

## Well-defined Polymer Grafted Fullerene C<sub>60</sub>

C. Mathis\*, F. Audouin, R. Nuffer and C. Picot

Centre National de la Recherche Scientifique  
Institut Charles Sadron, 6 rue Boussingault, 67083  
Strasbourg, France

The incorporation of fullerenes into polymers has attracted much attention as it allows bringing together the specific properties of both in a single material. But, to be able to take advantage of the full potential of such materials it is necessary not only to be able to adjust the amount of fullerene but also to perfectly control the electronic state of the incorporated C<sub>60</sub> and its distribution. That requires pure adducts where a defined number of chains of controlled length are grafted on each fullerene. Such well-defined polymer architectures can be prepared by combining the specific chemical reactivity of C<sub>60</sub> with the good control allowed by anionic or "controlled radical" polymerization.

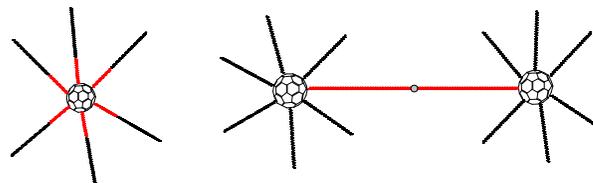
A simple addition of carbanions onto double bonds located on the fullerene is observed in non-polar solvents and a maximum of six chains can be grafted onto C<sub>60</sub> using "living" polystyrene (PS) [1], polyisoprene (PI) or blockcopolymers PI-PS. This upper limit of 6 grafts is a result of the structure of the C<sub>60</sub> (6 pyracyclene units) and the delocalization of the negative charge introduced onto the fullerene each time addition of a carbanionic chain takes place. Hexa-adducts with molar masses ranging from a few thousand to over two millions could be prepared by this route and count among the best defined six-branch polymer stars described up to now in the literature. The "model" aspect of these 6 arm-stars with a C<sub>60</sub> core is attested by the small angle neutron scattering (SANS) measurements, which will be presented. The results obtained in dilute solution for a wide range of molar masses (3 decades) confirm that hexa-adducts are obtained whatever is the length of the grafted chains and have allowed to test the validity of the Cotton-Daoud blob model. Labeling with deuterium - (PS<sub>D</sub>-PS<sub>H</sub>)<sub>6</sub>C<sub>60</sub> - gives access to the chain conformation in the vicinity of the core and a better determination of the inter-particle distribution function in semi-dilute solution and in the solid state.

Glassy (PS) and rubbery (PI) materials with a given concentration of homogeneously distributed fullerene hexa-adducts can so be easily prepared. These materials display interesting photo-optical and non-linear properties both in solution and in the solid state [2, 3].

An important factor to take into account for any potential application is the stability of the above described materials. We will present results concerning the thermal stability of 6-arm stars with a C<sub>60</sub> core.

Each addition of a "living" PS-Li or PI-Li on the C<sub>60</sub> introduces a carbanion onto the fullerene cage and, under our experimental condition (glass apparatus sealed under high vacuum using the break-seal technique) this carbanions are completely stable. So, up to 6 carbanions can be located onto the same conjugated molecule. The particularity of this specific situation is that the reactivity of one of these carbanions will depend on the total number of negative charges present on the same fullerene; the reactivity increases if this number increases. We have

shown that only one of the 6 carbanions located on the fullerene core of the "living" hexa-adducts is reactive enough to open the double bond of a monomer like styrene or isoprene so that a single PS or PI chain grows out from the 6-arm star leading to the formation of "palm-tree" like polymer architectures [5]. The out-growing chain bearing on its end a carbanion, two such structures can be attached together using an adequate coupling agent to form "dumbbells" like architectures. A set of these latter, where two identical six-arm stars (PS<sub>H</sub>)<sub>6</sub>C<sub>60</sub> stars are connected by a deuterated PS chain, has been synthesized and studied by SANS. By this selective labeling of the connecting chain and by adjusting the contrast, it has been possible to characterize the conformation of the link as well as the interaction between the two attached stars in dilute solution.



Scheme 1 : Star and dumbbell like blockcopolymers.

By combining recent advances in the field of Atom Transfer Radical Polymerization (ATRP) with the easy addition of radicals onto fullerene C<sub>60</sub>, an alternative synthetic route toward model polymer adducts could be developed. Halogen terminated PS chains of low polydispersity prepared by ATRP can be converted to macro-radicals using an atom transfer reaction and so attached in a controlled way to the fullerene. We have found conditions where only di- and tetra-adducts are formed. The characterization of these star-shaped macromolecules will be presented and the particular reaction mechanism discussed.

A further step toward more complicated polymer architectures can be done by combining radical and carbanion addition on fullerene. The principle consist of preparing first di- and tetra-adducts by grafting macro-radicals followed by additional "saturation" of the C<sub>60</sub> core by reaction with a "living" PS-Li or PI-Li. Through this route, asymmetric- [2(4) PS chains of one length + 4(2) PS chains of a different molar masse) and hetero-stars [2(4) PS + 4(2) PI] have been obtained.

The synthesis of blockcopolymer architectures, where incompatible polymer segments are attached in various ways to fullerenes, may lead to new materials. PS-PI block copolymers are known to form lamella, cylindrical, spherical, etc... structures. It should then become possible to develop materials where the fullerene is not longer homogeneously dispersed in the matter, but becomes located in specific domains ordered in space.

### References :

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