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Grafting of Polystyrene from Narrow Disperse Polymer Particles by Surface-Initiated Atom Transfer Radical Polymerization

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ABSTRACT: Grafting of polystyrene from narrow disperse polymer particles by surface-initiated atom transfer radical polymerization was investigated. Poly(DVB80) particles prepared by precipitation polymerization were used as starting particles. Their residual surface vinyl groups were hydrochlorinated to form chloroethylbenzene initiating sites for subsequent ATRP of styrene using CuBr/2bipy as catalyst system. Polystyrene was found grafted not only from the particle surfaces but also from within a thin shell layer, leading to particles size increases from 2.96 to 3.07 μm. The surface layer of polystyrene improved colloidal stability and facilitated formation of colloidal arrays. Block copolymers of poly(styrene-*b*-4-methylstyrene) were grown from the particles, and the living nature of surface-initiated ATRP is discussed.

Introduction

The modification of particles or planar surfaces by grafting of polymer chains has attracted much academic and industrial interest. Particular attention has been given to polymer "brush-type" layers with properties such as being able to change their swelling volume in response to changes in pH or ionic strength,[1] temperature,[2] solvent quality, or mechanical force.[3,4] The grafted surfaces may be formed by either a "grafting-onto" or a "grafting-from" approach.

In the former case (Scheme 1a), preformed polymer chains carrying an active terminal group are coupled onto a reactive surface. This approach allows careful control of the polymer chains but tends to suffer both from low grafting rates[5] and from low final graft density,[6] since already tethered chains try to maintain their coil shape in good solvents and hence hinder further grafting in their vicinity. As well, the overall amount of grafted polymer first increases with increasing molecular weight but subsequently decreases due to the steric exclusion.

The "grafting-from" technique (Scheme 1b) allows polymer chains to initiate from every active site on the substrate, giving high grafting densities because monomers can easily diffuse to the propagating sites.

Rühe et al.[7] 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.[8] Moreover, this approach is not suitable for preparing block copolymers.

Living polymerization methods, on the other hand, are able to generate grafted homopolymers and block copolymers of uniform lengths. Schouten's group[9] reported the addition of *sec*-butyllithium (*s*-BuLi) 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[10] 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 yielded densely grafted polymer brushes with a thickness of 18 ± 0.2 nm and a surface roughness of 0.3−0.5 nm.

In most cases, the study of grafting-from process through ionic polymerization involved planar surfaces, or particles, based on carbon black,[11] carbon fiber,[12] graphite,[13] and silica.[14] The sensitivity of ionic polymerizations to polar impurities, as well as to ionic repulsion at high initiator loading, can limit their utility for grafting polymers from solid surfaces.

Controlled/living radical polymerizations such as atom transfer radical polymerization (ATRP)[15] have a number of advantages over both conventional free radical and ionic polymerization. ATRP has a highly living nature, allowing for the synthesis of block copolymers[16] and graft copolymers,[17] and is particularly tolerant of water[18] and functional groups.[19] Several groups have worked on applications of ATRP in grafting polymers from solid surfaces. Patten et al. reported the preparation of structurally well-defined polymer−nanoparticle hybrids by ATRP.[20] Spherical silica particles with an average diameter of 70 nm were tethered with surface ATRP initiator (2-(4-chloromethylphenyl)ethyl)-dimethylethoxylsilane, followed by ATRP of styrene at 130 °C in the presence of CuCl/dNbipy as catalyst. The size of the particles increased with conversion, consistent with the molecular weight of the grafted polymer. The grafted polymer chains were cleaved from the support particles using 5% aqueous HF and aliquot 336 and showed narrow molecular weight distribution with a PDI of about 1.3.

ATRP were also carried out on the inside of glass capillaries[21] to be used for electrophoresis and from initiator patterned onto a gold substrate[22] for generating barriers to wet chemical etchants of gold.

The ease of attaching initiators through silyl coupling agents, and the ease of detaching the formed polymer chains to determine their molecular weight and molecular weight distribution, led to significant use of glass,[23]

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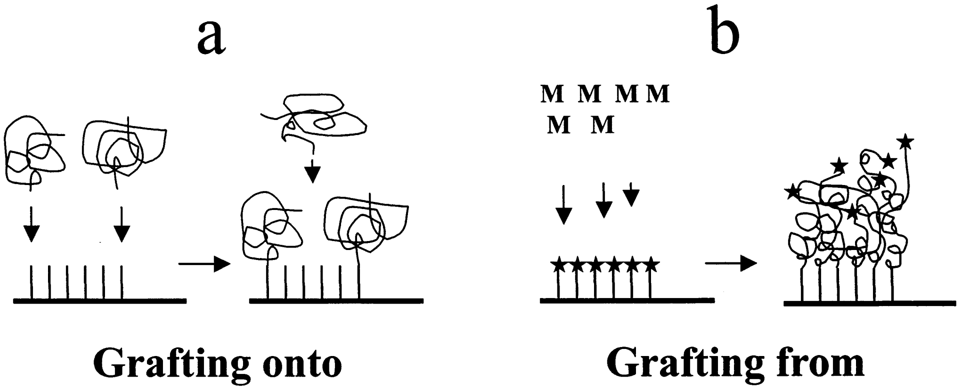
Scheme 1. Surface Grafting of Polymer Chains



silicon wafers,[24] silica gel,[25] and silica particles[26] as support surfaces for ATRP. In contrast, few reports deal with ATRP grafting from organic polymeric particles.[27,28]

We report here the modification of organic polymeric particles by grafting styrene from poly(divinylbenzene) (PDVB80) microspheres using ATRP. The PDVB80 microspheres are prepared by precipitation polymerization of DVB80 using AIBN as initiator in the absence of added stabilizer or surfactant. However, they do have residual vinyl groups on their surface, which were easily converted into 1-chloroethylbenzene groups by hydrochlorination. The bulk ATRP of styrene took place from benzyl halide initiator sites in the presence of CuBr/2bipy as catalyst.

Experimental Section

Chemicals. DVB80 (70−85% DVB isomers, Fluka, Oakville, Canada), acetonitrile (HPLC grade, Aldrich), tetrahydrofuran (THF, 99+%, Aldrich), methyl ethyl ketone (MEK) (99+%, Aldrich), 2,2′-dipyridyl (bipy) (99+%, Aldrich), Cu(II)Br_2 (99%, Aldrich), and diethyl malonate (99%, Aldrich) were used as received. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Eastman Kodak Co.) was recrystallized from methanol. Styrene and 4-methylstyrene were purchased from Aldrich Chemical Co. and purified by distillation under vacuum prior to polymerization. Anhydrous hydrogen chloride in a steel cylinder was purchased from Matheson.

Methods. *Preparation of Starting Particles.* The starting PDVB80 particles were prepared by precipitation polymerization in neat acetonitrile as described earlier.[29] Divinylbenzene-80 (DVB80) (6.0 g, 46 mmol), acetonitrile (200 mL), and AIBN (0.12 g, 2 wt % relative to monomer) were placed in a 250 mL polyethylene bottle and shaken vigorously until the initiator was completely dissolved. The bottle was placed in a reactor equipped with horizontal rollers and a programmable temperature controller. The reactor gently agitates the sample by rolling the bottles at approximately 4 rpm. The temperature profile used for polymerization started with a 1 h ramp from room temperature to 60 °C followed by a 1 h and 40 min ramp to 70 °C where the temperature was kept constant for 24 h. The resultant microspheres were isolated by vacuum filtration through a 0.5 μm membrane filter with three subsequent washing with THF. The clean particles were dried at room temperature under vacuum for 24 h. The yield of particles was 3.4 g (56.7%), with the remainder being unreacted monomer.

Hydrochlorination of Particles. PDVB80 particles (2.00 g) were suspended in 20 mL of THF in a 50 mL two-neck round-bottomed flask for 2 h. Dry hydrogen chloride (HCl) was slowly passed through the suspension for 1 h at room temperature. The flow rate of HCl was controlled such that all HCl introduced dissolved in the THF. The HCl saturated suspension was kept for 2 h at room temperature. The resulting PDVB80−HCl particles were filtered and washed with THF. The final particles were dried at room temperature under vacuum for 24 h. The yield of particles was 2.07 g. A blank recovery test indicated that recovery after work up was quantitative.

Preparation of CuBr. Due to the low purity of CuBr purchased from Aldrich, the CuBr used in ATRP were prepared by the reduction of $CuBr_2$ with dimethyl malonate. $CuBr_2$ (10.0 g, 44.8 mmol) was added to 50 mL of dimethyl malonate/THF (1:1), and the mixture was refluxed for 3 h. The light yellow precipitate was filtrated through a 0.5 μm membrane filter and washed with methanol followed by hexane. The precipitated CuBr was stored under nitrogen prior to use. The yield was almost quantitative (6.26 g, 43.6 mmol/97.5%).

Grafting Polymers from Particles. The ATRP took place in bulk styrene. Particles PDVB80−HCl (3.00 g) and CuBr (0.26 g, 1.81 mmol) were placed in a flask and degassed/purged with three cycles of vacuum/nitrogen. Subsequently, degassed 2,2′-bipyridine (bipy) (0.58 g, 3.71 mmol) in 10.0 g of styrene was added through a double-tipped needle. The mixture was stirred with a magnetic bar, heated to 110 °C under nitrogen, and the reaction continued for 19 h. The resulting blue-green particles were isolated by centrifugation and redispersed three times in THF, several times in methanol/glacial acetic acid (95/5) until the particles were almost white, and finally twice in diethyl ether prior to drying. The resulting particle yield was 3.34 g. The polymerization solution was very viscous due to the formation of polystyrene through thermal autoinitiation in solution. This polymer was precipitated into methanol, and 4.5 g of polystyrene ($M_n = 2.65 \times 10^4$, $M_w = 4.43 \times 10^4$, and $M_w/M_n = 1.67$) was obtained.

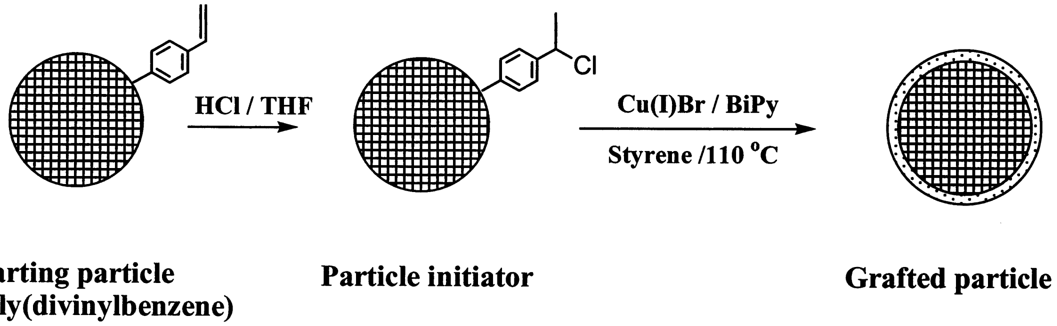
Similar polymerizations were carried out for the preparation of grafted particles with different polymerization times, with samples taken via syringe at each time interval. These samples were centrifuged and purified as described above. The first supernatants were used for determining molecular weight of the polymer in solution.

The second grafting, of poly(4-methylstyrene), from particles previously grafted with polystyrene, used a procedure similar to the first grafting: poly(styrene) grafted particles (1.00 g) and CuBr (78 mg, 0.54 mmol) were placed in a flask with a magnetic stir bar and degassed. Subsequently, degassed bipy (255 mg, 1.63 mmol) dissolved in 4-methylstyrene (3.4 g) was added, and the mixture reacted at 110 °C for 11 h. The resulting particles were purified by centrifugation as described above. The final yield was 1.09 g.

Particle Size Analysis. The particle sizes and size distributions were measured using a 256-channel Coulter multisizer interfaced with a computer. A 30 μm aperture tube was chosen to accommodate the particles size range of 1−10 μm. A small amount of particles, dispersed in acetone, was added to 25 mL of Coulter Isoton II electrolyte solution and stirred for 1 min with a mini-stirrer provided with the instrument.

The Coulter multisizer measurements were confirmed using a Philips ElectroScan 2020 environmental scanning electron microscope (ESEM). The samples for the measurement of ESEM were prepared by dispersing particles in THF and

Scheme 2. ATRP from Surface of Particle Initiators



casting a drop of this particle suspension on a piece of glass glued to an electron microscope stub with double-sided adhesive tape. The samples were dried under vacuum for 2 h and sputter-coated with 5 nm of gold. The quoted diameters are averages from 50 to 100 particles and were measured using UTHSCSA ImageTool software.

The particle sizes in the solvent swollen state were measured on a laser light scattering instrument, a Coulter LS230 particle sizer which operates on the principle of Fraunhofer diffraction for large particles (>0.4 μm) and polarization intensity differential scattering (PIDS) for small particles (<0.4–0.8 μm). A good solvent for polystyrene, methyl ethyl ketone was used to disperse the particle samples.

Molecular Weight Analysis. The soluble polymers were analyzed by size exclusion chromatography using a Waters model 590 pump, equipped with three Waters 5 μm Ultrastyragel linear columns and with a Waters 410 differential refractometer set to 40 °C. Tetrahydrofuran was used as mobile phase at 1 mL/min, and narrow disperse linear polystyrene standards were used for calibration.

FT-IR Analysis. Fourier transform infrared analysis was performed on a Bio-rad FTS-40 FT-IR spectrometer. All samples were prepared as pellets using spectroscopic grade KBr in a Carver press at 15 000 psi. The spectra were scanned over the range of 4000–400 cm^{-1}, in the transmission mode.

Elemental Analysis. Elemental analysis of the particles was carried, in triplicates, out by Guelph Chemical Laboratories Ltd., in Guelph, Ontario, Canada.

Results and Discussion

Introduction of Initiator Sites on the Particles. The narrow dispersed PDVB80 particles prepared by precipitation polymerization have diameters of 2.96 μm. As a direct result of their formation mechanism,[30] they have a thin surface layer consisting of lightly cross-linked and swellable poly(divinylbenzene). This surface gel layer facilitates redispersing the particles in a range of good solvents for modification and grafting reactions. The particles contain residual vinyl groups both within and on their surfaces, as indicated by the CH out-of-plane deformation of monosubstituted vinyl groups, seen at 990 cm^{-1} in the FT-IR spectrum. These residual vinyl groups can be hydrochlorinated to form 1-chloroethylbenzene groups, which are typical ATRP initiators. In comparison to the native PDVB80 particles, the FT-IR spectrum of the hydrochlorinated PDVB80 particles showed a decrease in the intensity of the peak at 990 cm^{-1} relative to an asymmetrical conjugated double bond stretch, 1603 cm^{-1}, due to the aromatic rings. The intensity ratio of the two peaks at 990/1603 cm^{-1} changed from 0.38 to 0.22, indicating significant conversion of the residual vinyl groups. While the addition of HCl to molecular styrene can be accompanied by formation of significant amounts of dimer,[31] in our case, the residual styrenic double bonds in the particles are immobilized by the polymer backbone, which should prevent excessive dimerization during hydrochlorination.

Our hydrochlorination of PDVB80 particles led to a weight gain of 3.5%, corresponding to the formation of PDVB80–HCl. According to the following equation

$$\frac{XM_{\mathrm{DVBHCl}}}{M_{\mathrm{DVB80}}} + (100 - X) = 103.5$$

where X is the percentage of DVB80 units in the PDVB80 particles converted to 1-chloroethylbenzene, M_{DVBHCl} is the molecular weight of DVB–HCl, and M_{DVB80} is the average molecular weight of DVB80, this weight gain corresponds to 12.5% of DBV80 units in the starting particles having been hydrochlorinated. Elemental analysis revealed the presence of 3.19 wt % chlorine in the PDVB–HCl particles, which corresponds to 12.1% of DVB80 units converted to 1-chloroethylbenzene, using the following equation:

$$X = \frac{Y\dfrac{M_{\mathrm{DVB}}}{M_{\mathrm{Cl}}}}{100 + Y\dfrac{M_{\mathrm{DVB}}}{M_{\mathrm{Cl}}} - Y\dfrac{M_{\mathrm{DVBHCl}}}{M_{\mathrm{Cl}}}}$$

where Y is the weight percentage of chlorine in the PDVB–HCl particles and M_{Cl} is the atomic weight of chlorine.

If the outer layer of the starting particles were not cross-linked and if the particles had uniform density distribution, then the observed chlorine could be accounted for by a hypothetical complete hydrochlorination of the pendant vinyl bonds, in an outer shell of the starting particles with 4.3% radial thickness. In fact, the particles have a cross-linking gradient that decreases from the core to the surface and that ends in a partially cross-linked gel layer at the surface.[32] Correspondingly, the amount of pendant double bonds decreases from the surface toward the core of the particles. Moreover, hydrochlorination will depend on penetration of the hydrogen chloride into the particle structure. Hence, the hydrochlorinated layer in the particles should exceed 4.3% in radial thickness and show its own gradient by favoring surface hydrochlorination. The starting particles used in this experiment are about 3 μm in diameter. Therefore, the initiator sites in the particles should be found at least up to ~100 nm from the surface. This shell layer should become swollen with the newly formed polystyrene.

Graft Polymerization of Styrene from Particles. The polymerization of styrene from these initiator sites

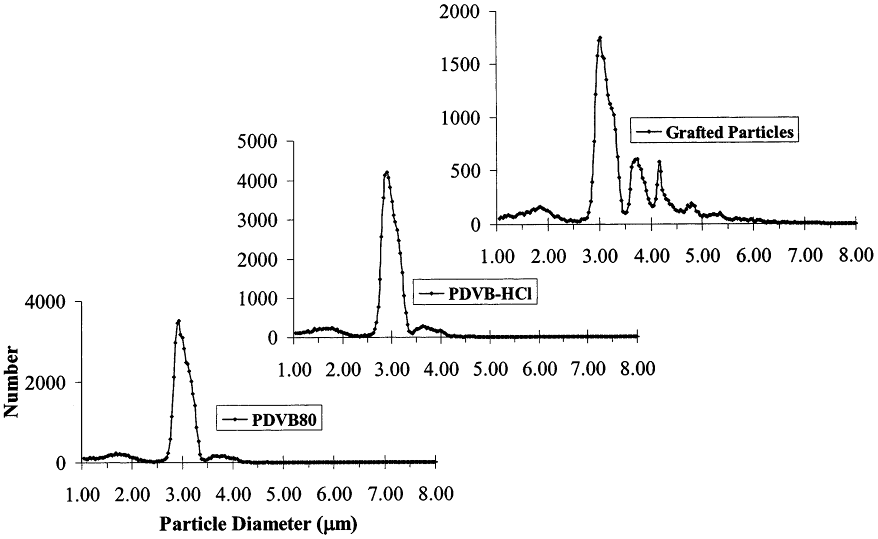


Figure 1. Particle size distributions of starting particles, particle initiators, and polystyrene-grafted particles.

was conducted at 110 °C in the presence of the catalyst, CuBr/2bipy (Scheme 2).

The grafted polystyrene changed both the properties of the particle surfaces and the size of the particles. Figure 1 shows the measurement of the particle sizes before and after graft polymerization, using a Coulter multisizer.

Number-average particle diameters, $\overline{Dn}$ of 2.88, 2.88, and 3.10 μm, with coefficients of variation, CV, of 18, 21, and 43%, were found for PDVB80, PDVB80−HCl, and grafted particles, respectively. The size of the PDVB−HCl particles remained unchanged from that of PDVB particles, which indicated that the hydrochlorination increased the density of the particles as the total weight of the particles increased. On the other hand, the diameter of the styrene-grafted particles increased about 4% compared to that of both PDVB−HCl and PDVB80 particles. The 4% increase in particle diameter corresponds to a 12.5% increase in particle volume, which is consistent with the observed weight increase of 11.3%. The density of the particles is considered to be similar to that of the grafted polystyrene, at 1.05 g/mL. The apparent coefficient of variation, CV, of the grafted particles was larger than those of the PDVB80 and PDVB−HCl particles. This is due to the enhanced formation of doublets and triplets of the polystyrene coated particles during the Coulter sizing in an aqueous medium. In Figure 1c, on the right side of the large peak there are two smaller peaks due to transient particle doublets and triplets that contribute significantly to the large CV. The mean particle diameters were taken from the main peak in the Coulter histogram. The sizes of the grafted particles were confirmed by ESEM (Figure 2).

The images showed that all particles have very smooth surfaces and remain unagglomerated. The ESEM images were taken from dried samples and should correspond to the diameters measured by Coulter multisizer using an aqueous medium in which the surface chains should be collapsed. The measured of particles from these ESEM images are 2.96, 2.96, and 3.07 μm for PDVB80, PDVB80−HCl, and grafted particles, respectively, which is consistent with the particles diameters obtained from the Coulter multisizer. The ESEM size data reflect averages over about 100 particles each. It is noteworthy that the ESEM images show no large particles, which confirms that the two small peaks in Figure 1c correspond to transient particle doublets and triplets.

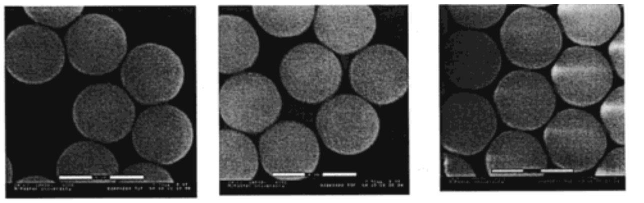

2.96 μm **Starting particles** **2.96 μm** **Particle initiators** **3.07 μm** **PS-grafted particles**

Figure 2. ESEM images of starting particles, particle initiators, and polystyrene-grafted particles.

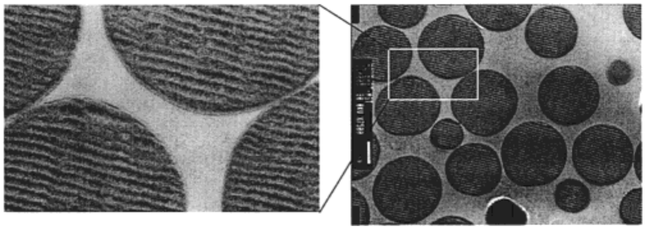


Figure 3. TEM images of poly(styrene-*b*-4-methylstyrene) grafted particles.

The internal structure of the grafted particles was shown by TEM (Figure 3**)** to consist of a hard core and a very thin surface layer.

The reaction on the particles was also confirmed by elemental analysis. The 3.19 wt % chlorine in particle initiators was converted to 1.79 wt % chlorine and 0.33 wt % bromine in grafted particles. The bromine found in particles showed that ATRP has taken place on the particles. The bromine came from Cu(I)Br by way of an exchange equilibrium during the ARTP. The percentage of chlorine was higher than the percentage of bromine in the grafted particles. Two causes might be responsible. One is some chlorine in the particles might be not accessible to the relatively large catalyst complex $(bipy)_2Cu(I)$ and hence would not become involved in the ATRP reaction. The other is that the Cl−C bond in benzyl chlorides (68 kcal/mol) is stronger than the Br−C bond in benzyl bromide (51 kcal/mol), which would suggest that benzylic chloride should dominate in the

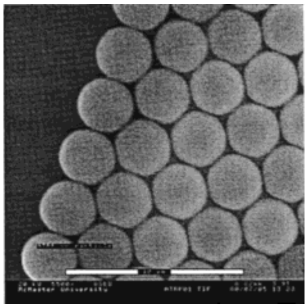


Figure 4. ESEM image of 2-D array of poly(styrene) grafted particles.

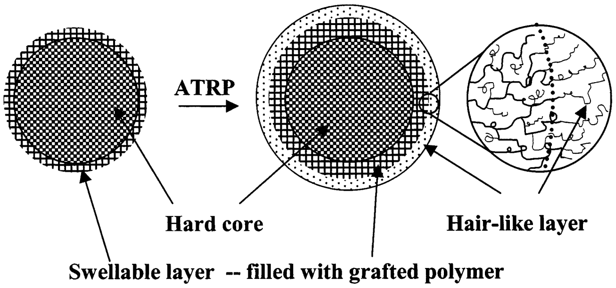
Cu-catalyzed benzylic halide interchange. In fact, Matyjaszewski et al.[33] studied the halide exchange during ATRP, using mixed halide initiation systems. Model studies of (1-chloroethyl)benzene/CuBr in the presence of 2 equiv of dinonyl-bipy showed that an equilibrium of 88% (1-chloroethyl)benzene and 12% (1-bromoethyl)-benzene was reached after 40 min at 110 °C.

The decrease of the total halogen percentage in our grafted particles compared with the particle initiator indicated that the formation of polymer grafted on the particles, as well as partial chain termination, led to an increase of the total carbon and hydrogen percentage. The fraction of polymer chain termination can be estimated on the basis of the weight increase of the grafted particles and the total halogen percentage. If the observed bromine weight percentage (0.33 wt %) were converted into the equivalent theoretical chlorine percentage (0.15 wt %), then the total chlorine in the grafted particles would be 1.94 wt %. The total chlorine in grafted particles should be 2.87 wt %, assuming all propagating groups survived. Hence, about 32.4% of propagating species were terminated, presumably at an early stage of reaction before the near steady-state concentration of Cu(II) was achieved.[34] Afterward, the reaction becomes a controlled/living polymerization. This has been confirmed by the subsequent addition of another polymer block to these particles, discussed below.

The hairlike polymer layer on the particle surface, which leads to the aggregation of the particles in a bad solvent, could conversely stabilize the particles in a good solvent. Although the surface graft on the particles cannot prevent sedimentation, they do prevent particle aggregation in good solvents and promote the formation of two- or three-dimensional arrays upon deposition from a good solvent onto a surface. Asher et al.[35] used highly charged polystyrene particles to build two- or three-dimensional arrays for use as photonic crystals. In their case, the charges on the particles helped the formation of arrays. Our particles are another example of the formation of particle arrays, helped by the grafted polymer on the particle surfaces.

Figure 4 shows a two-dimensional hexagonal array formed by adding a drop of the grafted particles dispersed in a good solvent such as THF onto a glass plate. In contrast, nongrafted PDVB80 and PDVB−HCl particles do not generate such arrays with this procedure. The results confirmed that the grafted particles have polymer chains of significant molecular weight on their surfaces. Auroy et al.[36] pointed out that for the formation of a crystalline packing of grafted particles, two essential conditions, namely particles having polymer chains with high molecular weight and a low polydispersity, must be met.

Scheme 3. Surface and Outer Layer Grafting of Polystyrene by ATRP



Interestingly, the grafted particles dispersed in a good solvent can be induced to aggregate by adding a poor solvent such as hexanes. The resulting particle aggregates prepared from a poor solvent were very easy to redisperse in a good solvent. On the other hand, the grafted particles dried from a good solvent formed hard clusters that were difficult to redisperse in a good solvent, likely due to entangling of the grafted polymer between particles.

The surface grafts were also confirmed by measuring the particle size in the swollen state by light scattering in MEK suspension. The sizes of PDVB80, PDVB80HCl, and grafted-particles were 3.26, 3.26, and 3.70 μm, respectively. Compared with their dry diameters of 2.96, 2.96, and 3.07 μm, the size of the polystyrene grafted particles increased much more than the other two particles, which demonstrates the effects of both particles swelling and the graft layer on the particle surface expanding in a good solvent.

Size Growth of Particles. In terms of the growth of polymer chains on the surface, polymer grown on planar surfaces is much easier to study than polymer on spherical particles. This is because certain surface techniques with high precision, such as ellipsometry, are only suitable to measure the thickness of coatings on a planar surface.

Fortunately, our grafted particles gave high enough increases in particle size and are easy to measure by Coulter multisizer and ESEM. The size increase is attributed to two contributions: grafted polymer grown on particle surfaces and grafted polymer grown within the outer layer of the particle initiators. In other words, graft polymerization in the outer layer of particles amplified the size increase by filling polymers into the relatively lightly cross-linked network. As discussed above, initiator sites may be located as deep as 100 nm below the particle surface, and ATRP of styrene should take place mainly within this layer of the particles. Scheme 3 shows the increase of particle sizes contributed by polymers grown on the surface and in this outer layer.

Controlled/Living Polymerization Properties. The concentration of initiators on solid surfaces usually is lower than in solution polymerization. It will produce an extremely low concentration of Cu(II) species that are needed to generate dormant species in a controlling equilibrium. Inadequate Cu(II) levels will result in loss of control of the polymerization. To help control the polymerization, free initiators[37] or Cu(II) compounds[38] may be added to help establish the required equilibrium between active and dormant species in grafting polymerizations from solid surface. However, a well-controlled system will have a relatively slow polymerization. In the case of our large particles, a slow grafting

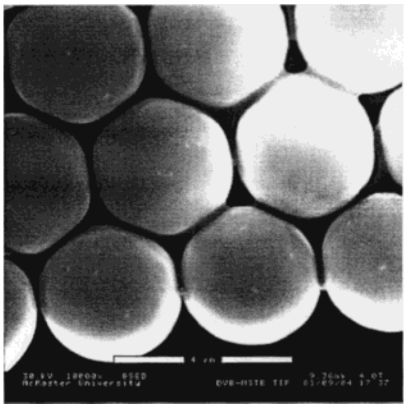


Figure 5. ESEM image of poly(styrene-*b*-4-methylstyrene) grafted particles.

polymerization might not generate a thick enough polymer layer to detect. Hence, we used Cu(I)Br as the only copper source without the addition of Cu(II) or free initiators. The amount of catalyst CuBr/2bipy was 65% equivalent to the total initiating sites (0.94 mmol/g) in particles calculated from the chlorine elemental analysis. The molecular weight and molecular weight distribution of grafted polymer could not be determined in these reactions because of their covalent linkage to the particle. However, the molecular weight and perhaps the molecular weight distribution of grafted polymer may be roughly estimated by measuring the polymer formed in solution. The molecular weight and molecular weight distribution of soluble polymer was $M_n = 2.65 \times 10^4$, $M_w = 4.43 \times 10^4$, and $M_w/M_n = 1.67$. This soluble polymer would be initiated thermally but would then be terminated by reaction with Cu(II) present in the system. A detailed comparison of surface grafted and soluble polymer, however, is beyond the scope of this paper.[35]

The living nature of the polymerization should improve as soon as the Cu(II) levels increase due to some early stage termination. As elemental analysis showed the existence of halogen, the grafted particles could still be used as particle initiators to form block copolymer. A second grafting polymerization of 4-methylstyrene on polystyrene grafted particles was accordingly carried out for 11 h at similar polymerization conditions as in the first grafting. Successful growth of poly(4-methylstyrene) was confirmed by the increase of the particles to 3.17 μm as measured by Coulter multisizer.

The size increase was confirmed by ESEM. Figure 5 shows the image of the second grafted particles. The particles deformed at contact points, which implies that the surface layers of the particles are soft and consist largely of linear polymer.

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