organometallic fragments to a suitable ligand polymer. In fact, nearly complete metallation of a mesogenic polyacrylate was realized, to obtain π-allyl and π-crotyl Pd(II) derivatives. This did not cause loss of mesomorphism, although a significant decrease in the mesophase stability range (more significant for the allyl than for the crotyl complexes) was observed, possibly due to the steric encumbrance of the π-allyl Pd(II) groups and to the related decrease in the axial ratio of the pendant groups. Such an effect, also detected here in related low molecular mass compounds, was observed previously in similar metallated polymers [10] and monomers [19].

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