

## Application of Living Ionic Polymerizations to the Design of AB-Type Comb-like Copolymers of Various Topologies and Organizations

David Lanson, Fumi Ariura, Michel Schappacher, Redouane Borsali, and Alain Deffieux\*

Laboratoire de Chimie des Polymères Organiques, UMR CNRS-ENSCP 5629, Université Bordeaux I France

Received September 28, 2006; Revised October 30, 2006

**Abstract:** Living anionic and cationic polymerizations have been combined to prepare various types of comb-like copolymers composed of polystyrene (PS) and polyisoprene (PI) blocks, with a precisely controlled architecture. According to the relative placement of these elementary building blocks, combs with randomly distributed PS and PI or with poly(styrene-*b*-isoprene) diblock branches (**I** & **II**, respectively) can be prepared. The reaction procedure initially includes the synthesis of a poly(chloroethylvinyl ether) using living cationic polymerization, which is used as the reactive backbone to successively graft  $\text{PS}\cdot\text{Li}^+$  and  $\text{PI}\cdot\text{Li}^+$  or  $\text{PI-}b\text{-PS}\cdot\text{Li}^+$  to obtain structures (**I**) or (**II**). The synthesis of Janus-type PS-comb-*b*-PI-combs (**III**) initially involves the synthesis of a diblock backbone using living cationic polymerization, which bears two distinct reactive functions having either a protected or activated form. Living  $\text{PS}\cdot\text{Li}^+$  and  $\text{PI}\cdot\text{Li}^+$  are then grafted, in two separate steps, onto each of the reactive functions of the backbone, respectively.

**Keywords:** , living anionic polymerization, comb-like copolymers, topology, organization, polystyrene, polyisoprene.

### Introduction

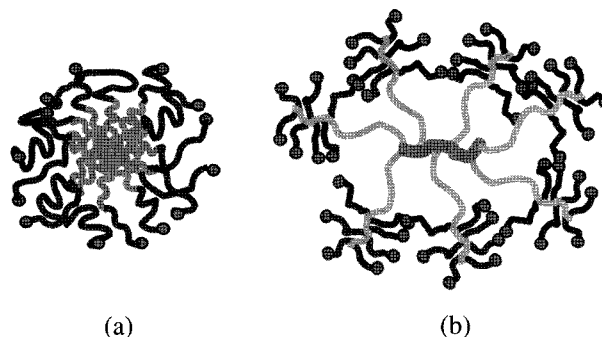
An important challenge in polymer-based advanced materials aimed at the fabrication of individualized functional molecular objects exhibiting specific and well-defined properties to be used as nano-devices. The design of such objects at the molecular scale can be achieved using two distinct and complementary main routes. The first one is based on the self-assembly of elementary polymer chains, typically linear block copolymers, into well-organized nanoscale superstructures,<sup>1-6</sup> such as micelles (Scheme I(a)), cylinders, vesicles, etc. The second strategy involves the construction of single giant macromolecules with specific architecture and controlled internal topology such as combs<sup>7-9</sup> or hyperbranched polymers<sup>10-14</sup> (Scheme I(b)).

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 relative precise contour and shape, and a capacity to remain as isolated entities even at high concentration in solution or in the solid bulk (Figure 1).

This specific characteristic is illustrated by the comparison of data collected in Table I for a linear and comb polysty-

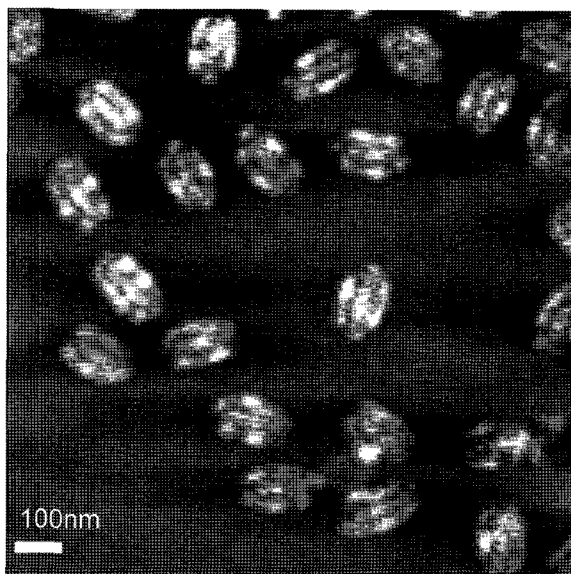
rene of same molar mass ( $M_w = 7.10^6$  g/mol). Assuming a spherical shape for the two isolated macromolecules  $R_g$  decreases by a factor of 4 and density increases by about 60 when going from the linear to the comb polystyrene.

The synthesis of molecular objects with precise shape and dimensions requires the use of well-controlled “living” polymerization and functionalization reactions that should allow the control of the main parameters (molar masses, molar mass distribution, chemical composition, monomer distribution, chain end functionality,...) of the elementary chains or blocks that are constitutive parts of the final macromolecular objects. On this ground polymer based nano-



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

\*Corresponding Author. E-mail: deffieux@enscpb.fr



**Figure 1.** Topographic AFM image of isolated PS comb molecules (backbone  $\overline{DP}_n=300$ , PS branch  $\overline{DP}_n=200$ ) deposits on graphite (HOPG) surface.

**Table I. Influence of Chain Architecture on the Dimensions and Characteristics of Macromolecules (in Toluene): Linear Versus Ps Comb of Same Mw:  $7 \times 10^6$  g/mol**

Chain Architecture	$R_g$ (nm)	Density (g/cm <sup>3</sup> )
Linear PS	134	1.2
Comb PS (764/81) <sup>a</sup>	34	69

<sup>a</sup>Respective  $\overline{DP}_n$  of backbone and PS branches.

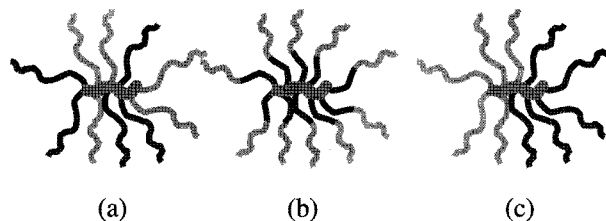
devices having well controlled architecture and dimensions, and exhibiting an homogeneous behavior and response toward the environment and external stimuli, can be expected.

This paper will focus on comb-type macromolecules that in many aspects behave already as individual macromolecular entities in solution and in the bulk. The influence of internal organization of block-like type comb copolymers on their behavior is in particular examined.

## Experimental

The synthesis of comb polymers by the grafting of anionically prepared living polymer chains onto a poly(chloroethylvinylether) backbone has already been described.<sup>15,16</sup> The specific changes applied for the preparation of the different type of combs with block-like structures, see Scheme II, has been described for combs with diblock PI-*b*-PI branches<sup>17</sup> and will be the subject of forthcoming publications for combs with randomly distributed PS and PI branches and for comb-PS-*b*-comb-PI Janus type copolymers.<sup>18,19</sup>

AFM images were recorded in air with a dimension microscope (Digital Instruments, Santa Barbara, CA). Samples



**Scheme II.** Different types of block-like comb copolymers with branches. (a) randomly distributed (**I**), (b) diblock-type (**II**), and (c) comb A-*b*-comb B (**III**).

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.<sup>20</sup>

## Results and Discussion

Comblike polymers can be visualized as unimolecular micelles, each elementary chain (branch) being attached at one end to a central backbone. This permanent link constitutes an advantage since in contrast to multimolecular micelles made from the assembly of linear block copolymers the corresponding comb structure is stable and preserve its integrity, independently of the presence of additives, the quality of the solvent (good or selective), the temperature and the concentration. Three different types of polystyrene (PS) and polyisoprene (PI) based block-like copolymers have been prepared, (**I**) with PS and PI branches randomly distributed along the backbone, (**II**) with PS-*b*-PI diblock branches, and (**III**) with PS and PI branches introduced in two sequences along the backbone, to form comb-PS-*b*-comb-PI, see Scheme II(c). Their solution and bulk properties were then investigated.

In this series comblike copolymers with diblock branches, Scheme II(a), constituted by the association of two incompatible macromolecular blocks, for example, PS and PI, represent a relatively close model of conventional micelles, which are formed by self-assembly of the corresponding diblock copolymers. They can be readily prepared by grafting living anionic diblock PI-*b*-polystyryl lithium (PI-PS, Li<sup>+</sup>) chains onto a reactive backbone bearing electrophilic sites, such as the previously reported poly(chloroethyl vinyl ether) (PCEVE) chain. The later polymer (**II**) can be readily obtained by a living cationic polymerization process, which allows control of both the backbone dimensions from low to high molar mass (up to 100,000 g/mol) and the polydispersity. Moreover, the coupling reaction used to anchor the anionic PS ends onto the side chloroethoxy groups of the PCEVE was shown to be a rapid and very selective process. It yields combs constituted of a central PS core and a peripheral PI shell, an organization closely corresponds to PS-*b*-PI micelles formed in a selective solvent of the PI

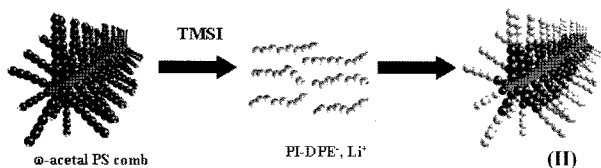
blocks.

The reverse diblock branch structure (II') with styrene blocks at the periphery can be synthesized in a similar way by reacting living PS-*b*-polyisoprenyl lithium chains end-capped with diphenylethylene onto the chloroether functions of the CEVE units.

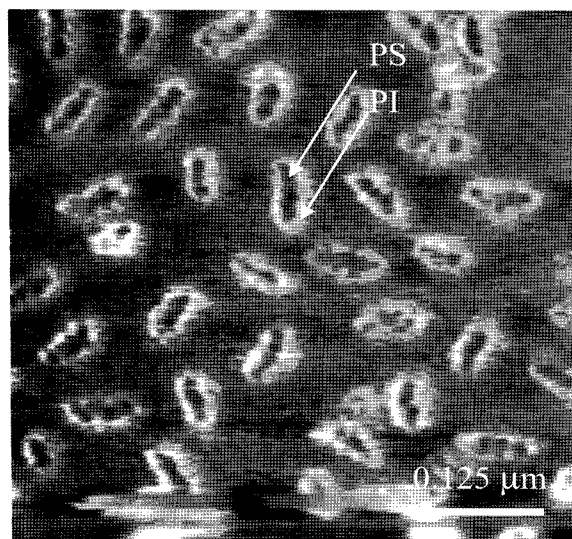
Grafting yields, which correspond to the number of diblock branches per 100 CEVE unit ranges from 60% for (II) to about 90% for (II'). In order to improve the grafting efficiency for (II), the later was prepared in two steps following a different strategy described in Scheme III. In a first step a PS comb bearing acetal groups at each PS branch ends was prepared. Coupling of the PI block at the PS end was then achieved by reacting DPE end-capped PI, Li<sup>+</sup> onto the acetal functions after their transformation by TMSI into  $\alpha$ -iodoether functions. Grafting yields close to 100% in PI blocks were reached using this strategy.

An AFM image of combs (II) is shown in Figure 2. It clearly shows individual macromolecules of homogeneous size (average length 65 nm, width = 35 nm) with a core-shell morphology constituted of a hard PS core (dark brown) surrounded by soft PI shell (white).

Comparison of the hydrodynamic radius ( $R_H$ ) of combs



**Scheme III.** Sketch of the two steps synthesis of PCEVE-*g*-(PS-*b*-PI) comb copolymers.



**Figure 2.** AFM phase image of PCEVE<sub>230</sub>-*g*-(PS<sub>106</sub>-*b*-PI<sub>115</sub>) combs on HOPG substrate obtained by evaporation of a diluted copolymer solution in dichloromethane.

(II) determined by DLS in THF a good solvent of the two blocks and in hydrocarbons, a selective solvent of the external PI blocks, shows that the size of the comb-like diblocks strongly varies with the solvent quality, Table II, as well as with the temperature, in particular in cyclohexane a  $\Theta$  solvent of the PS core and a good solvent of the PI shell, Table III. This can be attributed to the reversible contraction/expansion of the PS core, which can even completely collapse while the comb macromolecule remains fully soluble as a core-shell unimer in the different media examined.

Other types of block-like comb structures, see (a) and (c) Scheme II, are also of interest since in a selective solvent or in bulk they can self-organize intramolecularly to form nano-domains within the macromolecule and/or intermolecularly, thus forming aggregates and possibly very large micelles, as well as biphasic morphologies in the bulk.

Comb copolymers with randomly distributed PI and PS branches (I) can be easily prepared by adding the corresponding living PI, Li<sup>+</sup> and PS, Li<sup>+</sup> polymers in two successive steps (Scheme IV).

Interestingly, these structures are soluble both in selective solvents of PS (DMF) and PI (hydrocarbons), without any noticeable aggregation phenomenon. This suggests that each type of branches can alternatively protect the other one by developing selective interactions with the solvent, in a quite similar way than micelles of linear diblock can reverse their core-shell structure as a function of the solvent quality. For such combs with random PS and PI branches of about the same length ( $\overline{DP}_n$  of PS and PI branches of about 90-100) a

**Table II.** Evolution of the Hydrodynamic Radius ( $R_H$ ) of PCEVE<sub>230</sub>-*g*-(PS<sub>106</sub>-*b*-PI<sub>115</sub>) Combs with the Solvent Quality at 25 °C

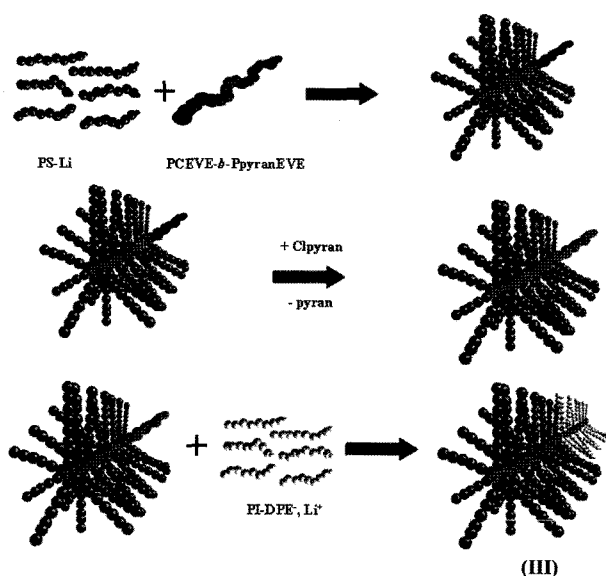
Solvent	THF	Heptane	Decane	Cyclohexane
$R_H$ (nm)	26.3	25.7	23.5	20.2

**Table III.** Evolution of the Hydrodynamic Radius ( $R_H$ ) of PCEVE<sub>230</sub>-*g*-(PS<sub>106</sub>-*b*-PI<sub>115</sub>) Combs with the the Temperature in Cyclohexane

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



**Scheme IV.** Sketch for the synthesis of combs with randomly distributed PS and PI branches.



**Scheme V.** Sketch for the synthesis of (PCEVE-*g*-PS)-*b*-(PCI-pyranEVE-*g*-PI).

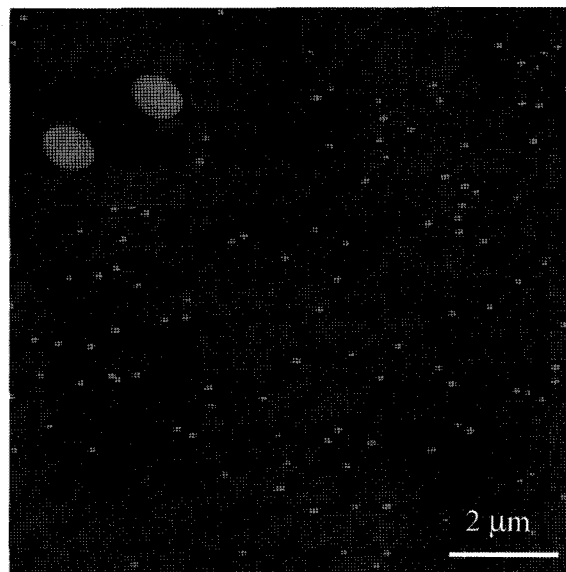
micro-phase segregation yielding a lamellar morphology was observed in the bulk.

Finally, Janus-type PS-comb-*b*-PI-comb structure (III) were prepared although their synthesis requires a longer and more complex approach (Scheme V).<sup>19</sup> It involves first the synthesis by living cationic polymerization of a diblock backbone bearing two types of reactive functions i.e., a PCEVE block and a poly(pyranoyloxyethyl vinyl ether) block that can be selectively obtained in a protected or activated form. Then, in a first grafting step PS<sup>Li</sup> was reacted with the active block bearing the CEVE function while the poly(pyranoyloxyethyl vinyl ether) block remained untouched. In a second step, after deprotection and then activation of the functions of the second backbone block, which consists in an exchange of pyranoyloxyethyl group by chlorobutylpyranoyloxyethyl ones, the grafting of PFLi<sup>+</sup> chains was achieved to yield the targeted PS-comb-*b*-PI-comb.

This diblock comb ( $R_H=30$  nm in THF a good solvent of both constitutive combs) was found to yield large spherical micelles in a selective solvent of one of the two constitutive monomer units ( $R_H=70$  nm in heptane a selective solvent of PI) (Table IV) as well as in the solid, as illustrated by the AFM image (Figure 3) of spherical to ovoid object (length 120 nm, section 90 nm) obtained from deposit of the comb-PS-*b*-comb-PI from heptane.

**Table IV.** Evolution of the Hydrodynamic Radius ( $R_H$ ) of (PCEVE-*g*-PS)-*b*-(PCI-pyranEVE-*g*-PI) Combs in a Good and Selective Solvent Quality at 25 °C

Solvent	THF	Cyclohexane
$R_H$ (nm)	30	80



**Figure 3.** AFM topographic image ( $10 \times 10 \mu\text{m}^2$ ) of the (PCEVE<sub>390</sub>-*g*-PS<sub>60</sub>)-*b*-(PCI-pyranEVE<sub>370</sub>-*g*-PI<sub>60</sub>).

## Conclusions

The synthesis of block-like comb copolymers of different topologies open new opportunities in the design of nanometric size macromolecular objects. According to their internal organization, in particular the repartition of the two types of constitutive blocks these objects can behave as isolated unimolecular micelles or can aggregate to form larger micelles. They constitute an interesting alternative to conventional micelles and other self-assembled superstructures. Core-shell combs are much more stable than multimolecular systems based on self-assembly processes. Moreover it is possible to control their size and shape by adjusting the backbone and graft dimensions. It is, for example, possible to get in similar conditions spherical to very long cylindrical combs unimolecular “micelles” simply by varying the backbone length. Further investigation of the properties of these nanosize macromolecules are in progress.

## References

- (1) D. E. Discher and A. Eisenberg, *Science*, **297**, (5583) 967 (2002).
- (2) Ikkala and G. Ten Brinke, *Chem. Commun.*, **10**, 2131 (2004).
- (3) H. Klok and S. Lecommandoux, *Adv. Mater.*, **13**, 1217 (2001).
- (4) T. P. Lodge, *Macromol. Chem. Phys.*, **204**, 265 (2003).
- (5) G. Riess, *Prog. Polym. Sci.*, **28**, 1107, 1170 (2003).
- (6) P. L. Soo and A. Eisenberg, *J. Polym. Sci., Polym. Phys.*, **42**, 923 (2004).
- (7) K. Ishizu, *Polym. J.*, **36**, 775 (2004).
- (8) K. Ishizu, K. Tsubaki, J. Satoh, and S. Uchida, *Designed Monomers and Polymers*, **5**, 23 (2002).

- (9) J. Pyun, T. Kowalewski, and K. Matyjaszewski, *Macromol. Rapid Comm.*, **24**, 1043 (2003).
- (10) A. Hirao, M. Hayashi, S. Loykulnant, K. Sugiyama, S. W. Ryu, and N. Haraguchi, *Prog. Polym. Sci.*, **30**, 111 (2005).
- (11) K. Ishizu, A. Mori, and T. Shibuya, *Designed Monomers and Polymers*, **5**, 1 (2002).
- (12) J. Bernard, M. Schappacher, A. Deffieux, P. Viville, R. Lazzaroni, M. T. Charreyre, and M. Charles, *Bioconjugate Chem.*, **17**, 6 (2006).
- (13) J. Bernard, M. Schappacher, P. Viville, R. Lazzaroni, and A. Deffieux, *Polymer*, **46**, 6767 (2005).
- (14) M. Schappacher and A. Deffieux, *Polymer*, **45**, 4633 (2004).
- (15) A. Deffieux and M. Schappacher, *Macromolecules*, **32**, 1797 (1999).
- (16) M. Schappacher, C. Billaud, C. Paulo, and A. Deffieux, *Macromol. Chem. Phys.*, **20**, 2377 (1999).
- (17) D. Lanson, M. Schappacher, A. Deffieux, and R. Borsali, *Macromolecules*, **39**, 7107 (2006).
- (18) D. Lanson, *Thesis in preparation*, Bordeaux.
- (19) D. Lanson, M. Schappacher, A. Deffieux, and R. Borsali, *to be submitted*.
- (20) E. Minatti, P. Viville, R. Borsali, M. Schappacher, A. Deffieux, and R. Lazzaroni, *Macromolecules*, **36**, 4125 (2003).