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EFFECT OF METAL COMPLEXATION ON THE BEHAVIOR OF LIQUID CRYSTALLINE POLYMER

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ABSTRACT

Liquid crystalline side-chain polymers (**3b–3f**) crosslinked by a *trans* Pt(II) complex were synthesized by a ligand exchange reaction with dichlorobis(benzonitrile)platinum(II) and poly(methylsiloxane) (**3a**) bearing a *p*-cyanobiphenyloxy mesogen unit attached to the polymer backbone by a flexible spacer group. The amount (x) of *p*-cyanobiphenyloxy mesogen coordinating to the Pt(II) ion in polymers **3b**, **3c**, **3d**, **3e**, and **3f** was 4.9, 9.7, 14.8, 20.2, and 49.6 mol%, respectively. The effect of Pt(II) coordination on the thermotropic liquid crystalline behavior of **3a** was examined by DSC, x-ray diffraction, and polarizing microphotography. Polymers **3a–3d** exhibited a nematic mesophase between T_g and T_c . On the other hand, **3e–3f**, which have a large amount of Pt(II)-coordinating mesogen, did not show a definite nematic mesophase, but exhibited an ambiguous one. The introduction of Pt(II) ion into **3a** resulted in a crosslinked structure and consequently prevented the formation of the ordered nematic mesophase.

INTRODUCTION

Recently, interest in crosslinked liquid crystalline polymers (LCP) with elastic properties has increased because the LC phase can be well oriented by a small mechanical strain [1–6], and this property is not reversible [7]. With this in mind, Zentel [8] proposed a device that transforms a mechanical strain signal into an optical signal or a piezo element that transforms a mechanical strain signal into an electrical response. Such crosslinked LCPs have thus far been prepared by the reaction of some of the olefinic double bonds of the polymer with the Si–H groups of oligo(dimethylsiloxane) [3, 5–8], by reaction of the hydroxy groups of the polymer with the isocyanate groups of the diisocyanate compounds [1, 4, 7, 11], by formation of enamel from the oligoester diol and melamine resin [9, 10], or by copolymerization of vinyl and divinyl monomers [2]. In the present paper we report the synthesis and properties of crosslinked LCP in which the crosslinkage is achieved by Pt(II) coordination of cyano groups in mesogenic side-chains. This research is part of a series of our studies on metal-containing LCP [12–14].

EXPERIMENTAL

Syntheses of Liquid Crystalline Polysiloxane (3a)

LC polysiloxane **3a** was prepared by the addition of vinyl monomer to the polysiloxane **1** according to the literature [15].

To a mixture of 0.150 g (2.50×10^{-3} mol) polysiloxane **1** (DP = 34, Shin-Etsu Chemical Co., Ltd.) and 0.960 g (2.75×10^{-3} mol) 6-(*p*-cyanobiphenyloxy)hexyl acrylate **2** [13] was added 2.5 mL tetrahydrofuran containing 100 ppm $\text{H}_2\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$ as catalyst. The solution was stirred at 50°C for 24 h under a nitrogen atmosphere. After concentrating, the polymer **3a** was reprecipitated from methanol and dried under vacuum. Yield: 0.92 g; IR (KBr): 2220(ν_{CN}), 1720($\nu_{\text{C=O}}$), 1600, 1485 cm^{-1} (aromatic). Disappearance of 2160(ν_{SiH}) and 1635 cm^{-1} ($\nu_{\text{C=C}}$).

Analysis. Calculated for $(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{Si})_n$: C, 67.44; H, 6.66; N, 3.42%. Found: C, 67.13; H, 6.54; N, 2.97%.

Introduction of Pt(II) Ion into 3a

A typical procedure for introducing Pt(II) ion into **3a** is described below. Toluene was distilled and bubbled with nitrogen for 15 min prior to use.

(A) In 10 mL toluene was dissolved 55 mg (1.34×10^{-4} mol) of **3a**, and then 2 mL toluene containing 1.57 mg (3.31×10^{-6} mol) dichlorobis-(benzotrile)platinum(II) [16] was added. The resultant solution was heated to 50°C for 1 h under a nitrogen atmosphere. After evaporating, methanol was added to precipitate. Crosslinked LCP **3b** having 4.9 mol% as the content of the Pt(II)-coordination unit was obtained. Yield: 37 mg; IR (KBr); 2280 (ν_{CN} coordinating to Pt(II)), 2220 (ν_{CN} noncoordinating to Pt(II)), and 340 cm^{-1} (*trans* $\nu_{\text{Pt-Cl}}$).

Analysis. Calculated for $(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{SiPt}_{0.5}\text{Cl})_{0.049n}(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{Si})_{0.951n}$: C, 66.39; H, 6.54; N, 3.37; Pt, 1.15%. Found: C, 65.69; H, 6.81; N, 3.00; Pt, 1.15%.

(B) In 10 mL toluene was dissolved 55 mg (1.34×10^{-4} mol) of **3a**, and then 2 mL toluene containing 4.88 mg (1.05×10^{-5} mol) dichlorobis-(benzotrile)platinum(II) was added. After the treatment described in (A), LCP **3c** having 9.7 mol% as the content of the Pt(II)-coordination unit was obtained. Yield: 27 mg.

Analysis. Calculated for $(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{SiPt}_{0.5}\text{Cl})_{0.097n}(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{Si})_{0.903n}$: C, 65.39; H, 6.44; N, 3.32; Pt, 2.24%. Found: C, 65.93; H, 6.51; N, 2.98; Pt, 2.24%.

(C) In 10 mL toluene was dissolved 55 mg (1.34×10^{-4} mol) of **3a**, and then 2 mL toluene containing 6.26 mg (1.32×10^{-5} mol) dichlorobis-(benzotrile)platinum(II) was added. After the treatment described in (A), LCP **3d** having 14.8 mol% as the content of the Pt(II)-coordination unit was obtained. Yield: 40 mg.

Analysis: Calculated for $(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{SiPt}_{0.5}\text{Cl})_{0.148n}(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{Si})_{0.852n}$: C, 64.36; H, 6.34; N, 3.26; Pt, 3.36%. Found: C, 63.87; H, 6.33; N, 2.89; Pt, 3.36%.

(D) In 10 mL toluene was dissolved 55 mg (1.34×10^{-4} mol) of **3a**, and then 2 mL toluene containing 7.90 mg (1.68×10^{-5} mol) dichlorobis-(benzotrile)platinum(II) was added. The elastic material was precipitated immediately. After stirred for 1 h at 50°C under a nitrogen atmosphere, the elastic precipitate was filtered off and washed with methanol. Upon drying, crosslinked LCP **3e** having 20.2 mol% as the content of the Pt(II)-coordination unit was obtained. Yield: 38 mg.

Analysis. Calculated for $(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{SiPt}_{0.5}\text{Cl})_{0.202n}(\text{C}_{23}\text{H}_{27}\text{NO}_4\text{Si})_{0.798n}$: C, 63.30; H, 6.24; N, 3.21; Pt, 4.51%. Found: C, 63.86; H, 6.12; N, 2.79; Pt, 4.51%.

(E) In 10 mL toluene was dissolved 55 mg (1.34×10^{-4} mol) of **3a**, and then 2 mL toluene containing 22.06 mg (4.69×10^{-5} mol) dichlorobis-(benzotrile)platinum(II) was added. The elastic material was precipitated immediately. After stirred for 1 h at 50°C under a nitrogen atmos-

phere, the elastic precipitate was filtered off and washed with methanol. Upon drying, the highly crosslinked LCP **3f** having 49.6 mol% as the content of Pt(II)-coordination unit was obtained. Yield: 35 mg.

Analysis. Calculated for $(C_{23}H_{27}NO_4SiPt_{0.5}Cl)_{0.496n}(C_{23}H_{27}NO_4Si)_{0.504n}$: C, 58.09; H, 5.72; N, 2.95; Pt, 10.17%. Found: C, 58.86; H, 6.00; N, 2.67; Pt, 10.17%.

Measurements

A Hitachi 170-70 atomic absorption spectrometer was used to determine the Pt(II) content. IR spectra were obtained by a Jasco IRA-302. DSC was recorded on a Rigaku DSC-10A apparatus at the rate of 10°C/min in air. Wide-angle x-ray diffraction patterns were photographed with a Rigaku Geigerflex (35 kV, 25 mA, CuK_{α} line). Optical microphotography was performed on a Nikon polarizing microscope, equipped with a Mettler hot stage FP82 apparatus.

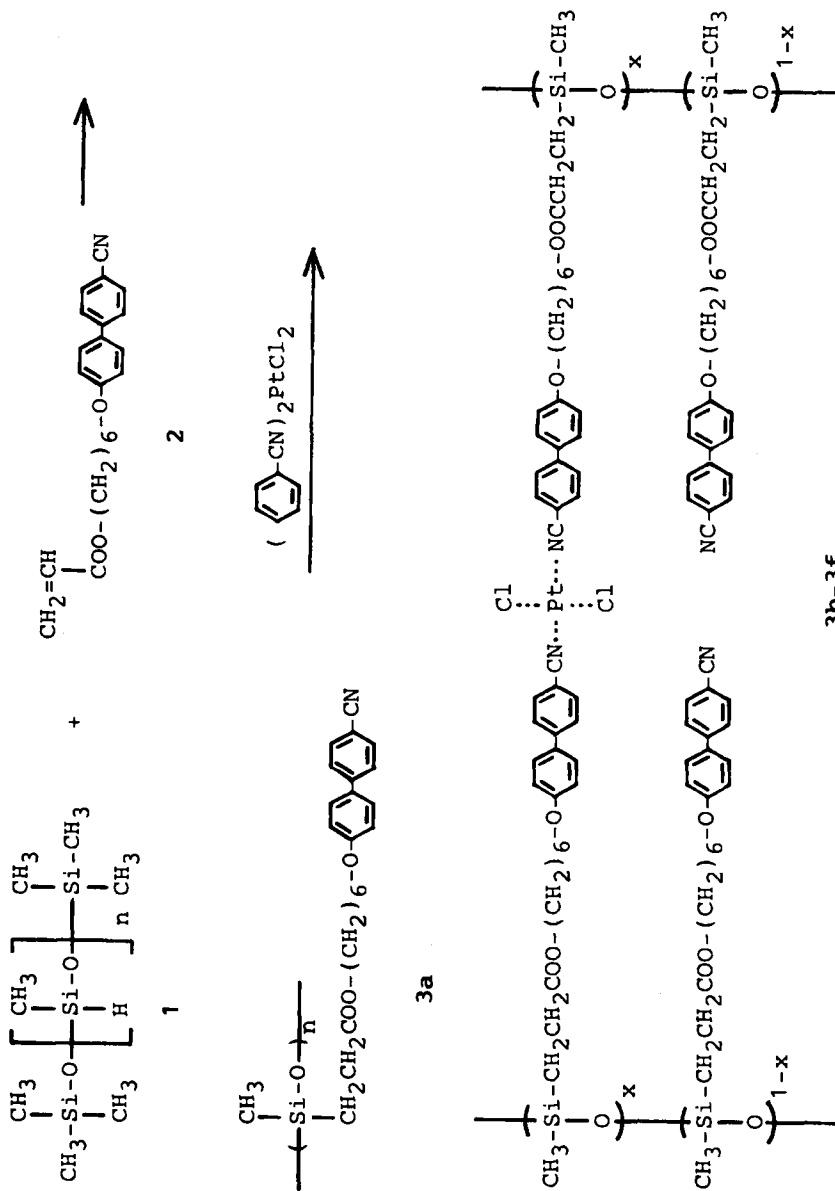
RESULTS AND DISCUSSION

Synthesis of Crosslinked Liquid Crystalline Polymers

A side-chain type of LCP **3a** bearing a *p*-cyanobiphenyloxy mesogen unit attached to the polysiloxane backbone by a flexible spacer group was prepared by the addition of 6-(*p*-cyanobiphenyloxy)hexyl acrylate **2** to the reactive hydrogen of the polysiloxane **1** according to Scheme 1. Crosslinked polymers **3b–3f** exhibiting elasticity similar to a rubber, in which the crosslinkage was achieved by *trans* Pt(II) complexation, were synthesized by a ligand exchange reaction with **3a** and dichlorobis(benzonitrile)platinum(II) (Scheme 1). The polymers and their abbreviations are summarized in Table 1, where *x* indicates the mol% of Pt(II)-coordinating mesogen as determined by atomic absorption spectroscopy. The structure of the Pt(II) complex in **3b–3f** was assigned *trans* [17] because only one terminal Pt–Cl stretch was observed in the far-IR spectrum (ν_{Pt-Cl} 340 cm^{-1}).

Thermal Behavior

Figure 1 shows the DSC heating curves of **3a–3f**. The thermal behavior of **3a** is characterized by a glass transition (T_g) into a nematic mesophase



SCHEME I.

TABLE 1. Abbreviations of Prepared Polymers and Mol% of Side-Chain Coordinating to Pt(II)

Sample	x (mol%)
3a	0
3b	4.9
3c	9.7
3d	14.8
3e	20.2
3f	49.6

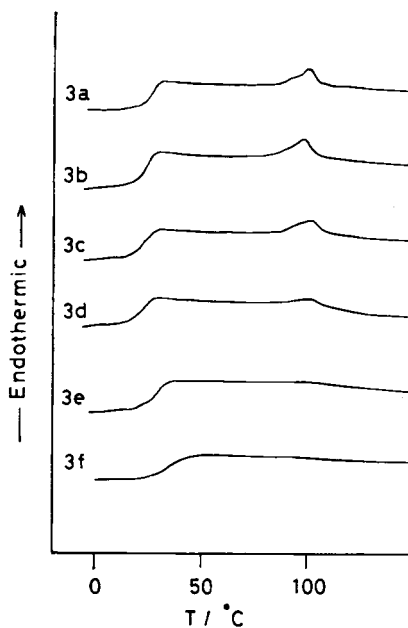


FIG. 1. DSC third heating curves of **3a**–**3f** (heating rate: 10°C/min).

at $\sim 30^\circ\text{C}$ and a clearing point (T_c) at $\sim 100^\circ\text{C}$ which corresponds to the transition from a nematic mesophase into an isotropic melt. Crosslinked LCPs **3b–3d**, which contain the Pt(II)-coordinating mesogen in contents less than 15 mol%, showed similar DSC heating curves to that of **3a**. However, if the Pt(II)-coordinating mesogen in the side-chain is more than ~ 20 mol%, the corresponding T_c disappeared in their curves (**3e** and **3f** in Fig. 1).

X-Ray Diffraction

The x-ray diffraction patterns in the cases of **3a–3c** exhibited a diffuse halo at a wide scattering angle and a second diffuse ring at a small angle (Table 2). The former corresponds to a distance of 4.3 Å, which is related to the lateral interferences between the mesogenic cores, while the latter corresponds to that of 22.6 Å, which is close to the length of the side-chain in the extended conformation. On the other hand, it is noteworthy that the diffuse ring at a small angle, related to a long-range order, is not observed with **3d–3f** having the Pt(II)-coordinating mesogen over ~ 15 mol%.

Polarizing Microscopy

Polarizing microphotographs of **3a–3f** are shown in Fig. 2. Typical Schlieren textures with disclination of the nematic mesophase were observed for **3a–3c** between T_g and T_c . As these textures disappeared above T_c it can be concluded that the endothermic peaks near 100°C are the transition from the nematic mesophase into the isotropic melt. With respect to **3d–3f**, the distinct Schlieren texture was no longer observed, although the birefringence still remained. Therefore, it is thought that the

TABLE 2. Spacings of **3a–f** Determined by X-Ray Diffraction

Sample	Spacing	(Å)
3a	4.3	22.3
3b	4.2	22.6
3c	4.3	22.6
3d	4.2	—
3e	4.2	—
3f	4.2	—

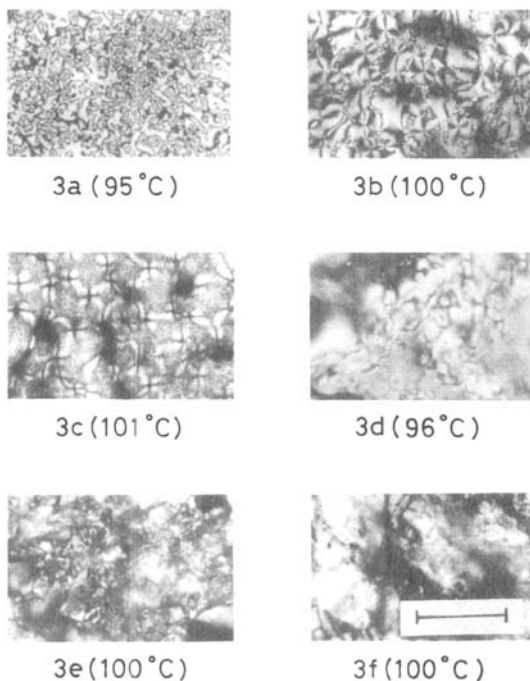


FIG. 2. Polarizing microphotographs of **3a–3f**. Bar represents 100 μm .

mobility of the mesogenic segments in **3d–3f** is reduced due to the restriction of side-chain segments by the higher level of crosslinking through the Pt(II) complex.

CONCLUSIONS

The LC elastomers (**3b–3f**), in which crosslinking was achieved by a *trans* Pt(II) complexation, were prepared by coordination of the cyano groups in the side-chain of LCP (**3a**). The properties of these elastomers were dependent on the extent of crosslinking, that is, the mol% of mesogen unit forming a Pt(II) complex. Thermal properties of **3a–3d** were characterized by a glass transition (T_g) and a clearing point (T_c), whereas **3e** and **3f** showed only T_g . X-ray diffraction patterns of **3a–3c** exhibited both a short-range and a long-range order. In polarizing microphotographs, typical Schlieren textures with disclination were observed for **3a–**

3c. Crosslinked LCPs **3b** and **3c** possessed a nematic mesophase similar to that of the parent LCP **3a**. However, **3d-3f** containing the Pt(II)-coordinating mesogen in excess of 20 mol% did not show a definite nematic mesophase. The introduction of high levels of Pt(II) ion crosslinks into **3a** prevented the formation of a nematic mesophase.

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