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# Giant dendrimer-like particles from nanolatexes†

**Chantal Larpent,**[*a] **Cécile Geniès,**[a] **Anne Paula De Sousa Delgado,**[a] **Anne-Marie Caminade,**[b]
**Jean-Pierre Majoral,**[b] **Jean-François Sassi**[c] **and Frédéric Leising**[c]

[a] Université de Versailles-St Quentin en Yvelines, SIRCOB UMR-CNRS 8086, 45 Avenue des Etats-Unis, 78035 Versailles, France. E-mail: Larpent@chimie.uvsq.fr; Fax: +33 1 39254452; Tel: +33 1 39254413
[b] Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France. E-mail: caminade@lcc-toulouse.fr. E-mail: majoral@lcc-toulouse.fr; Fax: +33 5 61553003
[c] Rhodia, Centre de Recherche, 69192 Saint-Fons and 93308 Aubervilliers, France
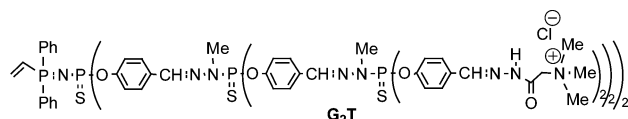
**A straightforward grafting of a polycationic phosphorus-containing dendritic shell onto polystyrene nanoparticles leads to dendronized nanoparticles showing unique behavior.**

During the last decade, nanoparticulate materials have attracted widespread attention due to their unique properties. Among them, aqueous suspensions of polymer nanoparticles, so-called nanolatexes, may find a wide range of applications in chemistry, for the development of special nanomaterials and supported reagents with improved activity,[1] as well as in life science, for the development of carriers, sensors or probes that are suitable for intracellular transport and measurements.[2] In this context, the design of nanomaterials with improved stability and tailored functionalities is a challenging endeavour and the control of the surface characteristics assumes paramount importance because of the high surface-to-volume ratio and the high specific area of the particles. Although dendrimers and dendrons have already been used for surface modification[3–5] or as templates[6–9] and protecting peripheral ligands in the case of inorganic nanocrystals,[10,11] there are limited reports of dendronized polymer particles, despite existing strategies toward dendronized polymers[12] and resin-bound dendrimers.[13] Dendrimer mediated immobilization of latex on flat solid supports and adsorption of amphiphilic dendrons on polystyrene particles[3,14] have been studied, but, to our knowledge, there is no example of chemical modification of polymer particles with dendrons or dendrimers.

In this paper, we wish to describe a simple and straightforward synthesis of dendronized nanolatexes in aqueous medium using a convergent approach, *i.e.* by attaching dendrons covalently at the focal point to anchor groups of functionalized nanoparticles. Unique behavior of these new types of nanolatexes will be pointed out.

The dendrons $G_nT$ of generation 0, 1, 2 with 2, 4, 8 ammonium extremities respectively are prepared by condensation of a stoichiometric amount of the Girard-T reagent on the aldehyde end groups of dendrons $G_n$[15] (Fig. 1).

The aqueous suspensions of cyclam-functionalized cross-linked nanoparticles, **NLCyc**, with a polymer content of about 4% wt, are obtained in two steps by copolymerization of styrene and 4-vinylbenzyl chloride in ternary oil-in-water microemulsions stabilized with a cationic surfactant, dodecyltrimethyl ammonium bromide (DTAB), followed by post-functionalization with cyclam

(Scheme 1).[16] The nanoparticles have an average diameter of 15 nm with a narrow size distribution and contain about 0.2 mmol of cyclam residues per g of polymer.

The grafting of the dendron is readily performed at room temperature by adding the dendron $G_nT$ to the as-prepared nanolatex **NLCyc**. The decrease of the amount of dendron in solution, monitored by $^{31}P$ NMR, indicates that the reaction is complete after 48 h. The translucent suspension remains stable during the reaction and the excess of unreacted dendron is readily removed by dialysis. The dendron loads, deduced from P and S elemental analyses of the isolated and purified polymer particles, are 230, 130 and 70 μmol $G_nT$ per g for $n = 0$, 1 and 2, respectively. The linkage of dendrons is further evidenced by the presence of P–O–C vibrations at 1200 and 900 cm$^{-1}$ in the IR spectra of the polymers **NLG$_n$T**. It is noteworthy that the maximum functionalization yield is achieved in the presence of only a slight excess of dendron (2 equiv.). Assuming an area of about 2.5, 5 and 8.5 nm$^2$ per dendron for $G_0T$, $G_1T$, and $G_2T$ respectively, it corresponds to an almost complete coverage of the surface. For a low generation dendron, $G_0T$, the reaction is quantitative with up to statistically 1 dendron grafted per cyclam residue. The average number of larger dendrons grafted per cyclam residue, about 0.7 $G_1T$ and 0.4 $G_2T$, is lower because the surface reaction is limited by steric hindrance and electrostatic repulsions.



**Fig. 1** Formula of dendron $G_2T$.
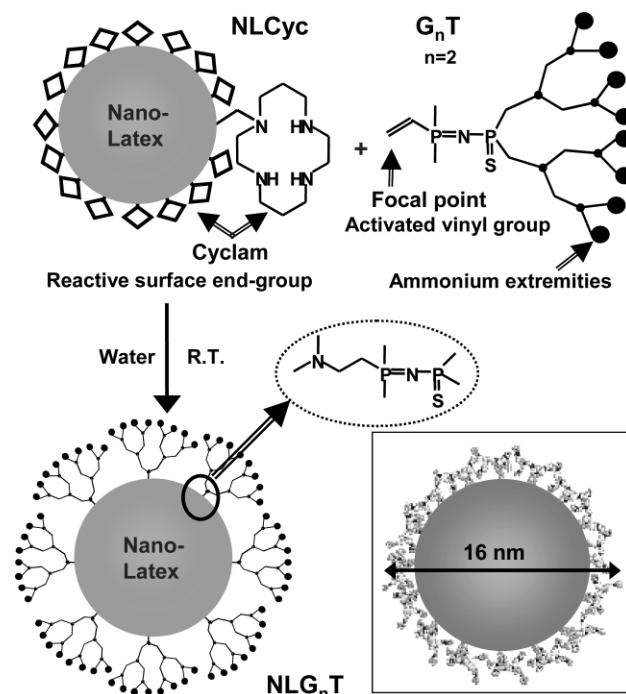
**Scheme 1** Synthesis of dendronized nanolatexes **NLG$_n$T**. Insert : scaled cross-section of a dendronized nanoparticle **NLG$_1$T** showing the thin $G_1T$ shell as CPK space filling molecular models.

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Moreover, the particle size and distribution, deduced from QELS analyses, remain unchanged upon grafting. Thus, this simple and straightforward reaction gives access to translucent aqueous suspensions of nanoparticles with an average diameter of 16 nm and containing about 300 $G_0T$, 150 $G_1T$ and 90 $G_2T$ residues per particle, respectively. Remarkably, these dendronized nanoparticles are comparable to high 10th generation dendrimers (diameter 15.5 nm as observed by TEM) in their size and functionality.[17] Regardless of the dendrimer generation, the charge per particle is large enough to prevent aggregation (600 to 800 ammonium groups per particle). The polycationic dendritic shell provides a remarkable improvement of the colloidal stability since the suspensions $NLG_nT$ remain stable with no change in the particle size when the surfactant is completely removed by dialysis, while the starting nanolatexes $NLCyc$ are stable only in the presence of DTAB (0.15% wt or more) and aggregate in the absence of surfactant.[1] Moreover, the surfactant-free suspensions of dendronized particles $NLG_nT$ exhibit a good tolerance to an increase of the ionic strength. Their critical flocculation concentrations in the presence of added sodium chloride (0.1, 1, and 5 mol $L^{-1}$ respectively for $NLG_0T$, $NLG_1T$ and $NLG_2T$) increase with the dendron generation. Furthermore, the $NLG_nT$ dendrigrafted particles can be redispersed in water after drying which is not the case for $NLCyc$.

The surfactant free dendronized nanolatexes $NLG_nT$ at 2 to 4% wt form rigid stable translucent hydrogels upon standing at room temperature for 1 week, whatever the grafted dendron. About 105 000, 185 000 and 345 000 water molecules are estimated to be gelled by a grafted molecule of a dendron of generation 0, 1 and 2 respectively.[18]

In the same way, the dendritic shell has a remarkable influence on the solid-state thermal behaviour of the polymer nanoparticles as illustrated by thermogravimetric analyses. The starting cyclam-functionalized particles $NLCyc$ are completely decomposed at 450 °C, while a plateau with 40–45% remaining weight is observed for up to 510 °C for dendrigrafted-particles $NLG_0T$ and 550 °C for $NLG_1T$ and $NLG_2T$. These results clearly indicate an improvement of the thermal stability of the polymer, since the dendron loads are respectively 19%, 23% and 26% in $NLG_0T$, $NLG_1T$ and $NLG_2T$. Moreover, the dendrons $G_nT$ decompose upon heating according to a retrosynthetic step by step process starting from the ammonium extremities; at 450 °C, the percentage of mass retained (about 50%) corresponds to the phosphorus backbone. The observed improvement of the thermal stability of the dendronized polymer particles $NLG_nT$ may thus be attributed to the fireproofing properties of the phosphorus-based[19] dendritic shell.

Remarkably, in addition to the profit brought by the dendritic layer, the dendronized nanoparticles retain their metal-complexing ability with a Cu(II) binding capacity of 0.2 mmol per g of polymer. The metal-binding capacity of the covalently sandwiched cyclam residues is not altered thus demonstrating the permeability of the dendritic shell.

In conclusion, we have described a versatile new convergent procedure for the synthesis of polystyrene core-dendrimer shell nanoparticles in an aqueous suspension, that proceeds under very mild conditions. The added value of grafting a polycationic phosphorus-containing dendritic shell onto nanoparticles is obvious for different reasons: (i) the colloidal stability is improved, due to the charge; removal of surfactant does not provoke the aggregation of the dendronized latexes in marked contrast with what is observed with "classical" nanolatexes. Moreover the dendronized nanolatexes can be redispersed in water after drying thereby demonstrating that the dendritic shell acts as a protective coat, (ii) the thermal stability is improved, due to the dendritic backbone bearing many phosphorus groups, (iii) the complexing properties of the cyclam polymer core are retained. Moreover the grafting of the dendrons onto cyclam functionalized nanolatexes permits the formation of copper containing hydrogels. Therefore the dendronized nanoparticles can be considered as "multilayered systems": each layer (cyclam and phosphorus dendrons) carries out its designed task, (iv) the formation of stable hydrogels at low overall dendron contents opens new perspectives in the field of nanomaterials and colloidal chemistry.

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