Elaboration of Corona Functionalized Regular Unimolecular Hyperbranched Polystyrene Nanoparticles

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Summary: Functional arborescent graft polystyrenes prepared by the "graft-on-graft" technique, involving the iterative grafting of end functional polymer chains onto reactive polymer backbones were synthesized. The zero-generation comb polymers and then the first generation hyperbranched structures were obtained by the coupling reaction of living α-acetal polystyryllithium onto linear or comb chains of poly(chloroethyl vinyl ether) (PCEVE) of controlled $\overline{DP}_n$ and structure. Both the PS grafts and the PCEVE reactive backbones were synthesized individually by living polymerization techniques. Initiation of styrene polymerization from acetal functionalized lithium derivatives yield the ω-functionalization of all external polystyrene branches. Derivatization of these acetal branch termini allowed the generation of aldehyde, hydroxyl and carboxyl groups as well as the introduction of functional organic molecules at the periphery of the nanoparticles.

Introduction

We have recently reported a new method for the synthesis of monodisperse polystyrene stars, combs and arborescent unimolecular particles with well-controlled chain characteristics (backbone dimensions and architecture and number and size of branches). The method is based on the highly selective coupling of living polystyryllithium onto poly(chloroethyl vinyl ether) chains; both the PS grafts and the poly(CEVE) building blocks are prepared individually by living polymerizations[1-5]. The synthesis of arborescent graft polymers with a dendritic-like architecture i.e. "dendrigrafts" using this approach allowed us to prepare in a few steps and with a good control of the different structural parameters (number and position of branching points, elementary polymer segment length) nanometric objects with molar masses ranging from 10^5 to more than 10^8 g/mole and narrow molar mass distribution (<1.2).

The corona functionalization of the final objects by the introduction of organic functions and molecules at each branch termini as well as the impact of corona modification on the solubility of the particles in organic solvents is reported.

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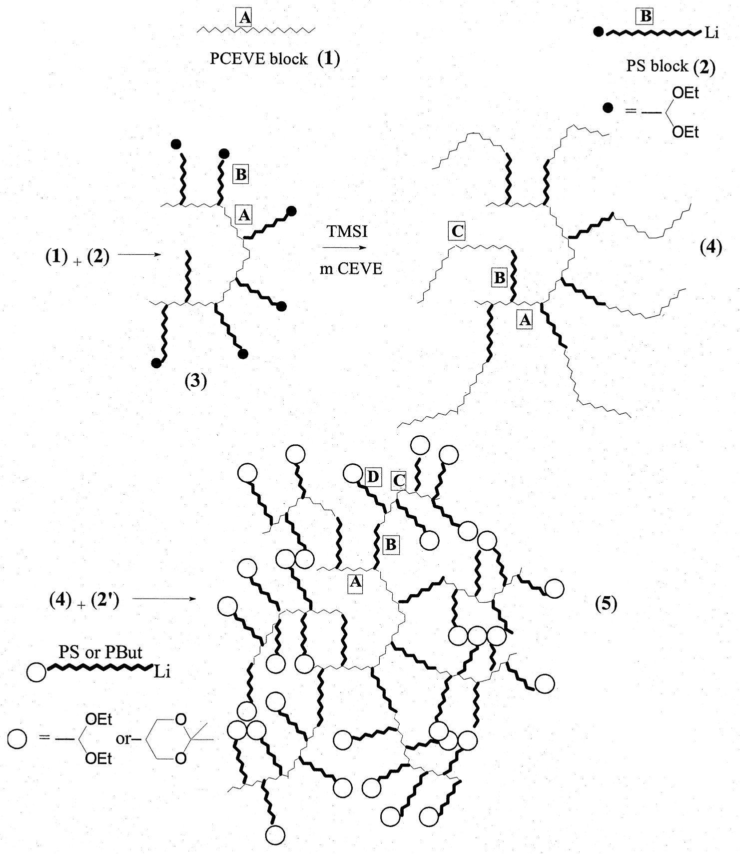
Results and Discussion

The general approach to the synthesis of ω-acetal branch functionalized PS dendrigrafts is described in Scheme 1. The strategy consists in grafting living polystyryllithium chains **(2,2')** onto poly(chloroethyl vinyl ether) chains (PCEVE) of controlled $\overline{DP}_n$. The ω-diethylacetal polystyryllithium grafts were prepared in benzene, using propyl lithium diethylacetal as initiating system[4]. PCEVE$_1$ homopolymers **(1)** were synthesized as previously described by living cationic polymerization and were used as precursors for the preparation of zero generation branched macromolecules (comb architecture), Scheme 1. The grafting reaction of anionic ω-diethylacetal PSLi chains was achieved by adding the living carbanionic solutions onto a known quantity of PCEVE.



scheme1

The living/controlled character of the cationic chloroethyl vinyl ether polymerization was further used to grow PCEVE blocks from the macromolecular chain precursor (**3**) using the acetal ends of polystyrene branches as chain precursor[5].

A typical SEC chromatogram of a $PCEVE_1$-*g*-PS_1 with acetal branch termini used as multifunctional precursor and the corresponding $PCEVE_1$-*g*-(PS_1-*b*-$PCEVE_2$) comblike copolymer are presented in Figure 1(a-e). After purification of (**4**) by selective precipitation, ω-acetal functional arborescent polystyrene dendrigrafts (**5**) were finally obtained by grafting in a similar way ω-acetal PSLi chains (**2'**) or another anionic living block (polybutadiene,...) onto the $PCEVE_1$-*g*-(PS_1-*b*-$PCEVE_2$) combs (**4**), see Scheme 1. Due to the large difference in their molar masses, the hyperbranched structure could be easily separated from ungrafted polystyrene ω-acetal PS_2 by selective precipitation.

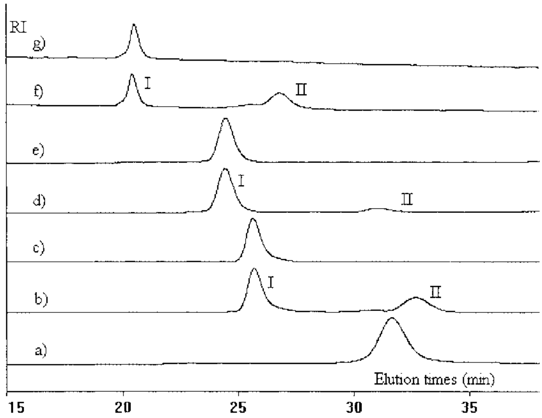


Figure 1 : SEC chromatograms of : a) poly(CEVE) precursor, app$\overline{M_n}$=4 700 g/mol (I= 1.06); b) crude poly(CEVE-g-S), fraction II corresponds to ungrafted polystyrene ; c) purified poly(CEVE-*g*-S), app$\overline{M_n}$= 55 000 g/mol (I=1.03); d) crude poly(CEVE-*g*-(S-b-CEVE)) copolymer, fraction II corresponds to homo poly(CEVE)) ; e) purified poly(CEVE-*g*-(S-*b*-CEVE) copolymer, app$\overline{M_n}$= 117 000 (I=1.04) ; f) crude poly(CEVE-*g*-(S-*b*-CEVE-*g*-But) copolymer, fraction II corresponds to ungrafted polybutadiene, and g) purified poly(CEVE-*g*-(S-*b*-CEVE-*g*-But) copolymer, app$\overline{M_n}$= 2 000 000 (I=1.09). App $\overline{M_n}$ are relative to a calibration curve with linear polystyrene.

A second type of lithio acetal derivative consisting of isopropylidene-1,1 dihydroxymethyl-1-(1-lithio butoxy)butane, was also recently used to synthesize PS grafts with ω-geminal dihydroxymethyl termini a function with very specific coupling capacities towards aldehydes [6], see 2, Scheme 2.

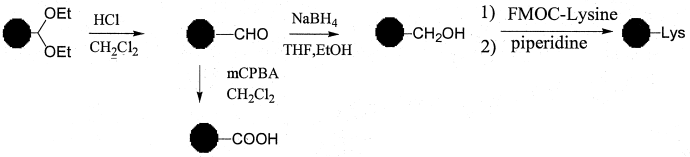
Table 1: Characteristics of poly($CEVE_1$-*g*-(S_1-*b*-($CEVE_2$-*g*-ω-acetal S_2))) dendrigrafts:

samples	PS_2	Dendrigrafts				
		RI detector[a)]		LS detector[a)]		
$\overline{DP}_n$ of elementary blocks	$\overline{M}_n$ exp[a)]	$\overline{M}_{n\,\mathrm{th}}$ [b] (g/mol)	$\overline{M}_{n\,\mathrm{exp}}$ (g/mol)	$\overline{M}w_{\mathrm{exp}}$ (g/mol)	$\overline{M}_{n\,\mathrm{exp}}$	R_g (nm)
26/150/50/50	5440	7.7 10^6	7.0 10^5	5.8 10^6	5.0 10^6	30.5
26/51/82/50	5400	11.0 10^6	3.1 10^5	9.6 10^6	9.4 10^6	27.3
36/180/67/37	3800	7.9 10^6	7.2 10^5	7.3 10^6	6.9 10^6	29.0
56/39/39/15	1590	3.5 10^6	3.3 10^5	2.7 10^6	2.5 10^6	18.0.
56/31/21/45	4700	5.7 10^6	6.7 10^5	5.2 10^6	5.0 10^6	27.0
764/81/50/39	4060	1.5 10^8	3.1 10^6	1.3 10^8	1.2 10^8.	77.5

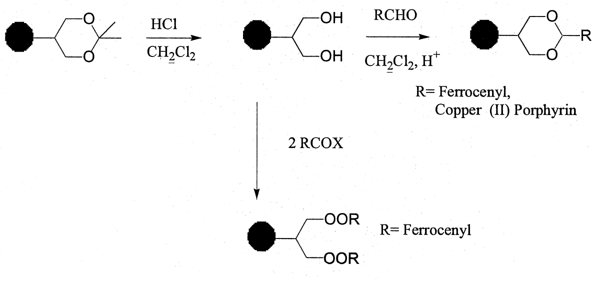
.[a)] $\overline{M}_n$ and $\overline{M}w$ determined by SEC using refractive index (RI) or light scattering (LS) detectors; dn/dc =0.177 in THF at25°C.

[b)] $\overline{M}_n$ Caculated from $\overline{DP}_n$ $PCEVE_1[\overline{Mn}\ PS_1 + (\overline{DP}\ n\ PCEVE_2\ x\overline{Mn}\ PS_2)]$

Some chemical derivatization of the acetal end groups are depicted in Scheme 2.



2) Dendrigraft isopropylidene 1,1-dihydroxymethyl functionalized:



Scheme 2

Conversion of the diethyl acetal function into aldehyde can be readily achieved by treatment of the polymer particle in toluene with acidic amberlyst thus yielding potential grafting site for aminoacids and peptides. Further reduction of the aldehyde functionalized polymer with sodium borohydride (1, Scheme 2) as well as hydrolysis of the isopropylidene 1,1 dihydroxymethyl group (2, Scheme 2) yield respectively the corresponding mono and dihydroxyfunctionalized particles. The latter was recently used to quantitatively graft ferrocenyl, see NMR spectra Figure 2, and porphyrine groups on each branch termini[6] ,thus yielding particles surrounded by metal-organic molecules. Finally, oxidation of the aldehyde function by peroxybenzoïc acid allowed to prepare the carboxy functionalized particles and their salts. On the basis of NMR it may be considered that most of these transformations are quantitative. SEC analysis show that molar mass distributions of the particules remain unimodal and narrow after the different treatments, in agreement with the absence of chain degradation and/or crosslinking.

Solubility parameters and aggregation characteristics of the differently corona functionalized nanoparticles have been investigated. Although the introduction of hydroxyl functions does not allow solubilization or dispersion of the particles in water, the transformation of each PS branch termini into carboxylate yields water dispersable particules as shown by dynamic light scattering Figure 3: strong aggregation persists however as indicated by the increase in diameter size (from about 50nm to approximately 500 nm) and polydispersity.

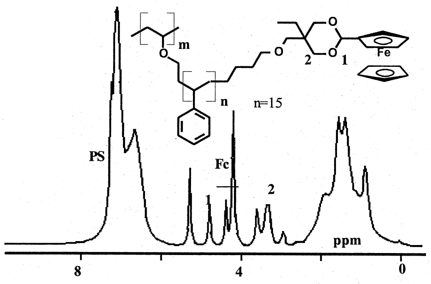


Figure 2

Proton NMR spectrum of PS nanoparticules with ferrocenyl corona.

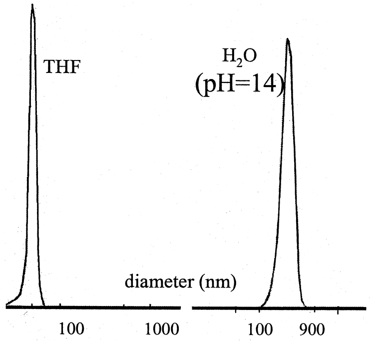


Figure 3

Size and distribution of PS nanoparticules with acetal (THF) and ammonium carboxylate (H_2O) corona functions .

In conclusion the synthesis in a few steps of a series of corona functional unimolecular nanoparticles based on covalent assembly of elementary macromolecular blocks followed by chemical derivatization has been developed. The possibility to adjust the structure and dimensions of the different building elements allows a good control of the size, shape, and surface functionality of the final objects. This opens interesting possibilities in tuning their properties for specific applications such as host- guest interactions, soluble polymer supported catalysts, etc…

Further hydrophilization of the surface particle by water soluble organic groups or macromolecular blocks, in order to make them soluble or at least dispersable in water, are in progress.

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