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Grafting-from Nanoparticles Using Aldol Group Transfer Polymerization

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In surface-initiated polymerization from nanoparticles ("grafting-from" approach),[1] a variety of techniques have proven useful, perhaps most prominently controlled free radical polymerization methods,[2−5] such as atom transfer radical polymerization (ATRP), reversible addition−fragmentation chain transfer (RAFT) polymerization, and nitroxide-mediated radical polymerization (NMRP). Styrenic and methacrylic monomers are used extensively in such grafting chemistry. However, the difficulties inherent to controlled free radical polymerization of vinyl acetate (VA) reduce its potential feasibility in the grafting-from technique. Indeed, only a few reports describe controlled free radical polymerization of VA, for example using metal complexes[6] or RAFT.[7−10] Even RAFT has significant limitations for controlling VA polymerization relative to other monomers and of course also requires the synthesis of chain transfer agents tailored for each system. Nonetheless, the importance of poly(vinyl acetate) (PVAc), its hydrolysis product poly(vinyl alcohol) (PVOH), and numerous PVOH derivatives in applications such as adhesives, barrier polymers, interlayer plastics, and pharmaceuticals makes desirable the availability of different methods for tailoring nanoparticles with such polymers.

Webster and Sogah reported a group transfer polymerization (GTP) method for the preparation of PVOH.[11] Aldol GTP is the Lewis acid-assisted polymerization of vinyloxytrialkylsilane monomers, initiated by benzaldehyde or benzyl halides, to give silyl ether-protected PVOH. Deprotection by hydrolysis or with fluoride ion affords PVOH. The advantage of aldol GTP over cationic polymerization of vinyloxytrialkylsilane monomers[12,13] is found in better control over polydispersity and the feasible use of a wide temperature range, as opposed to the low temperatures required for the cationic case. The simplicity of initiating functionality inherent to aldol GTP over other techniques suggests good applicability to grafting-from polymerization in conjunction with a wide variety of aldehyde and benzyl halide-functionalized surfaces, including the nanoparticles described here.

Two types of nanoparticles, one with an inorganic core structure and the other with a polystyrene core structure, and both with benzyl chloride functionality, were chosen for this grafting-from study using vinyloxytrialkylsilane monomers. The monomer vinyloxy-*tert*-butyldimethylsilane (VO-*t*BDMS) was prepared by *tert*-butyldimethylsilyl chloride quenching of the lithium enolate obtained by anionic ring-opening of tetrahydrofuran.[14] While we were able to perform grafting-from chemistry with VO-*t*BDMS by aldol GTP, particle dispersibility problems led to inefficient deprotection. Thus, subsequent experiments were performed with vinyloxytrimethylsilane (VOTMS) as the monomer exclusively.

The inorganic nanoparticles were prepared by condensation of (4-chloromethyl)phenyltrimethoxysilane with ammonium hydroxide solution in ethanol (Supporting Information). This procedure gave SiO_x nanoparticles ($x \sim 1.5$), typically ∼30 ± 10 nm in diameter, with residual benzyl chloride functionality. The polystyrene particles were ∼60 nm average diameter, also containing benzyl chloride functionality, as supplied by Eastman Kodak Co. Following grafting-from chemistry, characterization of the polymer grafts and grafted particles was performed by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), and transmission electron microscopy (TEM).

The application of aldol GTP to benzyl chloride functionalized nanoparticles is depicted in Scheme 1. In a typical procedure, VOTMS and anhydrous zinc bromide (0.01 mol % relative to monomer) were added to a dichloromethane dispersion of the nanoparticles. The mixture was stirred at 35 °C for 24 h and then quenched with methanol. The polymer-grafted particles obtained in this fashion were collected by precipitation in excess methanol, followed by centrifugation to afford the nanoparticles as a light yellow solid. Repeated centrifugation and filtration revealed no ungrafted polymer that would result from nonsurface initiation mechanisms, an appealing aspect of

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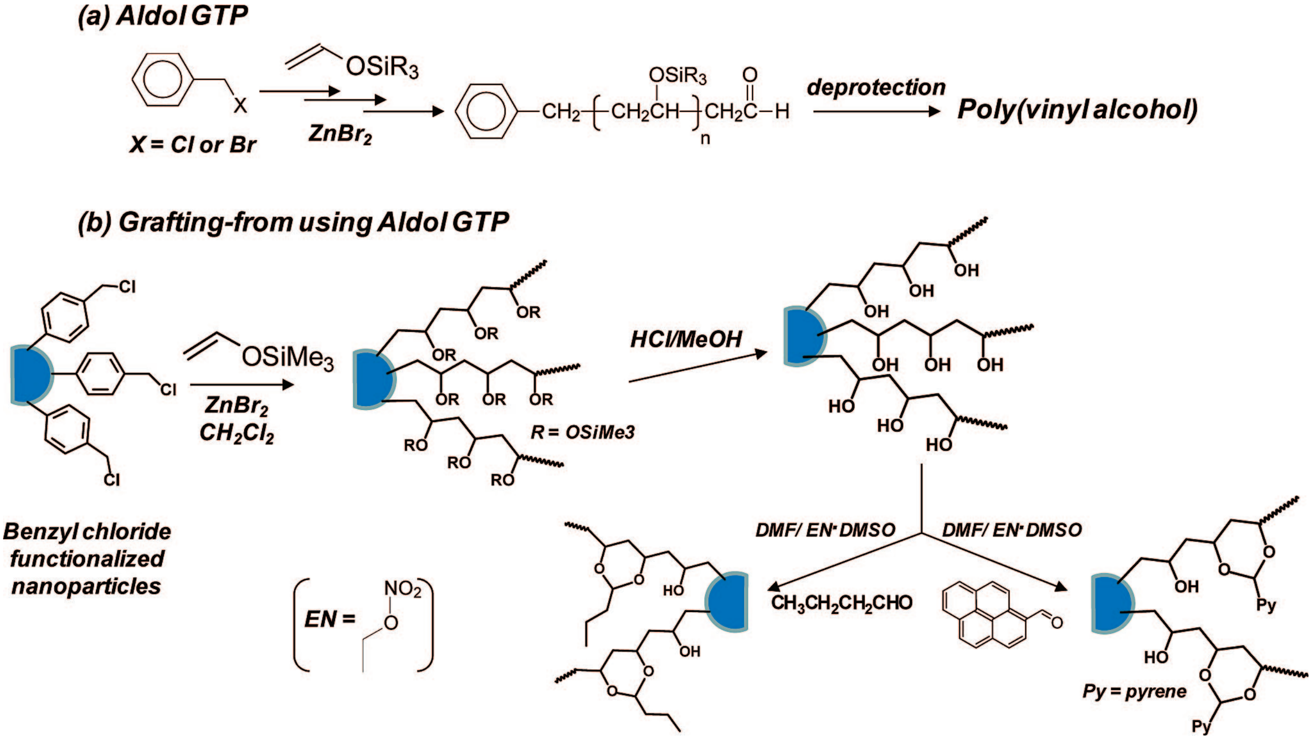
Scheme 1



aldol GTP as a grafting-from method. Also, the temperature at which the polymerization was carried out, and the successful use of these monomer-to-catalyst ratios, is consistent with the aldol GTP process.[11–13]

FT-IR spectroscopy of the polymer-grafted inorganic and PS nanoparticles showed signals at 3285 cm^{-1} (broad OH stretching) and 2954 and 2856 cm^{-1} (C–H stretching from TMS ethers). The polymer-grafted PS particles showed a characteristic C–Si signal at 1200 cm^{-1}. ^{1}H NMR spectra recorded on the polymer grafted particles in d_6-DMSO confirmed the presence of the PVOH chains, including hydroxyl (4.26–4.50 ppm), methine (4.03 ppm), and methylene (1.37–1.10 ppm, br, m)

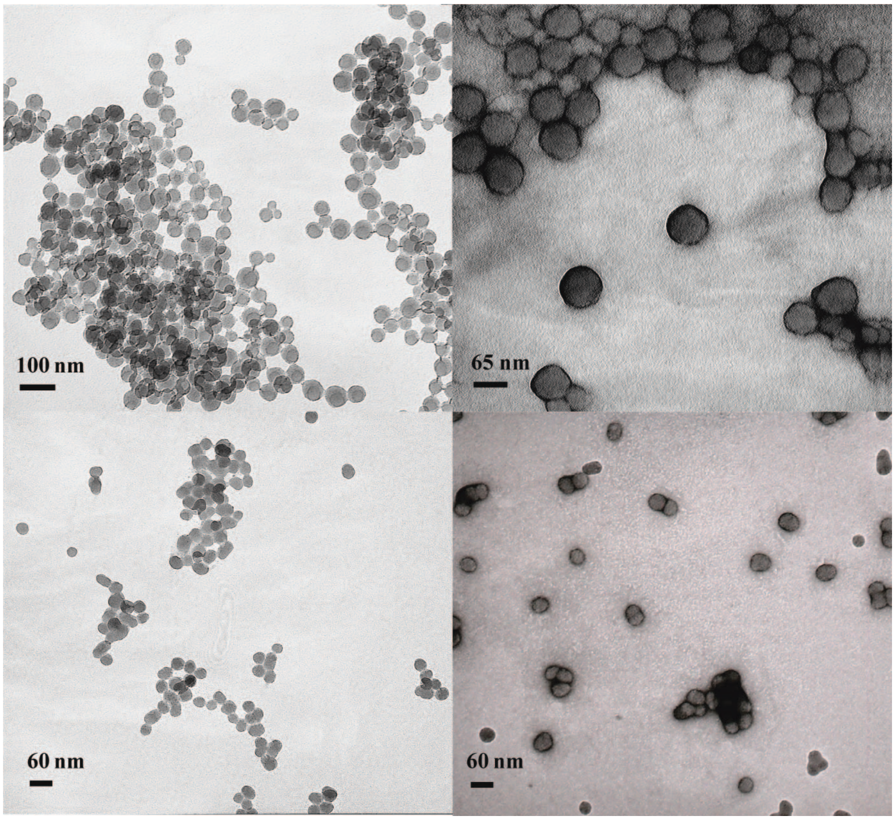


Figure 1. TEM images of nanoparticles: (a) PS before grafting; (b) PVOH-covered PS; (c) $SiO_{1.5}$ before grafting; (d) PVOH-covered $SiO_{1.5}$. All samples were stained with 2% phosphotungstic $acid_{(aq)}$.

resonances as well as weak TMS−methyl resonances at 0 ppm after precipitation into methanol (∼10% of the original TMS groups remained). Complete hydrolysis of the polymer grafts followed stirring the polymer-grafted particles in methanolic HCl. The PVOH-grafted nanoparticles were found to disperse in water (∼10−15 mg/mL for the $SiO_{1.5}$ and 20−30 mg/mL for the PS). As solutions in D_2O, the particles gave ^1H NMR resonances at 4.27 ppm (methine) and 1.84−1.90 ppm (methylene). The ^1H NMR spectra in d_6-DMSO show the expected three hydroxyl signals from 4.26−4.50 ppm, representing isotactic, heterotactic, and syndiotactic triads.[15] The peak intensities show the PVOH grafts to be largely heterotactic (∼50%), with lesser degrees of syndiotactic (∼30%) and isotactic (∼20%) character. This tacticity is also consistent with the aldol GTP process rather than cationic.[16]

For the inorganic nanoparticle case, the polymer grafts were characterized independently following degradation of the core in aqueous HF and precipitation of the polymer into methanol. The isolated PVOH grafts were converted back to silyl ethers by reaction with hexamethyldisilazane (HMDS) and then characterized by GPC as solutions in THF. GPC indicated that polymer grafts were obtained by aldol GTP over a range of degrees of polymerization (DPs), from ∼30 to >100, corresponding to molecular weights of ∼3000 to ∼15 000 g/mol. Unexpectedly, variation of monomer-to-nanoparticle ratio (i.e., monomer-to-initiator ratio) did not result in a systematic variation in graft molecular weight, perhaps due to changes in dispersibility of the particles during the course of the grafting chemistry, such that the level of molecular weight control known for solution aldol GTP is more difficult to achieve in the grafting-from cases studied here. Studies directed toward improved molecular weight control upon grafting are in progress. As the PS nanoparticles cannot be degraded readily, independent characterization of the grafts was not performed.

Reaction of PVOH-grafted inorganic and PS nanoparticles with butyraldehyde, performed in DMF using conditions described by Dass for PVOH acetylation,[17] gave the corresponding butyral-substituted polymer grafts. These acetal-functionalized particles were dispersible in DMF, DMSO, ethanol, and water, to extents depending on the percent functionalization of the grafts. At greater than 70% hydroxyl consumption, the particles were dispersible in DMSO and ethanol at ∼20−25 mg/mL. Such grafting, to give poly(vinyl butyraldehyde)-like grafts, is of interest for tailoring nanoparticles of this type for composite materials applications. The PVOH shell was also functionalized with pyrene carboxyaldehyde as a fluorescent tag to obtain fluorescent nanoparticles, dispersible in water at appropriate extent of pyrene functionalization.

Transmission electron microscopy was employed to examine the benzyl chloride- and polymer-functionalized nanoparticles. Figure 1 shows representative micrographs of the nanoparticles before and after grafting, in each case following staining to provide core−shell contrast. The micrographs of Figure 1b,d show a distinct core−shell morphology that is not present in the ungrafted samples. The dark shell is relatively thin (consistent with the modest molecular weights of the polymer grafts revealed by GPC) and is not seen for the particles without the PVOH layer. To date, we have not been able to grow thick PVOH shells using the aldol GTP method; work along these lines is in progress.

In summary, we have described the application of aldol GTP to grafting-from polymerization on benzyl chloride-functionalized inorganic and polymer nanoparticles. We expect this technique to prove generally useful for grafting from many types of appropriately functionalized surfaces, particles, and insoluble functional resins and supports.

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Supporting Information Available: Experimental details and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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