

# SURFACE-GRAFTED HYPERBRANCHED POLYMERS BY SELF-CONDENSING VINYL (CO)POLYMERIZATION VIA ATRP

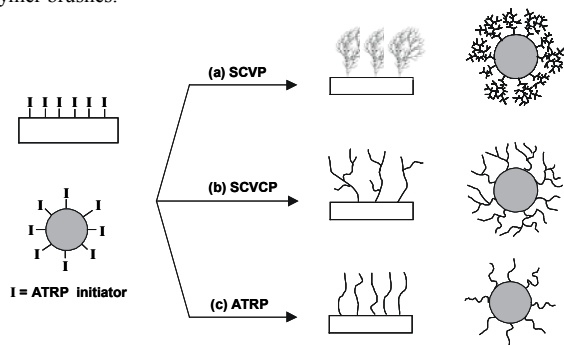
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## Introduction

Highly branched polymers play an increasingly important role in interface and surface sciences, since their distinctive chemical and physical properties can be used advantageously as functional surfaces and as interfacial materials. Hyperbranched polymers grafted onto surfaces have also become a field of growing interest. Depending upon the substrates, it can be divided into 3D, 2D, and 1D hybrids, which correspond to products grafted on spherical particles, planar surfaces, and linear polymers, respectively. Previously, synthesis of dendrimers and hyperbranched polymers grafted onto surfaces has been mainly conducted by "grafting to" techniques.<sup>1,2</sup> A series of repeated "grafting from" steps have been also employed.<sup>3</sup> However, both approaches have the disadvantage that many tedious synthetic steps are necessary to reach the defined surface structures.

We describe here a novel synthetic concept for preparing hyperbranched (meth)acrylates on 2D and 3D surfaces in which a silicon wafer or silica nanoparticles grafted with an initiator layer composed of an  $\alpha$ -bromoester fragment were used for self-condensing vinyl polymerization (SCVP) via atom transfer radical polymerization (ATRP) (Scheme 1). Surface-initiated self-condensing vinyl copolymerization (SCVCP) was also applied as a method for the synthesis of highly branched polymers grafted from surfaces. In contrast, surface-initiated ATRP resulted in the preparation of linear polymer brushes.



**Scheme 1.** Synthesis of hyperbranched, branched, and linear polymer brushes from planar surfaces and spherical particles.

## Experimental

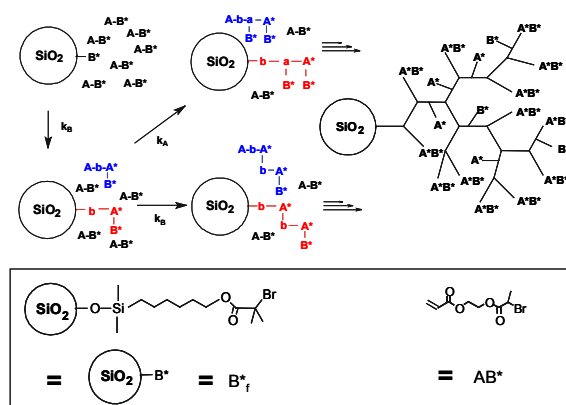
**Materials.** The synthesis of an acrylic AB\* inimer, 2-(2-bromopropionyloxy)ethyl acrylate (BPEA), was conducted by the reaction of an  $\alpha$ -bromoacid halide with 2-hydroxyethyl acrylate. The  $\alpha$ -bromoester initiator attached to silica particles was prepared by the reaction of a trichlorosilyl derivative with silica particles (Aerosil 200, Degussa, mean particle diameter = 16 nm). All polymerizations were carried out in bulk in a round-bottom flask sealed with a plastic cap under nitrogen. CuBr/N,N,N',N'',N'''-pentamethyldiethylenetriamine was used as the ATRP catalyst. The branched structures were evaluated by characterization of the soluble polymers using conventional GPC, GPC/viscosity, and <sup>1</sup>H NMR measurements.

**Instrumentation.** Bright-field transmission electron microscopy (TEM) was performed using a Zeiss electron microscope (CEM 902) operated at 80 kV. Scanning force microscopy (SFM) images were taken on a Digital Instruments Dimension 3100 microscope operated in Tapping Mode. Field-emission scanning electron microscopy (FE-SEM) was performed using a LEO 1530 Gemini microscope equipped with a field emission cathode. Dynamic light scattering (DLS) was performed at room temperature on an

ALV DLS/SLS-SP 5022F compact goniometer system with a He-Ne laser ( $\lambda_0$  = 632.8 nm) using an ALV 5000/E correlator. X-ray photoelectron spectroscopy (XPS, Leybold) with a monochromatic Mg K $\alpha$  X-ray source ( $E_{\text{exc}}$  = 1256.3 eV) was used to characterize the surface composition.

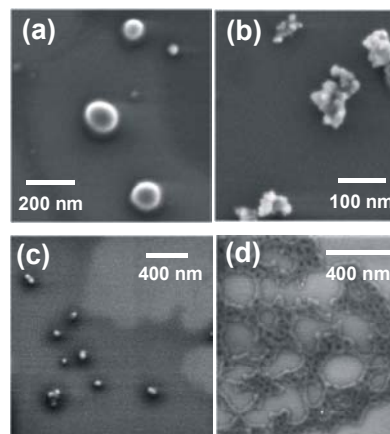
## Results and Discussion

**Hyperbranched Polymers Grafted from Spherical Particles** The synthesis of hyperbranched polymer-silica hybrid nanoparticles was conducted by self-condensing vinyl polymerization (SCVP) via ATRP from silica surfaces.<sup>4</sup> The synthesis is based on an initiator-monomer ("inimer") of the general structure AB\*, where the double bond is designated A and B\* is a group capable of initiating the polymerization of vinyl groups. The formation of a 2-bromoisobutryl fragment (B\*) layer on the silica surface was conducted by the reaction of a trichlorosilyl derivative with the silica particles. Because both the AB\* inimer and the functionalized silica particles have groups capable of initiating the polymerization, the chain growth can be started from both B\* in the initiators immobilized on the silica particles, and a B\* group in the inimer. Further addition of AB\* inimer or dimer to A\* and B\* centers results in hyperbranched polymers.



**Scheme 2.** SCVP of an AB\* inimer (BPEA) from a functionalized silica particle (B\*). Capital letters indicate vinyl group (A) and active centers (A\*, B\*), and lowercase letters stand for reacted ones (a, b).

The bulk polymerization of BPEA with the functionalized silica particles yielded well-defined hybrid nanoparticles comprised of silica cores and hyperbranched polymer shells having multifunctional bromoester end groups. Such surface multifunctionality is ideally independent of the surface curvature of the core particle and the layer thickness of the polymer shell, which could not be achieved by linear polymers.

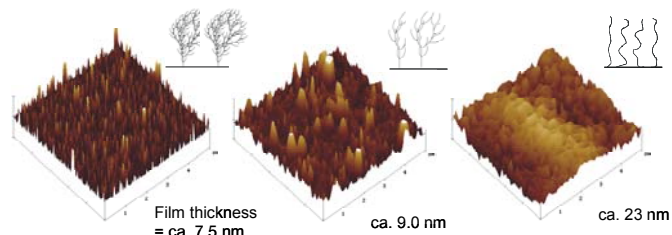


**Figure 1.** Representative FE-SEM images of the branched PtBuA-silica hybrid nanoparticles obtained by SCVCP of BPEA and tBuA at  $\gamma = [\text{tBuA}]_0/[\text{BPEA}]_0 = 6.1$  (a,b) and  $\gamma = 1.1$  (c,d).

Self-condensing vinyl copolymerization (SCVCP) of BPEA and *tert*-butyl acrylate (tBuA) from the functionalized silica nanoparticles created branched PtBuA-silica nanoparticles. The functionality of the end groups on the surface, and the chemical composition as well as the structure of the branched polymers grafted on the silica nanoparticles could be controlled by composition in the feed during the SCVCP, as confirmed by elemental analysis and FT-IR measurement.

FE-SEM (**Figure 1**), TEM, SFM, and DLS measurements indicate that the hybrid nanoparticles comprising the silica core and the hyperbranched polymer shell exist as isolated and aggregated forms. Novel hybrid nanoparticles with branched polyelectrolytes, poly(acrylic acid) (PAA)-silica, were obtained after hydrolysis of linear segments of the branched PtBuA. These polymers grafted on the nanoparticles can be designed to have a fairly open structure, allowing the functional materials, such as metal ions, to penetrate the film more easily than in conventional linear polymer layers. SCVCP was also applied for the synthesis of branched PAAs having different molecular weights and degree of branching.<sup>5</sup>

**Hyperbranched Polymers Grafted from Planar Surfaces.** The synthesis of hyperbranched (meth)acrylates on a planar surface was conducted by surface-initiated SCVP. SCVP of BPEA was found to yield polymer films with a high degree of branching and with a characteristic surface topography. SFM and XPS were used to investigate the surface topography and chemical composition of the grafted hyperbranched polymers. The size and density of the nano-scale protrusions obtained on the surface and the film thickness were observed to depend on the polymerization conditions. In this way, we have been able to create novel surface architectures, in which the characteristic nano-protrusions with different densities and sizes are composed of hyperbranched polymers tethered directly to the surface. The SCVCP gave an intermediate surface topography and film thickness between the polymer protrusions obtained from SCVP of an AB\* inimer and the polymer brushes obtained by ATRP of a conventional monomer (**Figure 2**). The difference in the Br content at the surface between hyperbranched, branched, and linear polymers was confirmed by XPS, suggesting the feasibility to control the surface chemical functionality. Hence, the one-step self-condensing ATRP from the surface can be regarded as a novel and convenient approach towards the preparation of smart interfaces.



**Figure 2.** SFM images of hyperbranched, branched, and linear polymers grafted from functionalized silicon wafers (mean roughness = 3.1, 5.0, and 1.0 nm, respectively).

**Theoretical Considerations.** A series of theoretical studies of the SCV(C)P have been reported<sup>7-13</sup>, which give valuable information on the kinetics, the molecular weights, the molecular weight distribution (MWD), and the degree of branching (DB) of the polymers obtained. **Table 1** summarizes the calculated MWD and DB of hyperbranched polymers obtained by SCVP and SCVCP under various conditions. All calculations were conducted, assuming an ideal case, i.e., no cyclization, no excluded volume effects, no side reactions.

The calculated MWD of polymers formed in SCVP without initiators (conventional SCVP in bulk or solution) is broader than that obtained from SCVP in the presence of *f*-functional initiators.<sup>9,10</sup> The presence of multifunctional initiators, B\*<sub>*f*</sub>, leads to a considerable narrowing of the polydispersity index, which decreases with increasing initiator functionality, *f*. Thus, the molecular weights and MWD of the ungrafted polymer obtained in solution might be different from those of the grafted polymer produced by a surface-initiated SCVP. On the other hand, the effect of the *f*-functional initiators on the DB was calculated to be negligible under batch conditions

used here (inimers and initiators grafted on the surface are mixed instantaneously).<sup>9</sup> This indicates that the DB does not depend on whether polymer is formed in solution or on the surfaces. Therefore, it is reasonable to suppose that SCVP of the inimer with functionalized silica particles (or silicon wafers) provides surface-grafted poly(acrylate) having a highly branched structure, even if the correlation of the molecular parameters of the soluble polymers with the polymers grafted on the surface is not confirmed experimentally.

**Table 1.** Molecular parameters of polymers obtained by self-condensing vinyl polymerization and copolymerization

	SCVP of AB*	Copolymerization of AB* + M ( $\gamma : [M]_0/[AB^*]_0$ )
Polymerization without initiator	$DB \approx 1/2$ <sup>7,8)</sup> $\overline{M}_w/\overline{M}_n \approx 1 + \overline{DP}_n$	$DB \approx 2/(\gamma + 1)$ ( $\gamma \gg 1$ ) <sup>11)</sup> $\overline{M}_w/\overline{M}_n = 1 + \overline{DP}_n/(\gamma + 1)$
Polymerization with multifunctional initiator (batch)	$DB \approx 1/2$ <sup>9)</sup> $\overline{M}_w/\overline{M}_n = 1 + \overline{DP}_n/f^2$	$DB \approx 2/(\gamma + 1)$ ( $\gamma \gg 1$ ) <sup>12)</sup> $\overline{M}_w/\overline{M}_n = 1 + \overline{DP}_n/(\gamma + 1) f^2$
Polymerization with multifunctional initiator (semi-batch)	$DB \approx 2/3$ <sup>10)</sup> $\overline{M}_w/\overline{M}_n = 1 + 1/f$	$DB \approx 2/(\gamma + 1)$ ( $\gamma \gg 1$ ) <sup>13)</sup> $\overline{M}_w/\overline{M}_n = 1 + 1/f$

DB: degree of branching *f*: initiator functionality  
Semi-batch = slow monomer addition

## Conclusions

One-step SCV(C)P from the surfaces was used for the development of new hyperbranched polymer-inorganic 2D and 3D hybrid materials. Because these hyperbranched polymers contain a high density of functional groups, they are suitable for a number of technological applications including corrosion inhibition, chemical sensing, cellular engineering, or catalysts. Further, the 3D hybrids having various functional groups, such as carboxylic acid groups, can be used as fundamental building blocks for the synthesis of macromolecular clusters with a higher order of complexity. Thus, a well controlled synthesis for these materials is considered to lead the creation of an entirely new category of materials that are controllable on nanoscopic scale and have chemically sensitive interfaces.

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