Versatile and efficient functionalisation of multiallylic dendronised polymers: can dense packing be reached?†

Firmin Moingeon,[a] Jérôme Roeser,[ab] Patrick Masson,[a] Françoise Arnaud[b] and Stéphane Méry*[a]

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Surface modification of a multiallylic dendronised polymer was performed using hydrosilylation, hydroboration or radical addition of thiols to cover the polymer with various functional moieties; surface congestion is expected to occur when bulky groups are grafted.

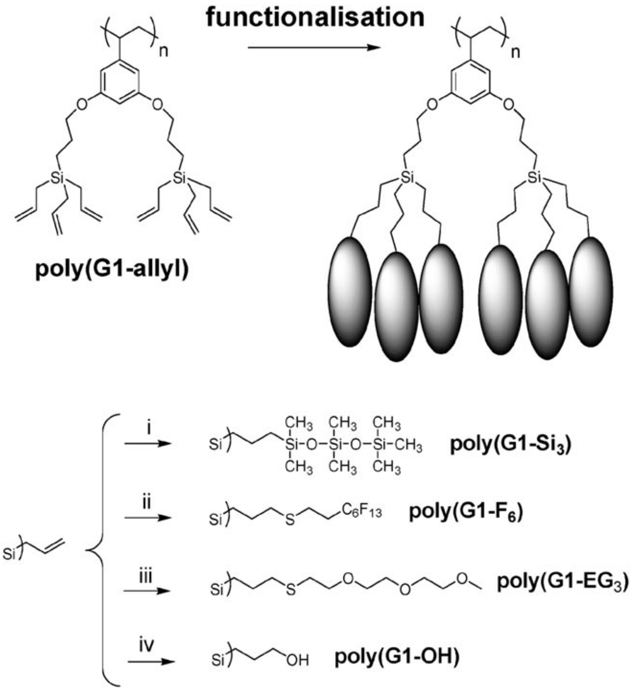
Polymer-analogous reactions are well known and abundantly used to confer or adjust specific properties on polymer materials.[1] Not much work has been devoted, however, on grafting polymers with a very high density of functional groups, *i.e.* containing more than two functional groups per monomer repeat unit. Dendritic architectures are unique materials for hyperfunctionalisation because they offer a large number of potentially reactive branches at the dendron periphery.[2] Moreover, the preferred end-branches distribution at the outer surface of the macromolecule, associated with a sterically-induced shape persistency of dendritic structures, allows for the preparation of surface-functionalised nano-objects.[2,3]

Dendronised polymers (denpols) are a particular case of branched linear polymers where a dendron is carried on each monomer repeat unit.[4] When sterically demanding dendrons are tightly attached to the polymer backbone, these denpols are shown to adopt a wormlike morphology.[5,6]

Some dendronised polymers with peripheral functional groups have already been reported.[4] They were prepared by using a stepwise building of the dendron onto a preformed polymer or else by polymerisation of a dendritic macromonomer. Typical examples of reactive functional groups that have been introduced at the dendron periphery are (protected) amines,[7] (protected) hydroxyls[8] and allyls.[6,9,10] Although these functionalities are quite valuable for chemical modification, they have not been much exploited to functionalise the surface of the denpols.[7b,9,11] In this context, only a few publications report on the preparation of functional denpols *via* a post-polymerisation process.[9,11]

In this communication, we describe a simple and straightforward hyperfunctionalisation of multiallylic dendronised polymers by means of hydrosilylation reaction, radical addition of thiols and hydroboration reaction. By using either of the above cited reactions, it is possible to graft a large variety of functional groups onto the allyl end-branches. The surface functionalisation of the denpols by siloxane moieties, perfluorinated chains, oligo(ethylene glycol) chains and hydroxyl groups are given here as examples.

The starting multiallylic denpols **poly(G1-allyl)** are polystyrenes substituted by two allyl-ended carbosilane dendrons as shown in Scheme 1. They were prepared by living anionic polymerisation of the dendritic styrene precursors, as already published.[10] The use of a living polymerisation technique could offer well-defined denpols of monomodal molecular weight distribution and of low polydispersity. It also permitted to produce dendronised block-copolymers. All surface-



Scheme 1 Example of surface-functionalisation of the multiallylic dendronised polymers. *Reagents and conditions*: (i) 1,1,2,2,3,3,3-heptamethyltrisiloxane, Karstedt catalyst, toluene; (ii) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol, AIBN, heptane; (iii) 2-methoxy(2-ethoxy(2-ethoxy))-1-ethanethiol, AIBN, toluene; (iv) (a) 9-BBN, THF, (b) NaOH, H_2O_2.

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[a] *Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS-GMO), UMR 7504 CNRS-ULP, 23 rue du Loess, BP43, 67034 Strasbourg Cedex 2, France. E-mail: mery@ipcms.u-strasbg.fr; Fax: +33 388 107246; Tel: +33 388 107165*

[b] *Laboratoire de Chimie-Physique, Département des Sciences Analytiques, Institut Pluridisciplinaire Hubert Curien, ULP, CNRS, ECPM, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France. E-mail: farnaud@chimie.u-strasbg.fr; Fax: +33 390 242747; Tel: +33 390 242749*

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Table 1 Characteristics of the functionalised polymers

			Functionalisation, *f* (%)	
Functionalised polymer	$\overline{M_n}^a$/Da	PDI[b]	^{1}H NMR	Elemental analysis[c]
Poly(G1-Si$_3$)	51 100	1.13	85	79 (Si)
Poly(G1-F$_6$)	64 000[d]	nd[e]	100	98 (F)
Poly(G1-EG$_3$)	36 400	1.21	97	97 (S)
Poly(G1-OH)	nd[e]	nd[e]	>95	97 (C)

[a] Unless specified, measured by multi-angle laser light scattering (MALLS). [b] Polydispersity calculated from SEC refractometer results. [c] From elemental analysis (Si: silicium, F: fluorine, S: sulfur, C: carbon). [d] From MALDI-TOF. [e] Not determined owing to insolubility reasons.

functionalisations presented here were performed on multiallylic polymers of same characteristics (M_n = 13 200 Da, PDI = 1.11). The resulting functional polymers were characterised by different techniques (see synthesis and characterisation data in ESI†). Table 1 gives the measured values of the molecular weight, polydispersity and grafting content.

Hydrosilylation allows the grafting of many different types of silyl derivatives, *via* the addition (usually platinum-catalysed) of a silane (Si–H) functionality onto an insaturation (generally an ω-olefin).[12] The addition is highly regioselective and essentially leads to anti-Markovnikov's type of addition. This reaction was used here to graft a short siloxane moiety (1,1,3,3,5,5,5-heptamethyltrisiloxane) using Karsdedt catalyst.[12b] It was found that in average, more than five siloxane chains could be grafted by a monomer unit of **Poly(G1-Si$_3$)**. This corresponds to a very high siloxane content when considering the close attachment of the sterically demanding[13] siloxane moiety and the required platinum insertion complex intermediate.[12] Moreover, the functionalisation was found to proceed without polymer coupling as demonstrated by the polydispersity which remained unaffected through the functionalisation process (PDI = 1.13 *vs.* 1.11) (see Fig. 1). To our knowledge, this **Poly(G1-Si$_3$)** polymer contains the highest siloxane chain density ever grafted on a polymer.

Radical addition of thiols is well-known for the chemical modification of olefin-based polymers. It has already been used to graft polymers with fluorinated chains[14] or with carboxylic groups.[15] In particular, Frey and co-workers showed its remarkable effectiveness to functionalise dendrimers with perfluorinated chains up to the third generation.[16] In this work we used radical addition of thiols to introduce both perfluorinated and oligo(ethylene glycol) chains to produce **Poly(G1-F$_6$)** and **Poly(G1-EG$_3$)**, respectively.[17] Radicals were generated by thermal decomposition of AIBN initiator. The experimental conditions were found to be crucial for avoiding side-reactions such as polymer inter-chain couplings (see Fig. 1). The addition of both types of chains proceeded almost to completion as shown by the results obtained from NMR, FTIR and elemental analysis (Table 1). The MALDI-TOF mass spectrum of **poly(G1-F$_6$)** (Fig. 2) even allows to visualise the few missing mercaptan chains ($M_{\text{R–SH}}$ = 380.0 Da) onto the entirely substituted polymer fractions (the molecular weight of the perfluorinated monomer repeat unit is 2800.3 Da).

Hydroboration of alkenes represents another versatile method of functionalisation.[18] The most convenient 9-borabicyclo[3.3.1]nonane (9-BBN) reagent is known to exhibit a remarkable chemo- and regio-selectivity during hydroboration reaction. The resulting organoboranes then constitute valuable intermediates since they can be converted to C–O, C–N, C–S, C–Hal... or C–C bonds.[18,19] We herein report the transformation of allyls into propanol chains *via* the hydroboration with 9-BBN, with a subsequent oxidation[19c] with H_2O_2/OH^- to produce the polymer **poly(G1-OH)**. This procedure already proved to be quite successful in the polyhydroxylation of carbosilane dendrimers, up to the third generation.[20] Applied to our denpols, this hydration-like reaction was found to proceed almost quantitatively (>95%), giving an anti-Markovnikov type of addition, exclusively.

To comment on the steric effects brought by the denpol hyperfunctionalisation, it is clear that grafting a high density of (bulky) chains, closely attached to the backbone, as described here, may lead to a congestion of the macromolecule.

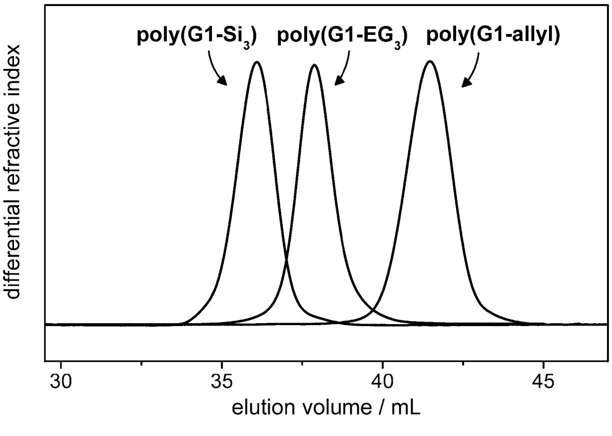

Fig. 1 SEC peaks of the starting multiallylic polymer **poly(G1-allyl)** and its silylated (**poly(G1-Si$_3$)**) and PEGylated (**poly(G1-EG$_3$)**) analogues.

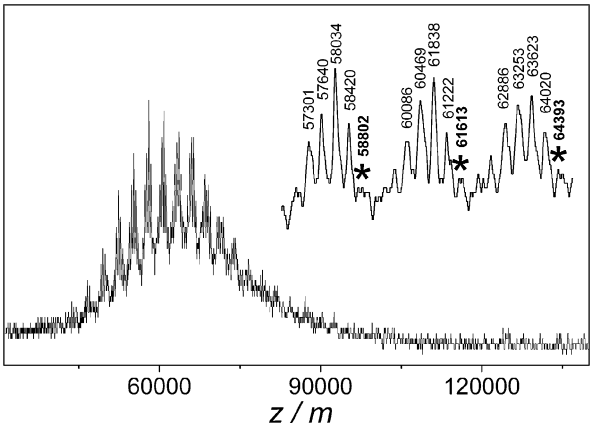

Fig. 2 MALDI-TOF mass spectrum of the perfluorinated polymer **poly(G1-F$_6$)**. Entirely substituted polymer fractions (all allyl branches of all repeat units are functionalised) are indicated by an asterisk (*).

To assess the congestion phenomenon, the available surface for grafting was evaluated using a straight geometrical approach. Knowing this surface and the transverse molecular area of the functional groups, their maximum number can then be estimated. Thus, considering that the starting multiallylic denpol adopts a cylindrical interface for functionalisation (assuming the polymer is fully stretched and of infinite length), the available area for functionalisation Σ can be calculated from eqn (1), where h is the maximum distance between each monomer repeat unit (h = 2.54 Å); V is the volume of the multiallylic monomer repeat unit and was calculated from dilatometric measurements (V = 860 Å^3). The maximum number (n) of functional groups that can be grafted onto the surface Σ can then be deduced from eqn (2)

$$\Sigma = 2\sqrt{\pi V h} \tag{1}$$

$$n = \Sigma/\sigma \tag{2}$$

where σ, is the transverse molecular area of the functional groups (σ = 41 Å^2 for oligo(dimethylsiloxane) chain,[13] 31 Å^2 for fluorocarbon chain,[21] and ~21 Å^2 for ethylene glycol chain[21] or hydroxyl group). This calculation indicates that the maximum number of chains that can be grafted (per monomer repeat unit) is n = 4.0 siloxane chains, 6.6 perfluorinated chains and 7.8 oligo(ethylene glycol) chains or hydroxyl groups. These results clearly show that the polymer grafted with siloxane chains (the most sterically demanding) should be congested. Moreover, the fact that it was possible to exceed the limit average number of grafted chains (~5.0 *vs.* 4.0) can be explained from (i) a deformation of the grafting interface that may no longer be cylindrical and (ii) a contribution of the end polymer chains (the macromolecule has a finite degree of polymerisation: $\overline{DP_n} \approx 25$) which allows the dendrons at both extremities of the polymer to relax and absorb overcrowding.

To conclude, allyl functionalised denpols are demonstrated to be a versatile platform toward highly functionalised polymers. The peripheral allyl branches allow the grafting of a broad variety of functional groups by means of hydrosilylation, hydroboration or radical addition of mercaptans. Despite the high steric hindrance, the grafting efficiency was excellent, leading to a quasi-complete conversion of the allyl groups. In the case of the most sterically demanding siloxane chains, a surface congestion of the polymer is expected to be reached. Covering the surface of the polymer with such a high density of functional groups (up to six per monomer repeat unit) naturally provides the polymer with remarkable properties in many domains. For instance, covering the denpols with siloxane or perfluorinated chains induces a liquid-crystal supramolecular organisation of the polymers; moreover, covering the denpols with ethylene glycol chains confers to polymers a sharp and reversible temperature-induced demixtion in water (*i.e.* a low critical solution temperature: LCST). The detailed properties of these surface-functionalised denpols will be described in subsequent papers.

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