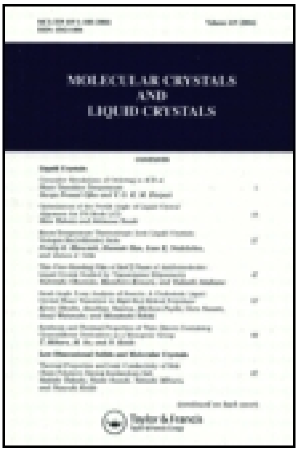

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Synthesis of PS-g-TiO$_2$ Nanocomposites through a Simple Method of Surface Initiated Radical Polymerization

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Version of record first published: 27 Sep 2012.

To cite this article: Long Giang Bach , Md. Rafiqul Islam , Yeon Tae Jeong , Chan Park & Kwon Taek Lim (2012): Synthesis of PS-g-TiO$_2$ Nanocomposites through a Simple Method of Surface Initiated Radical Polymerization, Molecular Crystals and Liquid Crystals, 568:1, 162-169

To link to this article: http://dx.doi.org/10.1080/15421406.2012.710392

*Mol. Cryst. Liq. Cryst.*, Vol. 568: pp. 162–169, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.710392

# Synthesis of PS-*g*-TiO$_2$ Nanocomposites through a Simple Method of Surface Initiated Radical Polymerization

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*Hybrid nanocomposites of polystyrene (PS) and TiO$_2$ were prepared by the facile surface thiol-lactam initiated radical polymerization (TLIRP). At first, the surface of TiO$_2$ nanoparticles was modified by 3-mercaptopropyl-trimethoxysilane to prepare TiO$_2$-SH. Subsequently, a radical polymerization of styrene was accomplished in the presence of TiO$_2$-SH and butyrolactam to afford PS-g-TiO$_2$ nanocomposites. The nanocomposites were investigated by $^1$H-NMR, FT-IR, GPC and XPS. The morphology of the nanocomposites was captured on TEM images, showing the encapsulation of TiO$_2$ with PS. The TGA data suggest that the thermal stability of PS was enhanced upon inclusion of TiO$_2$ nanoparticles. The dispersability of TiO$_2$ nanoparticles was improved significantly after functionalization of PS chains.*

**Keywords** Polymer brush; PS-*g*-TiO$_2$; surface initiated polymerization; TiO$_2$ nanoparticles; TLIRP.

## Introduction

Recently, enormous attention have been concentrated to the polymer-inorganic hybrid nanocomposites in conformity with the fast development of nanotechnology for wide applications in optics, electronics, mechanics, membranes, catalysis, sensors, and biomedical science [1–3]. Of the many classes of inorganic compounds, TiO$_2$ is coated with different polymers for the improvement of mechanical and dielectrical properties prior to being used for electronic ink material, dielectric ceramics, solar cells and optoelectronic devices [4–6]. For the preparation of hybrid nanocomposites, among numerous procedures the controlled/living radical polymerization techniques, such as ATRP, NMP, and RAFT are most frequently used for functionalization of nanosized inorganic particles [7–9]. There techniques are allowed for the preparation of high graft density polymer brushes in which molecular weight and polydispersity are controlled. However, most of these techniques require many reaction steps to introduce functional groups to the inorganic surface for

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polymerization with complex structures and/or it is tedious to remove the catalyst completely from the reaction products.

Now a days, surface bonded thiol groups are being used as chain transfer agents in free radical polymerization because of their high chain transfer constant. Zhou et al. found that ultra thin polymer films can be obtained *via* a surface chain-transfer reaction using (3-mercaptopropyl)-trimethoxysilane as silane coupling agent [10]. Thiol alone is able to initiate polymerization *via* a charge transfer complex of comonomers such as methyl methacrylate/N-cyclohexylmaleimide [11,12]. Hu et al. observed that the addition of *n*-dodecylmercaptan with $\varepsilon$-caprolactam or 2-pyrrolidinone in bulk polymerization of styrene, methyl methacrylate led to the polymerization of monomers [13,14]. Recently, we found that thiol group with the aid of butyrolactam (BL) is a facile approach for surface initiated radical polymerization [15,16].

To the best of our knowledge, there is hardly any report of a facile strategy like the thiol-lactam initiated radical polymerization (TLIRP) on the surface functionalization of $TiO_2$ has been published, even through, it has a great potential for surface modification of inorganic materials. Grafting polymerization of Styrene on $TiO_2$ nanoparticles was performed following a two-step synthetic procedure: employing a one-step direct anchoring of initiator preferably thiol group onto the $TiO_2$ surface and subsequent grafting polymerization from $TiO_2$ based on chain transfer to thiol groups on $TiO_2$ surfaces. The surface modification reaction and the modulated properties of surface-modified $TiO_2$ nanoparticles were characterized by FT-IR, XPS, $^1$H-NMR, TGA, GPC and TEM.

## Experimental

### *Materials*

Titanium dioxide nanoparticles ($TiO_2$, anatase), butyrolactam (BL), (3-mercaptopropyl) trimethoxysilane (MPTMS), toluene were purchased from Aldrich and used as received. Styrene (St) were dried over $CaH_2$ and distilled under reduced pressure before use.

### *Grafting of MPTMS onto $TiO_2$ Nanoparticles*

The grafting procedure of MPTMS on the surface of $TiO_2$ is as follows: after dispersing 10 g of $TiO_2$ nanoparticles in 200mL of toluene, an excess amount of MPTMS was added and the resulting solution was stirred for 24 h under argon atmosphere. Modified $TiO_2$ was isolated by centrifugation and washed repeatedly with toluene. Finally, it was dried at 50°C under vacuum for 24 h.

### *Synthesis of PS-g-$TiO_2$ Nanocomposites by TLIRP*

A typical method for synthesizing PS-*g*-$TiO_2$ nanocomposites by TLIRP is as follows: 1 g of styrene, 0.2 g of $TiO_2$-SH, 0.5 g of BL, 4 mL of toluene and a Teflon-coated stir bar were placed in a 25 mL round flask equipped with a reflux condenser. The flask was purged with $N_2$, heated to 100°C and kept stirring. After polymerization, the flask was cooled to room temperature and the reaction mixture was precipitated in methanol. The product was filtered and dried in a vacuum oven. The product was dissolved in toluene and centrifuged to collect the PS-*g*-$TiO_2$ free from the unbound polystyrene.

To investigate the dependency of number average molecular weight ($M_n$) and polydispersity index ($PDI = M_w/M_n$) of the grafted PS with reaction time, PS brushes were cleaved from the $TiO_2$ surface in the following way: 100 mg of the PS-*g*-$TiO_2$ were dissolved in

1 mL of HCl (2 M) and 10 mL of toluene. The solution was allowed to stir at 80°C for 24 h. The cleaved PS in the organic layer was precipitated in methanol.

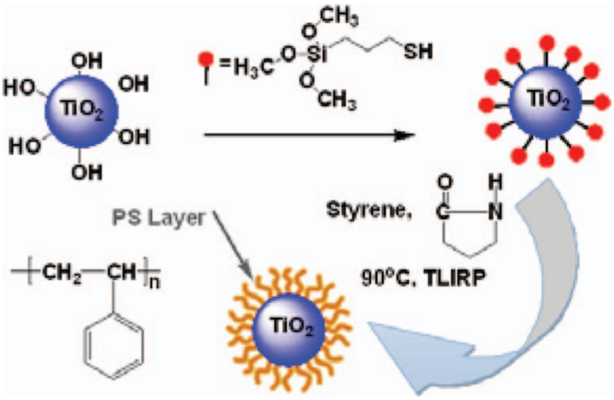
### *Instrumentation*

Transmission Electron Microscopy (TEM) images were recorded using a Hitachi H-7500 instrument operated at 80 kV. Fourier-transformed infrared spectrophotometry (FT-IR) was employed to characterize the change in the surface functionalities of $TiO_2$ using a BOMEM Hartman & Braun FT-IR spectrometer. Thermogravimetric analysis (TGA) was conducted with Perkin-Elmer Pyris 1 analyzer (USA). Surface composition was investigated using X-ray Photoelectron Spectroscopy (XPS) (Thermo VG Multilab 2000) in ultra high vacuum with Al K$\alpha$ radiation. GPC was performed using an Agilent 1200 Series equipped with PLgel 5 $\mu$m MIXED-C columns, with tetrahydrofuran as the solvent. Calibration was carried out using polystyrene standards. The $^1$H NMR spectrum of PS brush cleaved from the $TiO_2$ surface was recorded using a JNM-ECP 400 (JEOL) Spectrophotometer with $CDCl_3$.

## Results and Discussion

The synthetic route for the preparation of PS-*g*-$TiO_2$ is shown in Scheme 1. In order to realize chemical bond between $TiO_2$ nanoparticles and PS *via* TLIRP, it is necessary to immobilize thiol groups onto the surface of $TiO_2$ nanoparticles *via* reaction between the hydroxyl groups on the surface of $TiO_2$ and triethoxysilane groups of MPTMS to form Ti–O–Si linkages. MPTMS-anchored $TiO_2$ nanoparticles were utilized as initiators for TLIRP, where BL was used as a radical generating agent for the polymerization. The well-structured PS-*g*-$TiO_2$ nanocomposites were successfully synthesized by the TLIRP protocol and subsequently subjected to characterization by FT-IR, $^1$H NMR, XPS, TGA, GPC, and TEM.

The chemical bond of MPTMS on the surface of $TiO_2$ and PS grafting on the $TiO_2$ surface were confirmed by using FT-IR spectroscopy (Fig. 1). The $TiO_2$ nanoparticles exhibited broad absorption bands at 3421 and 1633 cm$^{-1}$ assignable to the –OH stretching vibrations and H–O–H bending vibrations, respectively. The strong absorption bands between 400 and 800 cm$^{-1}$ were ascribed to the vibrations of Ti–O and Ti–O–Ti framework. The MPTMS modified $TiO_2$ surface shows the characteristic absorptions at 2821 and 2927 cm$^{-1}$ which



**Scheme 1.** The synthetic route of PS-*g*-$TiO_2$ nanocomposites.

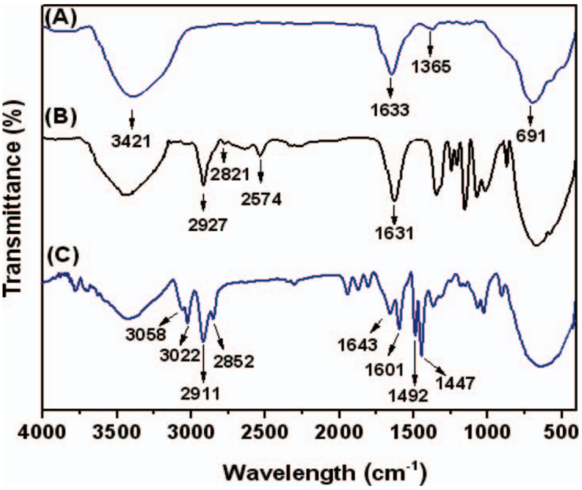


**Figure 1.** FT-IR spectra of (A) $TiO_2$, (B) $TiO_2$-SH and (C) PS-*g*-$TiO_2$.

are assigned to $CH_2$-groups of the MPTMS coupling agent and a weak but visible band at 2574 $cm^{-1}$ assigning to the S–H stretching band. The characteristic bands of PS-*g*-$TiO_2$ were observed for the PS arising from the C-H aromatic stretching vibration at 3058 and 3022 $cm^{-1}$, the C-H aliphatic stretching vibration at 2911 and 2852 $cm^{-1}$, and the phenyl ring stretching vibration at 1447, 1492, and 1601 $cm^{-1}$ (Fig. 1C). The presence of these vibration bands strongly suggests that PS was successfully attached onto the surface of $TiO_2$ nanoparticles.

The surface chemical composition of $TiO_2$, $TiO_2$-SH and PS-*g*-$TiO_2$ were further studied by XPS. The immobilization of the initiator on the surface of $TiO_2$ is suggested by the characteristic signals of O1s at 531.5 eV, Ti2p at 460.0 eV, C1s at 286.1 eV, S2p at 163.6 eV and Si2p at 102.4 eV (Fig. 2B). The binding energy (BE) of S2p at 163.6 eV in the XPS spectrum clearly demonstrates the existence of S–H groups in $TiO_2$-SH. After

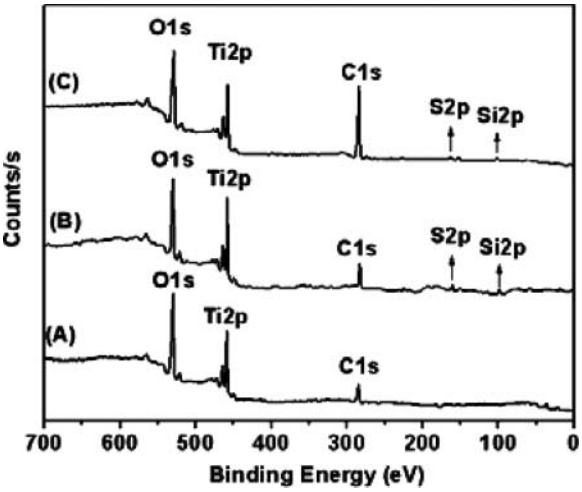


**Figure 2.** Wide-scan spectra of (A) $TiO_2$, (B) $TiO_2$-SH and (C) PS-g-$TiO_2$.

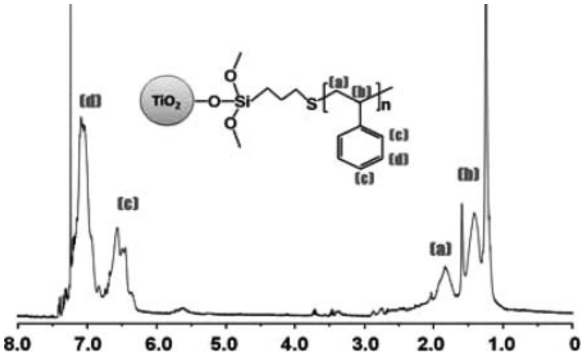


**Figure 3.** $^1$H-NMR spectrum of the cleaved PS brushes from PS-*g*-$TiO_2$ in $CDCl_3$.

grafting of PS onto $TiO_2$ nanoparticles, the XPS scan of PS-*g*-$TiO_2$ shows that the C1s peak with high intensity slightly shifted to a higher BE, indicating that the polymeric chains were directly grafted from the surfaces of $TiO_2$ nanoparticles.

At the primary stage of polymerization, BL induces hydrogen transfer from $TiO_2$-SH to form two free radicals, $TiO_2$-S· and BL-H·. The radical polymerization is then initiated *via* radical addition to styrene with unstable $TiO_2$-S·. In order to analyze the polymer, the grafted polymers from PS-*g*-$TiO_2$ nanocomposites were cleaved with aqueous HCl for subsequent $^1$H-NMR and SEC analyses. The $^1$H-NMR spectrum of the PS which was cleaved from the surface of $TiO_2$ shows peaks at 6.3–7.2 ppm (Fig. 3), assigned to the phenyl protons of PS.

The polymerization on $TiO_2$-SH nanoparticles were attempted for different reaction times ranging from 6 to 18 h. The molecular weight ($M_n$) and PDI values of the time dependent TLIRP are summarized in Table 1. From the GPC analysis, it was observed that the $M_n$ of the PS increased with the polymerization time from 21.4 to 52.2 kg/mol, indicating the control nature of TLIRP. The GPC traces indicate the PDIs are unimodal and narrow. All of these results explicitly suggest that the polymerization of styrene on $TiO_2$ by TLIRP was successful in controlled manner.

The amount of MPTMS and the grafted PS onto the $TiO_2$-SH were quantitatively measured by TGA analysis (Fig. 4). When pure $TiO_2$ was heated from room temperature to 800°C the weight loss was 2.1%, which may be due to the hydroxyl groups or adsorbed gases on $TiO_2$ nanoparticles. The $TiO_2$-SH shows the weight loss of 7.2% between 50 - 800°C, and thus the content of the coupling agent grafted onto the surface of $TiO_2$ is ca. 5.1 wt% (Fig. 4B). The PS-*g*-$TiO_2$ nanocomposites show thermal decomposition at temperature range from 285 to 420°C, which is due to the decomposition of grafted PS. The amount of grafted polymer on the surface of $TiO_2$ is estimated to be ca. 40%, which

**Table 1.** Molecular weight ($M_n$) and PDI of cleaved PS at different polymerization time

| Sample | $M_n$ (kg/mol) | PDI |
|---|---|---|
| PS-*g*-$TiO_2$ (6 h) | 21.4 | 1.49 |
| PS-*g*-$TiO_2$ (12 h) | 39.6 | 1.67 |
| PS-*g*-$TiO_2$ (18 h) | 52.2 | 1.68 |

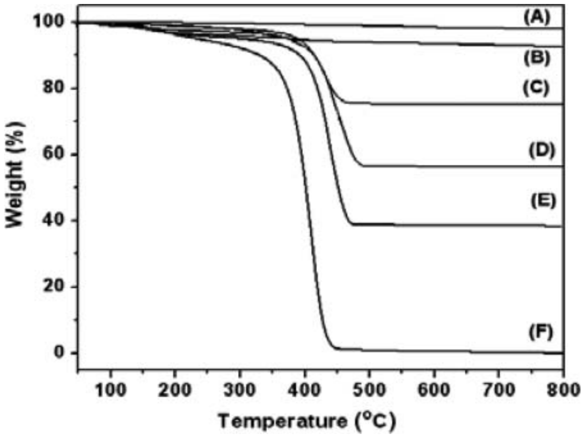


**Figure 4.** TGA spectra of (A) TiO$_2$, (B) TiO$_2$-SH, (C, D, and E) PS-*g*-TiO$_2$ after polymerization for 6 h, 12 h, and 18 h, respectively, and (F) grafted PS cleaved from PS-*g*-TiO$_2$ nanocomposites (polymerization for 12 h).

suggests that the functionalization of PS on the surface of TiO$_2$ nanoparticles was achieved by "*grafting from*" approach.

The morphology of the pure TiO$_2$ and PS-*g*-TiO$_2$ nanocomposites were studied using TEM analysis. Figure 5 shows aggregation of TiO$_2$ nanoparticles and the electron diffraction pattern (inset Fig. 5A) consisting of rings indicates the good crystal structure of the TiO$_2$ nanoparticles. The agglomeration might arise from the large surface area of TiO$_2$ nanoparticles. The important challenge is the prevention of agglomeration of TiO$_2$ nanoparticles in the polymer matrix, which was successfully overcome by the covalent

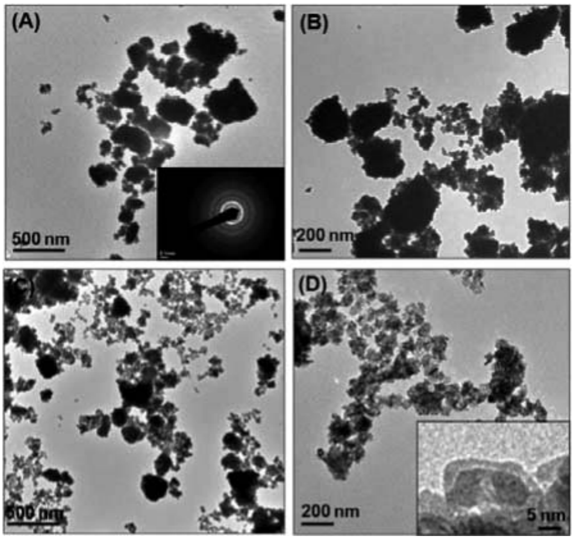


**Figure 5.** TEM pictures of (A) TiO$_2$ nanoparticles and (C) PS-*g*-TiO$_2$ nanocomposites. Pictures (B) and (D) are higher magnifications of (A) and (C).

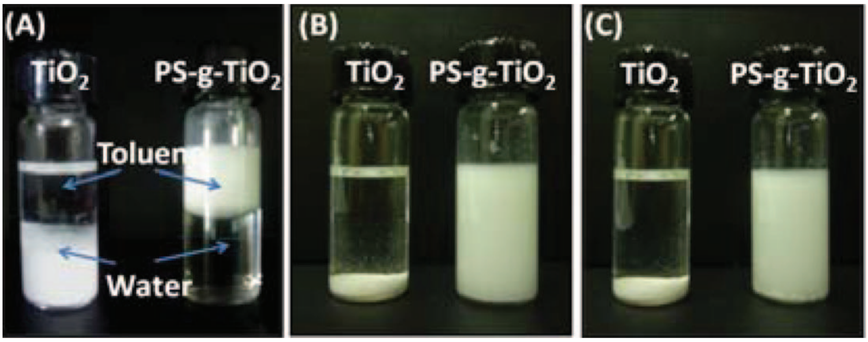


**Figure 6.** Photographs of (A) $TiO_2$ and PS-*g*-$TiO_2$ dispersed in the mixture of toluene and water; photographs of $TiO_2$ and PS-*g*-$TiO_2$ dispersion in toluene after (B) 5 min, and (C) 12 h.

connection between $TiO_2$ and MPTMS. The HR-TEM image of the nanocomposites (inset Fig. 5D) further illustrates that $TiO_2$ nanoparticles are wrapped by the soft PS polymer layer.

The colloidal stability of $TiO_2$ was improved significantly by the covalent PS chain functionalization. The photographs of $TiO_2$ and PS-*g*-$TiO_2$ nanocomposites in the mixture of toluene and water are shown in Figure 6A for the comparative study. The PS-*g*-$TiO_2$ exhibits good dispersion in toluene, while pure $TiO_2$ are well dispersed in the water phase. The $TiO_2$ precipitated in toluene within a few minutes, whereas the PS-*g*-$TiO_2$ remained well dispersed in toluene for prolonged period (Fig. 6B, C). This remarkable difference in dispersibility between pure $TiO_2$ and PS-*g*-$TiO_2$ could be explained in such a way that the PS chain might act as a steric stabilizing layer to prevent agglomeration resulting in superior colloidal stability.

## Conclusions

A facile surface TLIRP strategy was employed to prepare PS-*g*-$TiO_2$ nanocomposites by using $TiO_2$-SH and BL as the initiating system. The FT-IR, $^1$H-NMR, TGA, XPS, and TEM analyses suggested that PS-*g*-$TiO_2$ nanocomposites were successfully afforded. After 18 h TLIRP, the $M_n$ and PDI of the cleaved PS from the $TiO_2$ surface were determined to be 52.2 kg/mol and PDI 1.68, respectively. The $TiO_2$ nanoparticles were encapsulated with the soft PS layer and the $M_n$ of the polymer was found to be time dependent. The anchoring of PS onto $TiO_2$ nanoparticles significantly increased the colloidal stability of the $TiO_2$ nanoparticles in toluene. It is expected that this TLIRP approach would be able to synthesize a range of polymer coated $TiO_2$ with versatile functionalities in the polymeric shell.

## Acknowledgments

This work was financially supported by the grant from the Industrial Source Technology Development Program (Project No. 10035163) of the Ministry of Knowledge Economy (MKE) of Korea and by Inter-Metropolitan Cooperation Development funded by the Presidential Committee on Regional Development.

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