Experimental report

24/08/2022

Proposal: **9-11-2058** **Council:** 4/2021

Title: Molecular structure of hybrid Triaryl amine/poly vinyl chloride gels

Research area: Soft condensed matter

This proposal is a resubmission of 9-11-2023

Main proposer: **Jean Michel GUENET**

Experimental team: Jean Michel GUENET

Local contacts: Bruno DEME

Samples: Tri aryl amine organogel/ $C_2Cl_4H_2$
Tri aryl amine organogel/ $C_2Cl_4D_2$
Tri aryl amine organogel/PVC/$C_2Cl_4H_2$
Tri aryl amine organogel/PVC/$C_2Cl_4D_2$
Tri aryl amine organogel/ C_6H_5Br
Tri aryl amine organogel/ C_6D_5Br

Instrument	Requested days	Allocated days	From	To
D16	3	3	01/10/2021	04/10/2021

Abstract:

We have recently shown that hybrid materials can be prepared from organogelators and poly vinyl chloride (PVC) thermoreversible gels. Of interest are Tri-aryl amine (TATA) molecules that self-assemble into long fibrils, which produces electrically-conducting networks in appropriate solvents. While PVC is an excellent insulating polymer, it becomes conducting after incorporation of the TATA organogel in tetra chloroethane. In bromobenzene, we have observed a crystalline form that differs from that in the solid state. Due to the very high content of chlorine atoms in tetrachloroethane, we could not study the crystalline structure by X-ray diffraction because of the very high photon absorption. From thermodynamic investigations, it is suspected that the crystalline form in this solvent is also different, and possibly a TATA/solvent molecular compound is formed. We further suspect that the conductivity in this solvent arises from this crystalline form. To overcome the problem of absorption, neutron diffraction is the appropriate tool. Also, by using hydrogenous solvents and deuterated solvents, one can decide whether the crystal structure consists of a TATA/solvent molecular compound.

This aim of this proposal was the determination of the molecular structure of conducting self-assembled triaryl tri-amine (TATA) fibrils as a function of the solvent type and of the fraction of PVC in hybrid PVC/TATA gels.

We have recently shown [1,2] that hybrid materials can be prepared from organogelators and poly vinyl chloride (PVC) thermoreversible gels (fig.1). Of particular interest are Tri-aryl triamine (TATA) molecules that self-assemble into long fibrils (fig.1), which produces electrically-conducting networks in appropriate solvents [3,4]. Conversely, PVC is an excellent insulating polymer subsequently used for jacketing electric wires. We have observed that PVC gels become conducting after incorporation of the TATA organogel, particularly in tetra-chloroethane (C2H2Cl4; TCE).

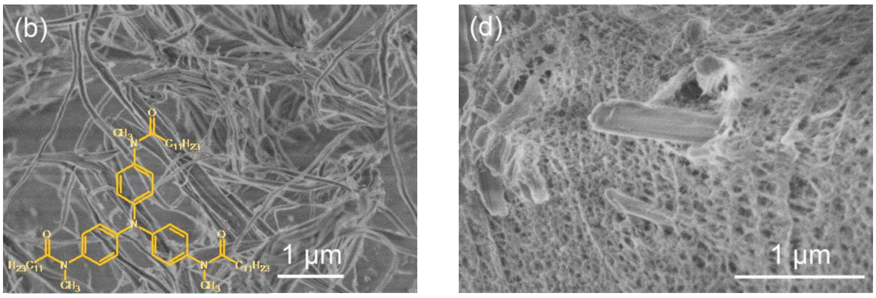

Fig 1: *left: SEM of TATA organogel (molecular structure inserted); right SEM of hybrid gel. Here the TATA fibrils are easily distinguished from the PVC smaller mesh size.*

The hybrid gel is merely a combination of both gels as one can easily distinguish the organogel fibrils from the PVC gel from SEM investigations (fig.1). Thermodynamic investigations reveal that the organogel formation and melting are not altered by the presence of the surrounding PVC network. This conductivity in TCE suggests the occurrence of another crystalline structure, the more so as TATA molecules already possess several crystalline forms in the bulk state and in TATA/bromobenzene organogels (ref. 2). This is reminiscent of the piezo-electric properties of PVDF that are only observed for one crystalline structure [5]. Further the existence of a crystalline form of the type TATA/solvent **molecular compound** is contemplated. The very high content of chlorine atoms made it impossible to study the crystalline structure by X-ray diffraction due to high photon absorption. Conversely, the study of these systems by neutron diffraction is feasible as the scattering length of chlorine atoms is close to that of carbon (0.96 against 0.662). In addition, by using hydrogenous solvents and deuterated solvents one can find out whether the crystal structure does consist of a TATA/solvent molecular compound as the intensity of the peaks is strongly dependent upon the solvent labelling [5].

Neutron diffraction is therefore the appropriate tool for such a study, the more so as the solvent scattering amplitude can be changed. Indeed, the general expression for the diffracted intensity by any kind of radiation for a binary system simply reads:

$$I(q) = \overline{A}_i^2(q)S_i(q) + \overline{A}_j^2(q)S_j(q) + 2\bar{A}_i(q)\bar{A}_j(q)S_{ij}(q) \tag{1}$$

where, depending upon the subscript, $\bar{A}$ is the averaged scattering amplitude, and S(q) the structure factor of the different species, while Sij(q) is a cross-term related to the intermolecular terms between species. In the present case, namely TATA fibrils and a liquid, there are two possible cases: 1) the solvent is totally excluded from the crystal unit cell, then I(q) reduces to:

$$I(q) = \overline{A}_{TATA}^2(q)S_{TATA}(q) + \overline{A}_{solv}^2(q)S_{solv}(q) \tag{2}$$

with obvious meaning for the subscripts.

Equation 2 implies that changing the value of $\bar{A}_{solv}$ will not alter the diffraction pattern of the crystalline TATA fibrils, in particular the relative intensity of the peaks with respect to one another as $S_{solv}(q)$ is the structure factor of a liquid, chiefly featureless except for a broad maximum.

Conversely, if a molecular compound is formed, then the cross-term in relation 1 cannot be discarded any longer. Changing the contrast of the solvent, $\bar{A}_{solv}$, is therefore to alter significantly the diffraction pattern [5].

The occurrence of molecular compounds can be demonstrated by comparing the diffraction patterns obtained by neutron diffraction of systems prepared in hydrogenous and in deuterated solvents as already shown for polymer-solvent molecular compounds [6].

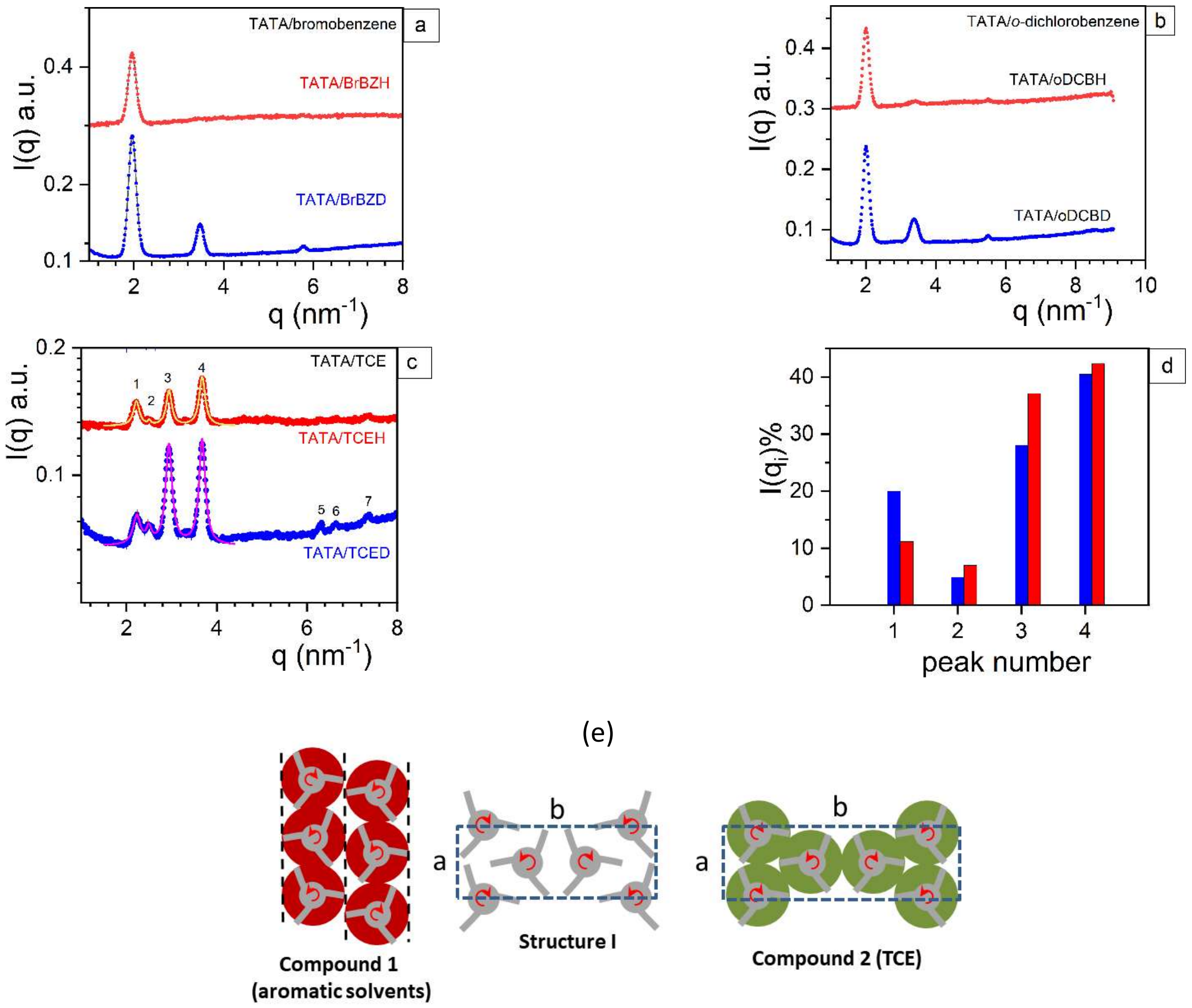

Figure 2: *(a)* neutron diffraction pattern for TATA/bromobenzene (C_{TATA}= 0.07 g/cm^3); *(b)* neutron diffraction pattern for TATA/o-dichlorobenzene (C_{TATA}= 0.07 g/cm^3); *(c)* neutron diffraction pattern for TATA/tetrachlorethane (C_{TATA}= 0.07 g/cm^3). The full lines correspond to a fit with Lorentzian functions (relation 3); *(d)* relative intensities of the first five peaks vs the solvent labeling as determined by a fit with Lorentzian functions (relation 3) *(e):* helix packing in structure I from ref. 7, and tentative for compounds. For compound 1 (left), red, hollow discs are used for representing the solvation shell with bromobenzene; correlation between TATA helices occurs only within the rows highlighted by dashed lines. Rows are not correlated, right and left-handed helices are randomly distributed. For compound 2 (right) a tentative orthorhombic unit cell reminiscent of that of solid I except that the TATA helices are wrapped in a solvent shell (green, hollow discs). For details about the lattice parameters see ref. 7.

Diffraction patterns obtained on D16 for TATA systems in hydrogenous solvents and deuterated solvents are shown in figure 2a-c. There are two types of diffraction patterns depending upon the solvent type. TATA gels in bromobenzene and o-dichlorobenzene display virtually the same diffraction pattern, while that in tetrachloroethane differs significantly.

In all cases, the diffraction pattern for TATA/hydrogenous solvent differs from that in deuterated solvents. This effect is rather strong for systems in bromobenzene and in o-dichlorobenzene, but less pronounced with TCE. In the latter case, the relative intensities of the first 4 peaks depend upon the solvent labelling, which further confirms the occurrence of a molecular compound with this solvent (figure 2d).

The intensity of each reflection is calculated by integration of the peak after performing a fit with a Lorentzian function:

$$I(q) = S_B + \frac{2C}{\pi}\left[\frac{\Delta q}{4(q-q_o)^2+\Delta q^2}\right] \quad (3)$$

where q_o is the position of the peak, Δq is the full width at half maximum, S_B is the residual flat background and C is a calibration constant.

It is worth mentioning that the peaks 5 and 6 are absent in the TATA/TCEH systems unlike in their TATA/TCED counterpart (figure 2c), which is further consistent with the occurrence of a molecular compound.

In addition to the structure put forward for TATA/Bromonebenzene systems (fig. 2e and ref. 2), a new crystalline structure is considered for TATA/TCE gels as shown in figure 2e. It corresponds typically to structure I observed in the bulk state [2] but it incorporates solvent molecules.

All these results have been published in reference 7.

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