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Preliminary Communications

The synthesis and mesomorphism of a new series of silver(I) complexes showing glassy mesophases

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Reaction of 3,4-dialkoxystilbazoles (*n*-3,4-OPhVPy) with silver dodecylsulphate (AgDOS) leads to complexes of the formula [Ag(n-3,4-OPhVPy)$_2$][DOS]. These complexes are polycatenar liquid crystals and show mesophases which are characteristic of this structural type, namely, hexagonal, columnar and cubic. On cooling, some of the materials do not crystallize, but form stable glasses instead. All the mesophases have been fully characterized by small angle X-ray diffraction.

The glassy state is a particular phase of the solid state, characterized by the absence of crystallization, which usually appears when compounds or mixtures of compounds present a very high viscosity in the temperature region where they might be expected to crystallize. In theory [1], all substances can reach the glassy state below their melting point. However, in most cases, crystals (thermodynamic products) are more stable than glasses (kinetic products) and therefore crystallization occurs more often than vitrification.

Glass formation has long been known in polymeric materials and in recent years [2], it has been of great interest to combine the macromolecular properties of polymers (for instance the glass-forming tendency) with the remarkable properties of low molar mass liquid crystals (electro-optics). Thus, side chain liquid crystal polymers combined for the first time the anisotropy of liquid crystals with the glassy behaviour of polymers. As a result, new applications were discovered, one of them being optical information storage [3].

The use of liquid crystal polymers presents several problems as it is often difficult to reproduce exactly the same 'polymer' each time, whereas low molar mass materials can be readily reproduced time after time. Thus glasses obtained from low molar mass systems would have a certain attraction, particularly as they could properly be described as anisotropic glasses [4]. In general, glassy states of low molar mass systems have been obtained by rapid cooling of the mesophase, but more recently it has been reported that anisotropic glasses can be obtained by slow cooling of pyrene-based liquid crystals [5].

After a few examples reported in the literature, one can notice that the common feature of all these molecules is their rather unconventional structures. A structural model representing the relationships between vitrification and mesogenity in low molar mass compounds has been formulated [6]. It states that the elongated shape of the molecules, which guarantees the existence of mesophases, can be disturbed by several structural fragments. In almost all cases, the mesophase stability is reduced, whereas the tendency to vitrification is strengthened. In order to obtain glassy liquid crystalline materials, the molecule must be designed to be able to form both liquid crystal and glass. It should be underlined that some degree of compromise is necessary to satisfy these two potentially antagonistic conditions.

The materials now described differ from these systems in that they are metal complexes with a much more conventional liquid crystal structure which form glasses.

As part of our studies of metal-containing liquid crystals, we have extensively examined the mesomorphism of silver(I) complexes of alkoxystilbazoles (see the figure: $Y_1 = Y_2 = Y_4 = \mathrm{H}$, $Y_3 = \mathrm{OC}_n\mathrm{H}_{2n+1}$, $X = \mathrm{BF}_4$, NO_3, $\mathrm{CF}_3\mathrm{SO}_3$, $\mathrm{C}_m\mathrm{H}_{2M+1}\mathrm{OSO}_3$ for $m = 8, 10, 12, 14$). In one part of this study [7] we had examined silver complexes based on fluorinated stilbazoles (2-fluorinated: $Y_1 = \mathrm{F}$ and $Y_2 = \mathrm{H}$, 3-fluorinated: $Y_1 = \mathrm{H}$ and $Y_2 = \mathrm{F}$) and had found

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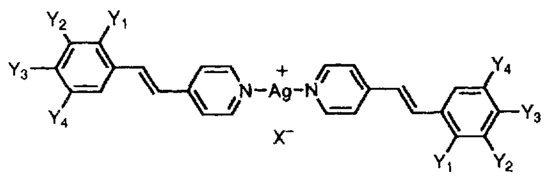


Figure 1. Silver(I) complexes of substituted stilbazoles (see text).

that in some 2-fluorinated derivatives with $X = C_{12}H_{25}OSO_3$, glass formation was favoured over crystallization on cooling.

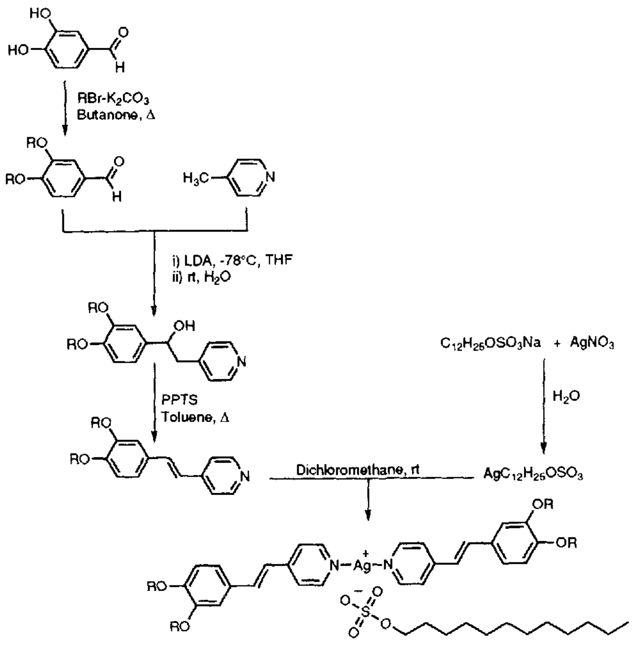
It is very sensible to think that substituents larger than fluorine such as alkoxy chains would certainly give compounds with higher viscosity than fluorinated compounds and even lower melting points. In order to try to make related materials for which glass formation might be further promoted, we undertook the synthesis of polycatenar silver complexes of stilbazoles, using dialkoxystilbazoles as ligands (see the figure: $Y_2 = Y_3 = OC_nH_{2n+1}$, $Y_1 = Y_4 = H$, $X = C_{12}H_{25}OSO_3$).

These silver salts with more than 3 chains can be identified as polycatenar materials. Polycatenar compounds can be defined as hybrids between a rod-like and disc-like molecules (a rigid core ending in one or two half-disc shaped moieties). This structural type of mesogen is known to exhibit an exceptional mesomorphism. Indeed, it presents the mesomorphism associated with calamitic mesogens (N, S_C, Cub) and discotic mesogens (columnar phases of the type ϕ_h, ϕ_{rd}, ϕ_{ob}).

The ligands were readily prepared in three steps according to the scheme. Thus, 3,4-dihydroxybenzaldehyde was reacted with the appropriate 1-bromoalkane in butanone using potassium carbonate as base to give the 3,4-dialkoxybenzaldehyde in yields between 70 and 85 per cent after work-up. The benzaldehyde was then added to a solution in THF containing 4-picoline and lithium di-isopropylamine (LDA) to give the secondary alcohol intermediate which was then dehydrated using pyridinium *p*-toluenesulphonate in boiling toluene to give the product in 80 per cent yield and exclusively *trans* ($J_{AB} = 17$ Hz). None of these new stilbazoles was mesomorphic.

The stilbazoles were then reacted with silver dodecylsulphate (from silver nitrate and sodium dodecylsulphate) to give the complexes in good yield and of analytical purity.

In principal, the complexes can be identified as tetracatenar 2(mp) + 2(mp) systems according to the nomenclature proposed by Malthête *et al.* [8], but this classification is confused by the presence of the dodecylsulphate anion which we assume acts as a lateral group, particularly as single crystal evidence [9] shows the sulphate group to be closely associated with the silver cation, and conductivity studies of related species imply that the tight ion pair survives into the mesophases.



Scheme

In common with other 2(mp) + 2(mp) polycatenar systems, these complexes show hexagonal columnar (ϕ_h) and cubic phases, but by contrast, no S_C phases are seen. We attribute the last observation to the presence of the lateral chain (dodecylsulphate anion) which reduces the tendency for lateral interactions. No liquid crystalline behaviour has been observed for $n = 3$, but a cubic phase was found for $4 \leq n \leq 9$ and a ϕ_h phase was found for $6 \leq n \leq 12$. Representative examples are listed below (first heat). Glasses were obtained for $4 \leq n \leq 8$. All the glasses are cubic and therefore isotropic. By contrast, for $n = 1$, and 2, the complex seems to have a completely different structure. It seems that a mono-ligand complex, [Ag(stilbazole)][DOS], contaminated by one equivalent of the free ligand was formed instead. Evidence for this formulation was provided by the fact that the elemental analysis was accurate for an empirical formula of [$Ag(stilbazole)_2$][DOS]. However on heating, partial melting occurred at the melting point of the free stilbazole, followed by a total melting at a higher temperature. The monotropic nematic phase observed was in a biphasic system with an isotropic liquid which we assumed to be the free stilbazole.

$n = 5$	Cr 82 cub 118 I	1st heat
	I 110 cub 68 g	1st cool
$n = 6$	Cr 70 Cub 122 ϕ_{hd} 160 I	1st heat
	I 146 ϕ_{hd} 117 Cub 57 g	1st cool
$n = 11$	Cr(I) 73 Cr(II) 86 ϕ_{hd} 178 I	1st heat
	I 170 ϕ_{hd} 40 Cr	1st cool

All of the phases were characterized by their optical textures and the hexagonal and body-centred cubic phases were confirmed by a combination of X-ray scattering studies and freeze-fracture microscopy [10]. In the case of the materials exhibiting only the cubic phase, the optical identification was based on the observation of distorted air bubbles, and also on the high viscosity of the isotropic phase.

In the case of polycatenar mesogens, both the structures of the thermotropic bicontinuous cubic phase and of the hexagonal phases are assumed to be based on aggregates of columns. The columnar phase arises from the rearrangement of the columns in an hexagonal array. The $Ia\bar{3}d$ cubic phase (the most commonly encountered in thermotropic systems) is made of portions of these cylinders (or columns) which interconnect coplanarly 3-by-3 to form two, periodical 3-dimensional continuous networks [11]. Thus, in our system, it was not surprising that our materials show these two phases, as the aliphatic matrix was big enough to envelop the rigid cores of the columns. Also, by analogy with the polycatenar systems, it is likely to assume that the molecules aggregate in planar clusters which stack together to form the columns. Dilatometry experiments and freeze-fracture electron microscopy are still in progress in order to propose a model of the molecular organization within both the hexagonal and cubic phases and maybe improve our understanding of cubic phase *formation* in thermotropic systems.

On cooling, some of the species do not crystallize, but form a glassy state instead. The glass transition temperature decreases with the number of carbon atoms in the alkoxy chains. The glasses were characterized by DSC. However, the measurements of ΔC_p were not always possible due to poor resolution. In some high homologues, the glassy state has persisted for more than 5 months and is still present. It is very important to point out here that the glassy state can be obtained on *slow* cooling of the materials, implying that crystallization is very much disfavoured.

The results that we obtained for this series lead us on to study fully this structural type and hopefully we will be able to formulate some structure–property relationships. Indeed, we intend to observe:

(*a*) the effect of di-3,5 and tri-3,4,5 substitutions by alkoxy chains on the mesomorphism (see the figure, (i) $Y_1 = Y_3 = \mathrm{H}$, $Y_2 = Y_4 = \mathrm{OC}_n\mathrm{H}_{2n+1}$ and (ii) $Y_1 = \mathrm{H}$, $Y_2 = Y_3 = Y_4 = \mathrm{OC}_n\mathrm{H}_{2n+1}$);

(*b*) the role of the counter anion on the mesomorphism by modifying its size (see the figure, $X = \mathrm{CF_3SO_3}$ and $\mathrm{C_8H_{17}OSO_3}$);

(*c*) the influence of different metals and therefore different coordination structures.

We have therefore obtained isotropic (or cubic) glasses. We think that the glass formation is due to (i) the bulkiness and all the alkoxy chains of the silver complex and (ii) the reduction of the free volume and the high viscosity in the low temperature region of the phase which would dramatically decrease the mobility of the molecules and then avoid a reorganization into a crystal packing.

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