CHEMISTRY OF MATERIALS

VOLUME 1, NUMBER 5 SEPTEMBER/OCTOBER 1989

Communications

Nematic Phases in Ionic Melts: Mesogenic Ionic Complexes of Silver(I)

Duncan W. Bruce,* David A. Dunmur,
Peter M. Maitlis, and Peter Styring

Department of Chemistry, The University
Sheffield S3 7HF, England

Miguel A. Esteruelas,[†] Luis A. Oro,[†] M. Blanca Ros,[†]
Jose-Luis Serrano,[†] and Eduardo Sola[†]

Instituto de Ciencias de Materiales de Aragon
Universidad de Zaragoza, CSIC
50009 Zaragoza, Spain

Received January 23, 1989

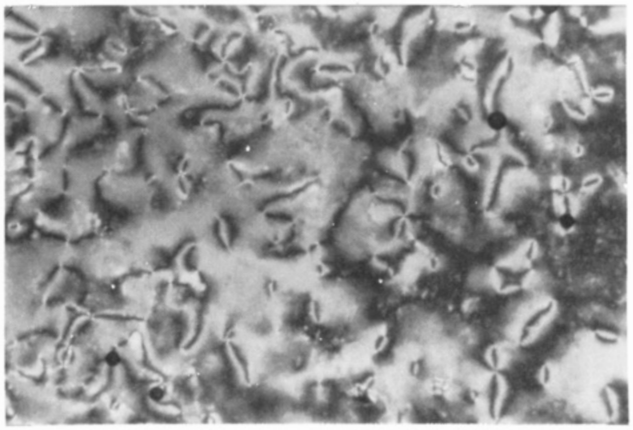
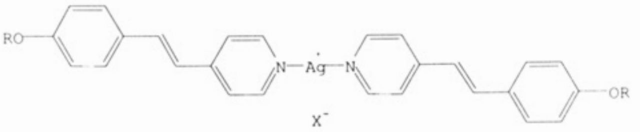


Figure 1. Photomicrograph of IIc in its nematic phase at 154 °C viewed between crossed polars.

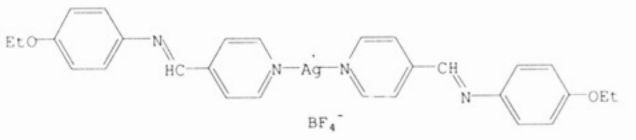
Anhydrous ionic mesogens have been recognized for many years, and their phase behavior has been reported.[1] In general, the materials show a complex solid-phase behavior, but on heating they eventually melt to a lamellar (smectic like) phase that clears to an isotropic liquid at higher temperatures. We recently reported[2] that the phase behavior of (alkyloxy)stilbazole complexes of silver(I) differed from that usually associated with ionic amphiphiles. For example bis((octyloxy)stilbazole)silver dodecyl sulfate showed a viscous phase of mosaic texture in addition to the lamellar phase characteristic of ionic materials: on the basis of its texture, the mosaic phase was assigned as smectic B.[2] Some of the higher homologues showed smectic C phases.[3] These were the first materials to combine the phase behavior of ionic and neutral mesogens in one material. Some *N*-alkylpyridinium halides have also been found to have smectic A[4] or smectic B[5] phases, although polymorphism was not observed.

We now report the silver complexes I–III, which we believe to be the first examples of anhydrous, ionic materials showing a thermotropic *nematic* phase.[6] The phase



I: $X = CF_3SO_3$ $R = C_4H_9$

II: $X = C_{12}H_{25}OSO_3$ $R =$ (a) CH_3
(b) C_2H_5
(c) C_3H_7
(d) C_4H_9



III

[†] In part.

(1) See, e.g.: Tiddy, G. J. T. *Phys. Rep.* **1980**, *57*, 1, and references therein.

(2) Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Maitlis, P. M.; Styring, P. *Nature (London)* **1986**, *323*, 791.

(3) Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Maitlis, P. M.; Styring, P., manuscript in preparation.

(4) Bazuin, C. G.; Guillon, D.; Skoulios, A.; Nicoud, J. F. *Liq. Cryst.* **1986**, *1*, 181.

(5) Bazuin, C. G.; Guillon, D.; Skoulios, A.; Zana, R. *J. Phys. (Les Ulis, Fr.)* **1986**, *47*, 927.

0897-4756/89/2801-0479$01.50/0 © 1989 American Chemical Society

Table I. Thermal Data for $[AgL_2][X]$

complex	chain length	X	transition	T/°C	ΔH/(J g^{-1})	ΔH/(kJ mol^{-1})	ΔS_m/R
I	4	TFMS	K-N	227	50.4	38.5	9.2
			N-I	234	2.7	2.1	0.5
II	1	DOS	K-N	128	39.6	31.5	9.4
			N-I	159	5.3	4.2	1.2
II	2	DOS	K-N	131	46.8	38.6	11.5
			N-I	163	3.1	2.6	0.7
II	3	DOS	K-N	146	49.9	42.5	12.1
			N-I	159	0.8	0.7	0.2
II	4	DOS	K-N	147	36.7	32.3	9.2
			N-I	166	0.7	0.6	0.2
III	2	BF_4	K-N	192			
			N-I	not detected			

behavior was investigated by using hot-stage optical microscopy and differential scanning calorimetry (Table I). All complexes showed only a nematic mesophase.

The identity of the nematic phase has been assigned mainly on the basis of optical textures, and the photomicrograph of the nematic phase of IIc at 154 °C (Figure 1) shows the characteristic[8] two- and four-brush isogyres at the termination of disclination lines. Miscibility studies were inconclusive, and contact preparations with *N*,*N*′-bis((octyloxy)benzylidene)-*p*-phenylenediamine led to isotropic areas, while similar preparations with pentylcyanoterphenyl resulted in an injected smectic A phase.

The silver complex I appeared stable in the isotropic state in the absence of air, leading to the formation of good optical textures on cooling and good DSC curves; the DSC curve obtained for I is shown in Figure 2. Complex III slowly decomposed in the nematic phase, and the complexes II decomposed in the isotropic state, although the decomposition was slow and was not a problem if the complexes were quickly cooled from the isotropic state. Although the thermal stability of I was quite good, the X-ray stability of crystals was not, and attempts to obtain a single-crystal structure of I resulted in the total loss of diffraction after only 2 h.

In our earlier work on these materials,[2] we observed a lamellar phase in complexes IIc and IId but did not detect a nematic phase. We believe that the reason for this difference is in the method of preparation and that the samples reported as showing a lamellar phase contained a very small amount of residual water.[9] However complexes IIc and IId prepared by the route described in ref 6 showed the nematic phase in place of the lamellar phase. This is supported by the observation that a sample of IIc having a nematic phase can be made to show a lamellar phase (replacing the nematic phase) after treatment with wet acetone.

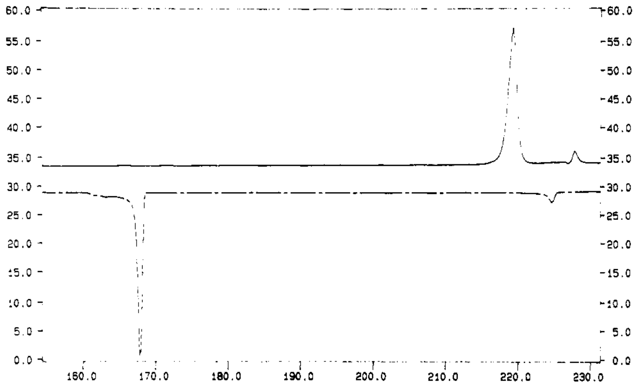


Figure 2. DSC curve for IId obtained at 10 K/min, using a Perkin Elmer DSC7 instrument. Power in milliwatts (*y* axis) plotted against temperature (*x* axis). Solid line is the heating cycle; broken line is the cooling cycle.

The formation of liquid crystalline mesophases in ionic melts is at first sight surprising. Orientationally ordered mesophases form from molecules with strong angle-dependent intermolecular forces, but Coulombic forces are isotropic and would tend to favor the formation of solid, crystal phases. Liquid, crystal phases of anhydrous ionic amphiphiles are known,[2] and some aqueous solutions of rodlike micelles form nematic phases.[10] In these lyotropic nematics the charges on the polar head-groups are partially cancelled by adsorbed counterions, and the high permittivity of the aqueous environment screens the Coulombic interactions. For our new materials the permittivity is likely to be low, and we have no evidence of aggregation. It is possible that the anions associate with the silver ion bearing the localized positive charge, forming uncharged ion pairs, and this idea is supported by the low electrical conductivity measured in the nematic phase of IIa.[11]

One conclusion from this and our other related work[2,12,13] is that the existence of anisotropic liquid, crystal phases is very widespread and not confined to "conventional" mesogenic molecules. The ability to produce fluids in which the molecules are orientationally ordered has led to switchable signal-processing devices but also has possibilities in enhanced catalytic activity and selective chemical reactivity. Anisotropic ionic melts could be used to increase the efficiency and selectivity of electrochemical processes, if suitable ionic systems can be discovered that have nematic phases at low enough temperatures. The use

---

(6) The complexes were prepared as follows. I: Stirring a solution of 4-(butyloxy)-4′-stilbazole[7] (2 equiv) with silver triflate (1 equiv) in dry acetone for 2 h in the dark led to a colorless precipitate, which was filtered off, washed with acetone, and dried under vacuum at room temperature, yield 96%. II: 4-(alkyloxy)-4′-stilbazole (2 equiv) was stirred with silver dodecyl sulfate (1 equiv) in dichloromethane for 5 min in the dark. The solvent was removed under vacuum, and the residue crystallized from hot acetone to give the product as a pale yellow solid in 75% yield. III: 4-(ethyloxy)-*N*-(4-pyridylbenzylidene)aniline (2 equiv) and $AgBF_4$ (1 equiv) were stirred in ethanol for 20 min in the dark under nitrogen. The resulting yellow suspension was concentrated under reduced pressure, filtered off, washed with ethanol, and vacuum dried, yield 75%. All new complexes gave satisfactory analyses.

(7) Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Maitlis, P. M.; Styring, P. *Liq. Cryst.* **1988**, *3*, 385.

(8) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978.

(9) Previously, the complexes II were prepared from their BF_4 analogues by metathesis with NaDOS in acetone, and it is possible that water was introduced via the NaDOS, which is very difficult to dry. A better preparation is that described in ref 6, where stilbazole is reacted directly with AgDOS (prepared from NaDOS and $AgNO_3$ and rigorously dried).

(10) Yu, L. J.; Saupe, A. *J. Am. Chem. Soc.* **1980**, *102*, 4879, and references therein.

(11) Dunmur, D. A.; Orr, R., unpublished results.

(12) Bruce, D. W.; Lalinde, E.; Styring, P.; Dunmur, D. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1986**, 581.

(13) Adams, H.; Bailey, N. A.; Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Marcos, M.; Ridgway, C.; Smith, A. J.; Styring, P.; Maitlis, P. M. *Liq. Cryst.* **1987**, *2*, 381.

Chemistry of Materials 1989, *1*, 481–483 481

of room-temperature isotropic ionic melts as solvents for electronic spectroscopy has recently been demonstrated.[14]

Acknowledgment. We thank Sarah Hudson for the preparation of some complexes, and we acknowledge support from the EC Twinning (Grant No. ST2J-0387-c), the Royal Society, the SERC, and the Spanish Ministry of Education.

---

(14) Appleby, D.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Nature (London)* **1986**, *323*, 614.

Colloidal Metal Particles Dispersed in Monomeric and Polymeric Styrene and Methyl Methacrylate

Kenneth J. Klabunde,* Jan Habdas,† and
Galo Cárdenas-Triviño‡

Department of Chemistry, Kansas State University
Manhattan, Kansas 66506, and
Department of Chemistry, University of Concepción
Castilla 3-C, Concepción, Chile

Received February 14, 1989

Introduction

As Kay has stated, "the physical and chemical behavior of small metal clusters in dielectric thin-film matrices is of considerable interest both from a fundamental and potential applications point of view".[1] Thus, Kay and co-workers have reported interesting properties of gold clusters in fluorocarbons polymer composite films, which were prepared by plasma methods.[1,2] Andrews and Ozin[3] have also reported broad, fundamental studies of metal atoms and clusters in liquid polymeric materials, and Wright[4] has reported interesting synthetic approaches to the synthesis of polymer-trapped metal clusters based on atom agglomeration in organic monomers.

In this communication we report a synthetic approach to preparing metal clusters trapped in solid, organic polymers based on our earlier work involving the preparation of colloidal metals in nonaqueous solvents.[5-7] This method, which involves deposition of metal vapor (atoms) with low-temperature organic solvents followed by controlled/limited atom accretion, is wide in scope and can be employed with a variety of metals and solvents. It allows fairly large-scale preparation of such colloidal solutions, which are of great interest in colloid chemistry, film formation processes, and other areas.[8-11]

Table I. Polymerization Studies of Au–Styrene Compared with Styrene Alone

styrene or Au–Styrene (mL)	mol % AIBN added	yield of poly-styrene, %	mol wt of poly-styrene[a]	color
styrene (10)	0.1	2.0	128 000	white
styrene (10)	0.2	2.3	83 000	white
styrene (10)	0.5	4.2	65 000	white
styrene (10)	1.0	6.2	47 000	white
Au–styrene (10)[b,d]	0.1	2.1	53 000	light purple
Au–styrene (10)[b,d]	0.2	3.2	50 000	light purple
Au–styrene (10)[b,d]	0.5	6.2	24 000	white
Au–styrene (10)[b,d]	1.0	7.3	21 000	white
Au–styrene (10)[c,d]	0.1	2.2	72 000	purple
Au–styrene (10)[c,d]	0.2	6.6	41 000	purple
Au–styrene (10)[c,d]	0.5	11.0	32 000	purple
Au–styrene (10)[c,d]	1.0	16.6	22 000	purple

[a] These are relative molecular weights since we used viscosimetry (in benzene at 25 °C); the Kuhn equation is most applicable for linear polymers only, and these may not be linear. [b] 1.09 × 10^{-3} M in gold. [c] 1.5 × 10^{-3} M in gold. [d] Very light loadings of Au were used for the studies reported in this table. Much higher loadings, such as 9 × 10^{-2} M, were possible, giving darker purple colloid solutions.

Results and Discussion

Three approaches to preparing these cluster–polymer composites have been employed:

(1) Codeposition of Metal Atoms with Styrene (or Methyl Methacrylate) Vapor at −196 °C. A typical metal vapor reaction[12,13] where 0.9 g of gold vapor was codeposited with 53 mL of liquid styrene (as a vapor) at −196 °C over 2 h yielded a deep purple matrix. On warming, a purple liquid was formed that was stable at room temperature for several days. Transmission electron microscope (TEM) measurements indicated gold particle sizes ranging from 7 to 15 nm, which are similar to colloids we have prepared in acetone, isopropyl alcohol, and other solvents.[5-7]

(2) Deposition of Metal Atoms into Liquid Styrene or Methyl Methacrylate. With utilization of a rotating metal vapor reactor[14] where liquid monomer (30 mL) was held at −78 °C, metal vapor (e.g., 0.4 g of gold) was evaporated, and the atoms were immersed in the liquid. In this case with Au, a purple liquid was again obtained, and on isolation this colloidal dispersion was very stable at room temperature. TEM again indicated particle sizes from 7 to 15 nm.

(3) Deposition of Metal Atoms into Dissolved Polymer. Again with utilization of a rotating metal atom reactor, 5 g of polystyrene was dissolved in 50 mL of toluene, giving a viscous liquid. Gold atoms (0.05 g) were deposited into this liquid at −78 °C; after warming to room temperature, the toluene solvent was evaporated, leaving a purple solid. Microtoming to 70 nm followed by TEM studies showed particle sizes from 7 to 15 nm.

Polymerization Studies. Colloidal solutions of the cluster monomers were polymerized by conventional means. Thus, AIBN was added to aliquots (all manipulations were carried out under pure N_2), followed by heating to 65 °C for 3 h. Methanol was added to precipitate the polymer, which was filtered off, washed, and dried under vacuum.

---

* To whom correspondence should be addressed at Kansas State University.

† 4000C Katowice, Silesian University, Poland.

‡ University of Concepcion.

(1) Kay, E. *Z. Phys. D: At., Mol. Clusters* **1986**, *3*, 251–262.

(2) Perrin, J.; Despax, B.; Kay, E. *Phys. Rev. B* **1985**, *32*, 719–732.

(3) Andrews, M. P.; Ozin, G. A. *Chem. Mater.* **1989**, *1*, 174–187, and references therein.

(4) Wright, R. 196th National Meeting of the American Chemical Society, Los Angeles, September 1988, paper I and EC, 32, and private communications.

(5) Lin, S. T.; Franklin, M. T.; Klabunde, K. J. *Langmuir* **1986**, *2*, 259–260.

(6) Franklin, M. T.; Klabunde, K. J. *ACS Symp. Ser. No. 333* **1987**, 246–259.

(7) Cardenas-Trivino, G.; Klabunde, K. J.; Dale, B. *Langmuir* **1987**, *3*, 986–992.

(8) Turkevich, J.; Stevenson, P. C.; Hillier, J. *Discuss. Faraday Soc.* **1951**, *11*, 55–75.

(9) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*; Lagowski, J. J., Ed.; Marcel Dekker: New York, 1977; pp 453–466.

(10) Shaw, D. J. *Introduction to Colloid and Surface Chemistry*, 2nd ed.; Butterworths: London, 1970; pp 157–158.

(11) Cardenas-Trivino, G.; Klabunde, K. J.; Dale, B. *Proc. SPIE—Int. Soc. Opt. Eng.* **1987**, *821*, 206–213.

(12) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic Press: New York, 1980.

(13) Klabunde, K. J.; Efner, H. F.; Murdock, T. O. *Inorg. Synth.* **1979**, *19*, 70–72.

(14) Timms, P. L. In *Cryochemistry*; Moskovits, M., Ozin, G., Eds.; Wiley-Interscience: New York, 1976; pp 61–136.

0897-4756/89/2801-0481$01.50/0