Application of Living Ionic Polymerization Reactions to the design of Functional NanoObjects

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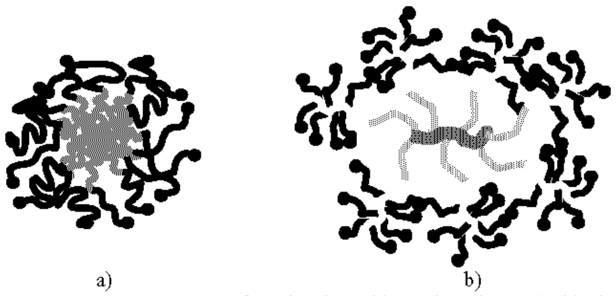
Introduction

An important challenge in polymer-based advanced materials aimed at the fabrication of individualized functional molecular objects exhibiting specific and well-defined properties to be used as nano-devices. The design of such objects at the molecular scale can be achieved using two distinct and complementary main routes. The first one is based on the self-assembly of elementary polymer chains, typically block copolymers, into well-organized nanoscale superstructures, such as micelles, cylinders, vesicules, etc.. The second strategy involves the construction of single giant hyperbranched macromolecules with controlled architecture and topology. In contrast to linear macromolecules which form highly diffuse random coils which can interpenetrate at elevated concentration, macromolecular assemblies and hyperbranched macromolecules are characterized by density profiles showing high monomer units concentration, a precise contour and shape and a capacity to remain as isolated entities even at high concentration or in bulk.

The synthesis of both types of precise molecular objects requires the use of well controlled "living" polymerization and functionalization reactions that allow the control of the parameters (molar masses, molar mass distribution, chemical composition monomer distribution, chain end functionality,...) of the elementary chains or blocks that will serve as the constitutive parts of the final macromolecular objects. On this basis we can expect the preparation of nano-devices showing a good definition in structure and dimensions and exhibiting an homogeneous behavior toward the environment and toward external stimuli.

Our presentation will be focused on the design of comb copolymers, that can behave as macromolecular object.



Scheme 1. Two types of molecular objects based on a) block copolymer chain assemblies and b) single hyperbranched macromolecules

Experimental

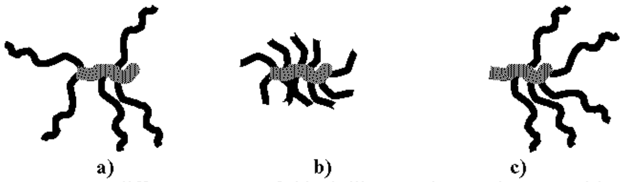
The synthesis of comb polymers by the grafting of anionically prepared living polymer chains onto a poly(chloroethylvinylether) backbone has already been described [1,2]. The specific changes applied for the preparation of the different type of combs with block-like structures, see Scheme 2, will be described in detail in forthcoming publications[3,4].

AFM images were recorded in air with a Dimension microscope (Digital Instruments, Santa Barbara, CA). Samples were prepared by solvent casting on highly oriented pyrolytic graphite. Static and dynamic scattering measurements were performed using an ALV (Langen-FRG) apparatus as previously described.[5]

Results and discussion

Comblike polymers can be visualized as unimolecular micelles, each elementary chain (branch) been attached at one end to a central backbone This permanent link constitutes an advantage since in contrast to micelles made from linear block copolymers the corresponding comb structures are stable and preserve their integrity, independently of the presence of additives, the quality of the solvent (good or selective), the temperature and the concentration.

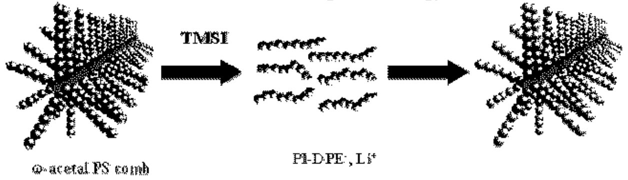
In this series comblike copolymers with diblock branches, scheme 2 a), constituted by the association of incompatible macromolecular blocks, for example polystyrene (PS) and polyisoprene (PI), represent a relatively close model of conventional micelles that are formed by self-assembly of diblock copolymers. They can be readily prepared for example by grafting living anionic diblock polyisoprene-*b*-polystyryl lithium chains onto a reactive backbone. The later is a poly(chlorethyl vinyl ether) (PCEVE) chain of controlled $\overline{\mathrm{DP}}_n$ prepared by living cationic polymerization. This yields a PS core PI shell structure, **C1**, corresponding to PS-*b*-PI micelles in a selective solvent of the PI blocks.



Scheme 2. different types of block-like comb copolymers with branches a) randomly distributed, b) diblock –type, c) forming block-combs.

The reverse diblock branch structure **C2** with styrene blocks at the periphery can be synthesized in the same way by reacting living polystyrene-*b*-polyisoprenyl lithium chains end-capped with diphenyl ethylene onto the chloroether functions of the CEVE units.

Grafting yields, corresponding to the fraction of diblock branches per CEVE units ranges from 0.6 for **C1** to about 0.9 for **C2**. In order to improve the grafting efficiency with **C1**, the later was prepared in two steps as described in Scheme 3. Coupling of the external PI block was achieved by reacting DPE end-capped PILi onto the acetal ended PS branches of a PS comb after activation by TMSI. Grafting yields close to 100% in PI blocks are reached using this strategy.



Scheme 3 : Sketch of the two step synthesis of PCEVE-*g*-(PS-*b*-PI) comb copolymers

An AFM image of **C1** combs is shown in Figure 1. It clearly shows individual macromolecules with a core-shell morphology constituted of a hard PS core (dark brown) surrounded by soft PI shell (white).

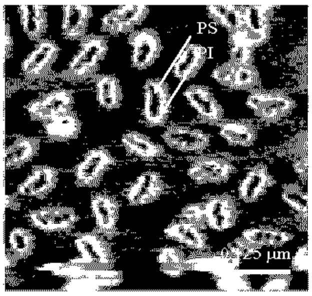


Figure 1 AFM phase image of $\mathrm{PCEVE_{230}}$-*g*-($\mathrm{PS_{106}}$-*b*-$\mathrm{PI_{115}}$) combs

Comparison of the hydrodynamic radius (R_H) of the **C1** combs determined by DLS in THF a good solvent of the two blocks and in hydrocarbons, selective of the external PI blocks, shows that the size of the diblock combs strongly varies with the solvent quality, Table 1, and temperature, Table 2, due to the reversible contraction/expansion of the PS core, which can even completely collapse while the comb macromolecules remain as fully soluble core-shell unimers in the different media.

Table 1: Evolution of the hydrodynamic radius (R_H) of PCEVE$_{230}$-*g*-(PS$_{106}$-*b*-PI$_{115}$) combs with the solvent quality at 25°C

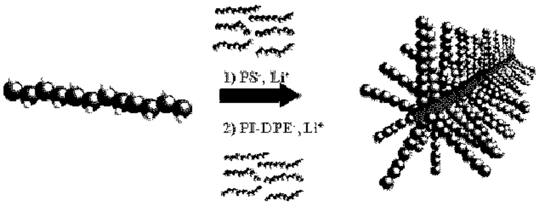
solvent	THF	Heptane	Decane	Cyclohexane
R_H (nm)	26.3	25.7	23.5	20.2

Table 2: Evolution of the hydrodynamic radius (R_H) of PCEVE$_{230}$-*g*-(PS$_{106}$-*b*-PI$_{115}$) combs with the the temperature in cyclohexane

Temperature °C	8	25	35	55
R_H (nm)	20.2	23.2	24.5	25

Other types of block-like comb structures, see a) and c) scheme 2, are also of interest since in a selective solvent or in bulk they can self-organize intra-molecularly to form nano-domains within the macromolecule and/or inter-molecularly, yielding aggregates and possibly large micelles, as well as biphasic structures in the bulk.

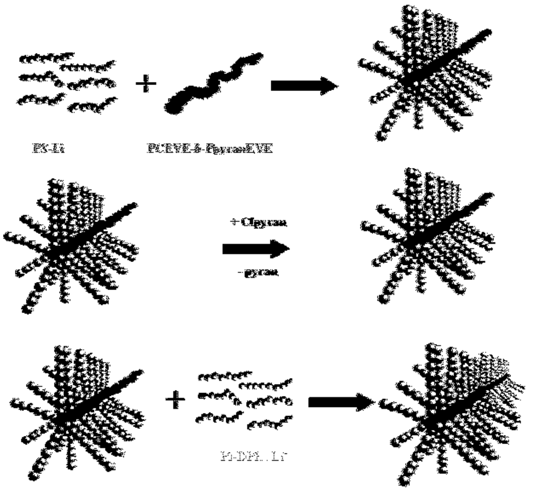
Comb copolymers with randomly distributed PI and PS branches can be easily prepared, by adding the corresponding living PILi and PSLi polymers in two successive steps (Scheme 4).



Scheme 4 : sketch for the synthesis of combs with randomly distributed PS and PI branches

Interestingly, these structures are soluble both in selective solvents of PS (DMF) and PI (hydrocarbons) suggesting that each type of branch can alternatively protect the other ones, by developing interactions with the solvent. For PS and PI branches of about the same length ($\overline{DP_n}$ about 90-100) no micelle formation was noticed in solution while a micro-phase segregation yielding a lamellar morphology was observed in the bulk.

The synthesis of Janus-type PS-comb-*b*-PI-comb is more complex. It involves first the synthesis of a diblock backbone bearing two types of reactive functions that can be selectively activated and protected. In a first grafting step PSLi are reacted with the active block of the backbone polymer. Then in a second, after deprotection/activation of the second backbone block the grafting of a second set of PILi is achieved.



Scheme 5 : sketch for the synthesis of (PCEVE-*g*-PS)-*b*-(PCl-pyranEVE-*g*-PI)

These super diblock structures formed by the association of two combs form spherical micelles in a selective solvent of one of the comb as illustrated by the AFM image obtained from deposit of the comb-PS-b-comb-PI from a selective solvent of PI.

Table 3: Evolution of the hydrodynamic radius (R_H) of (PCEVE-*g*-PS)-*b*-(PCl-pyranEVE-*g*-PI) combs in a good and selective solvent quality at 25°C

solvent	THF	Cyclohexane
R_H (nm)	30	80

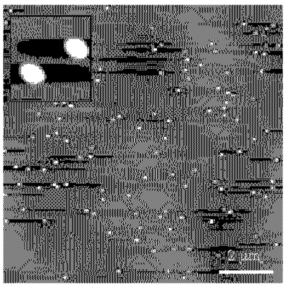


Figure 2 :AFM topographic image (10x10 µm^2) of the (PCEVE$_{380}$-*g*-PS$_{60}$)-*b*-(PCl-pyranEVE$_{370}$-*g*-PI$_{60}$).

Conclusions

The synthesis of block-like comb copolymers is an interesting alternative to conventional micelles and other self-assembled superstructures. Combs are much more stable than systems based on self-assembly processes. Moreover it is easier to control their size and shape by adjusting the backbone and graft dimensions. It is for example also possible to get in similar conditions spherical to very long cylindrical combs unimolecular "micelles" simply by varying the backbone length.

References

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