

LIVING /CONTROLLED GRAFTING FROM POLYMER MICROSPHERES

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Abstract A review is given of grafting-from methods using living polymerizations, with emphasis on grafting from polymer microspheres using ATRP.

Keyword Living controlled polymerization, Grafting, ATRP, Microspheres

INTRODUCTION

Grafting polymerizations provide an important route to new materials. They can be used to attach functional polymers to linear and branched backbones, carbon nanotubes, inorganic and polymeric microspheres, flat surfaces and three-dimensional monoliths. Three approaches, grafting-on, grafting-from, and grafting-through, can be combined with a variety of polymerization mechanisms to create a vast array of functional materials ranging from biomaterials to new opto-electronic devices. The covalent nature of the attachment provides for permanent binding, in contrast to surface modifications involving deposition of block copolymers.

This review focuses largely on grafting polymers from polymer microspheres, an area that has received increasing attention in recent years due to the development of new methods for living/controlled radical polymerizations.

Stable Free Radical Polymerization (SFRP)^[1], Atom Transfer Radical Polymerization (ATRP)^[2], and Reversible Addition Fragmentation chain Transfer Polymerization (RAFT)^[3, 4] not only permit the formation of homo polymers, block copolymers and random copolymers of controlled molecular weight, but can be applied in dispersed systems^[5] and enable chains to be grafted from solid surfaces functionalized with initiating groups. Solid surfaces of interest include both flat and microspherical silica and polymers. In particular, the use of microspheres as solid phases for synthesis, chromatography, and drug delivery may be enhanced by grafting processes^[6]. Bruce Merrifield's solid phase peptide synthesis in fact represents an early example of grafting well-defined polyamides from polymeric microspheres^[7].

GRAFTING

Below, we will compare different polymerization methods and graft directions used, and provide a summary of our work on ATRP and ROP grafting of styrenic and methacrylic polymers from either hard or swellable polymer microspheres prepared by precipitation polymerization.

Grafting on, through and from Surfaces

Grafted surfaces are usually formed by either a "grafting-on" or a "grafting-from" approach.

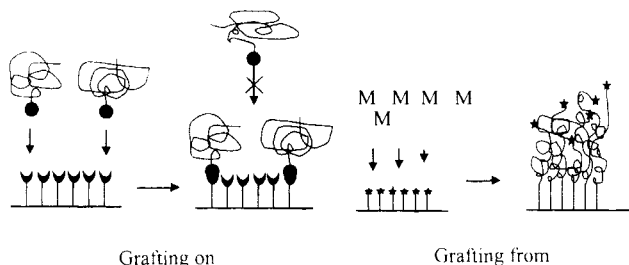
In the "grafting-on" approach, pre-formed polymer chains carrying a reactive group are coupled to a

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complementary reactive surface. This approach allows careful control of the polymer chains through, for example, living anionic polymerization, but tends to give low grafting rates^[8] and graft densities^[9], since initially grafted chains hinder further grafting in their vicinity, especially for higher molecular weight grafts.



Scheme 1

In the “grafting-from” approach polymerization is initiated from active sites on the substrate. This results in higher graft densities because monomers can easily diffuse to these propagating sites.

A third approach, grafting-through, involves a copolymerization that passes through polymerizable groups attached to a surface^[10].

Grafting using Ring-Opening Metathesis Polymerization (ROMP) and Ring Opening Polymerization (ROP)

Buchmeiser and coworkers reported the Ring-Opening Metathesis Polymerization (ROMP) grafting of a variety of chiral norbornene-based monomers from brominated styrene-divinylbenzene beads and silica particles, using both Schrock and Grubbs type catalysts^[11], as well as ROMP grafting to form chromatographic supports for reverse phase and ion-exchange chromatography^[12]. Nouvel *et al.* described the ROP grafting of ϵ -caprolactone from granular starch particles in order to prepare hydrophobically coated starch and related composites^[13]. Our group reported the ROP grafting of ϵ -caprolactone from functionalized crosslinked polymer microspheres^[14].

Grafting by Free Radical Polymerization

Free radical polymerization has traditionally been used to grow grafts from inorganic supports^[15]. Rühle *et al.*^[16] reported the conventional free radical polymerization of styrene from the surface of silica gel coated with a monolayer of covalently bound azo-initiator. Graft polymers with high, controlled graft density could be obtained. However, conventional free radical polymerization, especially when confined to a thin layer, leads to a wide molecular weight distribution of the grafted polymers, largely due to termination reactions^[17]. Moreover, free radical polymerization is not suitable for preparing block copolymers.

Grafting by Living Ionic Polymerization

Living polymerization can be used to graft homopolymers and block copolymers of uniform lengths from suitably functionalized chains and surfaces. The use of living anionic polymerization to form complex polymer architectures has recently been reviewed^[18].

Most ionic grafting-from polymerizations involve planar surfaces, or particles, based on carbon black^[19], carbon fiber^[20], graphite^[21], and silica^[22]. An interesting class of branched polymers are the arborescent graft copolymers, formed by successive chloromethylation and grafting-on using polystyryl anions^[23].

The sensitivity of ionic polymerizations to polar impurities, as well as to ionic repulsion at high initiator loading, requires careful handling and may limit the graft density achievable on surfaces.

Schouten's group^[24] reported the addition of *sec*-butyllithium to a layer of 4-trichlorosilylstyrene immobilized on a silica surface, and the subsequent living anionic polymerization of styrene and isoprene from the resulting surface-bound initiator groups. Ulman's group^[25] used self-assembled monolayers of biphenyllithium moieties on gold substrates as initiation sites for the anionic polymerization of styrene. The polymerization of styrene through this grafting-from method was reported to yield densely grafted polymer brushes with a thickness of 18 ± 0.2 nm and a surface roughness of 0.3–0.5 nm.

Zhao and Brittain recently described the sequential carbocationic and ATRP graft block copolymerization

of, respectively, styrene and MMA from a functionalized silica substrate^[26].

Grafting by Living Radical Polymerization

SFRP, ATRP and RAFT are the three major living radical polymerization processes, all introduced during the past 10 years. They share the ability to lower the steady state concentration of free radicals and effectively suppress bimolecular termination processes. In addition, Hadziioannou *et al.* reported the photoiniferter-mediated graft polymerization of styrene and MMA from functionalized silicon wafer and glass surfaces, including the formation of well-controlled block copolymers in thicknesses of up to 100 nm^[27].

SFRP Grafting

Stable Free Radical Polymerization (SFRP) is based on the reversible unimolecular dissociation of polymers terminated with nitroxyl radicals such as TEMPO^[1]. SFRP usually requires temperatures between 100°C and 135°C. It has been used to graft styrene and styrene copolymers from isotactic polypropylene surfaces, using ⁶⁰Co γ -radiation-induced surface hydroperoxides as initiators^[28]. Irgum and Frechet used 3-carboxy-PROXYL and 4-carboxy-TEMPO mediators to form porous monoliths with good flow properties, that could subsequently be pore-modified by grafting from the active chain ends^[29].

Chaumont *et al.* described the formation of thin layers of polystyrene grown from silica-bound nitroxide initiators, with high degrees of grafting and chain stretching^[30].

Riedl's group reported the very well controlled graft polymerization of styrene from peroxide-functionalized ultrafine silica using *N*-tert-butyl-1-diethylphosphono-2,2-dimethyl propyl nitroxide (DEPN) as mediator, yielding organic/inorganic composites with polystyrene grafts having M_n of up to 80,000 g/mol and PDI's of 1.2–1.3^[31].

RAFT Grafting

RAFT polymerization is a versatile living/controlled method that is compatible with a very wide range of monomer types, functional groups and reaction conditions. Polymers prepared by the RAFT method bear dithioester end groups. Following polymerization, the dithioester can be converted into a terminal thiol group and used to attach the chain to transition metal particles^[32]. Grafting has been carried out by attaching RAFT agents to different substrates^[33, 34]. The Centre for Advanced Macromolecular Design, CAMD, in Sydney, Australia, recently described the γ -initiated, RAFT mediated, graft polymerization of styrene on polypropylene SynPhase lanterns used as solid synthesis supports^[35]. Baum and Brittain described the use of RAFT to graft styrene, methylmethacrylate and *N,N*-dimethylacrylamide from silicone and silica surfaces using a surface-bound azo initiator^[36]. Due to its compatibility with many functional groups, RAFT may be expected to play a major role in future living/controlled polymerizations.

ATRP GRAFTING

Atom transfer radical polymerization^[2] (ATRP) was reported almost simultaneously in 1995 by the groups of Sawamoto and Matyjaszewski, and has since been developed into a very versatile method for the controlled living polymerization of a wide range of monomers. Several recent reviews cover the choice of catalysts, ligands, initiators and monomers available^[37, 38], as well as approaches to grafting using ATRP. Styrenic, acrylic and methacrylic monomers are all suitable for ATRP, with the only exception being acidic and anhydride monomers, due to their interference with the metal complexation. Grafting is a particularly attractive application for ATRP, as metal and ligand residues can easily be removed by washing/centrifugation steps. Inorganic as well as polymeric substrates of different shapes have been grafted using ATRP, and are briefly described below.

Inorganic Surfaces

The ease of attaching initiators through silyl coupling agents, and the ease of detaching the resulting polymer chains from the surface to determine their molecular weight and molecular weight distribution, led to significant uses of glass^[39], silicon wafers^[40], silica gel^[41] and silica particles^[42] as supports for ATRP. Matyjaszewski recently reviewed the synthesis of nanocomposite organic/inorganic hybrid materials using different

controlled/living radical polymerizations^[43]. Hallensleben described the formation of related hybrid materials by ATRP grafting from layered silicates, and related the layer spacing to the degree of polymerization^[44]. Muller and coworkers described the well-controlled grafting of hyperbranched polymers from silica surfaces by the self-condensing ATRP of a monomer carrying both an acrylic group and an initiating group^[45]. Brittain reported the ATRP graft block copolymerization of poly(styrene-*b*-acrylate) from flat silica surfaces^[46]. Tsujii *et al.* described the formation of patterned surface grafts by amplifying a primary electron beam derived initiator pattern using ATRP^[47]. Fukuda recently described the ATRP grafting of glucofuranose-carrying methacrylate on silica surfaces, in order to prepare model materials suitable for affinity binding studies involving the sugar residue^[48].

Wirth described grafting acrylamide from porous silica gel coated with a self-assembled monolayer of 1-trichlorosilyl-2-(*m/p*-chloromethylphenyl)ethane. The number-average molecular weights of the grafted polymers were up to 13–15 kDa, with PDI's below 1.3^[49]. Patten *et al.* reported the grafting of styrene from 70 nm silica-nanoparticles by ATRP^[50]. Recently, he reported the grafting of a series of polyelectrolytes from silica particles using surface initiated ATRP, and described their polyelectrolyte and materials properties^[51].

Klep and Luzinov described the covalent anchoring of a primary layer of poly(glycidyl methacrylate) on the surface of a range of substrates, followed by the conversion of the residual epoxy groups into ATRP initiators by reaction with bromoacetic acid^[52].

Finally, Bruening and Baker reported the ATRP grafting of PMMA with M_n of 44,500 g/mol and PDI of 1.30 from gold surfaces, using 2-bromo-propionates attached to the gold surface through a thiol spacer^[53]. Recently, they described the water-accelerated ATRP grafting of HEMA from gold surfaces, yielding 700 nm thick layers within 12 h^[54].

Molecular Brushes

Molecular brushes are a fascinating class of material, formed by using living/controlled graft polymerizations from usually linear backbones. Matyjaszewski and Sheiko recently briefly reviewed this class of compounds, and described the formation of molecular brushes containing a gradient of grafting density, based on using a gradient copolymer of MMA and protected hydroxyethylmethacrylate as macroinitiator^[55].

Grafting from Latex Particles

Brooks *et al.* reported the aqueous ATRP grafting of *N,N*-dimethylacrylamide from a polystyrene latex coated with a copolymer shell carrying 2'-chloropropionato initiator groups. They observed very high graft molecular weights M_n of over 600,000 g/mol, with corresponding hydrodynamic brush thicknesses of up to 800 nm^[56]. Very recently they found that grafting from analogous latex particles with low initiator loading, led to even higher molecular weight poly(*N,N*-dimethylacrylamide) grafts of 1,200,000 g/mol, with polydispersities of as low as 1.3^[57]. It appears that the graft environment is responsible for these unusually high molecular weights.

Min *et al.* described the grafting of methyl methacrylate and methyl acrylate from chloromethylated, 10% crosslinked styrene/divinylbenzene latex particles prepared by emulsifier-free emulsion polymerization^[58]. They observed small increases of the latex particle diameters of between 7 and 22 nanometer, which are likely predominantly due to surface grafting, given the fairly high crosslink density.

Suspension Polymer Particles

Haddleton's group^[59, 60] has described the attachment of ATRP initiators on Merrifield and Wang-type microbeads, and the subsequent grafting of methyl methacrylate, benzyl methacrylate, and hydrophilic *N,N*-dimethylacrylamide from these beads. Recently, Tirelli's group grafted several polar acrylamides and methacrylates including PEG methacrylate and *N*-isopropylacrylamide from PEG-containing suspension polymer beads in aqueous media. Depending on the resin used, they succeeded in grafting only from the surface, or throughout the microparticles. Tirelli also briefly reviews a number of living radical grafting-from reports^[61].

Filiz Senkal and Bizak reported the grafting of neat methyl methacrylate and ethyl acrylate from 10% DVB crosslinked polystyrene suspension beads, with weight increases of 380% for MMA after 6 h, and 160% for EA after 44 h^[62].

Other methods developed to form monodisperse microspheres such as Ugelstad's multi-step seeded swelling

polymerization^[63, 64, 65], and Okubo's single-step dynamic swelling polymerization^[66, 67], also offer interesting supports for grafting polymerization.

ATRP GRAFTING FROM POLYMER MICROSPHERES FORMED BY PRECIPITATION POLYMERIZATION

In the following we describe our research into grafting from crosslinked monodisperse microspheres prepared by precipitation polymerization. These microspheres have a number of properties that make them particularly useful as model supports for living radical graft polymerizations.

Precipitation Polymer Microspheres

These microspheres are prepared by polymerization of crosslinking monomers such as divinylbenzene in near-*theta* solvents or solvent mixtures^[68, 69, 70]. They form by controlled aggregation of oligomer radicals^[71], and hence have a gel surface layer that provides both colloidal stability, and residual vinyl groups for subsequent functionalization. No steric stabilizers or surfactants are used in this process, and the resulting microspheres are hence inherently clean.

A wide range of co-monomers including hydroxyethyl methacrylate (HEMA), MMA, MA, glycidyl methacrylate (GMA)^[72], maleic anhydride (MAN)^[73], and chloromethylstyrene^[74] have been incorporated into these particles^[75]. In addition, the microspheres can be made porous by adding a porogenic solvent such as toluene to the polymerization mixture^[76]. Core-shell particles can be prepared by adding a second monomer at a later stage of the polymerization^[77], and the overall crosslinking density can be varied to give both swellable and non-swellable microspheres^[78]. Finally, this polymerization process can be used with non-polar silane comonomers^[79] as well as with polar monomers such as PEG methacrylate and methacrylic acid^[80], by adjusting the solvent polarity to the monomer system.

Figure 1 shows an ESEM image of monodisperse microspheres prepared by precipitation polymerization of di(4-vinylbenzyl) diphenyl silane.

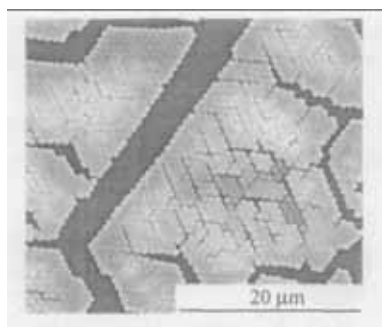


Fig. 1 ESEM image of microspheres prepared by precipitation polymerization of di(4-vinylbenzyl) dimethyl silane

Both highly crosslinked, nonporous^[81] as well as lightly crosslinked, swellable microspheres^[82, 83] were prepared for use as macroinitiators for the ATRP grafting of styrene and 4-methylstyrene, MMA, MA, dimethylamino ethyl methacrylate (DMAEMA), GMA, as well as for the ring-opening grafting polymerization of ϵ -caprolactone^[14].

ATRP Grafting From Poly(divinylbenzene-80) Macroinitiator Particles (D-Cl, D-Br)^[81]

Nonporous poly(divinylbenzene-80) particles (D) were prepared in polyethylene bottles containing 3 W/V% DVB80 (commercial mixture containing 80% divinylbenzene isomers) in acetonitrile, together with 2 W/W% AIBN relative to the monomer. The bottles were rotated horizontally at 70°C for 24 h at about 4 r/min to give approximately 50% yield of mono disperse microspheres (Fig. 2a) with diameters of about 3 micrometer.

These microspheres were converted to ATRP initiator particles by either hydrochlorination (*D-Cl*), or by

hydroboration followed by reaction with H_2O_2 and NaOH , and esterification of the resulting alcohol with 2-bromopropionyl bromide ($D\text{-Br}$).

Styrene was grafted from $D\text{-Cl}$ at 110°C , using Cu(I)Br and 2,2'-bipyridine (bipy) as catalyst system. Methacrylates were grafted from $D\text{-Br}$ at room temperature in THF, using $\text{Cu(I) Br/tetramethyl cyclam}$ (Me_4Cyclam). This catalyst system had earlier proven effective for the ATRP of N,N -dimethylacrylamide at room temperature^[84].

Grafting styrene from the nonporous $D\text{-Cl}$ initiator microspheres increased the number-average particle diameter D_n from 2.96 (Fig. 2a) to $3.07\ \mu\text{m}$ (Fig. 2b). The high crosslink density restricts both hydrochlorination and grafting to a thin layer near the surface. These grafted polymer chains promote the formation of two or three-dimensional microsphere arrays $D\text{-PS}$ (Fig. 2b). Precipitation into a poor solvent produces clusters that are easy to re-disperse in good solvents. On the other hand, drying from a good solvent such as THF forms chain-entangled composites that are difficult to re-disperse, even in good solvents.

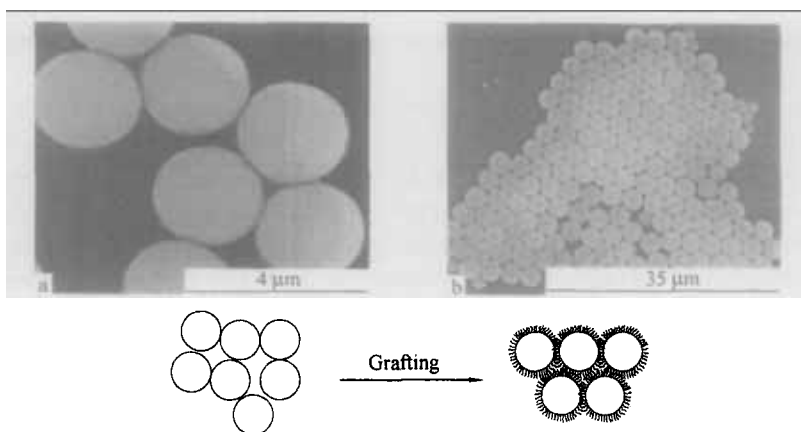
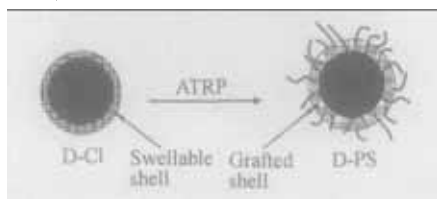


Fig. 2 Surface grafting helps particles self-assemble upon drying
a) $2.96\ \mu\text{m}$ starting microspheres D ; b) $3.07\ \mu\text{m}$ PS-grafted microspheres, $D\text{-PS}$

The observed finite size increase is attributed to both polymer grafted from the particle surface as well as polymer grafted from sites within the slightly swellable surface layer (Scheme 2).



Scheme 2 Grafting from swellable shell

Elemental analysis revealed the expected chlorine-to-bromine interchange during the ATRP, and a 32% decrease of total halogen, likely due to early radical termination^[85]. The remaining halide sites were able to initiate a second polymerization of 4-methylstyrene, leading to di-block grafted microspheres $D\text{-PS-}b\text{-P4MS}$ with a diameter of $3.17\ \mu\text{m}$. The environmental scanning electron microscope (ESEM) image in Fig. 3 now shows visible surface-grafted polymer between the $D\text{-PS-}b\text{-P4MS}$ microspheres.

Dimethylamino ethylmethacrylate (DMAEMA) was grafted directly from the analogous dense $D\text{-Br}$ microspheres. The resulting pDMAEMA chains were similarly confined to the surface regions of the microspheres. Potentiometric titration gave an amine loading of $0.8\ \text{meq/g}$ dry microspheres, commensurate with the 15% weight increase.

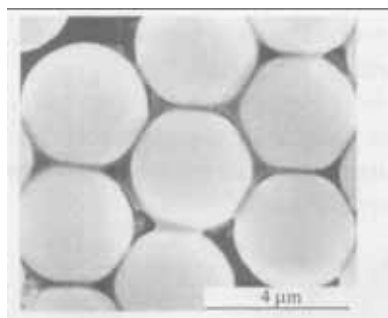


Fig. 3 D-PS-*b*-P4MeS with graft polymer visible between microspheres
Scale bar is 4 micrometer.

Grafting from such highly crosslinked nonporous polystyrene microspheres leads to largely surface-grafted particles, with applications as spacers for LCD displays, TEM size standards, and medium capacity ion exchange or separation resins. These highly cross-linked non-porous micro-spheres can withstand column backpressures of 69 MPa^[86]. Modification with a dense surface layer of long polymer chains could lead to improved chromatographic separation efficiency, compared to porous or swellable microspheres, and to enhanced capacity compared to non-grafted, purely surface functionalized supports. In addition, grafted block copolymer may further result in hydrophilic and hydrophobic domains that can facilitate selective retention, and be useful as stationary phases for direct analyses of hydrophobic drugs in serum, analogous to those described by Tanaka^[87].

Grafting from Swellable Poly(DVB80-co-HEMA) Microspheres H_1Br ^[82, 83]

Swellable macroinitiator particles may lead to even higher capacity resins suitable for supported syntheses^[88]. Advantages such as high product purity, and simplified work-up in high-throughput parallel syntheses, drives the development of new polymer-supported reagents^[89]. Many are based on lightly cross-linked polystyrene, which is stable in both basic and acidic media, but must be swollen in organic solvents and cannot be used in aqueous media. Bayer grafted polyethylene glycol (PEG) on lightly cross-linked polystyrene beads by anionic polymerization, forming the so-called TentaGels^[90]. These PEG-grafted polymer-supported reagents swell in many solvents, and are suitable for the solid-phase synthesis of peptides and nucleotides. However, their functional capacity is fairly low as functional groups are present only at the termini of the PEG chains. Bradley *et al.*^[91] increased the TentaGel capacity through an amidoamine-based dendrimerization process. In principle, small swellable microspheres grafted with a large amount of functional polymer should form resins having the maximum theoretical functional group loading. We have tested this concept using lightly crosslinked DVB-HEMA microspheres prepared by precipitation polymerization.

Grafting MMA and MA from H_1Br ^[82]

Lightly crosslinked, swellable microspheres were formed by copolymerization of four different ratios of DVB80 and HEMA, containing up to 82.5% HEMA (H_1). These microspheres were esterified with 2-bromopropionyl bromide to form initiator particles (H_1Br).

ATRP of MMA from H_1Br gave H_1 -PMMA-Br microspheres that showed weight increases of 313%, consistent with the high initiator loading, swellability and accessibility of H_1Br . The analogous ATRP of MA from H_1Br gave a weight increases of only 157%. These results resemble the loading achieved by Senkal and Bizak on analogous suspension polymer particles^[62].

Representative images of initiator particles H_1Br and H_1 -PMMA-Br are shown in Fig. 4(a) and (b), respectively. Grafting with MA and MMA led to increases in the number average diameter from 1.4 μm to 2.2 μm and 2.7 μm , respectively, indicating polymer chains growing not only from the surface, but also from initiator sites within these swellable particles. The rough surfaces of H_1 -PMMA-Br form during ESEM imaging and reflect the radiation sensitivity of the PMMA grafts. Optical images show smooth microsphere surfaces.

The resulting interpenetrating network formed between the macroinitiator particles and the graft should have a gradient composition as indicated in Scheme 3.

The TEM image of H_1 -PMMA-Br shown in Fig. 5 confirms this gradient composition. The surface layer of the particles, consisting of almost pure PMMA, decomposed under the electron beam and left a void indicated by a white ring. We are currently studying these compositional gradients, including core-shell structures, using scanning transmission x-ray microscopy (STXM)^[92].

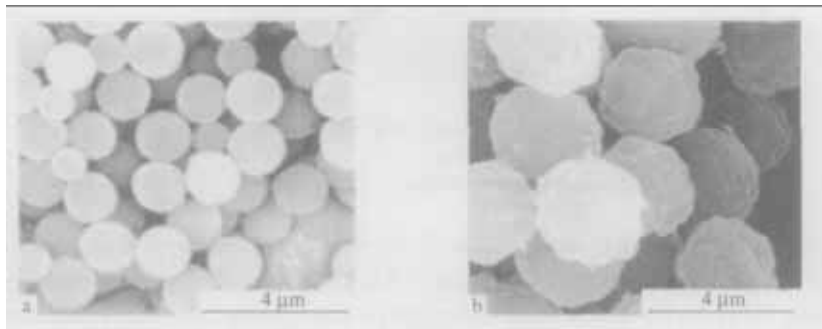
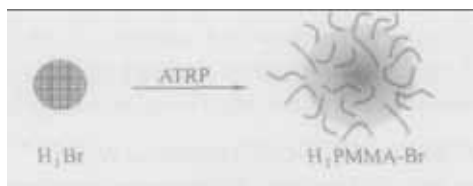


Fig. 4 ESEM images of (a) H_1Br ; (b) H_1 -PMMA-Br



Scheme 3 Interpenetrating network formed by grafting from both surface and interior of swellable microspheres

The living/controlled nature of the ATRP graft reactions was confirmed by the steady increase of the diameter of the H_1 -PMMA-Br microspheres with polymerization time (Fig. 6, only data for zero and four hours shown), as measured with a Coulter Multisizer II. The small peaks appearing to the right of the main peaks are attributed to temporary aggregates of two or more particles during passage through the Coulter Multisizer orifice.

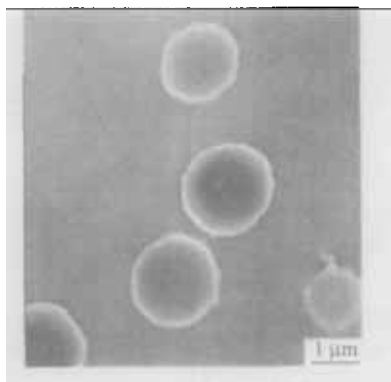


Fig. 5 TEM image of H_1 -PMMA-Br embedded in epoxy resin

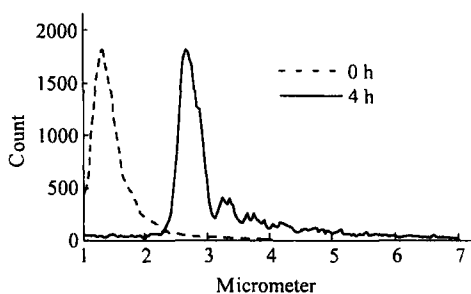


Fig. 6 Diameter of H_1 -PMMA-Br microspheres as function of polymerization time

Block copolymer: grafting HEMA and DMAEMA from H_1 -PMMA-Br^[82]

H_1 -PMMA-Br microspheres obtained after 4 h of polymerization were used as initiator particles for ATRP of HEMA and DMAEMA. The particle weights increased by 243% and 435%, respectively, while the diameter of the particles increased from 2.7 μm to *ca* 4.1 and 4.7 μm , respectively. These results confirmed that a significant

portion of the first grafts can be reactivated using ATRP catalysts. The resulting H_1 -PMMA-*b*-PDMAEMA microspheres showed capacities of 5.3 mmol amine/g dry microspheres by potentiometric titration. This high functional capacity is attributed to the tethering of many PDMAEMA blocks to the swellable scaffold formed by the H_1 -PMMA-Br precursor particles.

DMAEMA was also directly grafted from H_1 Br particles to give H_1 -PDMAEMA microspheres with weight increases of 398% and potentiometric amine loadings of 4.6 mmol/g.

Grafting functional acrylates and methacrylates by controlled/living ATRP from swellable microsphere initiators can hence lead to novel, highly functional polymer supports.

*Morphology of H_1 -PMMA-*b*-DMAEMA with different block lengths^[83]*

Block copolymers in solution and in matrices can adopt many different morphologies^[93]. There have been several reports of block copolymers grafted from polymeric initiators^[94]. However, few reports describe the morphology of block copolymers grafted in confined conditions, such as from surfaces^[95].

We prepared H_1 -PMMA-Br particles (Fig. 7a) and used them as macroinitiators for a second grafting of DMAEMA, to yield H_1 -PMMA-*b*-PDMAEMA particles (Fig. 7b). Viewed by optical microscopy under water, these microspheres all have perfectly spherical shape. The swellable, block copolymer grafted particles deform substantially upon drying from different solvents (Fig. 7b). We are investigating phase separations due to selective block interactions.

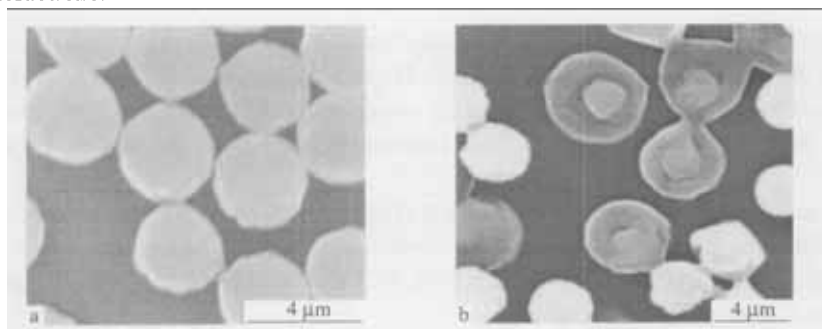


Fig 7 ESEM images of (a) H_1 -PMMA-Br and (b) H_1 -PMMA-*b*-PDMAEMA (PMMA/PDMAEMA = 2.1/10.2)

H_1 -PMMA-*b*-PDMAEMA was quantitatively converted into the corresponding quaternary trimethylammonium analog H_1 -PMMA-*b*-PTMAEMA, by treatment with methyl iodide. Both of these charged microspheres show falsely low diameters in Coulter Multisizer measurements, as the measurement current can now partly flow through the microspheres. H_1 -PMMA-*b*-PTMAEMA showed spherical or obloid shells, with some breakage visible (Fig. 8).

*H_1 -PMMA-*b*-PGMA^[83]*

Epoxy groups can be useful for subsequent functionalization of polymers, and for adhesion to polar surfaces. Accordingly, glycidyl methacrylate (GMA) was grafted from H_1 -PMMA-Br and the internal structure of the resulting H_1 -PMMA-*b*-PGMA studied by TEM (Fig. 9).

The dark H_1 core is visible in the particle, while the corona represents the PMMA-*b*-PGMA grafts. These grafts are swollen by the Spurr epoxy resin used for embedding. These GMA-grafted particles are currently being studied with regard to further functionalization of the epoxy ring, and as building blocks in interfacial film formation.

*Grafting of ϵ -Caprolactone and ϵ -Caprolactone-*b*-Dimethylaminoethyl Methacrylate from H_1 Microspheres by Ring-Opening Polymerization (ROP) and ATRP^[14]*

Choi and Langer recently described the surface-initiated tin octanoate catalyzed polymerization of *L*-lactide to form surfaces coated with biodegradable poly(ϵ -caprolactone)^[96]. The ROP of cyclic esters has been thoroughly

described^[97]. Aluminum alkoxides such as $\text{Al}(\text{OiPr})_3$ ^[98] and $\text{AlOR}(\text{Et})_2$ ^[99] have been reported to be efficient initiators toward polymerization and copolymerization of cyclic esters with narrow molecular weight distribution. Hamaide *et al.*^[100] reported the heterogeneous ROP initiated by $\text{Si}-\text{O}-\text{Al}(\text{OR})_2$ covalently attached to porous silica. The resulting $\text{SiO}-\text{Al}-[(\text{O}(\text{CH}_2)_5\text{CO})_n\text{OR}]_2$ linkage was hydrolytically labile, and hence more useful for producing ω -functionalized (oligo)copolymer, than for reliably modifying surfaces.

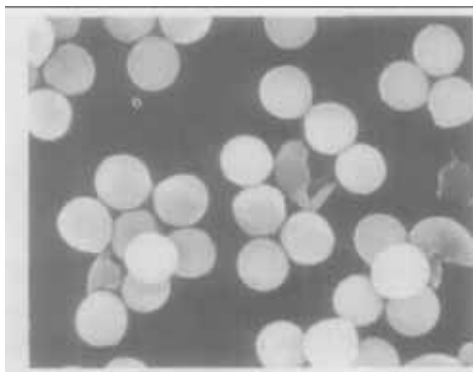


Fig. 8 ESEM image of H_1 -PMMA-*b*-PTMAEMA

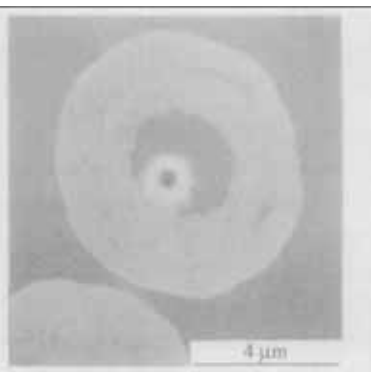


Fig. 9 TEM image of H_1 -MMA-*b*-GMA

We grafted ϵ -caprolactone from hydroxyl-functional microspheres using ring-opening polymerization (ROP) in the presence of $\text{Al}(\text{Et})_3$ and $\text{Al}(\text{OiPr})_3$. The particles H_1 , and H_3 , having 87.5% and 65% HEMA, respectively, were used to initiate the ROP of ϵ -caprolactone in the presence of $\text{Al}(\text{Et})_3$. Their weights after polymerization at 70 °C for 10 h increased by 107% and 37%, respectively, reflecting the higher swellability of the H_1 microspheres.

$\text{Al}(\text{Et})_3$ gave more efficient particle growth than $\text{Al}(\text{OiPr})_3$, as all chain growth was confined to the polymer-bound alkoxy. The resulting H_1 -PCL particles were reacted with 2-bromopropionyl bromide to form macroinitiators for ATRP of DMAEMA, leading to H_1 -PCL-*b*-PDMAEMA block graft copolymer with amine loadings as high as 5.10 mmol/g dry particles.

The H_1 -PCL-*b*-PDMAEMA particles approximately double in diameter due to grafting. Their shell of pDMAEMA swells in good solvents such as THF, fusing the particles into a film upon drying. Isolation from poor solvents such as diethyl ether yields individual particles.

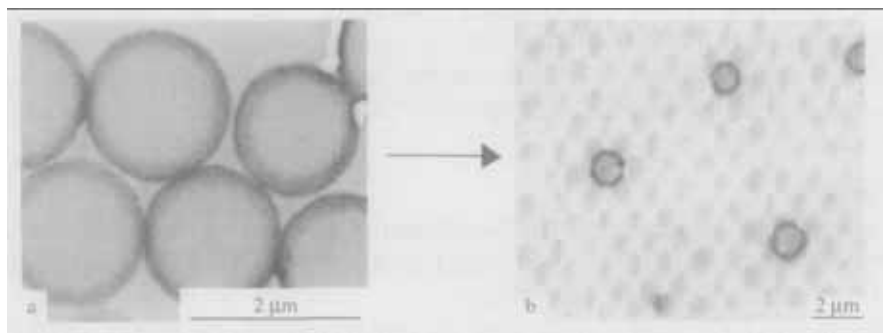


Fig. 10 TEM images of (a) H_1 -PCL; (b) H_1 -PCL-*b*-PDMAEMA

Figure 10 shows TEM images of poly-(ϵ -caprolactone) grafted microspheres. H_1 -PCL shows a core-shell structure with a dark corona of poly(ϵ -caprolactone) and a light core representing the swollen H_1 particle (Fig. 10a). After the second grafting, with DMAEMA, the resulting H_1 -PCL-*b*-PDMAEMA particle shows an irregular contour comprised mainly of linear poly(DMAEMA) around each core-shell particle (Fig. 10b).

These doubly grafted microspheres show functional amine loadings of up to 5.10 mmol/g. A typical gel ^1H -

NMR spectrum of H_1 -PCL-*b*-PDMAEMA, swollen in $CDCl_3$ is shown in Fig. 11. The high mobility of the grafted chains ensures significant local or segmental mobility to allow both ^1H and ^{13}C -NMR. Direct Polarization-Magic Angle Spinning (DP-MAS) NMR of these gel particles would result in high-resolution, solution-type spectra^[101].

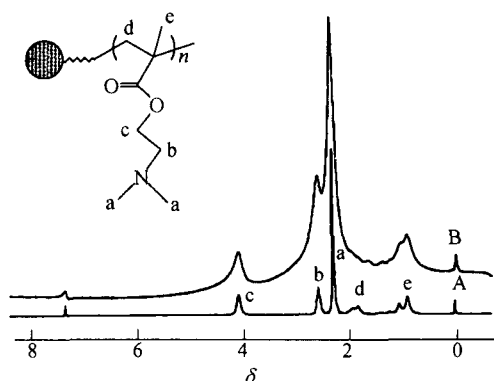


Fig. 11 Gel- ^1H -NMR of H_1 -PCL-*b*-PDMAEMA

A) linear poly(DMAEMA) in $CDCl_3$; B) H_1 -PCL-*b*-PDMAEMA swollen in $CDCl_3$

CONCLUSION

Grafting functional polymers from dense and swellable microspheres using living/controlled polymerizations can give access to new materials with potential uses in separation science and as solid supports. In particular, the use of swellable microspherical scaffolds results in very high functional group loading, due to the favourable ratio of functional load to support.

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