Q&A Supra-molecular Chemistry

1) What is supra-molecular chemistry?

Traditional or molecular chemistry focuses in particular on the synthesis of molecules, both small and large, by creating or breaking covalent bonds between atoms. These covalent bonds are called « chemical » bonds as they are strong bonds which, generally speaking, are not considered to be reversible.

In supra-molecular chemistry, the bonds holding together small or large molecules are weaker; these are physical bonds, which are reversible. Supra-molecular chemistry concerns an increasing number of fields in the world of chemistry. Arkema's R&D focuses in particular on its applications in the field of polymers, and, with regard to physical bonds, on hydrogen bonds.

2) What is a hydrogen bond?

Hydrogen bonds are one of the types of reversible physical bonds that are very much present in the world around us. These are the bonds, for example, which hold together in a reversible mode the two strands of the DNA molecule. They also play a role in the structure of proteins. It is thanks to hydrogen bonds that water, made up of very small H_2O molecules, is liquid at ambient temperature, whereas other molecules of a similar or a larger size but without hydrogen bonds, e.g. methane, CO_2, or propane molecules, produce gaseous substances at ambient temperature. Hydrogen bonds impart additional cohesion to solid or liquid bodies, but they can be « undone » or broken up by a trigger factor such as temperature.

3) What is a supra-molecular polymer? On which supra-molecular polymers is Arkema working ?

With the supra-molecular polymers we are working on, we draw a distinction between two major groups among them:

The first group consists of **supra-molecular polymers** formed by the association, between them, of small molecules through (reversible) hydrogen bonds. In this case, our small choice molecules are derived from vegetable oils; they are oily liquids to begin with (before any modification has taken place); our work consists in grafting onto them associative functions to ensure that the small molecules bond together and behave like polymers, i.e. large molecules. Therefore our oily liquids become sturdy solids at ambient temperature, and for some of them only need heating up to return to their liquid state.

With the second group, we start off with **large molecules, which are already polymers in the traditional chemical meaning of the word**, but their modification (through grafting) to make them associative in a reversible mode, will afford new properties. Hence it will be possible to break with the convention which states that to have certain good cohesive properties in the end-materials like mechanical strength and resistance to solvents, traditional polymers must have very long molecules, which makes them barely fluid as well as difficult to process (in particular by hot molding). The supra-molecular approach with polymer molecules made « associative » by hydrogen bonds, allows us to envisage medium size polymer molecules that will remain relatively fluid during processing (open hydrogen bonds which do not impair fluidity), while imparting to the materials outstanding mechanical strength and resistance to solvents (closed hydrogen bonds which impart cohesion).

4) Where does Arkema stand in relation to the work of ESPCI ?

For over 10 years now Arkema has enjoyed a special working relationship with the laboratory run by L. Leibler in a number of fields of polymer science, and, for the past eight years, regarding the application of the concepts of supra-molecular chemistry to polymers. Today the *Matière Molle et Chimie* (MMC) laboratory run by L. Leibler comprises the *Unité Mixte de Recherche* [Mixed Research Unit] between ESPCI [*Ecole Superieure de Physique et de Chimie Industrielles*] and CNRS [French National Center for Scientific Research], within which researchers from both institutions work, as well as Arkema. Two PhD dissertations co-financed by Arkema have already been defended on the subject (Philippe Cordier and Nicolas Dufaure), with a third one (Damien Montarnal) half-way through. In 2004, Arkema decided to establish an industrial research project aimed at developing new innovative products from this research.

Arkema is already developing products from supra-molecular chemistry. We currently have at a pilot stage supra-molecular polymers of two types (see above), i.e. those resulting from the grafting of small molecules to make them associative and behave like a « polymer », and those resulting from the grafting of conventional polymers to improve their performances (strength/fluidity compromise). We are working jointly with the MMC Laboratory on these two types of systems; the work published in Nature in February 2008 by the team of L. Leibler and F. Tournilhac concerns one of the possibilities, for the first group of products, i.e. whereby small molecules are modified. The article published in Nature describes rubber-like materials with astonishing self-repairing properties; with this same group using small molecules of vegetable origin, it is also possible to obtain non rubber-like, hence less elastic, polymers, but also with interesting properties nevertheless, e.g. adhesion. We have already reached a pre-industrial stage with these materials.

5) What is a self-healing and thermoreversible rubber from a supra-molecular assembly ?

The article in Nature describes these materials, obtained by grafting onto small molecules derived from vegetable oils, different associative groups, all of which are capable of forming hydrogen bonds.
The result is astonishing in more ways than one. Indeed, the synthesis process used in this instance leads to materials with rubber-like properties, i.e. capable of significant deformation (over 100%) and reversal of this deformation, while the main raw material is a perfectly liquid oily derivative of vegetable origin. This rubber is thermoreversible as theoretically it is possible to go from the rubber-like solid state to the liquid state and vice versa by heating it up or cooling it down respectively. The most surprising quality of these new materials is that of self-repair: take a piece of elastomer that is cut or cracked, place the two pieces in contact for a few minutes at ambient temperature, and the material will recover properties that are very similar, if not identical, to those of the original material. All this is possible thanks to the assembly structure, in the form of a supra-molecular network, obtained by the careful grafting of associative groups onto small molecules. It is the hydrogen bonds present at multiple points of the assembly that allow the elasticity and the good mechanical strength of the material at ambient temperature.
Additionally, the material retains its properties up to fairly high temperatures. It is also the hydrogen bonds which, by opening up - as they are thermoreversible -, allow the material to become malleable and in some cases fluid at high temperatures. Finally, it is the hydrogen bonds which, being less strong than chemical bonds, allow the material to break up, when stretched significantly, essentially by breaking up these bonds. When the two broken pieces

are stuck together again, the hydrogen bonds can find each other again and close up again without the need for heat, and thus allow the material to self-repair.

6) What are the applications of this technology ?

We can imagine all kinds of applications based on the properties of the products we are working on, be they supra-molecular polymers derived from small molecules bonded together, or traditional polymers that have been modified to be able to bond in a reversible mode.

If we take the former, for example, we have, on the one hand, the supra-molecular self-healing rubber with all the applications that our imagination can dream up once we have a rubber that, if broken, can self-repair on its own, without the need for glue or heat. This would be useful for a large number of articles manufactured from rubber, e.g. joints, seals, office equipment components, clothing parts, decorative parts, etc.

On the other hand, still in the same group, we also have non rubber-like supra-molecular polymers, which behave more like plastics or adhesives. These will be able to make up a new class of products, of vegetable origin, from which we could formulate glues and sealants, or coatings such as paints and varnishes.

Now, if we take traditional polymers modified by supra-molecular chemistry, we can envisage improving mechanical strength and resistance to solvents for many polymers in common use like acrylic glass (PMMA), polyamides, polyesters and many others, without having to sacrifice, as is often the case today, their fluidity during processing.