

Spatial Organisation of Fullerene C_{60} in a Polymer Matrix.

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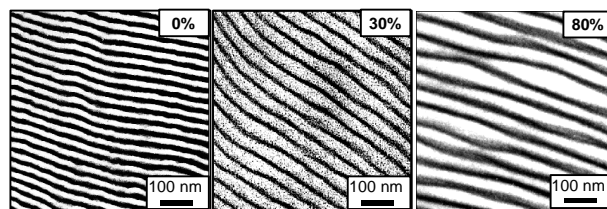
Fullerenes exhibit unique electronic properties, which are of interest for many applications in the field of all-plastic electronics. The main drawback for an extended use of fullerenes lies in their poor solubility and miscibility, which prevents efficient dispersion in a polymer matrix on a nanometric scale. The controlled grafting of polymer chains onto C_{60} constitutes a good way to overcome this difficulty. Indeed, if the exact number of grafted chains can be well controlled, the electronic properties of all the incorporated C_{60} will be defined and identical (same number of opened double bond). In addition, the attached polymer will provide compatibility, avoid aggregation and, if the length of the chains can be varied, the distance between the fullerene molecules can be adjusted. The presence of polymer grafts not only allows dispersing fullerenes homogeneously in a matrix, but should also give access to more sophisticated spatial distributions using the self-organization of block-copolymers.

In the last years we have developed synthetic routes toward well-defined polystyrene (PS) stars with a C_{60} core bearing exactly 2, 4 [1] or 6 arms [2] of adjustable length. These macromolecules exhibit interesting photo-physical [3] and nonlinear optical properties [4]. If the grafts are long enough ($> 15000 - 20000$), self-standing films can be cast from a solution. Small angle neutron scattering has shown that the distribution of C_{60} in them is homogeneous, that no aggregation takes place and that the distance between the fullerene cores is directly correlated to the molar mass of the polymer chains [5]. For small stars, blending with some high molar mass PS is necessary to form films. The optical limiting and nonlinear optical absorption properties of these polymer matrix made of $(PS)_x C_{60}$ stars have also been studied [6].

It is known that block-copolymers made of two incompatible sequences such as PS and polyisoprene (PI) self-organize in the solid state in order to minimize the contact between the incompatible blocks. Depending on the respective length of the two blocks, well-defined periodic and ordered microstructures such as lamellae and cylinders are formed in the matrix via self-assembling. It has also been reported that, if homo-PS or PI are mixed with a PI-b-PS block-copolymer, the homo-polymer is incorporated only in the lamellae (cylinder) of same chemical nature [7]. We thus envisioned the possibility to control the spatial arrangement of C_{60} by forming binary blends of $C_{60}(PS)_6$ stars and PI-b-PS block-copolymers having sequences of similar molar masses such as to form lamellar structures.

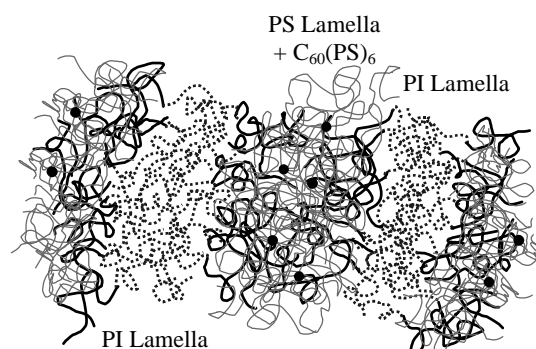
The structure of the samples was analyzed using Small Angle X-ray Scattering (SAXS), Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). Our results demonstrate that the $C_{60}(PS)_6$ stars are indeed confined in the PS lamellae of a PS-b-PI block-copolymer. The confinement leads to a progressive swelling of the PS lamellae with increasing wt% of stars with a C_{60} core. We also observed that the

lamellar microstructure is preserved for $C_{60}(PS)_6$ concentrations of up to 80wt%.



Evolution of the lamellar structure upon blending a PS-b-PI (30K-30K) with various weight % of $C_{60}(PS)_6$ (60K). PI lamellae stained black with OsO_4

However, with increasing $C_{60}(PS)_6$ concentration in the blends, we observe an increase of the fluctuations in lamellar spacing of the PS domains. The spatial organization is schematically represented below.



The chemistry described in ref. [2], based on the addition onto a double bond of C_{60} of the terminal carbanion of a "living" polymer chain prepared via anionic polymerization allows also to graft PI-b-PS block-copolymers onto C_{60} . Six-arm stars $(PI-b-PS)_6 C_{60}$ consisting of a central part made of PS surrounded by an outer shell made of PI, have been prepared and cast into films. In the case where the length of the PI and PS sequences are about the same, a lamellar structure is observed. Due to the architecture of these $(PI-b-PS)_6 C_{60}$ stars, the C_{60} core is located around the middle of the PS lamellae and no fullerene is present in the PI lamellae. So, the polymer matrix consists of "planes" of fullerenes separated by a distance of typically 10-100 nm depending on the length of the grafts.

A further step toward better defined fullerene "planes" with shorter distances between the C_{60} could be done by grafting directly the two incompatible chains onto the fullerene. In this case the C_{60} would be located at the interface of the lamellae and the distance between them function of the area occupied by each chain at this interface. Work in this direction is in progress.

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