Chem. Mater. **1992**, *4*, 1119–1123 1119

Transition Metals Complexed to Ordered Mesophases.[1] Synthesis and Mesomorphic Properties of Cyclopalladated 4,4′-Bis(hexyloxy)azoxybenzene Complexed to *N*-(4-(Dodecyloxy)salicylidene)-4′-alkylanilines

Mauro Ghedini* and Stefania Morrone

Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy

Oriano Francescangeli

Dipartimento di Scienze dei Materiali e della Terra, Università di Ancona, Via Brecce Bianche, I-60131 Ancona, Italy

Roberto Bartolino

Dipartimento di Fisica, Università della Calabria, I-87030 Arcavacata (CS), Italy

Received March 5, 1992. Revised Manuscript Received June 23, 1992

New mononuclear cyclopalladated liquid-crystalline materials whose molecular structure consists of two different thermotropic ligands, namely, 4,4′-bis(hexyloxy)azoxybenzene and *N*-(4-(dodecyloxy)-salicylidene)-4′-n-C_nH_{2n+1}-aniline (n = 0, 1–4, 6, 8), connected by a palladium atom, have been prepared. These lateral–lateral fused mesogens, obtained as mixtures of N,N-cis and N,N-trans isomers (about 1:5 ratio), display good thermal stability and mesomorphic properties which depend on the length of the n-C_nH_{2n+1} chain: monotropic nematic and/or smectic A (n = 0, 2, 4) and enantiotropic nematic (n = 1), nematic and smectic (n = 3), and smectic A (n = 6, 8). Contrarily, the clearing points for n = 1–4, 6, and 8 belong in a very narrow range: 143 ± 3 °C. Preliminary X-ray investigations in the solid and smectic phases show two different periodicities (nearly 45 and 28 Å for n = 0, 1–4; 25 and 29 Å for n = 6, 8) thus suggesting a peculiar molecular packing.

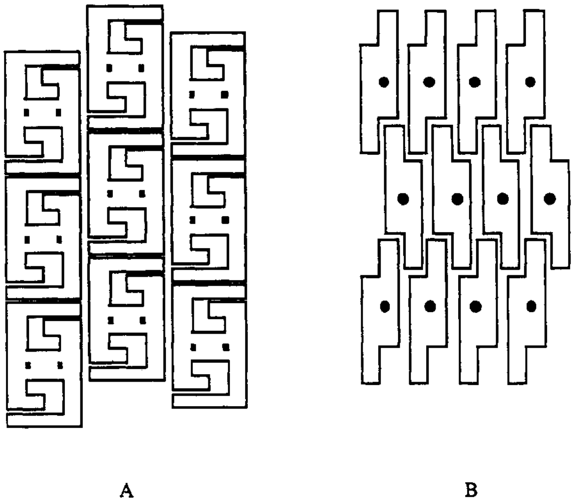
Introduction

The organic liquid-crystalline species whose rigid core is the azobenzene[2,3] or the salicylidene[2,4–7] fragment have been proved to be convenient starting materials for the preparation of metallomesogens. Thus, for example, from 4–methyl–4′-(dodecyloxy)azobenzene (I) or *N*-(4-(dodecyloxy)salicylidene)-4′-*n*-butylaniline (II) the respective palladium[8] (III) and copper[9] (IV) thermotropic derivatives have been obtained (Chart I).

The molecular shape of both these complexes is featured by two roughly parallel rodlike moieties mutually head-to-tail oriented and connected by the metals. They are classified as lateral–lateral fused mesogens,[10] the wider class of nondiscotic metallomesogens.[2] In such molecules the metallic core actually acts as a spacer between the two elongated fragments, and therefore the molecular width is larger for the palladium complex than for the copper one. In mesogenic compounds molecular geometry and mesomorphic character are intimately related; consequently, in comparing III and IV some differences should be expected.

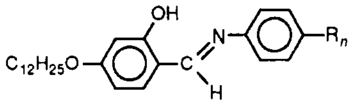
The molecular packing exhibited by III or IV in the different mesophases has been extensively investigated, and the data obtained from X-ray diffraction,[11] small-angle X-ray and neutron scattering,[12] and quasi-elastic neutron scattering[13] suggest two different molecular arrays indeed. Namely in III the molecules exhibit a structural conformation where the aliphatic chains are partially melted and folded (Scheme IA) while in IV the molecules appear strongly interdigitated (Scheme IB). Hence, with reference to the molecular geometry, these results should be ascribed to the different metallic cores and nature of mesogenic ligands.

Scheme I. Molecular Arrangement Suggested for Compounds III (A) and IV (B)[a]



[a] (■) Pd; (●) Cu.

Scheme II. General Formula of the R_nLH Schiff Bases



R_n = H, CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}

Compounds such as III or IV are homoligand complexes whose ligand (L) to metal (M) ratios are given by the

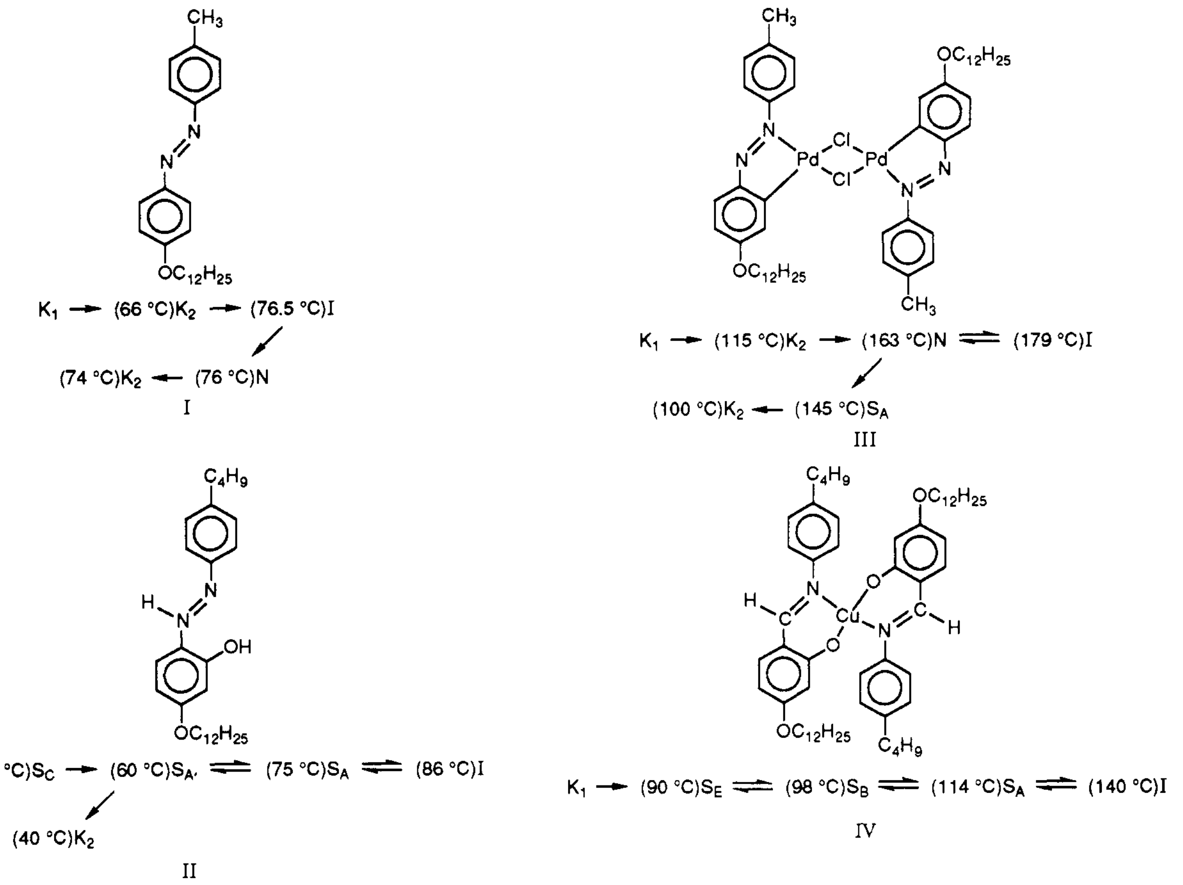
---

* To whom correspondence should be addressed.

(1) Part 10. Part 9: Ghedini, M.; Morrone, S.; Gatteschi, D.; Zanchini, C. *Chem. Mater.* 1991, *3*, 752.

(2) Giroud-Godquin, A. M.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* 1991, *30*, 375.

Chart I



general formula LM_2L or LML respectively. Worthy of note, while several thermotropic organometallic or coordination compounds having these stoichiometry are known, lateral–lateral fused heteroligand mesogens such as LM_2L' or LML′ have not been described up to now. Therefore, to get further insight about the relationship between molecular shape and mesomorphism, investigations have been recently prepared some LPdL′ species.[14]

Herein, we report on the synthesis, mesomorphic properties, and preliminary X-ray diffraction studies of a homologous series of LPdL′ complexes wherein LPd is the cyclopalladated 4,4′-bis(hexyloxy)azoxybenzene (hereafter Azoxy-6) and L′ is the anion, R_nL, arising from the thermotropic salicylideneanilines of general formula shown in Scheme II.

Table I. Thermal Behavior for H[Azoxy-6] and the R_nLH Compounds.

compd	transition temp (°C) and mesophases[a]
H[Azoxy-6][b]	$K \rightleftharpoons (80)N \rightleftharpoons (126)I$
HLH[c]	$K \rightarrow (60)I$
R_1LH[c]	$K \rightarrow (78)N \rightleftharpoons (83)I$ $(66)K \leftarrow$
R_2LH[c,d]	$K_2 \rightarrow (59)S_A \rightarrow (60)K_1 \rightarrow (63)N \rightleftharpoons (78)I$ $K_1(47) \leftarrow (60)S_A \leftarrow$
R_3LH[c]	$K \underset{39}{\overset{50}{\rightleftharpoons}} S_{A'} \rightleftharpoons (63)S_A \rightleftharpoons (72)N \rightleftharpoons (85)I$
R_4LH[c]	$K_2 \rightarrow (46)S_C \rightarrow (60)S_{A'} \rightleftharpoons (75)S_A \rightleftharpoons (86)I$ $(40)K_1 \leftarrow$
R_6LH[e]	$K_1 \rightleftharpoons (51)S_C \rightleftharpoons (90)S_A \rightleftharpoons (95)I$
R_8LH[e]	$K_1 \rightleftharpoons (45)S_C \rightleftharpoons (93)S_A \rightleftharpoons (101)I$

[a] K = crystal. When two different solid phases are detected, in K_2 the apparent molecular length is longer than in K_1; N = nematic; S = smectic; I = isotropic liquid. [b] From ref 17. [c] From ref 11c. [d] R_2 LH exhibits a reentrant solid phase (K_1) between the smectic A and the nematic phase. [e] From ref 1.

The transition temperatures and mesophases of these ligands are collected in Table I.

Experimental Section

General Procedures. All manipulation were carried out in air. The IR spectra (Nujol mull) were recorded on a Perkin-Elmer

---

(3) Hoshino, N.; Hasegawa, H.; Matsunaga, Y. *Liq. Cryst.* **1991**, *9*, 267.

(4) (a) Hoshino, N.; Murakami, H.; Shibuya, T.; Matsunaga, Y. *Inorg. Chem.* **1990**, *29*, 1177. (b) Hoshino, N.; Hayakawa, R.; Shibuya, T.; Matsunaga, Y. *Inorg. Chem.* **1990**, *29*, 5129. (c) Hoshino, N.; Kodama, A.; Shibuya, T.; Matsunaga, Y.; Miyajima, S. *Inorg. Chem.* **1991**, *30*, 3091.

(5) Caruso, U.; Roviello, A.; Sirigu, A. *Liq. Cryst.* **1991**, *10*, 85.

(6) (a) Baena, M. J.; Espinet, P.; Ros, M. B.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 711. (b) Ros, M. B.; Ruiz, N.; Serrano, J. L.; Espinet, P. *Liq. Cryst.* **1991**, *9*, 77.

(7) Borchers, B.; Haase, W. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 319.

(8) (a) Ghedini, M.; Armentano, S.; Neve, F. *Inorg. Chim. Acta* **1987**, *134*, 23. (b) Versace, C. C.; Bartolino, R.; Ghedini, M.; Neve, F.; Armentano, S.; Petrov, M.; Kirov, N. *Liq. Cryst.* **1990**, *8*, 481.

(9) Ghedini, M.; Armentano, S.; Bartolino, R.; Rustichelli, F.; Torquati, G.; Kirov, N.; Petrov, M. *Mol. Cryst. Liq. Cryst.* **1987**, *151*, 75.

(10) Demus, D. *Liq. Cryst.* **1989**, *5*, 75.

(11) (a) Ghedini, M.; Armentano, S.; Bartolino, R.; Torquati, G.; Rustichelli, F. *Solid State Commun.* **1987**, *64*, 1191. (b) Levelut, A. M.; Ghedini, M.; Bartolino, R.; Nicoletta, F. P.; Rustichelli, F. *J. Phys. (France)* **1989**, *50*, 113. (c) Torquati, G.; Francescangeli, O.; Ghedini, M.; Armentano, S.; Nicoletta, F. P.; Bartolino, R. *Il Nuovo Cimento* **1990**, *12D*, 1363.

(12) Formoso, V.; Pagnotta, M. C.; Mariani, P.; Ghedini, M.; Neve, F.; Bartolino, R.; More, M.; Pêpy, G. *Liq. Cryst.* **1992**, *11*, 639.

(13) Bartolino, R.; Rustichelli, F.; Scaramuzza, N.; Versace, C. C.; Ghedini, M.; Pagnotta, M. C.; Armentano, S.; Ricci, M. A.; Benassi, P. *Solid State Commun.* **1991**, *80*, 587.

(14) Ghedini, M.; Morrone, S.; De Munno, G.; Crispini, A. *J. Organomet. Chem.* **1991**, *415*, 281.

1330 spectrometer, and ^1H NMR spectra ($CDCl_3$, standard $SiMe_4$) on a Bruker AW 300 spectrometer.

Elemental analyses were carried out by the Microanalysis Laboratory of the Dipartimento di Chimica, Universitâ della Calabria.

The thermal behavior was monitored by means of a Mettler FP 80 thermosystem equipped with a FP84 microscopy cell, at a heating rate of 5 °C min^{-1}. The apparatus was calibrated with indium (156.6 °C, 28.4 J/g) as standard.

The textures of the mesophases were observed with a Zeiss Axioscope polarising microscope equipped for photography and with a Linkam CO 600 heating stage.

X-ray diffraction measurements were performed with the INEL CPS120 powder diffractometer equipped with a position sensitive detector covering 120° in 2θ. Ni filtered Cu Kα radiation (λ = 1.54 Å) was used, strongly collimated with an appropriate slit system. A calibration compound with well known 2θ values was used to determine the calibration function describing the 2θ vs channel number relation. The samples, about 1 mm thick, were placed between two thin Al sheets, fixed to a circular hole (1-cm diameter) in an Al matrix. Heating was achieved by a hot stage whose accuracy and stability were ±0.5 °C and ±0.1 °C, respectively.

Preparation of Compounds. The standard chemicals 4,4'-bis(hexyloxy)azoxybenzene (H[Azoxy-6], Eastman Kodak Co.) and $AgBF_4$ (Fluka A.G.) were used as supplied. The R_nLH ligands[1] and $[Pd(PhCN)_2Cl_2]$[15] were prepared as reported in the literature.

The palladium complexes **1**–**9** were synthesized according to the previously described procedures.[14] Colors, yields, elemental analyses, and selected ^1H NMR data (300 MHz, $CDCl_3$) are as follows:

[Pd(Azoxy-6)(μ-Cl)]$_2$, 1: yellow; yield 57%, mp dec at 298 °C. Anal. Calcd for $C_{48}H_{66}N_4O_6Cl_2Pd_2$: C, 53.34%; H, 6.15%; N, 5.18%. Found: C, 53.05%; H, 6.04%; N, 4.96%.

[Pd(Azoxy-6)(MeCN)$_2$]BF$_4$, 2: orange; yield 95%. Anal. Calcd for $C_{28}H_{39}BF_4N_4O_3Pd$: C, 49.96%; H, 5.84%; N, 8.36%. Found: C, 49.01%; H, 5.66%; N, 7.48%. IR (Nujol mull): ν(CN) = 2285 cm^{-1}; ν(B–F) = 1050 cm^{-1}.

[(HL)Pd(Azoxy-6)], 3: orange; yield 55%. Anal. Calcd for $C_{49}H_{68}N_3O_5Pd$: C, 66.36%; H, 7.65%; N, 4.54%. Found: C, 66.53%; H, 7.75%; N, 4.77%. ^1H NMR: N,N-trans δ 7.85 (s, 1 H, —C*H*=N—); N,N-cis δ 7.78 (s, 1 H, —C*H*=N—).

[(CH$_3$L)Pd(Azoxy-6)], 4: orange; yield 41%. Anal. Calcd for $C_{50}H_{70}N_3O_5Pd$: C, 66.75%; H, 7.84%; N, 4.78%. Found: C, 66.58%; H, 7.80%; N, 4.69%. ^1H NMR: N,N-trans δ 7.86 (s, 1 H, —C*H*=N—); N,N-cis δ 7.78 (s, 1 H, —C*H*=N—).

[(C$_2$H$_5$L)Pd(Azoxy-6)], 5: orange; yield 63%. Anal. Calcd for $C_{51}H_{72}N_3O_5Pd$: C, 67.04%; H, 7.94%; N, 4.62%. Found: C, 67.29%; H, 8.00%; N, 4.65%. ^1H NMR: N,N-trans δ 7.85 (s, 1 H, —C*H*=N—); N,N-cis δ 7.78 (s, 1 H, —C*H*=N—).

[(C$_3$H$_7$L)Pd(Azoxy-6)], 6: orange; yield 51%. Anal. Calcd for $C_{52}H_{74}N_3O_5Pd$: C, 67.32%; H, 8.04%; N, 4.55%. Found: C, 67.63%; H, 8.13%; N, 4.59%. ^1H NMR: N,N-trans δ 7.86 (s, 1 H, —C*H*=N—); N,N-cis δ 7.81 (s, 1 H, —C*H*=N—).

[(C$_4$H$_9$L)Pd(Azoxy-6)], 7: orange; yield 56%. Anal. Calcd for $C_{53}H_{76}N_3O_5Pd$: C, 67.59%; H, 8.13%; N, 4.48%. Found: C, 67.52%; H, 8.17%; N, 4.49%. ^1H NMR: N,N-trans δ 7.85 (s, 1 H, —C*H*=N—); N,N-cis δ 7.79 (s, 1 H, —C*H*=N—).

[(C$_6$H$_{13}$L)Pd(Azoxy-6)], 8: orange; yield 58%. Anal. Calcd for $C_{55}H_{80}N_3O_5Pd$: C, 68.11%; H, 8.30%; N, 4.35%. Found: C, 67.86%; H, 8.25; N, 4.42%. ^1H NMR: N,N-trans δ 7.86 (s, 1 H, —C*H*=N—); N,N-cis δ 7.78 (s, 1 H, —C*H*=N—).

[(C$_8$H$_{17}$L)Pd(Azoxy-6)], 9: orange; yield 63%. Anal. Calcd for $C_{57}H_{84}N_3O_5Pd$: C, 68.61%; H, 8.48%; N, 4.23%. Found: C, 68.56%; H, 8.53%; N, 4.27%. ^1H NMR: N,N-trans δ 7.84 (s, 1 H, —C*H*=N—); N,N-cis δ 7.78 (s, 1 H, —C*H*=N—).

Results and Discussion

Synthesis of the Complexes. The preparation of the palladium complexes has been accomplished according to the reaction scheme (Scheme III, eqs 1–3) previously tested for the synthesis of mixed–ligand compounds containing palladated *p*-azoxyanisole and salicylideneaminatoanilines.[14]

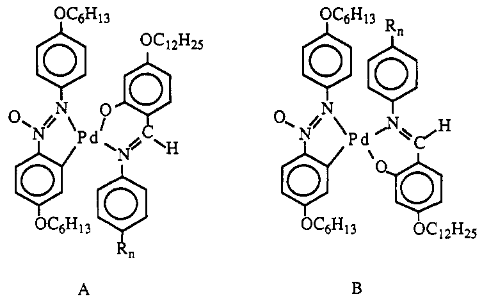


Figure 1. Proposed molecular structure of the [(R$_n$L)Pd(Azoxy-6)] complexes, N,N-trans (A) and N,N-cis (B) isomers.

Scheme III. Reaction Scheme for the Preparation of Compounds 3–9

$$2H[Azoxy\text{-}6] + 2[Pd(PhCN)_2Cl_2] \xrightarrow{EtOH} \underset{\mathbf{1}}{[Pd(Azoxy\text{-}6)(\mu\text{-}Cl)]_2} \quad (1)$$

$$\mathbf{1} + 2AgBF_4 \xrightarrow{MeCN} \underset{\mathbf{2}}{[Pd(Azoxy\text{-}6)(MeCN)_2]BF_4} \quad (2)$$

$$\mathbf{2} + R_nLH \xrightarrow{EtOH} \underset{\mathbf{3\text{–}9}}{[(R_nL)Pd(Azoxy\text{-}6)]} \quad (3)$$

The products **3**–**9** were characterized by elemental analyses and IR and ^1H NMR spectroscopies (Experimental Section). These experimental data were in agreement with the expected stoichiometry; moreover, the ^1H NMR findings[14] gave insights about the stereochemistry of the reaction reported in eq 3. In particular, since two different isomers could form, namely, N,N-trans and N,-N-cis (Figure 1), the analysis of the protonic spectra showed that both the isomers, in a cis to trans ratio of 1:5, are present in all the **3**–**9** products.

Both the cis and trans complexes which form the isomeric mixtures **3**–**9** contain a palladium atom in a square-planar bis-chelating environment formed by the cyclometalated H[Azoxy-6] molecule and homologous salicylideneaminato R$_n$L anions. The molecular structure of the strictly similar N,N-trans [*N*-(phenyl)-2-salicylideneaminato]-[4'-(methoxyphenyl-NNO-azoxy-*N*^{2})-4-methoxyphenyl-2-ato]palladium(II) was previously determined by single-crystal X-ray analysis.[4] By analogy, all the present compounds N,N-trans and N,N-cis are thought to display the molecular geometries sketched in parts A and B of Figure 1, respectively.

Mesomorphic Properties. The uncomplexed H[Azoxy-6] and the R$_n$LH ligands are liquid-crystalline compounds which give nematic[16] or smectic and nematic mesophases,[1,11a] respectively. Similar features are preserved in their palladium derivatives.

The mesogenic behavior of the isomeric mixtures **3**–**9** has been determined by optical microscopy and the mesophases identified by their optical textures and powder X-ray diffraction. All the investigated species display mesogenic properties and a good thermal stability, no decomposition being observed along several heating and cooling cycles. The transition temperatures are summarized in Table II.

The nematic phases, on either heating or cooling, display a schlieren texture. The smectic A phases exhibits the

---

[15] Karash, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

[16] Béguin, A.; Billard, J.; Bonamy, F.; Buisine, J. M.; Cuvelier, P.; Dubois, J. C.; Le, Barny, P. *Mol. Cryst. Liq. Cryst.* **1984**, *115*, 1.

Table II. Thermal Behavior for the Complexes [(R_nL)Pd(Azoxy-6)] (3–9)

compd	transition temp (°C) and mesophases[a]
3	$K \longrightarrow (122)I$ $K(98) \longleftarrow N(120) \longleftarrow$
4	$K \longrightarrow (141)N \rightleftharpoons (146)I$ $K(86) \longleftarrow S_A(131) \longleftarrow$
5	$K \longrightarrow (140)I$ $K(92) \longleftarrow S_A(126) \longleftarrow N(135) \longleftarrow$
6	$K \longrightarrow (136)S_A \longrightarrow (139)N \longrightarrow (143)I$ $K(100) \longleftarrow S_A(134) \longleftarrow N(141) \longleftarrow$
7	$K \longrightarrow (140)I$ $K(93) \longleftarrow S_A(132) \longleftarrow N(138) \longleftarrow$
8	$K \rightleftharpoons (128)S_A \rightleftharpoons (144)I$
9	$K \rightleftharpoons (125)S_A \rightleftharpoons (143)I$

[a] K = crystal; N = nematic; S = smectic; I = isotropic liquid.

Figure 2. Complex **6**, nematic schlieren texture. Crossed polarizers, 140 °C.

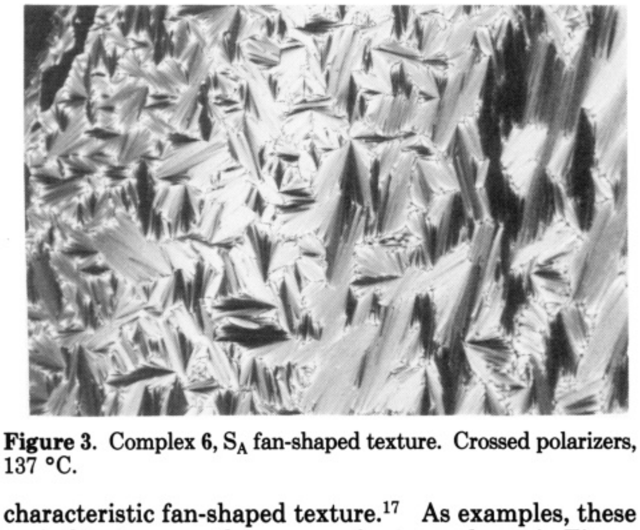


Figure 3. Complex **6**, S_A fan-shaped texture. Crossed polarizers, 137 °C.

characteristic fan-shaped texture.[17] As examples, these typical textures, as they appear for **6**, are shown in Figure 2 and 3, respectively.

Compounds **3**, **5**, and **7** (R_n = H, C_2H_5, and C_4H_9, respectively) show a monotropic behavior with a nematic phase only (**3**) or nematic and smectic A phases (**5** and **7**). Differently, **4** (R_n = CH_3) shows an enantiotropic nematic phase together with a monotropic smectic A phase and **6** (R_n = C_3H_7) exhibits both enantiotropic nematic and smectic A phases. Finally **8** (R_n = C_6H_{13}) and **9** (R_n = C_8H_{17}) give an enantiotropic smectic A phase. Therefore, with reference to the mesomorphic behavior, products **3–9** follow the trend usually observed for homologous series, i.e., the smectic mesophases result most common as the *n*-alkyl chains become longer.[18]

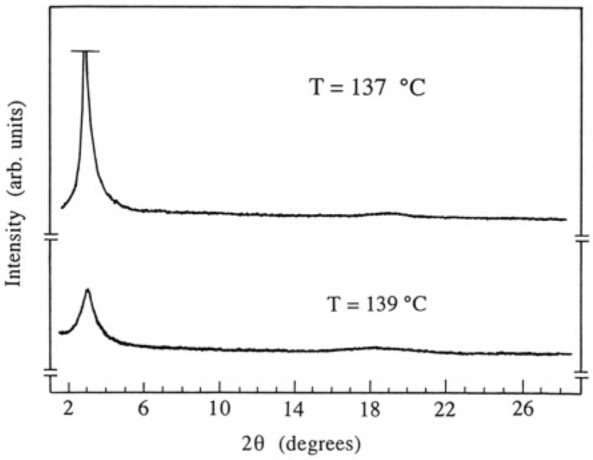


Figure 4. Complex **6**. X-ray diffraction patterns: S_A (137 °C) and N (139 °C; in an external magnetic field).

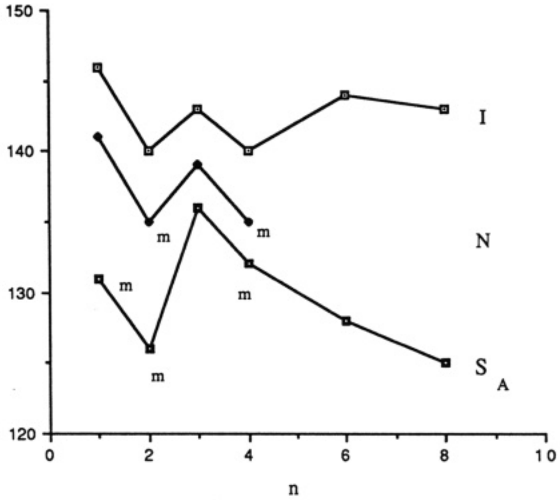


Figure 5. Plots of mesomorphic transition temperatures versus the R_n alkyl chain length (*n*) for compounds **4–9**.

The nature of the different mesophases has been confirmed by X-ray diffraction analysis. Representative diffraction patterns concerning both the S_A and N phases exhibited by **6** are reported in Figure 4. The diffraction pattern in the nematic phase was measured with the sample plunged in an external magnetic field in order to better point out the low angle diffuse peak. The peak in the smectic phase corresponds to a periodicity of about 28 Å.

Conclusion

The thermotropic species **3–9** are lateral–lateral fused mesogens. Regarding to the length of these molecules, the values calculated for the all-trans conformations of the aliphatic chains result slightly different for each couple of N,N-cis and N,N-trans isomers. Indeed such calculations afford a value of 36 Å for the **3–9** N,N-cis isomers and values ranging from 31 (**3–7**) to 35 Å (**9**) for the N,N-trans isomers. Therefore, along the **3–9** series the whole

---

[17] Demus, D.; Richter, L. *Texture of Liquid Crystals*; Verlag *Chemie*: Weinheim, West Germany, 1978.

[18] Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag Chemie: Weinheim, Germany, 1980.

molecular length is roughly unaffected by the R_n nature. The products **3**–**9** exhibit smectic A and/or nematic mesophases. The transition temperatures versus the number n of R_n carbon atoms are reported in Figure 5.

In homologous series of calamitic liquid crystals containing an *n*-alkyl chain as a terminal group, the clearing point and the transition temperatures normally display the odd–even effect and decrease with increasing the chain length.[18] For both the S_A and the N phases these effects are apparent for compounds **4**–**9** too (Figure 5). However, it seems remarkable that the clearing points, in spite of the large difference in the R_n length, belong in a quite narrow range (i.e., 6 °C). This behavior might be the result of the above described molecular geometry.

The role played by the complexed 4,4′-*n*-alkoxyazoxybenzene ligand could deserve a further comment. Actually, none of the previously reported $[(R_nL)Pd(Azoxy\text{-}1)]$ species,[14] wherein R_nL ($R_n = CH_3$, C_2H_5, and C_4H_9), is the deprotonated form of some of the R_nLH Schiff bases shown in Scheme II and [Azoxy-1] is the cyclometalated *p*-azoxyanisole, display thermotropic properties. Therefore, comparing the two homologous series $[(R_nL)Pd(Azoxy\text{-}6)]$ and $[(R_nL)Pd(Azoxy\text{-}1)]$, it is apparent that the building of mesogenic materials demands azoxybenzenes bearing the appropriate number of carbon atoms in the *n*-alkoxy chains.

The structure of the mesophases displayed by **3**–**9** has been investigated by X-ray techniques. In particular, for R_n ranging from zero to C_4H_9 (compounds **3**–**7**) two quite different periodicities (about 45 and 28 Å) characterize the low-angle diffraction pattern in the solid and smectic phases, respectively. In contrast, for $R_n = C_6H_{13}$ (**8**) or C_8H_{17} (**9**) the periodicities of 25 Å in the solid phase and 29 Å in the smectic one are seen. With reference to the molecular shape, in complexes **3**–**9** a metal atom binds two calamitic thermotropic ligands as in the bissalicylideneaminate copper mesogen IV. The X-ray analyses concerning the copper complexes gave apparent molecular lengths shorter than the theoretical values, and consequently an interdigitated molecular arrangement was proposed.[1,11] In the present case a molecular packing alike might be suggested for **8** and **9** only.

Finally, as far as the molecular structures are concerned, it should be pointed out that the mononuclear cyclopalladated liquid-crystalline materials reported up to now are acetyllacetonate derivatives of ortho-palladated imines[6a] or azoxybenzenes.[19] Both these species have asymmetric rodlike shapes; therefore, **3**–**9** are the first examples of lateral–lateral fused organometallic palladium mesogens.

Acknowledgment. This work was supported by the Italian CNR under the cover of "Progetto Finalizzato Materali Speciali per Tecnologie Avanzate" and Ministero dell'Università e Ricerca Scientifica e Technologica. We thank Johnson Matthey, Ltd., for a generous loan of $PdCl_2$.

Registry No. 1, 143064-01-1; 2, 143064-03-3; 3 (isomer A), 143064-04-4; 3 (isomer B), 143120-58-5; 4 (isomer A), 143064-05-5; 4 (isomer B), 143120-59-6; 5 (isomer A), 143064-06-6; 5 (isomer B), 143120-60-9; 6 (isomer A), 143064-07-7; 6 (isomer B), 143120-61-0; 7 (isomer A), 143064-08-8; 7 (isomer B), 143120-62-1; 8 (isomer A), 143064-09-9; 8 (isomer B), 143167-07-1; 9 (isomer A), 143064-10-2; 9 (isomer B), 143120-63-2.

---

(19) Ghedini, M.; Pucci, D.; Armentano, S.; Bartolino, R.; Versace, C. C.; Cipparrone, G.; Scaramuzza, N. Italian Patent VE 92A000003, Jan 16, 1992.

In Situ Polycondensation for Synthesis of Composites of Elastomeric Matrices and Wholly Aromatic Polyamides

Emmanuel Debeaupte, Masayoshi Watanabe, Kohei Sanui, and Naoya Ogata*

Department of Chemistry, Faculty of Science and Technology, Sophia University,
7-1 Kioi-Cho, Chiyoda-Ku, Tokyo 102, Japan

Received February 4, 1992. Revised Manuscript Received July 23, 1992

Composites of rubbers containing poly(*p*-phenylene terephthalamide) (PPTA) were prepared by solution polycondensation and interfacial polycondensation methods from terephthaloyl chloride (TPC) and *p*-phenylene diamine (PPD) in the presence of some elastomers, e.g., styrene–butadiene–styrene (SBS) triblock copolymers and acrylonitrile–butadiene (NBR) random copolymers. The morphology of these composite polymers was characterized by electron microscopy, and their mechanical properties were investigated. The morphology of the blends and the reinforcing effect of the PPTA were dependent on the matrix, the polycondensation method, and the PPTA content in the blend.

Introduction

The concept of molecular composites was first proposed by Takayanagi et al. in Japan[1] and Helminak et al. in the United States.[2] Many papers have since been published in that field.

However, only a few papers about molecular composites containing wholly aromatic polyamides, e.g., poly(*p*-phenylene terephthalamide) (PPTA) as reinforcing polymer, have been published. These were almost exclusively done by Takayanagi's group in Japan. Blends are achieved by different methods. One consists of solution blending of the rigid-rod polymer and the coillike flexible polymer. However, the insolubility of PPTA in common solvents renders this method futile. Therefore, only some composites with aliphatic polyamides have been prepared by this method in sulfuric acid, which is one of the few good solvents of PPTA.[3] Another method consists of chemical transformation of the surface of microfibrils of PPTA by

---

(1) Takayanagi, M. Japan Patent Application, 1977, 131436.
(2) Helminak, T. E. U.S. Patent, 1978, 902525.
(3) Takayanagi, M.; Ogata, T.; Morikawa, M.; Kai, T. *J. Macromol. Sci.-Phys. Ed.* 1980, *B17*, 591–615.

0897-4756/92/2804-1123$03.00/0