Notes

Novel Metallomesogenic Polymers Derived from η^1-Benzylideneaniline Palladium(II) Complex

Myongsoo Lee,* Yong-Sik Yoo, and Moon-Gun Choi

Department of Chemistry, Yonsei University,
Shinchon 134, Seoul 120-749, Korea

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Introduction

The area of metal-containing liquid crystalline polymers (metallomesogenic polymers) has received much attentions in recent years, and examples of metallomesogenic polymers with high magnetic anisotropy, ferroelectric behavior, and potential as optical storage devices have been reported.[1] A general strategy employed in designing novel metallomesogenic polymers is to prepare metal complexes with ligands that impart the rodlike or disklike mesogenic units in a main chain or side chain polymeric arrangement.[2]

A large and predominant class of metallomesogens is that of organometallic complexes derived from orthocyclopalladated imines[3] and azines[4] as well as azobenzenes.[5] This class of mesogens is represented by palladium derivatives mainly, because of the formation of stable complexes and the ease of the orthocyclopalladation reaction which produces an aromatic core with a planar structure, thus leading to the formation of a liquid crystalline phase. As a chemical diversity, these complexes offer many opportunities for the formation of novel palladium metal-based materials. Despite this intense interest, the current status of liquid crystallinity in cyclopalladated metallomesogens is limited by high melting points due to the increase of rigidity of the aromatic core caused by cyclometalation. A possible approach to overcome this limitation is to introduce the asymmetric molecular shape[6] or noncoplanarity.[5] The central noncoplanar structure of the complexes is expected to reduce intermolecular interactions due to perturbation of the crystal packing of the molecules. Consequently, the noncoplanar structure might lead to lower melting-transition temperatures.

Recently, we have synthesized mononuclear Pd(II) complexes with η^1-benzylideneaniline derivatives with the noncoplanar aromatic structure as novel metallomesogens.[7] In contrast to the Pd(II) orthometalated complexes derived from benzylideneaniline ligand described in the literatures,[3−5] the η^1-benzylideneaniline complexes provide an acyclic core structure which creates the noncoplanar aromatic core by free rotation around the Pd−N bond. Consequently, η^1-bonding of the complexes gives rise to the decrease of intermolecular interactions which leads to lower transition temperatures.

These design concepts can be extended to generate metallomesogenic polymers derived from η^1-benzylideneaniline palladium(II) complexes which may be an attractive way of creating novel liquid crystalline materials because they would lead to good solubility in common organic solvents and reduced transition temperature before thermal decomposition. We report herein the synthesis and characterization of metallomesogenic polymers based on bis[η^1(*N*)-3,4-dialkyloxybenzylidene-4′-dodecyloxyaniline]dichloropalladium(II) with octyl (**P-1**), decyl (**P-2**), dodecyl (**P-3**), tetradecyl (**P-4**), and hexadecyl (**P-5**) alkyl groups. We also describe the mesomorphic phase behavior of the resulting metallomesogenic polymers, characterized by a combination of differential scanning calorimetry (DSC) and optical polarized microscopy.

Experimental Section

Materials. 1-Bromooctane (99%), 1-bromodecane (98%), 1-bromododecane (97%), 1-bromotetradecane (97%), 1-bromohexadecane (97%), 1,12-dibromododecane (98%), 4-nitrophenol (98%), 3,4-dihydroxybenzaldehyde (97%), tin chloride(II) (98%), dichloropalladium(II) (99%) (all from Aldrich), and the conventional reagents were used as received. Bis(benzonitrile)dichloropalladium(II) and 3,4-dialkyloxybenzaldehydes were prepared according to a procedure described previously.[7]

Synthesis of 1,12-Di(4-aminophenyloxy)dodecane (6). 1,12-Di(4-aminophenyloxy)dodecane was prepared according to a procedure reported previously.[8]

Synthesis of 1,12-Bis{4-[(3,4-dialkyloxy)phenyliminomethyl]phenyloxy}dodecanes (7∼11). 1,12-Bis{4-[(3,4-dialkyloxy)phenyliminomethyl]phenyloxy}-dodecanes were all synthesized by using the same procedure. A representative example is described for 1,-12-bis{4-[(3,4-didecyloxy)phenyliminomethyl]phenyloxy}-dodecane (**8**). A mixture of **6** (0.25 g, 0.65 mmol), **2** (0.78 g, 1.6 mmol) and a catalytic amount of acetic acid in absolute ethanol (40 mL) was refluxed for 10 h. After cooling to room temperature, the obtained solid was filtered and recrystallized from ethyl acetate to yield 0.58 g (69%) of brownish crystals: mp 124−125 °C; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 12H, CH_3CH_2, J = 6.2 Hz), 1.28−1.49 [m, 56H, $CH_3(CH_2)_7$ and 16H, $OCH_2CH_2(CH_2)_8CH_2CH_2O$], 1.76−1.88 (m, 12H, OCH_2CH_2), 3.94−4.12 (m, 12H, OCH_2), 6.89−6.92 (m, 4H, *m* to N═CH−Ph and 2H, *m* to CH═N−Ph), 7.19 (d, 4H, *o* to N═CH−Ph, J = 6.8 Hz), 7.26 (dd, 2H, *o* to CH═N−Ph and *p* to 3-decyloxy, overlapped with $CHCl_3$ signal), 7.56 (d, 2H, *o* to CH═N−Ph and *o* to 3-decyloxy, J = 1.8 Hz), 8.36 (s, 2H, CH═N); IR (KBr) 1631 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{78}H_{124}N_2O_6$: C, 79.00; H, 10.54; N, 2.36. Found: C, 78.90; H, 10.64; N, 2.54.

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* Fax: 82-2-364-7050. E-mail: mslee@alchemy.yonsei.ac.kr.

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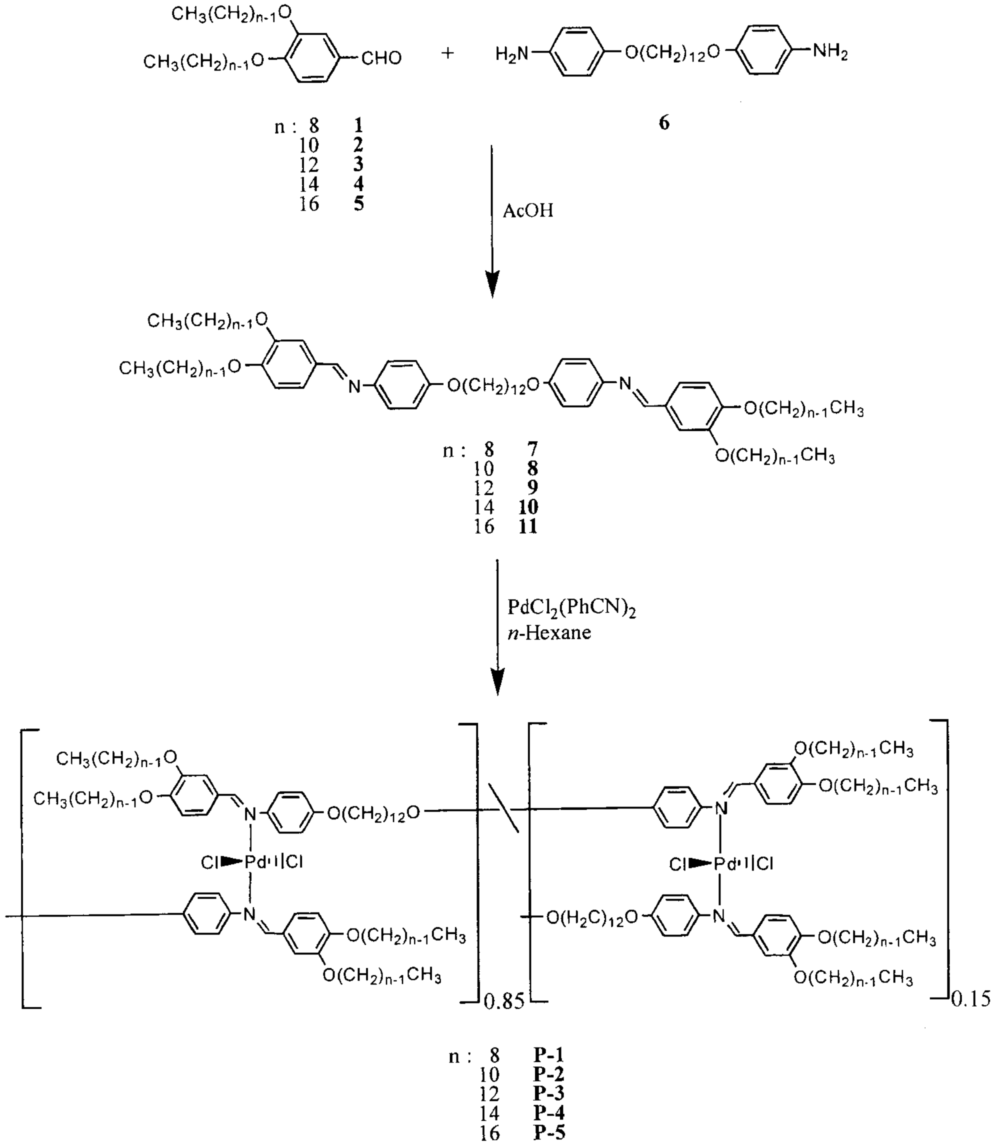
Scheme 1. Synthesis of Metallomesogenic Polymers P-*n*



Compound 7: yield 64%; mp 125−126 °C; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 12H, CH_3CH_2, $J = 6.6$ Hz), 1.26−1.48 (m, 40H, $CH_3(CH_2)_5$ and 16H, $OCH_2CH_2(CH_2)_8CH_2CH_2O$), 1.76−1.88 (m, 12H, OCH_2CH_2), 3.94−4.11 (m, 12H, OCH_2), 6.89−6.92 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph), 7.19 (d, 4H, *o* to N=CH−Ph, $J = 6.9$ Hz), 7.26 (dd, 2H, *o* to CH=N−Ph and *p* to 3-octyloxy, overlapped with $CHCl_3$ signal), 7.56 (d, 2H, *o* to CH=N−Ph and *o* to 3-octyloxy, $J = 1.6$ Hz), 8.35 (s, 2H, $CH{=}N$); IR (KBr) 1630 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{70}H_{108}N_2O_6$: C, 78.31; H, 10.14; N, 2.61. Found: C, 78.34; H, 10.24; N, 2.63.

Compound 9: yield 69%; mp 124−125 °C; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.88 (t, 12H, CH_3CH_2, $J = 6.4$ Hz), 1.26−1.48 [m, 72H, $CH_3(CH_2)_9$ and 16H, $OCH_2CH_2(CH_2)_8CH_2CH_2O$], 1.76−1.88 (m, 12H, OCH_2CH_2), 3.94−4.09 (m, 12H, OCH_2), 6.89−6.92 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph), 7.19 (d, 4H, *o* to N=CH−Ph, $J = 6.8$ Hz), 7.26 (dd, 2H, *o* to CH=N−Ph and *p* to 3-dodecyloxy, overlapped with $CHCl_3$ signal), 7.56 (d, 2H, *o* to CH=N−Ph and *o* to 3-dodecyloxy, $J = 1.9$ Hz), 8.36 (s, 2H, $CH{=}N$); IR (KBr) 1630 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{86}H_{140}N_2O_6$: C, 79.58; H, 10.87; N, 2.16. Found: C, 79.51; H, 11.11; N, 2.24.

Compound 10: yield 56%; mp 123−124 °C; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 12H, CH_3CH_2, $J = 6.0$ Hz), 1.26−1.48 [m, 88H, $CH_3(CH_2)_{11}$ and 16H, $OCH_2CH_2(CH_2)_8CH_2CH_2O$], 1.76−1.88 (m, 12H, OCH_2CH_2), 3.94−4.09 (m, 12H, OCH_2), 6.89−6.92 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph), 7.20 (d, 4H, *o* to N=CH−Ph, $J = 6.8$ Hz), 7.26 (dd, 2H, *o* to CH=N−Ph and *p* to 3-tetradecyloxy, overlapped with $CHCl_3$ signal), 7.56 (d, 2H, *o* to CH=N−Ph and *o* to 3-tetradecyloxy, $J = 1.8$ Hz), 8.35 (s, 2H, $CH{=}N$); IR (KBr) 1630 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{94}H_{156}N_2O_6$: C, 80.06; H, 11.15; N, 1.99. Found: C, 80.03; H, 11.34; N, 2.20.

Compound 11: yield 55%; mp 123−125 °C; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.89 (t, 12H, CH_3CH_2, $J = 6.4$ Hz), 1.26−1.48 [m, 104H, $CH_3(CH_2)_{13}$ and 16H, $OCH_2CH_2(CH_2)_8CH_2CH_2O$], 1.76−1.90 (m, 12H, OCH_2CH_2), 3.96−4.09 (m, 12H, OCH_2), 6.90−6.92 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph), 7.19 (d, 4H, *o* to N=CH−Ph, $J = 6.7$ Hz), 7.26 (dd, 2H, *o* to CH=N−Ph and *p* to 3-hexadecyloxy, overlapped with $CHCl_3$ signal), 7.55 (d, 2H, *o* to CH=N−Ph and *o* to 3-hexadecyloxy, $J = 1.8$ Hz), 8.35 (s, 2H, $CH{=}N$); IR (KBr) 1630 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{102}H_{172}N_2O_6$: C, 80.47; H, 11.39; N, 1.84. Found: C, 80.42; H, 11.60; N, 2.06.

Table 1. Characterization and Thermal Transition of Metallomesogenic Polymers (P-n)

					phase transition (°C) and corresp. enthalpy changes (kJ/mru[b])[c]	
polymer	yield (%)	$\bar{M}_n$ (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)	T_{di}[a] (°C) (TGA)	heating	cooling
P-1	66	23 000	2.4	210	k 106.4 (2.4) s_A 152.5 (6.6) i	i 153.2 (5.2) s_A 95.4 (1.5) k
P-2	82	80 000	1.3	194	g 58.9 s_A 122.5 (4.8) i	i 116.2 (4.6) s_A 60.4 g
P-3	71	12 000	2.3	170	g 59.8 n 101.1 (2.5) i	i 93.5 (2.4) n 59.4 g
P-4	72	24 000	2.2	236	g 59.6 n 81.8 (1.8) i	i 75.0 (1.2) n 56.8 g
P-5	57	34 000	1.8	234	g 68.5 i	i 63.1 g

[a] Initial decomposition temperature. [b] Mole repeating unit. [c] Key: k, crystalline phase; g, glassy phase; s_A, smectic A phase; n, nematic phase; and i, isotropic phase.

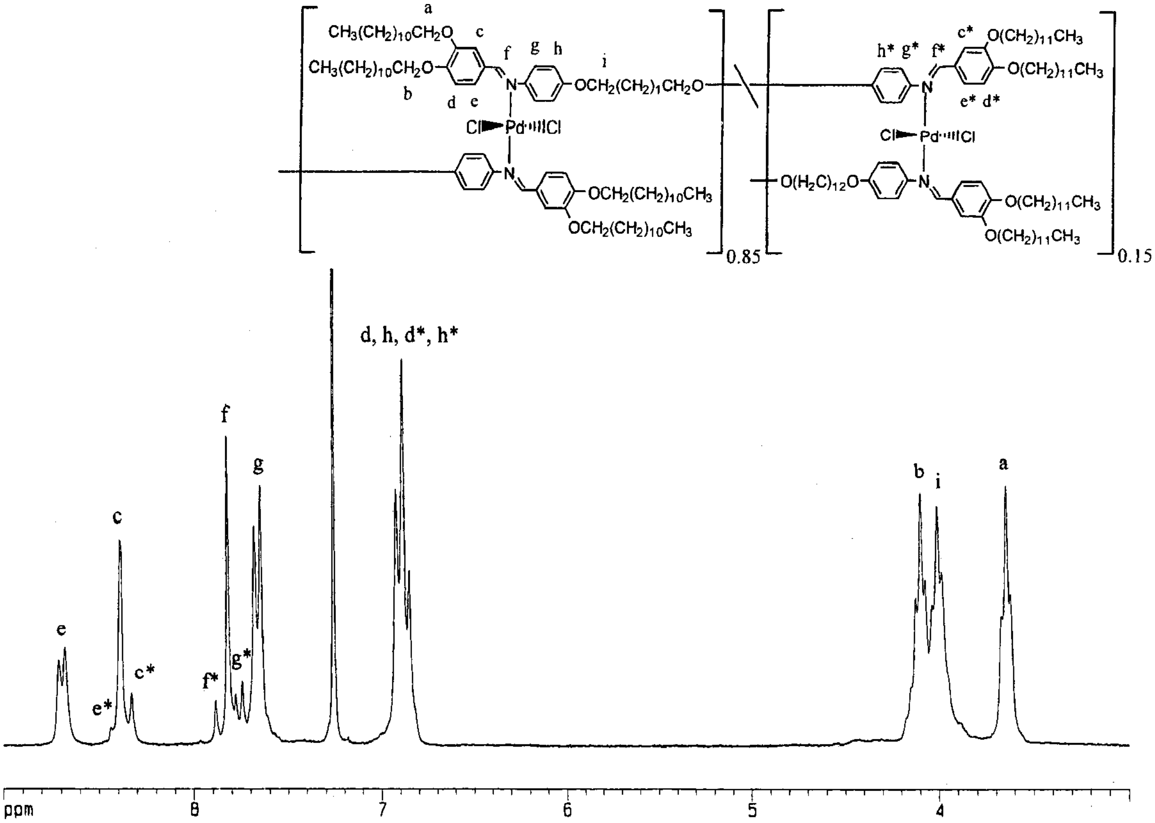


Figure 1. 250 MHz ^{1}H NMR spectrum of the metallomesogenic polymer **P-3**.

Synthesis of Poly[bis(1,12-bis{4-[(3,4-dialkyloxy)phenyliminomethyl]phenyloxy}dodecane)dichloropalladium(II)]s (P-1−5). Polymers were all synthesized by using the same procedure. A representative example is described for **P-2**. A mixture of **8** (92.8 mg, 78.2 μmol) and bis(benzonitrile)dichloropalladium(II) (30.0 mg, 78.2 μmol) in 10 mL of *n*-hexane was refluxed under nitrogen for 6 h. After the mixture was cooled, the solvent was evaporated on a rotavapor. The resulting polymer was purified by precipitation from CH_2Cl_2 solution into *n*-hexane and was then collected by filtration to yield 87 mg (82%) of yellow solids: ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.88 (m, 12H, CH_3CH_2), 1.29−1.57 [m, 56H, $CH_3(CH_2)_7$ and 20H, $OCH_2(CH_2)_{10}CH_2O$], 1.85 [m, 8H, $OCH_2CH_2(CH_2)_7CH_3$], 3.65 (m, 4H, OCH_2, *m* to CH=N−Ph), 3.96−4.09 (m, 4H, OCH_2, *p* to CH=N−Ph and 4H, OCH_2, *p* to N=CH−Ph), 6.75−6.93 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph; cisoid, overlapped with transoid), 7.66 (m, 4H, *o* to N=CH−Ph; cisoid, 7.76), 7.82 (s, 2H, CH=N; cisoid, 7.88), 8.39 (m, 2H, *o* to CH=N−Ph and *o* to 3-decyloxy; cisoid, 8.33), 8.69 (m, 2H, *o* to CH=N−Ph and *p* to 3-decyloxy; cisoid, 8.42); IR (KBr) 1615 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $(C_{78}H_{124}N_2O_6Cl_2Pd_1)_x$: C, 68.73; H, 9.17; N, 2.06. Found: C, 68.66; H, 9.30; N, 2.21.

P-1: yield 66%; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.89 (m, 12H, CH_3CH_2), 1.28−1.55 [m, 40H, $CH_3(CH_2)_5$ and 20H, $OCH_2(CH_2)_{10}CH_2O$], 1.84 [m, 8H, $OCH_2CH_2(CH_2)_5CH_3$], 3.64 (m, 4H, OCH_2, *m* to CH=N−Ph), 4.01−4.09 (m, 4H, OCH_2, *p* to CH=N−Ph and 4H, OCH_2, *p* to N=CH−Ph), 6.85−6.92 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph; cisoid, overlapped with transoid), 7.67 (m, 4H, *o* to N=CH−Ph; cisoid, 7.76), 7.83 (s, 2H, CH=N; cisoid, 7.88), 8.39 (m, 2H, *o* to CH=N−Ph and *o* to 3-octyloxy; cisoid, 8.33), 8.69 (m, 2H, *o* to CH=N−Ph and *p* to 3-octyloxy; cisoid, 8.40); IR (KBr) 1616 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $(C_{70}H_{108}N_2O_6Cl_2Pd_1)_x$: C, 67.21; H, 8.70; N, 2.24. Found: C, 66.40; H, 8.68; N, 2.44.

P-3: yield 71%; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.88 (m, 12H, CH_3CH_2), 1.28−1.55 [m, 72H, $CH_3(CH_2)_9$ and 20H, $OCH_2(CH_2)_{10}CH_2O$], 1.85 [m, 8H, $OCH_2CH_2(CH_2)_9CH_3$], 3.64 (m, 4H, OCH_2, *m* to CH=N−Ph), 4.01−4.09 (m, 4H, OCH_2, *p* to CH=N−Ph and 4H, OCH_2, *p* to N=CH−Ph), 6.85−6.93 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph; cisoid, overlapped with transoid), 7.67 (m, 4H, *o* to N=CH−Ph; cisoid, 7.76), 7.83 (s, 2H, CH=N; cisoid, 7.87), 8.39 (m, 2H, *o* to CH=N−Ph and *o* to 3-dodecyloxy; cisoid, 8.32), 8.69 (m, 2H, *o* to CH=N−Ph and *p* to 3-dodecyloxy; cisoid, 8.41); IR (KBr)

1615 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $(C_{86}H_{140}N_2O_6Cl_2Pd_1)_x$: C, 70.01; H, 9.56; N, 1.90. Found: C, 69.66; H, 9.17; N, 2.14.

P-4: yield 72%; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.88 (m, 12H, CH_3CH_2), 1.30−1.55 [m, 88H, $CH_3(CH_2)_{11}$ and 20H, $OCH_2(CH_2)_{10}CH_2O$], 1.85 [m, 8H, $OCH_2CH_2(CH_2)_{11}CH_3$], 3.64 (m, 4H, OCH_2, *m* to CH=N−Ph), 3.98−4.09 (m, 4H, OCH_2, *p* to CH=N−Ph and 4H, OCH_2, *p* to N=CH−Ph), 6.85−6.92 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph; cisoid, overlapped with transoid), 7.67 (m, 4H, *o* to N=CH−Ph; cisoid, 7.76), 7.82 (s, 2H, CH=N; cisoid, 7.88), 8.39 (m, 2H, *o* to CH=N−Ph and *o* to 3-tetradecyloxy; cisoid, 8.33), 8.69 (m, 2H, *o* to CH=N−Ph and *p* to 3-tetradecyloxy; cisoid, 8.42); IR (KBr) 1615 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $(C_{94}H_{156}N_2O_6Cl_2Pd_1)_x$: C, 71.12; H, 9.90; N, 1.76. Found: C, 70.68; H, 9.94; N, 2.05.

P-5: yield 57%; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.88 (m, 12H, CH_3CH_2), 1.26−1.55 [m, 104H, $CH_3(CH_2)_{13}$ and 20H, $OCH_2(CH_2)_{10}CH_2O$], 1.85 [m, 8H, $OCH_2CH_2(CH_2)_{13}CH_3$], 3.64 (m, 4H, OCH_2, *m* to CH=N−Ph), 4.00−4.13 (m, 4H, OCH_2, *p* to CH=N−Ph and 4H, OCH_2, *p* to N=CH−Ph), 6.85−6.92 (m, 4H, *m* to N=CH−Ph and 2H, *m* to CH=N−Ph; cisoid, overlapped with transoid), 7.67 (m, 4H, *o* to N=CH−Ph; cisoid, 7.76), 7.83 (s, 2H, CH=N; cisoid, 7.89), 8.39 (m, 2H, *o* to CH=N−Ph and *o* to 3-hexadecyloxy; cisoid, 8.33), 8.69 (m, 2H, *o* to CH=N−Ph and *p* to 3-hexadecyloxy; cisoid, 8.42); IR (KBr) 1615 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $(C_{102}H_{172}N_2O_6Cl_2Pd_1)_x$: C, 72.07; H, 10.20; N, 1.65. Found: C, 71.84; H, 10.28; N, 1.92.

Results and Discussion

Synthesis of the Metallomesogenic Polymers. The tetra alkoxy substituted dibenzylideneaniline ligands were prepared from the corresponding 3,4-dialkoxybenzaldehyde and 1,12-di(4-aminophenoxy)dodecane in ethanol in the presence of small amounts of glacial acetic acid as outlined in Scheme 1. The metallomesogenic polymers based on palladium(II) complexes with η^1-benzylideneaniline were prepared from the corresponding free ligands by a ligand exchange reaction as shown in Scheme 1. The elemental analyses for the metallomesogenic polymers given in the Experimental Section agreed well with the expected chemical structures. The IR spectra show that the stretching frequency of the C=N bond was shifted to a lower wavenumber (ca. 15 cm^{-1}) than for the free ligand after polymerization. This shift is due to the reduction of the double bond character of the C=N bond caused by the coordination of the nitrogen atom into the metal atom and is consistent with the results obtained from the cyclopalladated complexes described previously.[9]

The ^{1}H NMR spectra of the polymers are all very similar. Figure 1 presents the aromatic region of a typical 250 MHz ^{1}H NMR spectrum of **P-3** together with its proton assignments. As shown in Figure 1, all aromatic protons including the imine proton give rise to a pair of each signal. This result indicates the existence of the two isomers, transoid and cisoid, which are different dispositions of the ligand orientation[7] and which are in a ratio of about 85:15, as calculated from the intensity of the two types of proton resonances. The spectrum also exhibits a pair of imine proton resonances at 7.83 ppm for transoid and 7.87 ppm for cisoid, respectively, which represent an upfield shift for this proton upon complexation. This shift would result from the expected decrease in bond order due to nitrogen coordination and agrees well with the shifts reported for the orthometalated complexes.[3]

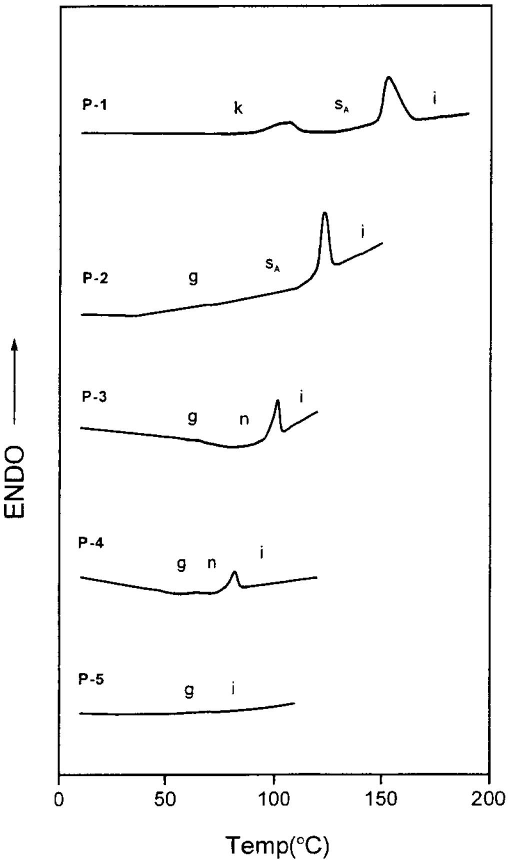


Figure 2. DSC traces (10 °C/min) recorded during the second heating scan of the metallomesogenic polymers.

It is well-known that molecular weight influences the properties of the polymers such as liquid crystalline phase behavior and especially influences those with low molecular weights.[10] Therefore, it is essential that the molecular weight of the polymer should be high in order to investigate its accurate phase behavior. The number-average molecular weights ($\bar{M}_n$) and molecular weight distributions ($\bar{M}_n/\bar{M}_w$) of the resulting polymers were measured by GPC with reference to polystyrene standards as summarized in Table 1. The molecular weight distributions are in the range from 1.3 to 2.4, and the number average molecular weights of the metallomesogenic polymers appear to be 12 000−80 000, indicating that molecular weights of the polymers are reasonably high. Table 1 also presents the initial decomposition temperature (T_{di}) of the metallomesogenic polymers obtained by thermogravimetric analysis (TGA) measured under a nitrogen atmosphere at a heating rate of 10 °C /min. All of the polymers show T_{di} values higher than 170 °C, indicating that they have good thermal stabilities, even the metallomesogenic polymers based on η^1-bonding. Furthermore, high-temperature ^{1}H NMR investigations with the metallomesogenic polymers performed at 90 °C in toluene-d_8 did not show any spectral changes. This result indicates that the η^1-Pd(II) complex appears to be a result of the lack of interconversion of the transoid and cisoid isomers up to 90 °C, and the η^1 structure persists even on heating of the polymer. As expected for the polymers based on the η^1-Pd(II) complex which gives rise to the semiflexible noncoplanar core structure resulting from

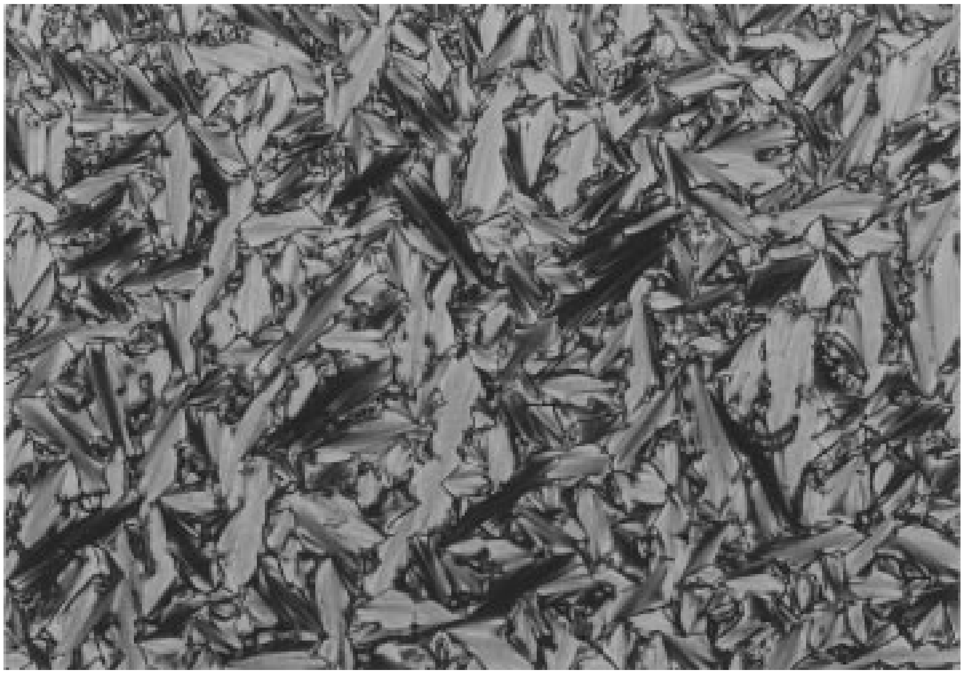


Figure 3. Representative optical polarized micrograph (100×) of the texture exhibited by the smectic A mesophase of **P-1** at 130 °C on the cooling scan.

η^1-ligand coordination, the polymers show good solubility in common organic solvents such as chloroform, methylene chloride, toluene, and THF.

Mesomorphic Phase Behavior. The phase behavior of the metallomesogenic polymers based on the η^1-Pd(II) complex was characterized by a combination of techniques consisting of differential scanning calorimetry and thermal optical polarized microscopy. The phase-transition temperatures and the associated thermal parameters obtained from DSC experiments for both the ligands and the polymers are summarized in Table 1. Figure 2 shows DSC traces obtained from the second heating scans of the polymers. In contrast to the monomer ligands which exhibit only a crystalline melting, all of the metallomesogenic polymers except **P-5** exhibit an enantiotropic liquid crystalline phase. **P-1** with octyloxy side chains melts into a smectic A phase at 106.4 °C on the heating scan. On cooling from the isotropic liquid, first baton-like growth of texture can be observed with a final development of focal conic domains which are characteristic of a smectic A mesophase exhibited by conventional calamitic mesogens.[11] **P-2** with decyloxy side chains shows phase behavior similar to **P-1**, which exhibits an enantiotropic smectic A mesophase. On the DSC heating scan, **P-2** exhibits a smectic A phase above a glass transition at 58.9 °C. The transition from the isotropic liquid on cooling can be seen by the formation of a focal conic fanlike texture, indicating a smectic A mesophase. A representative texture exhibited by the smectic A phase of **P-2** is presented in Figure 3.

On heating above the glass transition, both **P-3** and **P-4** display a nematic phase followed by an isotropization transition. On cooling from isotropic liquid of the polymers, schlieren texture can be observed, which is characteristic of a nematic phase exhibited by conventional nematogens.[11] In contrast, **P-5** with hexadecyloxy side chains is shown to be only amorphous. This behavior is mainly due to the disturbance of anisotropic packing of the aromatic cores caused by high thermal fluctuation of long side chains.[12]

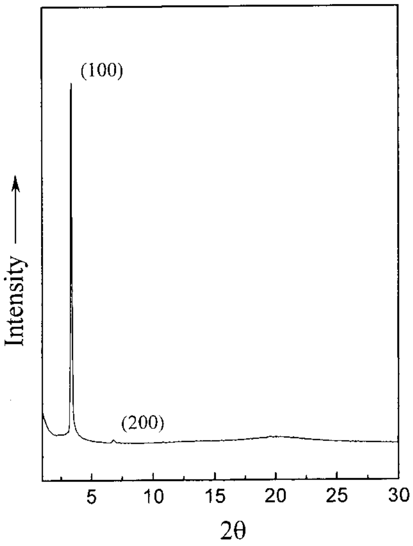


Figure 4. X-ray diffraction pattern of the polymer **P-2** at 105 °C on cooling. Spectrum was measured with synchrotron radiation at the 3C2 beamline ($\lambda = 0.154$ nm) at the Pohang Accelerator Laboratory.

To confirm the assignment of a smectic A phase, powder X-ray diffraction experiments were performed with **P-2** at 105 °C (Figure 4). The diffraction pattern displays two Bragg reflections with the relative positions of 1, 2 in the small angle region and a diffuse scattering in the wide-angle region. The positions of these reflections can be indexed as the (100) and (200) reflections of a lamellar structure. This result together with optical microscopic observations indicates that **P-2** displays a smectic A mesophase with a lattice constant of 2.6 nm.

Although the coordination of Pd(II) with η^1-benzylideneaniline gives rise to the noncoplanar aromatic core structure of the complexes, the appearance of a mesomorphic phase in these metallomesogenic polymers is notable. In addition, the appearance of good solubility and lower transition temperatures by coordination polymerization is very rare in main chain metallomesogenic systems[8,13] and is rewarding in terms of their potential processability without decomposition. This interesting thermal behavior can be attributed to the semiflexible noncoplanar core structure resulting from η^1-ligand coordination and the presence of tetraalkyl side chains.

Conclusion

We have been able to synthesize the polymers based on η^1-benzylideneaniline palladium(II) complex by a ligand exchange reaction of the dibenzylideneanilines with $[PdCl_2(PhCN)_2]$. The expected chemical structure with η^1-benzylideneaniline palladium(II) complex was identified by elemental analyses, IR, and ^{1}H NMR spectra. The resulting polymers appear to be thermally stable up to 170−200 °C without the appearance of decomposition, and they show good solubility in common organic solvents. In contrast to the imine ligand monomers which do not exhibit liquid crystalline phase, the polymers with octyloxy (**P-1**) and decyloxy (**P-2**) side chains exhibit a thermally stable enantiotropic smectic A mesophase. In addition, the polymers with dodecyloxy (**P-3**) and tetradecyloxy (**P-4**) side chains display an enantiotropic nematic phase, despite their semiflexible noncoplanar core structure resulting from η^1-ligand coordination. Further increasing the length of side chains as in the case of the polymer with hexadecyloxy (**P-5**) side chains suppresses liquid crystallinity and gives rise to only an amorphous polymer. These results suggest that novel Pd(II)metallomesogenic polymers with noncoplanar aromatic geometry can be created by η^1-imine ligand coordination polymerization.

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