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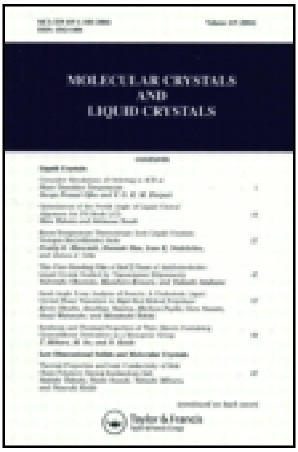

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Version of record first published: 24 Sep 2006.

To cite this article: C. Gang , X. Ping & Z. Rongben (1993): Effect of Palladium Coordination on Liquid Crystallinity of Imine Side Chain Polysiloxane, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 225:1, 373-381

To link to this article: http://dx.doi.org/10.1080/10587259308036241

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Mol. Cryst. Liq. Cryst., 1993, Vol. 225, pp. 373–381
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Effect of Palladium Coordination on Liquid Crystallinity of Imine Side Chain Polysiloxane

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(Received November 6, 1990; in final form June 6, 1991)

A new type of Pd-coordinating imine side chain liquid crystalline polysiloxane (Pd-ImLCP) has been synthesized by hydrolyzation reaction of *N*-(4-*n*-undecylenoxy-benzylidene)-4-dodecyloxyaniline with polymethylhydrogensiloxane (PMHS), then by ortho-palladation reaction of the obtained polymer ligand, imine side chain liquid crystalline polysiloxane (ImLCP), with various amounts of palladium acetate. The corresponding low molar mass Pd-coordinating imine complex (Pd-Im) has been also prepared for comparison. Their mesomorphic properties have been studied by polarizing microscopy, DSC and X-ray diffraction methods. The incorporation of Pd ions into the macromolecules ImLCP can affect the mesophase transitions in different ways. By increasing the molar percentage of Pd in the polymer, the textures turn from smectic to nematic phases and the transition temperatures almost stay constant up to 27 mole% and then decrease to 80 mole% at which crosslinking occurs. The clearing temperatures T_{cl} and enthalpy changes ΔH_i are lowered with rising molar percentage of Pd in the polymer. These results show a negative effect of coordinated Pd ions on the liquid crystallinity of the polymer ligand.

Keywords: palladium-coordinating LCP

In 1982, Takahashi[1] first reported the synthesis of lyotropic liquid crystalline transition metal-poly(-yne)organometallic compounds. Later on Hanabusa *et al.*[2] prepared the lyotropic liquid crystalline containing metalphthalocyanine moieties in side chains. Carfagna[3] and Moore[4] synthesized thermotropic metal-containing liquid crystalline polymers by incorporation of metal-complexing units into the polymer backbone. Hanabusa et al.[5,6] reported the preparation and liquid crystalline properties of metal-coordinating liquid crystalline polymers containing bipyridinediyl and 4'-cyano-4-biphenyloxyl groups, respectively. Before long, we have stated the synthesis of side chain β-diketone liquid crystalline polysiloxane (DKLCP) and its Copper complex.[7,8] Some preliminary results have been also presented for another two kinds of metal-coordinating liquid crystalline polysiloxanes containing azo and imine groups as ligands, respectively.[9] This paper is dealing with the synthesis and characterization of pd-coordinating imine-like polysiloxane (Pd-ImLCP) and the effect of incorporation of Pd ions on the liquid crystallinity.

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EXPERIMENTAL

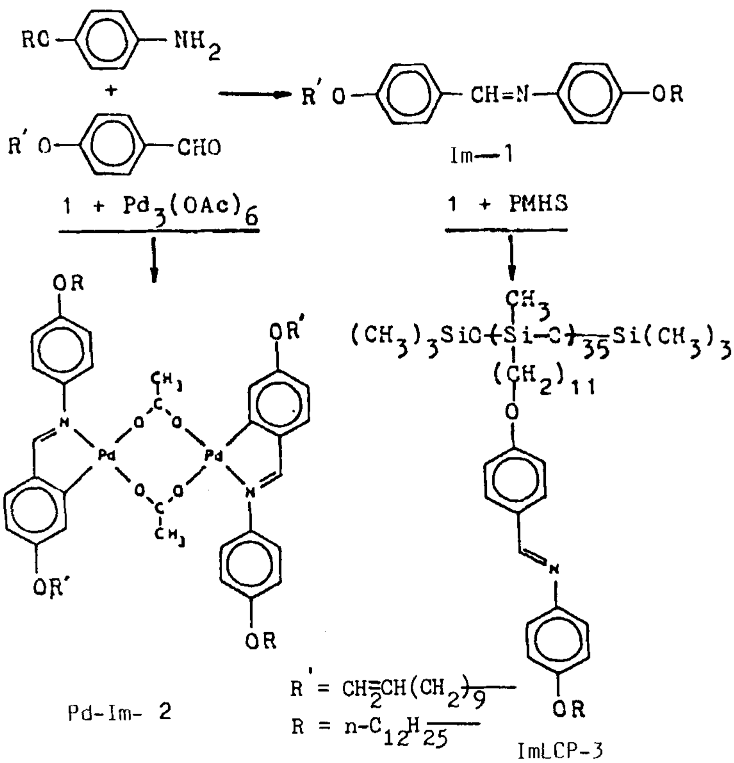
1. Materials and Techniques

Polymethylhydrogensiloxane (PMHS) was purchased from FLUKA company. Dicyclopentadinyl platinum dichloride (Cp_2PtCl_2) was synthesized as reported before.[10,11] Undecylene bromide was prepared according to the literature.[12] Palladium acetate was prepared by the method described elsewhere.[13,14] *p-n*-undecylenoxybenzaldehyde and *p-n*-dodecyloxyaniline were prepared by the known methods.[15,16] The elementary analysis was carried out on an ST-C2 elemental analyzer. FT-IR spectra were recorded using BRUKER-IFS-113V IR spectrometer. ESCA measurement was made on ES300 spectrometer. DSC study was performed with PE DSC-4 instrument. X-ray diffraction patterns were obtained on Rigaku D/max-3B diffractometer with 0.154 nm of wavelength of Cu-Kα radiation. The polarizing microphotographs were taken on XPIA-XINTIAN optical polarizing microscope.

2. Synthesis

The synthesis comprises the following steps as shown in Schemes I and II.

2-A Preparation of imine compound (Im-1) and its palladium complex (Pd-Im-2). Imine compound (Im-1) in Scheme I was formed by acetic acid-catalyzed condensation of aldehyde and aniline in ethanol as described elsewhere.[17] The



SCHEME I

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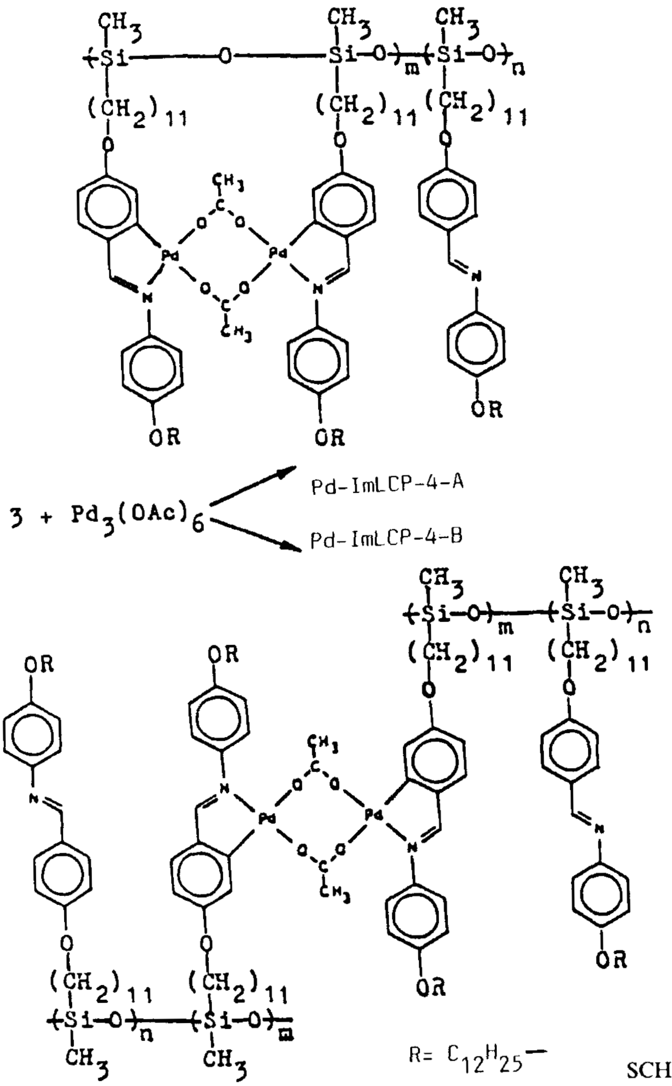


SCHEME II

corresponding Pd complex (Pd-Im) was prepared referring to the methods reported in literature.[18,19] To a solution of 1 g (1.9 mmol) of Im-1 in 50 ml of acetic acid at 80°C was added 0.42 g (1.9 mmol) of palladium acetate. The mixture was maintained isothermally for half an hour, then heated to reflux for 10 minutes in order to complete the reaction and minimize the black Pd formed by side reactions. After cooling the complex was precipitated out as yellow solid with trace amount of black Pd. After filtrating the solution of methylene dichlorids the obtained precipitate was recrystallized with ethyl acetate to give a yellow crystal. Yield: 80%. M.P. 178°C. The elementary analysis results of Im-1 and Pd-Im-2 are listed on Table I. The NMR, IR and ESCA data for these compounds are shown on Table II.

2-B Synthesis of imine side chain liquid crystalline polysiloxane ImLCP-3. The polymer ImLCP-3 was prepared according to Finkelmann's methods.[10,20] 5.5 g (10.3

TABLE I

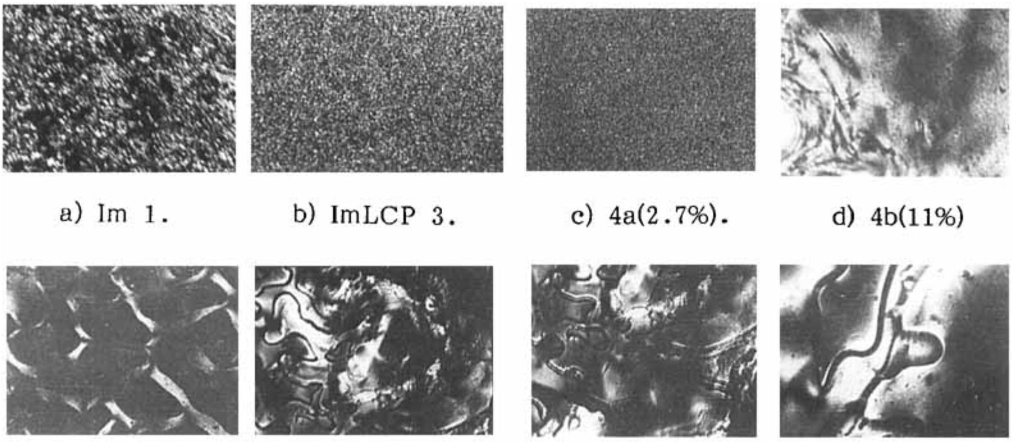
Elementary analysis data and the yields

Compound	N Found (Calcd.)	C Found (Calcd.)	H Found (Calcd.)	Pd Found (Calcd)	Yield(%)
1	2.66 (2.63)	81.05(81.05)	10.00(10.02)	0 (0)	92
2	2.00 (2.08)	64.86(64.14)	8.02(8.02)	15.18(15.21)	80
4b				2.0 (1.9)	90
4c				6.7 (6.5)	90

TABLE II

NMR, FT-IR and ESCA data

Compound	^{1}H-NMR(in ppm)				IR(cm^{-1})	ESCA(ev) Eb(Pd $3d_{5/2}$)
	CH=N	CH_2O	CH_2=CH	CH_3COO	CH=N	
1	8.36	4.0	4.8-6.0		1622(s)	0
2	7.42	3.7	4.8-6.0	1.84	1610(s)	337.4
3_{a-b}					1622(s)	
4_{a-g}					1622(w) 1607(s)	337.5



a) Im 1. b) ImLCP 3. c) 4a(2.7%). d) 4b(11%)

e) 4c(19%) f) 4d(27%) g) 4e (40%) h) 4f (54%).

FIGURE 1 Optical polarizing microphotographs of Im 1, ImLCP-3 and Pd-ImLCP-4(a–f) taken at 100°C. Magnification: × 125. The values in parentheses are molar ratio of Pd/Im in Pd-ImLCP 4(a–f).

mmol) of Im-1 (10 mol% excess over Si-H groups existed in PMHS (DP = 35) and 0.6 g (9.3 mmol of Si-H groups) of PMHS were dissolved in 25 ml of toluene (freshly distilled on sodium sand). After the solution was boiled and bubbled with Ar_2 for a few minutes, 0.6 ml (2.03×10^{-6} mole of Pt) of solution of dicyclopentadienyl platinum dichloride (Cp_2PtCl_2) in methylene dichloride was injected into the solution with stirring. The system was refluxed for 24 hrs at ca. 110°C and in turn 500 ml of methanol was slowly added. After cooling down to R.T. the pre-

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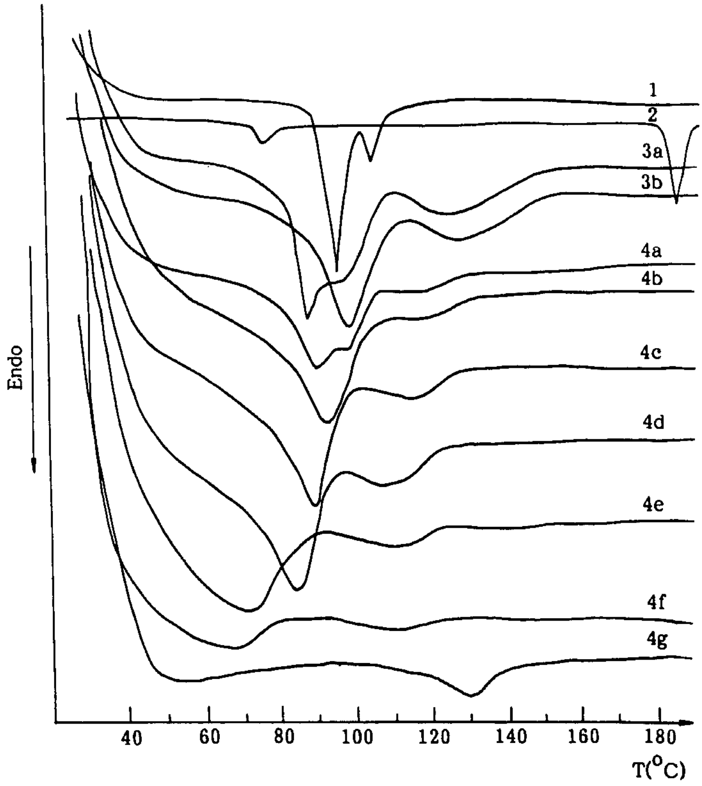

FIGURE 2 The DSC curves of Im-1, Pd-Im-2, ImLCP-3a & 3b (untreated & alkali-treated) & Pd-ImLCP-4(a–g). Heating rate: 20°C/min.

cipitate was filtered out and dried in vacuo to give a white powder ImLCP-3a, 4.5 g (Yield: 82%). The completeness of hydrosilylation was evidenced by the disappearance of the strong absorption peak of Si—H bond at 2180 cm^{-1} and the appearance of the strong absorption peak of CH=N bond at 1622 cm^{-1} in the IR spectra shown on Table II. In order to completely remove the residual unreacted Si-H groups which can not be observed by IR due to trace amount of it but cause the reduction of Pd acetate in complexation, to 50 ml of toluene solution of 4 g of formerly obtained ImLCP-3a was added a mixture of 50 ml of ethanol and 50 ml of 0.5% (weight ratio) aqueous solution of sodium hydroxide. The reaction was carried out at R.T. for one hr. Then the solution was decanted out and washed with distilled water twice and precipitated with 150 ml of MeOH. The precipitate was dried in vacuo to give a white solid ImLCP-3b, 3.6 g (90%).

2-B Synthesis of Pd-coordinating imine side chain liquid crystalline polysiloxane Pd-ImLCP. To a solution of ImLCP-3b in 20 ml of toluene at 80°C was added 10 ml of acetic acid and *X* mg (*X* = 1, 4, 7, 10, 15, 20, 25) of Pd acetate with stirring. After being maintained at 80°C for one hr, the system was heated slowly to reflux for half an hr to complete the coordination reaction without the formation of black Pd. The solvent was separated from the brown solution by distillation at

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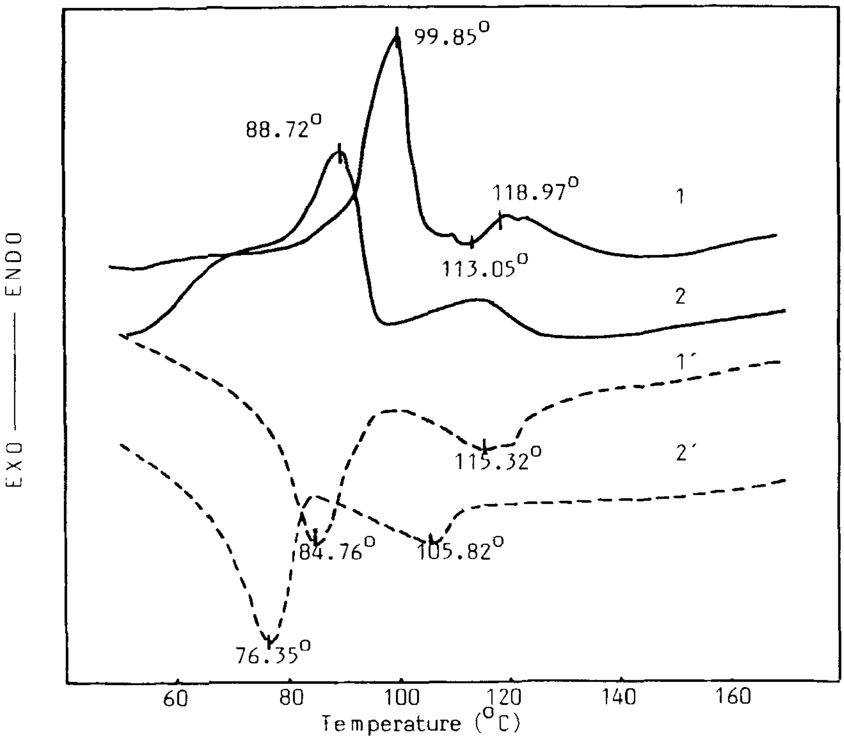

FIGURE 3 The DSC curves of ImLCP and Pd-ImLCP. Heating rate and cooling rate: 20°C/min. (1) ImLCP: heating run; (1') ImLCP: cooling run; (2) Pd-ImLCP-4c: heating run; (2') Pd-ImLCP-4c: cooling run.

reduced pressure. The remaining solid was dissolved in THF, filtered and freed from THF by carefully evaporating at R.T. and dried in vacuo to give the final products Pd-ImLCP 4a–g with yield 90%. The elementary analysis results of C, H and N for the polymer Pd-ImLCP 4a–g were not reported because they were not pure compounds of definite molecular weight. The data concerning IR and ESCA were shown on Table II. The determination of Pd content in Pd-ImLCP was performed by Ayres' method.[21] The sample was treated with aqua regia, percgloric acid and tindichloride in hydrochloric acid. The absorption intensity of sample-containing solution at 635 nm was determined with UV instrument and the Pd content was calculated. The analytical results indicated that the found values were almost identical with the added ones as shown on Table I.

RESULTS AND DISCUSSION

The polarizing microphotographs of low molar mass compounds (Im-1 and Pd-Im-2) and polymer samples (ImLCP-3 and Pd-ImLCP-4a–g) are shown in Figure 1. The DSC thermograms of these samples are given in Figure 2 and Figure 3. The untreated samples, ImLCP-3b and Pd-ImLCP-4c were examined by X-ray diffrac-

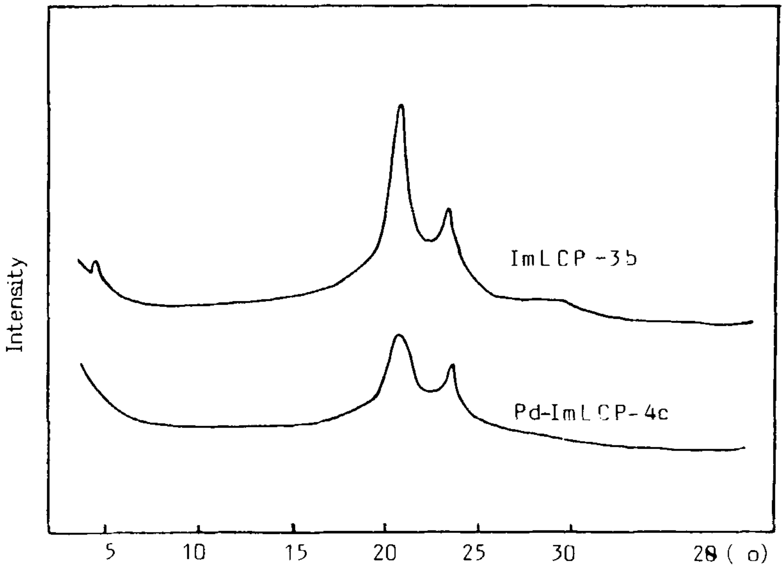

FIGURE 4 X-ray diffraction patterns ImLCP-3b and Pd-ImLCP-4c. The samples were obtained from solution without quenching or annealing.

tion as shown in Figure 4. The other X-ray diffraction data of the quenched samples (ImLCP-3a & 3b, and Pd-ImLCP-4a–g) are listed on Table III.

The structure of ortho-palladated imine was determined in the previous papers.[18,19,22,23] In the case of Pd-Im-2, ^{1}H-NMR, FT-IR, ESCA and elementary analysis confirm its acetato-bridged dinuclear ortho-palladated structure as shown in Scheme I. The polymeric complexes Pd-ImLCP-4a–g were characterized by IR and ESCA to prove the presence of ortho-palladated imine moiety as shown on Table II. The polymer ImLCP-3 and Pd-ImLCP-4a–f are all soluble in THF or toluene. So, it can be suggested that the coordination takes place intramolecularly and its structure (A) is illustrated in Scheme II. The title polymer Pd-ImLCP-4a–f exhibits good thermal stability. It does not decompose until ca. 200°C. Its stability is attributed to the ring-formation. The proposed structure of Pd-ImLCP-4a–f in Scheme II comprises three rings, two five-membered rings and a eight-membered ring, which are located between the two adjacent side chains and could stabilize the cis-configuration of the polymer Pd-ImLCP4a–f. It was observed that the viscosity of melted polymer Pd-ImLCP-4a–f increased with rise in Pd mole% especially when the molar ratio of Pd/imine was over 27%. A noticeable crosslinking could be found when the molar ratio was over 80%. It could be proposed that the structure (B) could exist as shown in Scheme II.

The influence of incorporation of Pd ions into the polymeric ligand molecule on its liquid crystallinity was investigated by polarizing microscopy, DSC and X-ray diffraction as followings:

1. The coordination of Pd ions can change the mesophase taxtures from smectic to nematic as shown in Figure 1.
2. A series of DSC curves in Figure 2 and Figure 3 have demonstrated two

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TABLE III

The DSC, X-ray diffraction and textures

Compound	Y*	DSC**		X-ray diffraction*** (Å)			Textures****
		$\frac{T\ (^{\circ}C)}{\Delta H\ (J/g)}$	ΔT (°C)	d_1	d_2	d_3	
Im------1	0	$K \xrightarrow[103]{96.9} S \xrightarrow[11.4]{106.8} I$	9.9				S(mosaic)
Pd-Im---2	100	$K \xrightarrow[3.4]{72.4} S \xrightarrow[36.0]{183.8} I$	111.4				S(mosaic)
ImLCP---3	0	$G \xrightarrow[47.7]{99.85} S \xrightarrow[14.4]{118.97} I$	39.6	19.9	4.3	3.9	S(mosaic)
Pd-ImLCP-4							
4a	2.7	$G \xrightarrow[44.7]{89.6} S \xrightarrow[1.1]{116.1} I$	26.5	19.5	4.4	3.9	S(mosaic)
4b	11	$G \xrightarrow[39.0]{92.7} S \xrightarrow[3.6]{115.6} I$	22.9	19.2	4.3	3.9	S(mosaic)
4c	19	$G \xrightarrow[33.4]{88.7} S \xrightarrow[4.5]{113.1} I$	25.6	19.0	4.3	3.9	S(mosaic)
4d	27	$G \xrightarrow[21.3]{85.1} S \xrightarrow[3.9]{111.1} I$	26.0	19.3	4.3	3.9	N(schlieren)
4e	40	$G \xrightarrow[14.1]{71.6} S \xrightarrow[2.6]{111.3} I$	39.7	----	4.4	----	N(schlieren)
4f	54	$G \xrightarrow[5.2]{67.9} S \xrightarrow[2.6]{110.7} I$	42.8	----	4.0	----	N(schlieren)
4g	80	Crosslinked					

*Y stands for the molar ratio of Pd/imine. **K = crystalline state; G = glass state; S = smectic phase; N = nematic phase; I = isotropic state; $\Delta T = T_{cl} - T_f$. T_f is the fluidizing temp. ***Samples were quenched from 100° to 0°C.

transitions in heating or cooling scans. The original polymers, ImLCP-3 and Pd-ImLCP-4a–g, obtained from solution were checked by X-ray diffraction as shown in Figure 4. The room temperature structure of ImLCP-3 is super-cooled smectic and that of Pd-ImLCP-4a–g must be some ordered solid or some super-cooled liquid crystal different from typical smectic form. It may be due to the coordination hindering the molecular motion to form regular layer structure at low temperature. By increasing the molar ratio of Pd/imine the phase transition temperatures and enthalpy changes of the samples change as shown in Figure 2 and Table III.

3. The X-ray diffraction patterns of the quenched samples in Figure 2 have indicated that the order-degree of Pd-ImLCP was lowered with increasing Pd content. It is consistent with the texture observation as shown in Figure 1 and the thermograms as shown in Figure 2.

From the above-mentioned results it could be understood that the coordination of Pd ion to polymer ligand would play an adverse effect on its liquid crystallinity, though complicated. The chelating moiety, ortho-palladated imine ring, possessing a book-open configuration[18,19,22,23] could disrupt the orderly arrangement of macromolecule ImLCP so that the liquid crystallinity would be reduced. To the contrary, Cu-coordinating β-diketone side chain liquid crystalline polysiloxane Cu-DKLCP[8] and Pd-coordinating (Chloro-bridged) imine side chain liquid crystalline polysiloxane[24] exhibit the positive effect of coordinated metal ions on the liquid

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crystallinity because of the complexing moieties are square-planar configuration and play roles of mesogens.

Acknowledgment

This work was supported by The National Natural Science Foundation of China, The Fund of Polymer Physics Laboratory of Academia Sinica and Beijing Zhongguncun Associated Center of Analyses and Measurements for providing Instrumental Facilities.

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