Supported ATRP and giant polymers

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Surface-initiated Atom Transfer Radical Polymerization (ATRP) produces surface-bound films with thicknesses up to tens of microns. We report on the possible existence of micron-sized, individual polymer chains in these films.

ATRP-related research is one of the fastest growing areas in polymer chemistry[1,2] and its potential applications in the tailor-made design of complex or functional polymeric structures[3–7] and hybrid materials[8–12] are of utmost interest.

In a recent study,[13,14] we applied ATRP to a grafting-from polymerization scheme, where supported initiators in the form of 2-bromoesters were used to start the on-bead polymerization of acrylic monomers dissolved in a water phase.

The polymerization proceeds only from water-exposed initiators, because they are accessible to both monomers and catalyst. Therefore, using wettable, but not water-swollen substrates (such as poly(styrene)-*gr*-poly(ethylene glycol) macrobeads), only the initiators on the surface are activated.

Another straightforward feature of ATRP is the negligible influence of termination reactions, at least with monomers such as (meth)acrylic esters, as already pointed out by Huang *et al.*.[15] This living character was confirmed in surface polymerization, by obtaining tens of microns-thick polymer layers.

These thick and conformal coatings can easily find application in the biocompatibilization and biofunctionalization of implants or in the modification of their adhesion properties.

The impressive thickness of these films has raised the question of whether they are composed of individual macromolecular chains of extraordinary dimensions; radical transfer processes to the polymer chain could have an influence too, promoting reinitiation and branching and thus generating a cross-linked material characterized by a more moderate kinetic chain length. Also non-radical processes could affect the architecture of the polymer chain, *e.g.* the occurrence of transesterification reactions; however, they do not change the kinetic chain length. Additionally, the physical entrapment of big, but not gigantic, polymer chains could play a role. Unfortunately, the direct detachment and analysis of the polymer chains from the substrates was not successful,† as also reported by other authors.[15]

In the present work we have functionalized silicon surfaces with an organic layer presenting an extremely low density of 2-bromoesters. We have chosen a flat surface such as that of silicon, because it allows easy detection of any surface-grown material. Given a sufficient spacing between initiator groups, one should thus be able to detect individual macromolecules.

With a high dilution of the initiators the effect of entanglements should be almost completely absent; the presence of micron-sized polymerized (and covalently linked) material should indicate that entrapped polymers do not play a major role in determining the thickness of the films.

It will also be possible to discriminate between two extreme cases: in the absence of radical transfer reactions, globular isolated macromolecules should be detected, even at extremely high monomer : initiator ratio (= extremely high MW and size). On the contrary, the massive occurrence of transfer reactions

should favour polymer coil coalescence and thus the formation of cross-linked films (Scheme 1).

If branching reactions occur among side chains, they are not sensitive to the dilution of initiators and can occur intra- or intermolecularly. Therefore, the above considerations about parasite radical processes (globules *vs.* films) remain valid even in the presence of cross-linking reactions between side chains. We have used 2-hydroxyethyl methacrylate (HEMA) as a monomer, because of the living character of its ATRP supported polymerization (Fig. 1).‡

Flat silicon surfaces were functionalized with a mixture of two trimethoxysilanes, one bearing a 2-bromoester group (silA), the second a short PEG chain (silB) (Scheme 2).

SilA was derived from allyl glycidyl ether, an attractive starting material, which possesses two orthogonally-reacting groups (considering hydrosilylation a polar reaction with a nucleophilic silicon, allyl glycidyl ether is equivalent to an a^α, a^ω synthon). An alcohol group was introduced through anionic ring opening of the epoxy ring with sodium methoxide in methanol (yield: 87%) and was then esterified with 2-bromoisobutyryl bromide according to a well-established literature procedure[14] (yield: 43% after purification on a silica column using hexane–ethyl acetate 4 : 1 as an eluent mixture).
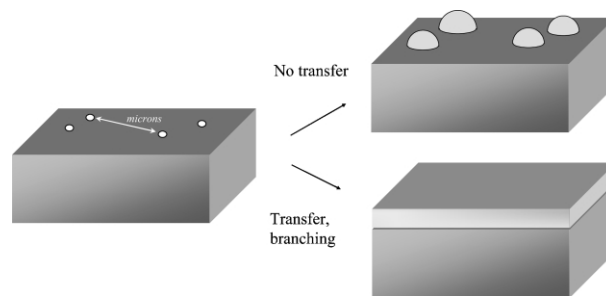
Scheme 1 A micron-spacing of the initiator groups can help in assessing the presence of transfer reaction in surface-supported ATRP.
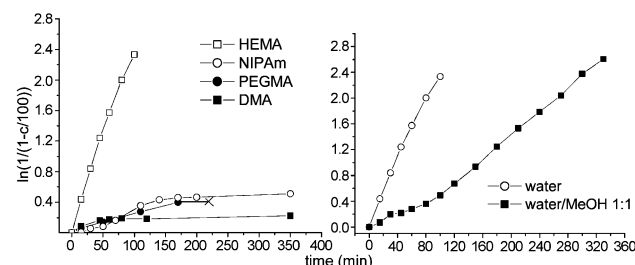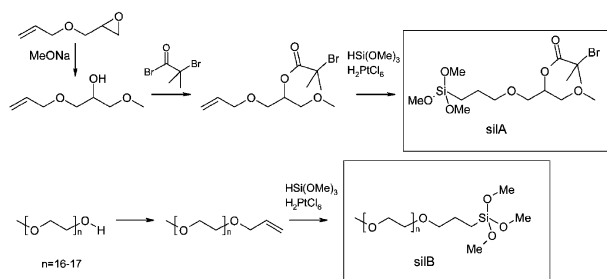

Fig. 1 Left: Conversion *vs.* time for several monomers polymerized on Rapp Tentagel M OH particles modified with 2-bromoester groups (0.14 mol g^{-1}) upon exposure to the Cu(bpy)$_2$Br complex in degassed water. **Right:** Conversion *vs.* time for HEMA polymerized in degassed water and in degassed water–MeOH 1 : 1 mixture. Conversion measured on a Nova-Pak® C$_{18}$ Water column (water–acetonitrile: gradient from 98% to 80% water in 10 minutes) as the concentration ratio between an internal standard (L-phenylalanine) and monomer.

Scheme 2 Synthesis of the silanizing agents.

Fig. 2 Left and centre: SEM pictures of poly(HEMA) coils on PEGylated silicon wafers; silB : silA = 10^4 (left) or 10^3 (centre). Right: optical microscopy picture of the sample with silB : silA = 10^4. The polymer coils are clearly detectable with optical analysis too.

Finally, hydrosilylation of the allyl group under hexachloroplatinic acid catalysis in ethanol–dimethoxyethane 1 : 1 mixture yielded the desired compound (yield: 52%, after purification on a sodium sulfate column using dichloromethane as an eluent). The same reaction was employed in the synthesis of silB (yield: 42% after sodium sulfate column and double precipitation in ice cold hexane), using as a substrate the allyl derivative of monomethoxy PEG750, synthesized according to a literature procedure.[16]

The introduction of this second, inactive silanizing agent provides a hydrophilic surface with a composition similar to that of our previous work (2-bromoesters in a poly(ethylene glycol)-rich environment), in order to safely adopt known polymerization conditions.

Even more important, in the silanization reaction silB competes with silA; due to the high excess of silB (see later), the condensation of silA with itself (co-localization) or in the proximity of other silA residues (proximal localization) is strongly unfavoured and the presence of clusters of initiators is therefore very unlikely.

The deposition conditions were first optimized for pure silB; silicon wafers (roughly 3 cm^2 in area) freshly treated with oxygen plasma were exposed to 30 ml of 1 mM toluene solution of silB for two hours, then rinsed and dried under nitrogen flux. AFM and XPS revealed the PEG-coating layer to be absolutely flat and with a negligible level of impurities.

A series of surface-functionalized silicon wafers was then prepared from reactand mixtures containing variable amounts of polymerization active silA. The silB : silA molar ratio was varied between 10^2 and 10^{12}, still keeping silB concentration = 1 mM. The successive polymerization experiments were performed under argon, adding a degassed water solution of HEMA into a tube containing the solid substrate and a degassed water solution of the polymerization catalyst (and copper(I) bromide–bipyridine–HEMA in 1 : 2 : 100 stoichiometric ratio, Cu(I)–silA used in the silanization experiment 1 : 1).

Polymerization took place from substrates treated with reactand mixtures with silB : silA ≤ 10^3; this number has been taken as a limiting value, above which silA was not effectively introduced onto the surface. If one assumes the two trimethoxysilyl groups to show the same reactivity, the silB : silA ratio should also indicate the surface area ratio between the two compounds (once corrected by their different mass) and from there the average inter-initiator distance. However, the existence of this limiting value hampers the use of the reactand ratio for a quantitative prediction.

Further experiments concentrated on values of this parameter between 10^2 and 10^3, which, without being related to a quantitative measurement, ensured the presence of initiators and at the same time their high dilution.

Under such conditions HEMA polymerization provided surface-tethered objects ranging in size from 100 nm to a few microns (Fig. 2). On increasing the amount of monomer, these objects coalesced in the form of films.

In a former study we observed HEMA polymerize from PEGylated surface-tethered initiators in a 'living' fashion until almost complete conversion; therefore, assuming termination reactions to be negligible, we believe that these objects are isolated, giant polymer coils.
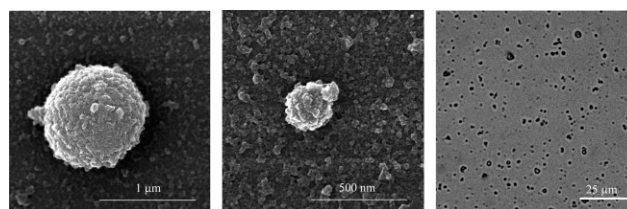
Their uncommon dimensions show that supported ATRP may provide macromolecules of exceptionally high molar mass and that, under such conditions, transfer reactions seem not to play a major role. However, their complete absence cannot be simply inferred from these observations and would require the analysis of the macromolecular material after careful detachment from the surface.

Notes and references

† No polymer could be extracted using organic solvents (THF, dichloromethane, NMP), suggesting the absence of physically entangled macromolecules. Due to the presence of an ester bond between polymer chains and surface, a basic treatment should cleave that group and also the side chains of the polyacrylate/polyacrylamide, delivering poly(sodium acrylate) in water solution. Unfortunately, only under very drastic conditions (boiling 5 M NaOH) was some polymeric material detached; furthermore it was characterized by low MW ($1–2 \times 10^3$). These values are far too low for this polymerization process (quantitative monomer conversion and monomer : initiator ratios ≫ 10^6) and were attributed to chain scission processes: radical transfer reactions cannot affect in such a marked way the MW.
‡ HEMA polymerizes in a living fashion also at high conversion, while other monomers (N-isopropylacrylamide (NIPAm), poly(ethylene glycol) methacrylate (PEGMA), dimethylacrylamide (DMA)) present limiting conversions (see Fig. 1). The possible transesterification of HEMA[17] does not hamper our study, and, with no transfer, just produces individual self-cross-linked chains.

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