

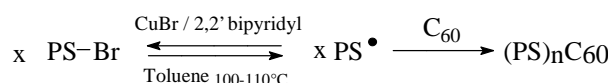
Controlled Macro-radical Grafting onto Fullerene C₆₀

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The addition of radicals on the 6-6 bonds of C₆₀ counts among the earliest observed reactions in fullerene chemistry [1]. The fullerene being highly reactive against radicals, this reaction is somewhat difficult to control. Nevertheless, the incorporation of fullerene in a polymer by radical polymerization of a monomer in the presence of C₆₀ has been studied by several groups [2-6]. If fullerene is indeed incorporated in this way, the mechanism is not completely understood and the structure of the polymer not controlled. The synthesis of well defined polymer architectures by macro-radical grafting has attracted much less attention even so "controlled" radical polymerization opens new possibilities. Atom Transfer Radical Polymerization ATRP [7], for example, allows to prepare polymer chains of controlled molar masses and low polymolecularity bearing on there end a bond which can be broken to produce macro-radicals able to add to a fullerene [8]. We will show in this report that it is possible to use an atom transfer mechanism to synthesis well defined polymer architectures such as polymer stars with a C₆₀ core [9].

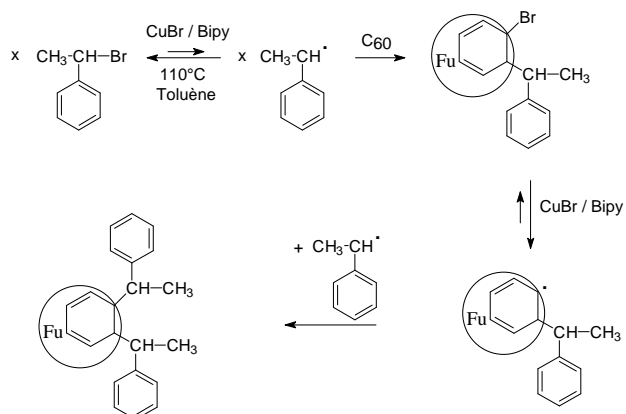
Polystyrene PS, polymethylmethacrylate PMMA and polyethyleneoxyde-block-polystyrene PEO-PS chains of low polydispersity have been produced by ATRP. These Br-terminated chains are converted in a reversible way to macro-radicals by an atom transfer mechanism.



In the presence of C₆₀, the macro-radicals add to the fullerene. But, if a 10 fold excess of C₆₀ over PS-Br is used, all the polymer is converted to a pure di-adducts. The addition of two chains in conditions where only mono-adducts are expected points to a specific mechanism favoring the addition of a second PS radical on an already mono-grafted fullerene over the addition of this macro-radical on a double bond of an unreacted C₆₀. Furthermore, what ever is the ratio PS-Br/fullerene, only addition products with an even number of chains are obtained. This peculiar mechanism results from the well known reduced stability of a direct bond to C₆₀ as compared to the corresponding "classical" bond. The addition of a macro-radical on a double bond introduces a radical onto the fullerene and, in the presence of CuBr₂ this radical is stabilized by the formation of a C₆₀-Br bond. But, as this latter bond is much easier to brake as the PS-Br bond, enough PS-C₆₀ radicals will always be present so that if a PS[•] radical is formed, it will preferably recombine with PS-C₆₀ to form a di-adduct rather than add to another double bond.

If the proposed mechanism is correct, the final polymers should contain no Br. To verify this point, we reacted under the same conditions, 1-bromophenylethane with C₆₀ and submitted the resulting adducts to elemental analysis. A Br content of about 0.2% was found as compared to the nearly 9% expected for a mono-adduct CH₃-CH(Ph)-C₆₀-Br. This confirms the validity of the

proposed mechanism.



We have produced pure di-adducts (PS)₂C₆₀ and (PEO-block-PS)₂C₆₀ as well as pure tetra-adducts (PS)₄C₆₀ and (PEO-block-PS)₄C₆₀. By reacting a di-adduct (PSa)₂C₆₀ with a PSb-Br of different chain length, asymmetric stars (PSa)₂C₆₀(PSb)₂ could be prepared by this macro-radical grafting.

A further step toward more complicated polymer architectures has been done by combining radical and carbanion addition on fullerene. Indeed, we have shown that up to 6 "living" PS-Li or PI-Li can add to a C₆₀ [10]. So, by reacting di- and tetra-adducts prepared by macro-radical grafting with an excess of "living" PS-Li or PI-Li, respectively four or two additional chains have been added to the fullerene core. Through this route, asymmetric- [2(4) PSa chains of one length + 4(2) PSb chains of a different molar masse) and hetero-stars [2(4) PS + 4(2) PI] have been obtained.

A-B block copolymers where A and B are incompatible are known to self-organize to form lamella, cylindrical, spherical, etc... structures. The synthesis of a variety of hetero-stars, where incompatible polymer segments are attached to a fullerene core, should allow to develop materials where the fullerene is not just homogeneously dispersed in the matter, but becomes located in specific domains ordered in space.

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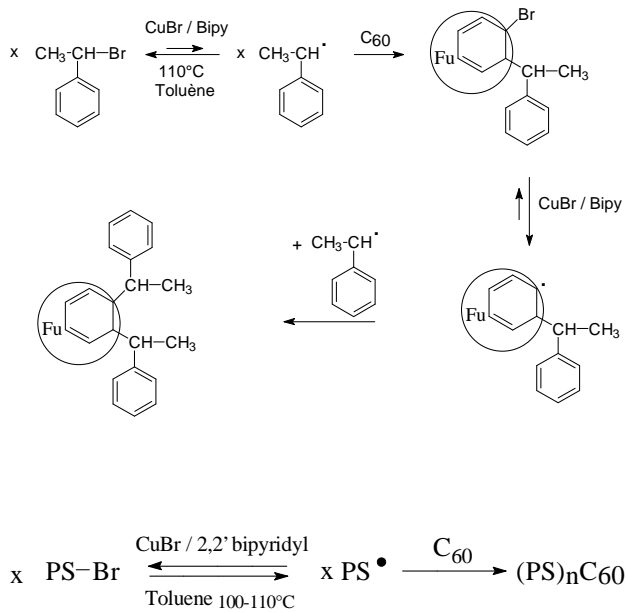


Figure 1 : Di-adduct $(\text{PS})_2\text{C}_{60}$ $M_w = 47000$ obtained by reacting PS-Br $M_w = 23400$ with C_{60} at 100°C in toluene in the presence of $\text{CuBr}/2,2'$ bipyridyl.

