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ORIGINAL PAPER

Grafting of polystyrene “from” and “through” surface modified titania nanoparticles

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Abstract We report the surface modification of titania (TiO_2) nanoparticles with azo-based radical initiator and vinyl (acrylate) polymerizable groups. This is achieved through the reaction of the surface hydroxyl groups of the titania with acid halides. Polymer (specifically, polystyrene) was grafted “from” the surface using the azo-modified titania, and “through” the surface of the vinyl-modified surface. Both conventional radical and reversible addition-fragmentation chain transfer (RAFT) polymerizations were performed. The surface-modified titania and the polystyrene-titania nanocomposites were characterized using IR spectroscopy, thermogravimetric analysis and gel permeation chromatography.

Keywords Nanocomposites · Titania · Grafting · RAFT polymerization

Introduction

One of the major issues facing the use of nanoparticles, particularly those of inorganic composition, is the ability to adequately disperse and process them [1–3]. For example, luminescent nanoparticles (e.g. quantum dots) such as CdS, silicate layers, silica and titania nanoparticles display properties that are largely dictated by their nanosized dimensions. However, these properties may alter, often detrimentally, if significant aggregation occurs. In order to overcome aggregation and often to impart particular functionality, particle surface modifications are commonly performed. Such reactions may enhance the properties of a particle such as wetting, electrolytic and redox characteristics, dispersability, or luminescence [2, 4]. There are a several approaches to particle surface modification, including condensation

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reactions (e.g. silations on the surface of silica) [3], or chain polymerizations that result in “grafting to”, “grafting from”, and “grafting through” polymerizations [5, 6]. We have previously successfully applied the latter two grafting methods for making polymer-layered silicate nanocomposites [7–10].

Titania (TiO_2) has many common uses, and continues to be widely studied because of potential applications in catalysis, heat and photo-stabilization [11], and photovoltaics [12]. TiO_2 is inexpensive, nontoxic, thermally stable, has a high refractive index, and a lack of absorbance of visible light. These properties give TiO_2 a good, practical use in many (nano) technologies. However, the surface chemistry of TiO_2 is rather complex [13], and as such there have been far fewer publications [14–17] dealing with polymer grafting to the surface of TiO_2 nanoparticles (or even submicron sized TiO_2), especially when compared with grafting onto silica particles (see, for example, references cited in [3]).

This paper reports the modifications of TiO_2 with azo-initiator and vinyl groups through the reaction of select acid halides with TiO_2 surface groups. Polymer can be grafted from the surface of the initiator modified TiO_2 or can be grafted through the vinyl modified surface. Synthesis and characterization of initiators, vinyl, and polymer modified TiO_2 nanoparticles is presented.

Experimental

Materials

Dichloromethane (DCM) (Pharmco) and tetrahydrofuran (THF) (Baker) were dried over of CaH_2 (Alfa Aesar). 4,4′-Azobisisobutyronitrile (AIBN) (Aldrich) was recrystallized from methanol. Acryloyl chloride (Acros), 4,4′-azobis(4-cyanopentanoic acid) (Fluka), 2-bromopropionyl bromide (Aldrich), *N*,*N*-dimethylacetamide (DMAc) (Aldrich), methanol (Baker), phosphorus pentachloride (Aldrich), were used without further treatment. Titanium dioxide P25 (Degussa) was dried under vacuum for more than 24 h. Styrene (Baker) was filtered with neutral alumina and dried and distilled over CaH_2 at reduced pressure. 2-Cyanoprop-2-yl dithiobenzoate was synthesized as previously reported [18].

Synthesis of 4-4′-azobis-4-cyanopentanoic acid chloride (ACPC)

ACPC was prepared according to previous literature [19]. The ACPC was dried in a vacuum oven for 3 days.

Synthesis of azo modified TiO_2

Azo-modified TiO_2 was prepared by using dry TiO_2 and dry ACPC. 2.0 g of TiO_2 was placed into a Schlenk flask under a N_2 atmosphere. 20.0 ml of DMAc was then added to the flask and the TiO_2 slurry was sonicated for 6 min. A solution of 0.23 g of ACPC and 20.0 ml DMAc was prepared in a N_2 atmosphere and added drop wise to the TiO_2 slurry. The reaction was carried out in an ice bath for 2 h and at room temperature for 16 h. The resulting product was separated and dried in a vacuum oven.

Synthesis of vinyl modified TiO_2

Vinyl-modified TiO_2 was prepared by using dry TiO_2 and acryloyl chloride. 0.50 g of TiO_2 was placed into a Schlenk flask under a N_2 atmosphere. 5.0 ml of DMAc was then added to the flask and the TiO_2 slurry was sonicated for 6 min. 5 mL of acryloyl chloride was added drop wise to the TiO_2 slurry at 0 °C. The reaction was carried out in an ice bath and then allowed to increase to room temperature over 18 h. The resulting product was separated and dried in a vacuum oven. The resulting powder was examined with FT-IR and TGA.

Synthesis of polystyrene azo-modified TiO_2 nanocomposite

0.20 g of the azo-modified TiO_2 and 10.0 ml of styrene were added to a Schlenk flask which was then subjected to three freeze-pump-thaw cycles, and then backfilled with N_2. The slurry was then sonicated for 6 min and the reaction took place at 65 °C for 17.3 h. The azo-PS modified TiO_2 was separated from non-bound polymer initially by rinsing with THF, centrifugation and soxhlet extraction in THF. PS bound to the nanoparticle surface was removed by etching the TiO_2 using a 5% HF aqueous solution.

Synthesis of polystyrene vinyl-modified TiO_2 nanocomposite

0.21 g of the vinyl-modified TiO_2, 0.11 g of AIBN, and 10.0 ml of styrene added to a Schlenk flask which was then subjected to three freeze-pump-thaw cycles, and then backfilled with N_2. The slurry was then sonicated for 6 min and the reaction took place at 65 °C for 17.3 h. The vinyl-PS modified TiO_2 was separated from non-bound polymer initially by rinsing with THF, centrifugation and soxhlet extraction in THF. PS bound to the nanoparticle surface was removed by etching the TiO_2 using a 5% HF aqueous solution.

RAFT polymerization of styrene with azo-modified TiO_2

0.1 g of the azo-modified TiO_2, 50.5 mg (3.1×10^{-3} mol) AIBN, 96.5 mg (4.62×10^{-4} mol) of 2-cyanoprop-2-yl dithiobenzoate and 5.0 ml of styrene (4.5×10^{-2} mol) were added to a Schlenk flask which was then subjected to three freeze-pump-thaw cycles, and then backfilled with N_2. The slurry was then sonicated for 6 min and the reaction took place at 65 °C for 39 h. The azo-PS modified TiO_2 was separated from non-bound polymer initially by rinsing with THF, centrifugation and soxhlet extraction in THF. PS bound to the nanoparticle surface was removed by etching the TiO_2 using a 5% HF aqueous solution.

Analytical techniques

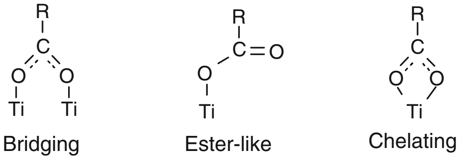
^{13}C and ^{1}H NMR spectroscopy (Bruker DMX400) were used to determine purity. Thermal gravimetric analyses (TGA) with N_2 purge and balance (Perkin-Elmer TGA7) and diffuse reflectance infra-red Fourier transfer (DRIFT-IR) (Bruker Vector 22) was used for surface analysis of the nanoparticles. Elemental analyses were performed by Prevalere Life Sciences, Inc., Whitesboro, N.Y.

Results and discussion

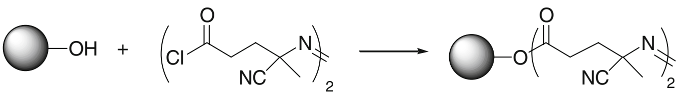
It is well know how to achieve surface modification of silica (SiO_2) particles [20–26]. However, the surface of TiO_2 is very different than that of SiO_2, partly because titanium is able to form multiple coordination systems whereas silicon forms a fourfold coordination system [13]. The size of the TiO_2 crystals may influence the coordination system of the titanium itself, ranging from a sixfold coordination system in larger crystals (>6 nm) to a fivefold or fourfold coordination system in smaller crystals (<6 nm). As a result, the attachment of compounds to the surface of the TiO_2 may vary from simple adsorption to chemical binding of many different types, including bridging, ester-like linkage, and chelating (Scheme 1) [13].

Since smaller crystal sizes form fivefold or fourfold titanium coordination systems, surface-modification is more likely to be chemical binding rather than simple adsorption because the titanium on the surface has the ability to bind to more compounds. Furthermore, for fivefold coordination systems, bridging or ester-like linkages are more apt to be the type of chemical binding, where as in fourfold coordination systems chelating is more likely. In larger crystal sizes where a sixfold coordination system exists, simple adsorption is more likely to occur through surface-modification because the titanium has already saturated its binding sites and there is no room for chemical binding to take place.

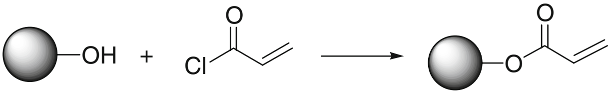
We anticipated that the addition of initiating and vinyl groups containing carboxy groups would interact with the TiO_2 surface such that it may be possible to form covalent bonding between the nanoparticle and polymer chains. Furthermore, we reasoned that surface OH groups might preferentially form covalent linkages (as opposed to bridging or chelating associations) if reacted with acid halide derivatives. Hence, two functionalities were introduced onto the TiO_2 surface, an azo group via the reaction of 4-4′-azobis-4-cyanopentanoic acid chloride (ACPC) with TiO_2, and a vinyl group through the addition of acryloyl chloride to the TiO_2 (Schemes 2, 3). The characterization of the surface of both unmodified and modified TiO_2 was performed using DRIFT FT-IR and TGA. Figure 1 shows the DRIFT-IR



Scheme 1 Types of chemical binding on the surface of TiO_2 nanoparticles [13]



Scheme 2 Surface modification of TiO_2 with ACPC



Scheme 3 Surface modification of TiO_2 with acryloyl chloride

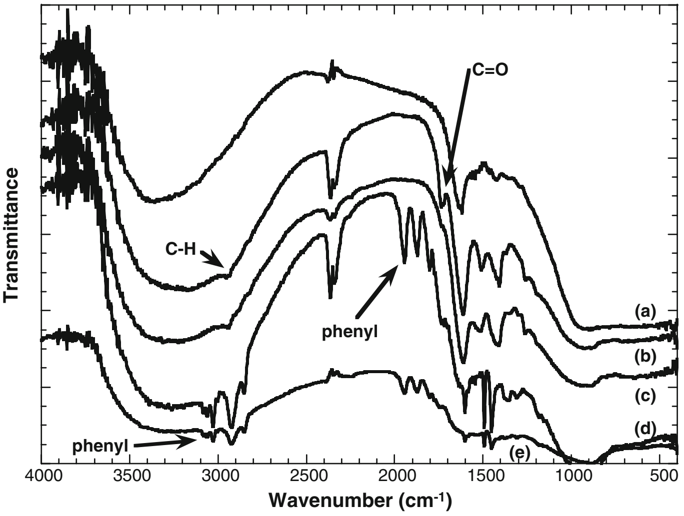


Fig. 1 DRIFT-IR spectra for (**a**) TiO_2 (**b**) vinyl-modified TiO_2, (**c**) azo-modified TiO_2 (**d**) vinyl-PS-modified TiO_2 (**e**) azo-PS-modified TiO_2

spectra for the unmodified TiO_2, vinyl-modified TiO_2 and azo-modified TiO_2 (along with FTIR spectra of PS vinyl-modified TiO_2 and PS azo-modified TiO_2, vide infra).

The spectra for TiO_2 (Fig. 1a) is used as a basis to show that modifications have been made to the surface of the TiO_2. All of the spectra have the same broad peak from 2,500 to 3,500 cm^{-1} and also show some peaks around 1,620 and 1,431 cm^{-1}. The IR spectra of the vinyl-modified TiO_2 and azo-modified TiO_2 are presented in Fig. 1b, c, respectively. The important peaks in Fig. 1b, c are the peaks at $\sim$2,950–2,960 cm^{-1} which are evidence of C–H vibrations and the peaks around $\sim$1,737 cm^{-1}. These are evidence of C=O vibrations from ester/carboxylic acid groups.

The amount of organics on the surface-modified TiO_2 (with either ACPC or acryloyl chloride) was characterized with the aid of TGA. By comparing the percent weight loss of TiO_2 and the modified TiO_2, a percent weight of organics attached to the surface of TiO_2 can be found. Figure 2 shows TGA plots comparing unmodified and modified TiO_2. These data indicate that there is approximately 2 wt.% of azo and vinyl functionality present on the modified nanoparticles.

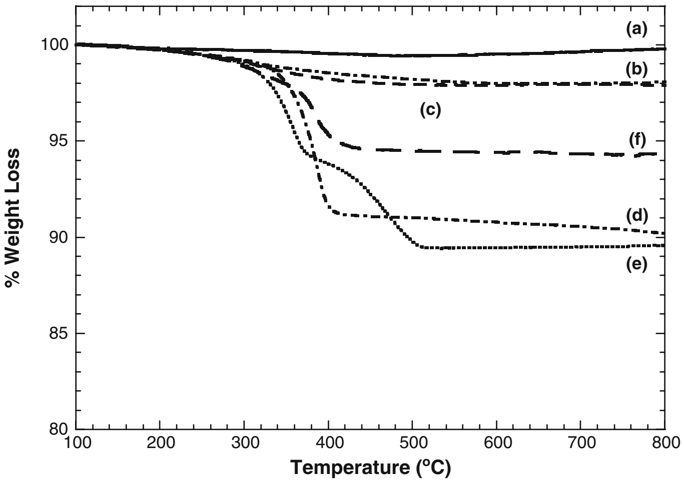


Fig. 2 TGA plots of (**a**) TiO_2 (**b**) vinyl-modified TiO_2, (**c**) azo-modified TiO_2 (**d**) vinyl-PS-modified TiO_2 (**e**) azo-PS-modified TiO_2, (**f**) azo-PS-modified TiO_2 after soxhlet extraction

Both versions of the modified TiO_2 were incorporated into (conventional) radical polymerizations of styrene. During these polymerizations some of the polymer chains are expected to be tethered to the TiO_2, while the rest will not be attached to the nanoparticles. For the azo-modified TiO_2, no extra initiator was added, hence untethered chains may result from decomposition of initiator molecules that are only attached via one of the two carboxy groups. For the vinyl-modified TiO_2, AIBN was added to the reaction, and hence all chains begin growth unattached to the TiO_2, but may become tether via propagation through a TiO_2-tethered acrlyate group. The free and tethered polymer chain populations were separated from each other through centrifugation. The component containing the TiO_2-PS was analyzed using FTIR and TGA, and these results are given in Figs. 1 and 2. The IR data clearly shows the presence of PS (notable peaks appearing from the phenyl ring at ~1,900 and ~3,000 cm^{-1}), and the TGA data shows approximately 10 wt.% of PS. However, the azo-modified TiO_2-PS composite was further processed by performing a soxhlet extraction, which reduced the PS content to around 5 wt.%. This lowering of the PS content may be an indication that some of the PS is adsorbed to the surface, rather than being covalently bonded (or chemisorbed) to the surface.

The molecular weights of the tethered and untethered fractions were measured, and are given in Table 1. The tethered polymers were removed from the TiO_2 by etching the TiO_2 using HF. These data show that with a low initiator concentration, due to the only initiator being attached to the TiO_2 nanoparticles, the molecular weight is quite high (M_n = 357,000 and 320,000). For the vinyl-modified TiO_2 case, where a much larger amount of initiator was added, the molecular weight is much lower (M_n = 54,000 and 57,000), as expected. The polydispersities were as expected for a conventional radical polymerization.

We also examined the use of reversible addition-fragmentation chain transfer (RAFT) polymerization [27, 28] in the production of PS-modified TiO_2. In this case

Table 1 Molecular weight data from PS-TiO_2 nanocomposites

Sample	M_n	M_w/M_n
Azo[a]	357,000	3.0
Azo[b]	320,000	2.2
Vinyl[a]	54,000	4.7
Vinyl[b]	78,000	5.6
RAFT[a]	9,000	1.35
RAFT[b]	12,500	1.26

[a] Untethered PS

[b] TiO_2-tethered PS

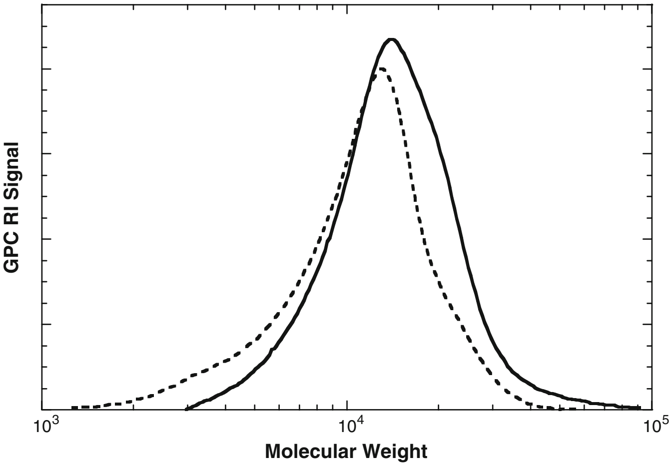


Fig. 3 Molecular weight distributions of untethered (*dashed line*) and tethered (*dotted line*) polystyrene from a RAFT polymerization of styrene using azo-modified TiO_2

we used the 2-cyanoprop-2-yl dithiobenzoate as the RAFT agent and azo-modified TiO_2. Figure 3 shows an overlay of the molecular weight distributions of the untethered PS, obtained from the supernatant liquid after centrifugation, and the tethered PS that was obtained after dissolving the TiO_2 nanoparticles using HF. These data show that both PS samples have much lower molecular weights and polydispersities compared with the previous conventional radical polymerizations conducted, and that the two samples (‘free’ and ‘bound’) are almost the same. This last observation indicates that growth of the polymer chains that are attached is the same as those that are unattached. Other workers have made similar observations during the grafting of polymers from SiO_2 particles [25, 26].

Conclusions

The surface of TiO_2 was modified with azo and vinyl (acrylate) groups through simple condensation with acid chlorides. These modified TiO_2 nanoparticles were then incorporated into conventional radical and RAFT polymerizations. This approach seems to be straight-forward, and could be applied to other functionalities to improve TiO_2 dispersibility or other properties that depend on the surface characteristics of the nanoparticle.

There are, however, still questions remaining about the mode of binding of the azo and vinyl groups, and hence also the polymer, to the TiO_2 nanoparticle surface. The stability of this connection will affect many of the properties of the nanocomposites. We are currently exploring other methods of polymer grafting and TiO_2 surface modification that may provide improved nanocomposites.

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