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Liquid Crystalline Polyacetylene Derivative Bridged with Metallomesogenic Substituent

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Metallomesogenic conjugated polymers were synthesized through complexations between liquid crystalline (LC) polyacetylene derivatives with cyanobiphenyl mesogenic groups in side chains and bis(benzonitrile)palladium dichloride. Coordinations of the cyano moieties of the side chains to the palladium cation generated crosslinked polymers with metallomesophase. Characterizations of the polymers were carried out in terms of mesophase stability and *cis-trans* isomerization.

Key words: polyacetylene derivative, conjugated polymer, palladium complex, metallomesogen, crosslink

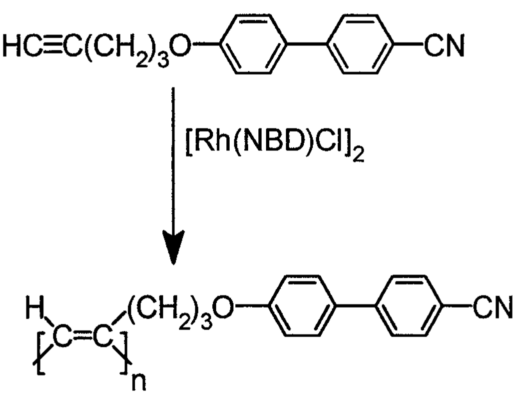
1. INTRODUCTION

It is well known that metal complexes coordinated with liquid crystalline (LC) ligands are called metallomesogens. Because of their profound potentialities in electromagnetic and optical properties, the metallomesogens have been intensively investigated for this decade[1]. However, there are less reported metallomesogenic polymers. Particularly, no metallomesogenic conjugated polymer has been reported so far as we know. Recently we developed a series of LC conjugated polymers by introducing mesogenic groups into side chains of the polymers[2-11]. Among the mesogenic groups, the cyano moiety adjacent with biphenyl mesogenic core is anticipated to coordinate to the metal cation. Namely, the complexation formed between the metal cation and mesogenic side chain of the LC conjugated polymer should give the metallomesogenic conjugated polymer. In the present study, we synthesized the metallomesogenic conjugated polymer by adopting the LC polyacetylene derivative with cyanobiphenyl group, as a ligand, to a palladium (II) cation. The optical and thermal characterizations are carried out.

2. EXPERIMENTAL

2.1 Synthesis of polyacetylene derivative

As shown in Scheme 1, the LC polyacetylene derivative with mesogenic group in side chain, *poly*[5-(4'-cyanobiphenyloxy)-1-pentyne], was synthesized using a rhodium catalyst under basic condition. To a solution of triethylamine, NEt_3 (5 ml) and tetrahydrofuran, THF (5 ml) was added the rhodium norbornadiene chloride dimer, $[Rh(NBD)Cl]_2$ (0.88 g, 0.19 mmol), and then the catalyst solution was aged for 30 min. The mono-substituted acetylene monomer (5 g, 19 mmol) dissolved in THF (40 ml) was added to the catalyst solution. After 24 hr, the reaction mixture was poured into a large amount of methanol several times and filtered off. The polymer was dried under reduced pressure to yield a yellow powder, 2.6 g (52 %).



Scheme 1.

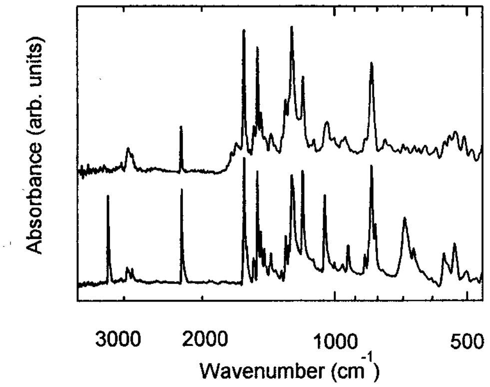
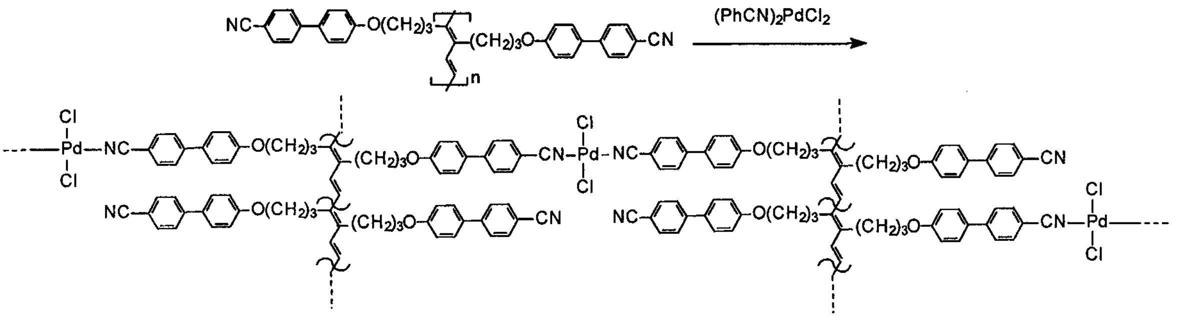


Figure 1. IR spectra of the monomer (bottom) and the polymer (top).

2.2 Preparation of metallomesogenic conjugated polymer

The complexations between LC polyacetylene derivatives and bis(benzonitrile)palladium dichloride[14] $[(PhCN)_2PdCl_2]$ were carried out, where the benzonitrile ligands were exchanged by the LC side



Scheme 2.

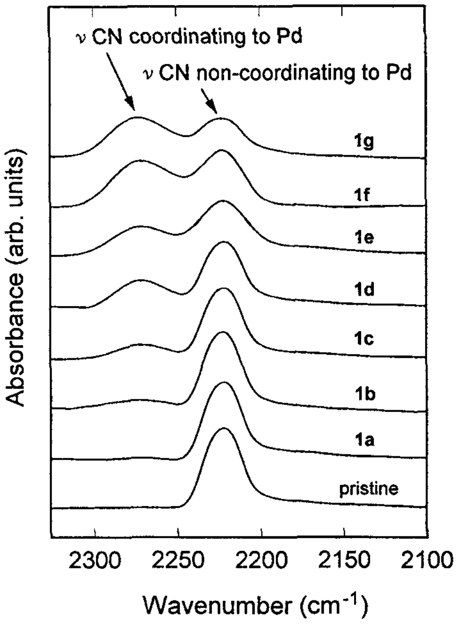


Figure 2. IR spectra of the pristine polymer and the polymers coordinating to the Pd(II) ion.

chains with cyanobiphenyl moiety. The procedure is as follows[15,16]. The polymer (0.2 g, 0.765 mmol) and (PhCN)$_2$PdCl$_2$ (2.90 ~ 38.16 mg, 0.0076 ~ 0.0995 mmol) were mixed in CHCl$_3$ at 60 °C. After 30 min., the reaction mixture was poured into a large amount of methanol, washed several times, and filtered off. The product was dried under reduced pressure to yield a brown powder.

3. RESULTS AND DISCUSSION

Number average (M_n) and weight average (M_w) molecular weights of the polymer were 16500 and 92500, respectively, according to polystyrene standard. Molecular weight distribution (M_w / M_n) was 5.4. Figure 1 shows IR spectra of the monomer and polymer. In the polymer was observed no absorption peak attributed to the acetylenic moiety of the monomer; C-H stretching vibration at 3270 cm^{-1} and C-H out-of-plane vibration at 696 cm^{-1}. This indicates that the opening of the acetylenic C≡C bond of the monomer has occurred to form conjugated double bonds. The polymer showed a schlieren texture under a polarizing optical microscope. X-ray diffraction (XRD) pattern showed a sharp halo and a broad one at $2\theta = 9.9$ (9.0 Å) and 20.5 (4.3 Å), respectively. Taking account of the diffraction pattern and corresponding distances, the sharp halo was assigned to the secondary diffraction of inter-layers in smectic phase. (The first diffraction was not observed.) The broad halo was assigned to the diffraction of inter-side chains. Thus, it may be argued from the polarizing optical microscope and XRD measurements that the present polymer forms a smectic C phase, where the side chain is not vertical to the polyene chain, but is substantially tilted. Table I summarizes the sample names of the polymers and incorporated Pd(II) contents. The polymers containing less than 13 mol% of palladium were soluble in ordinary organic solvent such as CHCl$_3$ and THF.

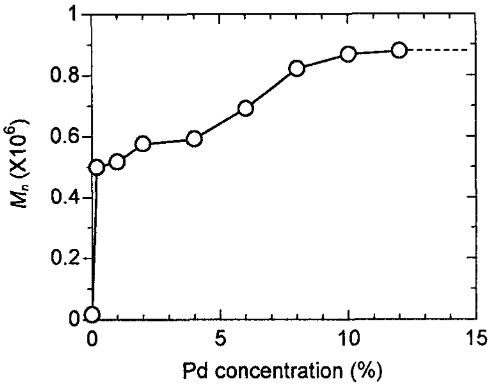


Figure 3. Number average molecular weight (M_n) of the polymers as a function of Pd(II) concentration.

Table I. Pd(II) contents in the polymers.

sample	Pd / mru[a] (mol)	Pd mol% vs. mru[a]
1a	0.0076/0.765	1
1b	0.0228/0.765	3
1c	0.0382/0.765	5
1d	0.0535/0.765	7
1e	0.0689/0.765	9
1f	0.0841/0.765	11
1g	0.0995/0.765	13

[a] mru: molecular repeating unit of the polymer.

The IR spectra of LC polyacetylene derivatives incorporating palladium atoms are shown in Fig. 2. The absorption peaks at 2220 and 2270 cm^{-1} decreased and increased in intensity, respectively, with increasing the palladium concentration. Therefore these peaks are assignable to CN stretching vibrations of mesogenic groups that are non-coordinating and coordinating to the Pd(II) ions, respectively. Note that although $(PhCN)_2PdCl_2$ has a C≡N stretching vibration of the benzonitrile moiety at 2290 cm^{-1}, no corresponding peak was observed after the complexion followed by the washing with methanol several times. It should be emphasized here that the random reactivity of metal ions leads to the coordination of ligand groups belonging to different polymeric chains. Hence, crosslinked polymers are obtained, as shown in Scheme 2.

In the gel permeation chromatography (GPC) measurement using THF were observed two peaks. The sharp and broad peaks were attributed to the polymers that were respectively non-incorporating and incorporating the palladium ions. As expected, the latter peak increased in intensity with increasing the Pd(II) concentration. Apparent increase in molecular weights of the polymers in accompany with the complexation is shown in Fig. 3. The transition temperatures of the pristine polymer and **1a**-**1c** estimated by DSC are summarized in Table II. The crosslink between different polymer chains via the palladium ions should have reduced the fusibility of the polymer. As a result, the LC temperature region became higher with increasing the Pd(II) concentration (**1a**-**1c**). Polarizing optical micrograph of **1a** is shown in Fig. 4. Although birefringence and fluidity of **1a**-**1c** was observed, no distinct optical texture was observed. As seen in Fig. 5, X-ray diffraction (XRD) pattern showed sharp and broad halos, which is very similar to the diffraction pattern of the pristine polymer. Thus, it can be argued that the metallomesogenic polymers of **1a**-**1c** also have smectic phase.

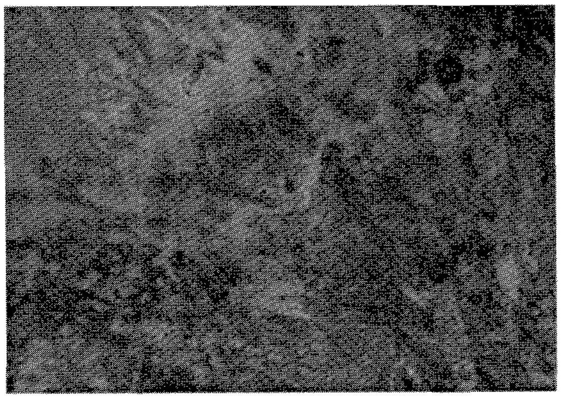


Figure 4. Polarizing optical micrograph of **1a** at 120 ℃.

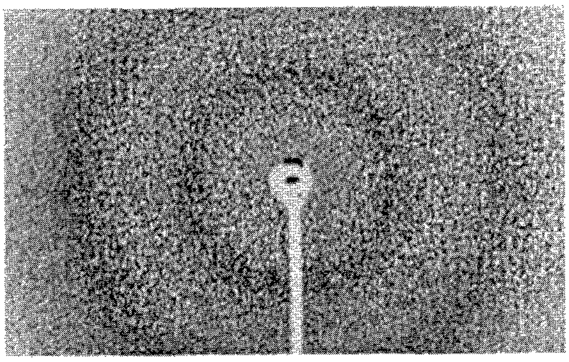


Figure 5. XRD pattern of **1a**.

Table II. Transition temperatures[a] of the polymers

sample	glassy-mesophase[b]	mesophase-isotropic[b]
pristine	80	137
1a	82	141
1b	83	145
1c	84	153

[a]determined by DSC and polarizing optical microscope in the second heating process. [b]unit: °C

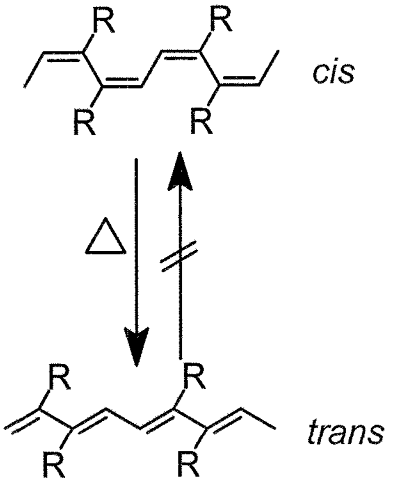


Figure 6. Thermally induced *cis-trans* isomerization of the polymer, where R is the substituent.

The polymers including more than 7 mol% of palladium contents (**1d**-**1g**) showed no birefringence under polarizing optical microscope. The *cis-trans* thermal isomerization of the substituted polyacetylene is illustrated in Fig. 6. In Table III are also summarized the isomerization temperatures and corresponding enthalpy changes. The isomerization temperatures shifted to the higher temperature region with increasing the Pd(II) concentration. This may be due to the formation of inter-chain crosslinkage, since it depresses the internal rotation around polymeric chain, necessary for the *cis-trans* isomerization.

Table III. *Cis-trans* isomerization temperatures and corresponding enthalpy changes of the pristine polymer and **1a**-**1g**.

sample	temperature (℃) [a]	enthalpy (J/g)
pristine	188	-32.0
1a	193	-28.2
1b	200	-25.8
1c	202	-23.2
1d	204	-21.2
1e	206	-15.6
1f	207	-10.4
1g	222	-5.45

[a] determined by DSC in the first heating process.

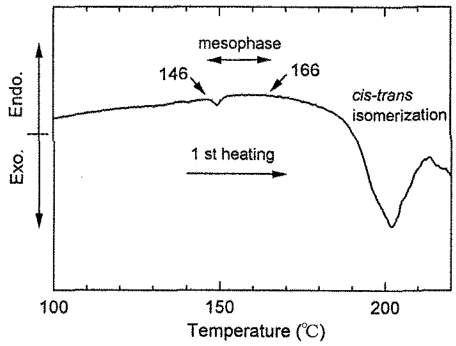


Figure 7. DSC curve of **1c** in the first heating process; Mesophase-isotropic transition temperature was determined by the polarizing optical microscopy observation.

It is of keen interest that the pristine polymer and **1a**-**1c** exhibited liquid crystallinity in the region lower than the *cis-trans* isomerization temperature in the first heating process, as exemplified in Fig. 7. Namely, even the *cis*-rich polymers showed liquid crystallinity, as in the *trans*-rich polymers, although the LC temperature region is narrower than the latter.

UV-Vis measurement of the pristine polymer dissolved in THF gave an absorption band around 300 nm due to π-π * transition in the main chain. However, no distinct red-shift was observed for this absorption after the complexation between the pristine polymer and the Pd(II) ion. This may be due to the situation that the effective conjugation of the main chain is not so strictly affected by the present complexation as in the case of the solubility and liquid crystallinity.

In summary, the novel metallomesogenic conjugated polymers were prepared through the complexation between palladium (II) and LC polyacetylene derivative with the cyano ligand group in the mesogenic side chain. The liquid crystallinity and solubility were retained in the polymers containing less than 7 and 13 mol% of palladium, respectively.

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