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Synthesis and mesomorphic properties of fishbone-like liquid crystalline polysilsesquioxanes†

V. Pd-coordinating, fishbone-like azo-based liquid crystalline polysilsesquioxanes

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New kinds of Pd-coordinating azo-based liquid crystalline polysilsesquioxanes, Pd-H-FBA and Pd-C-FBA, have been synthesized first by hydrosilylation reactions of a vinyl-terminated mesomorphic azo compound with ladder-like homopolyhydrosilsesquioxane (H-T) and copolymethylhydrosilsesquioxane (MH-T) to produce fishbone-like, azo-based liquid crystalline polysilsesquioxanes H-FBA and C-FBA, respectively, followed by a further *ortho*-palladation reaction with palladium chloride. The mesomorphic properties have been investigated by DSC, optical polarizing microscopy and temperature-variable X-ray diffraction. It is found that their clearing temperatures, T_{cl}, are much higher and the mesophase ranges, ΔT, are much wider than those of the corresponding comb-like polymers with a single main chain—by more than 100°C. This indicates that the double main chain structures of the title polymers have a positive effect on mesomorphic properties. The influence of the contents of Pd^{2+} ions on the liquid crystallinity is also discussed.

1. Introduction

In the early 1970s Platé *et al.* [2], Blumstein *et al.* [3] and Rinsdorf *et al.* [4] first reported comb-like liquid crystalline polymers (C-LCP) with a single main chain, and this new field has long attracted the interests of polymer chemists from the standpoints of their theoretical and potentially practical significance. Meanwhile, rapid developments in coordination chemistry were continuously leading to a great number of metal complexes with unique geometric forms. A combination of the chemistry of liquid crystalline polymers with that of coordination compounds has led to a surge of new metallomesomorphic chemistry. The incorporation of metal ions into liquid crystalline polymers can not only enrich liquid crystal chemistry, but also pave the way to exploring a new family of advanced materials largely used in high technologies. In 1981, Takahashi *et al.* [5] first described the synthesis of liquid crystalline transition metal-poly(-yne) organometallics, and later Carfagna *et al.* [6] and Moore and Stupp [7] synthesized thermotropic metal-containing liquid crystalline polymers by incorporation of metal-complexing units into the polymer backbone. Hanabusa *et al.* [8] then reported the preparation and mesomorphic properties of metal-coordinating liquid crystalline polymers containing bipyridiyl and 4-cyanobiphenyl-4′-yloxy groups. In recent years, Zhang *et al.* have reported metal-coordinating liquid crystalline polysiloxanes with different pendent mesogenic moieties incorporating diketone, imine and azo groups [9]. Serrano *et al.* also published papers relating to new types of Cu(II)-chelated polymers derived from hydroxy functionalized homo- and co-polyazomethines [10], and he has recently reviewed new developments in metallomesogenic polymers [11]. Also Serrano *et al.* have reported paramagnetic liquid crystal side chain polyacrylates containing Schiffs base Cu^{2+} complexes [12]. Bikchantaev *et al.* have also published recent results on liquid crystalline rare earth metallopolymers [13], and interestingly, Gangadhara

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†Part IV see ref. [1].

et al. have reported the synthesis and mesomorphic behaviour of metal-containing liquid crystalline networks [14].

Different from the metallomesogenic polymers with a single main chain mentioned above are a new kind of metal-coordinating liquid crystalline polymer with a ladder-like main chain. These are synthesized by a coordination reaction of fishbone-like side group liquid crystalline polymers and transition metal ions such as a Cu-coordinating β-diketone-based fishbone liquid crystalline polysilsesquioxane (Cu-FBDK) [15] and Pd-coordinating imine-based liquid crystalline polysilsesquioxane (Pd-FBI) [1]. These have been made in our laboratory recently. In comparison with the corresponding metallomesogenic polymers with a single main chain, these metallomesogenic polymers with a ladder-like main chain possess wider mesophase ranges and higher clearing temperatures, as well as an improved film-forming ability. This paper describes the synthesis and characterization of palladium-coordinated azo-based liquid crystalline polysilsesquioxanes (Pd-FBA). The characteristic mesomorphic behaviour gives the possibility of developing new functional polymer materials especially as photo-responsive films with high second harmonic generation non-linear optical activity and electro-conductive materials.

2. Experimental

2.1. *Materials*

All the reagents and solvents are commercially available and of analytical purities. The toluene used was purified with sulphuric acid to remove methylthiophene (which can inactivate the hydrosilylation catalyst Cp_2PtCl_2), and then distilled from sodium sand.

2.2. *Synthesis*

The vinyl-terminated azo-type mesomorphic compound, 4-undecenyl-4′-hexyloxyazobenzene ($CH_2{=}CH(CH_2)_9$–O–C_6H_4–N=N–C_6H_4–O–C_6H_{13}, m.p. 96·9°C, hereafter represented as Azo-C_{11}-C_6) was prepared following the procedure described in reference [16]. The catalyst was prepared according to Apfel's work [17]. The detailed synthetic procedures for obtaining ladder-like polyhydrosilsesquioxane (hereafter named H-T) and random copolymethylhydrosilsesquioxane (hereafter named MH-T) have been described in our previous paper [18]. The synthetic routes for the Pd coordinating azo-based liquid crystalline polysilsesquioxanes are shown in figure 1.

2.2.1. *H-FBA*

The hydrosilylation reaction was carried out in a similar manner to that for the corresponding comb-like azo-based polysiloxane described in reference [19]. At first, the reaction system was flushed with dry argon. Then a mixture of 0·2 g (0·44 mmol) of vinyl-terminated azo compound Azo-C_{11}-C_6 and 0·023 mg (0·43 mmol) of H-T was dissolved in 20 ml of methylthiophene-free toluene and heated at 80°C under argon. Next, 0·5 mg of Cp_2PtCl_2 dissolved in 0·5 ml of CH_2Cl_2 was added and the mixture was stirred for 48 h at 90°C. After that time about 0·1 ml of heptene was added and stirring was continued for several hours to ensure complete reaction with remaining Si–H groups. Then the reaction mixture

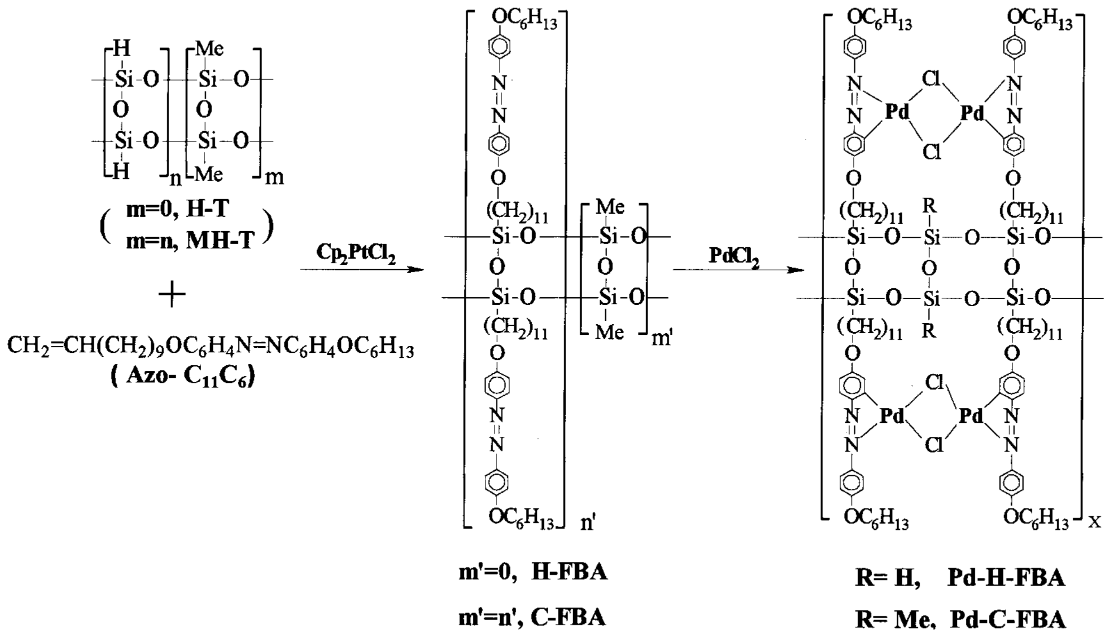


Figure 1. Synthetic route for Pd-H-FBA and Pd-C-FBA.

was filtered and 100 ml of dry methanol was added to the filtrate; the precipitate filtered off and then dissolved in toluene and again precipitated in methanol. Finally, an orange product was obtained after drying in a vacuum-oven in 84% yield.

2.2.2. *C-FBA*

Similarly to the above mentioned procedure for H-FBA, the system containing 0·2 g (0·44 mmol) of Azo-C_{11}-C_6 and 0·4 mmol of random copolymeric MH-T dissolved in 20 ml of freshly distilled, methylthiophene-free toluene was heated at 80°C under the protection of argon. Then heptene was added to react with the remaining Si–H groups. The reaction solution was filtered and methanol (100 ml) was added. The precipitate was filtered off and treated as above to give a yellow powder in *c*. 84% yield.

2.2.3. *Pd-H-FBA*

A solution containing 0·2 g of H-FBA dissolved in 30 ml of THF was added to 20 ml of an aqueous solution containing X mg ($X = 35{\cdot}3$; 17·7) of $PdCl_2$ and Y mg ($Y = 31{\cdot}5$; 15·8) of potassium chloride, respectively, followed by vigorous stirring for 72 h. The brownish solution was evaporated at room temperature. The remaining solid was dissolved in THF, the solution was filtered and the THF removed by carefully evaporating at room temperature. The residue was dried *in vacuo* to give the final products Pd-H-FBA (a) in 87% and Pd-H-FBA (b) in 83·6% yield.

2.2.4. *Pd-C-FBA*

Similarly to the above method for Pd-H-FBA, to a solution of 0·2 g of C-FBA in 30 ml of THF was added 20 ml of an aqueous solution containing X mg ($X = 31{\cdot}1$; 15·6) of $PdCl_2$ and Y mg ($Y = 27{\cdot}7$; 13·9) of KCl, respectively. After vigorous stirring for 72 h, the brown-reddish solution was evaporated at room temperature. The remaining solid was dissolved in THF, the solution filtered and the THF removed by carefully evaporating at room temperature. The residual product was dried *in vacuo* to give the products Pd-C-FBA (c) in 94·4% and Pd-C-FBA (d) in 92·5% yield.

2.3. *Analysis and characterization*

2.3.1. *Determination of the content of Pd^{2+} ions*

The determination of Pd^{2+} ions was carried out following the procedure reported in reference [20].

(1) Preparation of the sample solution. 3 ml of aqua regia was cautiously added to a flask containing 0·003–0·01 g of Pd-H-FBA or Pd-C-FBA. Then the sample was carbonized by heating and further carbonized after additions of 3 ml of nitric acid until no obvious reaction occurred. After adding hydrochloric acid, the solution was evaporated twice to destroy nitric acid and finally the sample solution was obtained.

(2) Determination by UV-visible spectroscopy. First, a standard working curve (A/C) was made, in which A was absorbance and C was the molar concentration of Pd^{2+} ions. The actual determination procedure was as follows: after introducing the sample solution from (a) above into a 25 ml volumetric flask, 10 ml of mixed acid (2·4 M in hydrochloric acid and 2·3 M in perchloric acid) were added. A green colour was developed by addition of 2 ml of 0·5 M tin(II) chloride solution which was 1 M in hydrochloric acid. The mixture was diluted to the required volume with distilled water. After 30 min, the absorbance was measured at 635 nm. The molar ratio of Pd^{2+}/Azo-unit could be found from the standard working curve. The analytical results are listed in table 1.

2.3.2 *Characterization*

The GPC and FTIR measurements were run in a routine manner. The differential scanning calorimetry (DSC) study was carried out using a Perkin-Elmer DSC-4. The temperature-variable X-ray diffraction was measured using a PW 1700 diffractometer (Phillips Co.) with a temperature-regulating attachment and Cu-K_α radiation with a wavelength of 0·145 nm. The birefringent behaviour was examined on an XPIA-XINTIAN optical polarizing microscope equipped with a hot stage. The determination of Pd^{2+} ion content was made using a UV-visible spectrophotometer 730 (Shanghai Analytical Factory). The atomic binding energy(E_b) of Pd($3d_{5/2}$) and nitrogen in the polymer was determined by X-ray photoelectron spectroscopy using the instrument ESCALAB 220 i-XL (VG Scientific Co.).

Table 1. Determination of Pd^{2+} content of Pd-H-FBA and Pd-C-FBA compounds.

				Molar ratio of Pd^{2+}/azo-unit	
Sample	No.	Wt of sample/g	Absorbance	Added	Found
Pd-H-FBA	(a)	0·0081	0·30	0·25 : 1	0·22 : 1
Pd-H-FBA	(b)	0·0045	0·36	0·5 : 1	0·41 : 1
Pd-C-FBA	(c)	0·0032	0·14	0·125 : 1	0·12 : 1
Pd-C-FBA	(d)	0·0030	0·23	0·25 : 1	0·25 : 1

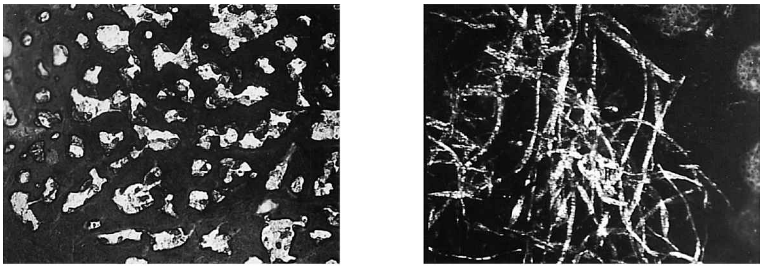
3. Results and discussion

The structure of the *ortho*-palladated azo-type compound was reported in a previous paper [9(*c*)]. As pointed out by Cope and Sickman [21] and by Ghedini *et al.* [22], the Pd^{2+} ions in related low molar mass systems are chelated with the N=N group and the *ortho*-carbon atom in the benzene ring to form a new disc-like chelating ring. In the polymeric systems under discussion here, this can significantly affect the mesomorphic properties of the parent materials H-FBA and C-FBA. All four polymeric complexes, (a)–(d) are readily soluble in THF or toluene, so it can be suggested that the coordination involving a given palladium atom takes place intramolecularly and that hardly any occurs between the polymeric chains. The structure is illustrated in figure 1.

Polarizing photomicrographs of the polymers are shown in figure 2. The mesomorphic properties examined by DSC and temperature-variable X-ray diffraction are listed in table 2. For comparison, the liquid crystalline properties of the corresponding comb-like, palladated azo-type liquid crystalline polysiloxane (Pd-LCP) are also listed in table 2. The title polymers Pd-H-FBA and Pd-C-FBA exhibited higher mesophase viscosities with increasing Pd^{2+} content. Especially high crosslinking would be found when the molar ratio of Pd^{2+}/Azo-unit approached to 1:1.

In the case of Pd-H-FBA and Pd-C-FBA, the discotic mesogenic system forming the chelating unit is of square-planar configuration, and the liquid crystalline features are comparatively complicated. The polarizing photomicrographs show some bright birefringent areas or bright bunches of lines.

Meanwhile, compared with the corresponding comb-like, single chain Pd-coordinating polymer, Pd-LCP, the clearing points T_{cl} are increased by 100°C. At the same time, the melting point temperature is decreased by about 30°C. Therefore, the mesophase ranges (ΔT) are extended by about 130°C. The significant increase in T_{cl} can be attributed to the great stiffness of the ladder-like



Sample (a), taken at 270°C

Sample (c), taken at 295°C

Figure 2. Polarizing photomicrographs of Pd-H-FBA (a) and Pd-C-FBA (c).

Table 2. Mesomorphic properties of Pd-H-FBA and Pd-C-FBA compounds.

Sample	No.	Molar ratio Pd^{2+}/azo	Phase transition by DSC $\frac{T/°C}{\Delta H/J\ g^{-1}}$	Mesophase range/°C ($\Delta T = T_{cl}\text{-}T_m$)	d/Å by XRD	Texture
Pd-H-FBA	(a)	0·22:1	$\mathrm{Cr}\xrightarrow[31{\cdot}1]{65{\cdot}9}\mathrm{LC}\xrightarrow[2{\cdot}7]{106{\cdot}7}\mathrm{LC}$ 310 dec.	244	4·43	birefringent areas and bright streaks
	(b)	0·41:1	$\mathrm{Cr}\xrightarrow[17{\cdot}1]{63}\mathrm{LC}$ 315 dec.	247	4·23	birefringent areas and bright streaks
Pd-C-FBA	(c)	0·12:1	$\mathrm{Cr}\xrightarrow[35{\cdot}5]{67{\cdot}5}\mathrm{LC}$ 315 dec.	247·5	4·25	bright lines
	(d)	0·25:1	$\mathrm{Cr}\xrightarrow[19{\cdot}7]{65{\cdot}6}\mathrm{LC}$ 315 dec.	249·4	4·67	bright lines
Pd-LCP[a]		0·11:1	$\mathrm{Cr}\xrightarrow[27{\cdot}1]{96{\cdot}7}\mathrm{N}_1\xrightarrow[24{\cdot}7]{135}\mathrm{N}_2$ 200 dec.	>104		N_D
		0·20:1	$\mathrm{Cr}\xrightarrow[2{\cdot}5]{97}\mathrm{N}_1\xrightarrow[7{\cdot}2]{159}\mathrm{N}_2$ 200 dec.	>103		N_D

[a] The data for the corresponding single main chain samples are from ref. [1].

polysilsesquioxane main chain which itself does not show a glass transition until decomposition occurs at 320°C [23].

The influence of the content of Pd^{2+} ion coordinated to the polymeric ligand on the liquid crystallinity was investigated by DSC, polarizing optical microscopy and temperature-variable X-ray diffraction. With increasing Pd^{2+} content, the mesophase range ΔT changes slightly, but the viscosity increases greatly. In the case of Pd-H-FBA, there are two mesomorphic transition peaks in the DSC curve for the sample (a). Meanwhile, compared with the X-ray diffraction curve of H-FBA coordinated with Pd^{2+}, the polymer (Pd-H-FBA), exhibits a small new peak in the small angle region on the right of original peak as shown in figure 3. This demonstrates that the polymer (Pd-H-FBA) forms a new layer structure involving the metal ion Pd^{2+}-coordinated units. Its layer separation is obviously shorter than that of polymer (H-FBA) un-coordinated to Pd^{2+}.

The metal-coordinated polymer was also examined by the method of X-ray photoelectron spectroscopy. The data indicate that the atomic binding energy (E_b) of Pd(3d$_{5/2}$) is 337·33 eV. Comparing this with the standard atomic binding energy (E_b) of Pd(3d$_{5/2}$) for K$_2$PdCl$_4$ ($E_b = 338{\cdot}1$ eV), the E_b chemical shift (ΔE_b) is $-0{\cdot}77$ eV.

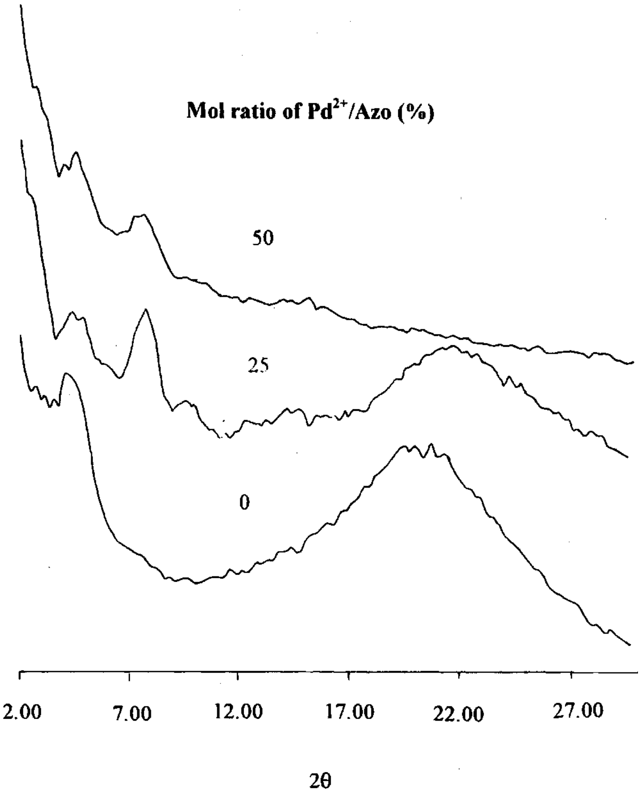


Figure 3. Variable-temperature X-ray diffraction curves of Pd-H-FBA compounds with different metal (Pd^{2+}) content at 180°C.

The nitrogen atomic binding energy graphics demonstrate that there are two types of nitrogens; one is the coordinated nitrogen (abbr. N$_A$) for which E_b(N1s) is 403·13 eV, and the other is the un-coordinated nitrogen (abbr. N$_B$) for which E_b(N1s) is 399·60 eV. The E_b chemical shift (ΔE_b) is $+3{\cdot}53$ eV. The peak area ratio N$_A$ to N$_B$ is 0·00544/0·03458. This indicates that the coordinated nitrogen atoms represent 13·5% of the total nitrogen atoms in the metal coordinated polymer. The data agree with the values determined by UV-visible spectrophotometry. This can be explained as follows. In the process of forming the complex, the azo-compound is the donor, the nitrogen contributing its lone pair of electrons to the Pd^{2+}. As a result, we have bonding between the Pd^{2+} and the nitrogen. The electron transfer therefore is from nitrogen to Pd^{2+}. When the complex is formed, the Pd^{2+} electronic density increases, while, the nitrogen electronic density decreases. Therefore the atomic binding energy of Pd^{2+} decreases (from 338·1 to 337·33 eV) and the atomic binding energy of nitrogen increases (from 399·60 to 403·13 eV).

The atomic binding energy graphics proves that only one type of Pd^{2+} peak occurs. This means there is only one type of Pd^{2+} in the metal-coordinated polymer. The metal-coordinated polymer does not therefore include unreacted PdCl$_2$ after the treatments involving dissolving in toluene and precipitation by methanol.

It is well known that the coordination geometry of the Pd^{2+} ion is square planar which leads to a hard discotic mesogen. The *ortho*-palladated chelating rings could well form a new type of mesophase, and the incorporation of Pd^{2+} ions into the polymeric ligand does have a very positive effect on the liquid crystalline properties. Reasonably speaking, the significant variations in liquid crystalline behaviour are mainly due to the high rigidity of the ladder-like main chain and the geometrical configuration of the metal discotic mesogens.

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