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ABSTRACT

This paper describes the synthesis and characterization of novel type poly (4-chloromethyl styrene-*graft*-4-vinylpyridine)/TiO₂ nanocomposite. Firstly, poly (4-chloromethyl styrene)/TiO₂ nanocomposite was synthesized by in situ free radical polymerizing of 4-chloromethyl styrene monomers in the presence of 3-(trimethoxysilyl) propylmethacrylate (MPS) modified nano-TiO₂. Thereafter, 1-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO-OH) was synthesized by the reduction of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). This functional nitroxyl compound was covalently attached to the poly (4-chloromethyl styrene)/TiO₂ with replacement of chlorine atoms in the poly (4-chloromethyl styrene)/TiO₂ with replacement of 4-vinylpyridine was initiated by poly (4-chloromethyl styrene)/TiO₂ nanocomposite carrying TEMPO groups as a macroinitiators. The coupling of TEMPO with poly (4-chloromethyl styrene)/TiO₂ was verified using ¹H nuclear magnetic resonance (NMR) spectroscopy. The obtained nanocomposites were studied using transmission electron microscopy (TEM), Fourier-transform infrared (FTIR) spectra, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and the optical properties of the nanocomposites were studied using ultraviolet–visible (UV–Vis) spectroscopy.

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1. Introduction

The past few years have witnessed a rapid development in the field of controlled radical polymerization for synthesizing tailormade polymers with well-defined architecture and predictable molecular weights [1–5]. A number of techniques have been explored to achieve this control: atom transfer radical polymerization (ATRP) [6,7], nitroxide-mediated radical polymerization (NMRP) [8], and reversible addition fragmentation process (RAFT) [9,10]. Nitroxide-mediated radical polymerization method is a controlled free radical methodology, which allows the synthesis

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of star and graft copolymers with controlled molecular weight under mild conditions. This polymerization method is based on the use of traditional radical initiator (e.g., B.P.O) in the presence of stable nitroxide radical (e.g., TEMPO). Compared with other graft copolymerization such as anionic polymerization, an advantage of 'living' free radical polymerization (LFRP) is that in the preparation of grafted copolymers, the terminal groups are stable in air at room temperature, and prepolymers can be isolated, stored, and used as needed. Moreover, in anionic polymerization, stringent polymerizations conditions are required [11–14].

Considering such novel chemical properties as acidity, basicity, and hydrophilic-hydrophobic balance, 4-vinylpyridine is of great importance. The homo or copolymers of 4-vinylpyridine are intriguing materials with many applications, such as in sensors and actuators, thin films, host/ligand of metal-containing chromophores, antimicrobial materials, and so on [15–18]. Controlled polymerization of P4VP has been achieved by living ionic polymerization [19,20], and recent reversible addition fragmentation chain transfer [21], polymerization studies have also reported successful controlled/living radical polymerization (CRP) syntheses of P4VP as well as polystyrene/P4VP triblock copolymers [22]. Studies with nitroxide-mediated polymerization [23,24] of





Abbreviations: LFRP, "Living" free radical polymerization; CRP, Controlled/living radical polymerization; NMRP, Nitroxide-mediated radical polymerization; TEMPO, 2,2,6,6-Tetramethyl-1-piperidinyloxy; B.P.O, Dibenzoyl peroxide; PCMS, Poly (4-chloromethyl styrene); P4VP, Poly (4-vinylpyridine); AlBN, 2, 2'-Azobis (isobutyronitrile); DMF, *N*,*N*-Dimethylformamide; TEM, Transmission electron microscopy; *T*_g, Glass transition temperature; DSC, Differential scanning calorimetry; TGA, Thermogravimetric analysis; BET, Specific surface area; MPS, 3-(Trimethoxysilyl) propylmethacrylate.

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4-vinylpyridine reported that "pseudo-living" polymerization was possible at a relatively high reaction temperature (T > 100 °C).

In recent years, polymer encapsulated submicron inorganic particles have attracted increasing because of their exceptional properties and use in technological applications [25-28]. Titanium dioxide (TiO₂) is one of the most important pigments and fillers used for a variety of scientific endeavors such as a dve in conjugated polymers for photoelectrochemical [29] or photoconductive agents [30] a photocatalyst in a photodegradable TiO₂-polystyrene nanocomposite films [31] and semiconductor electrodes in photoelectrochemical cells [32]. However, it is difficult to disperse inorganic nanoparticles in non-polar polymers due to the incompatibility at the interphase between the hydrophobic matrix and the hydrophilic oxide surface. Because of their extremely large surface-area/particle-size ratio, nanoparticles tend to strongly aggregate, hence reducing the mechanical properties of the resultant nanocomposite materials [33-37]. Many efforts have been taken to overcome this problem and to enhance the filler-matrix interaction, such as ultrasonic irradiation, which has been explored for dispersion of SiO₂, TiO₂, and Al₂O₃ nanoparticles during the synthesis of inorganic/polymer nanocomposite materials. However, this approach is restricted due to the limited interaction between the inorganic fillers and the organic matrix, compared with the very strong interaction between individual nanoparticles. Some methods have been explored to improve the dispersibility of inorganic nanoparticles in polymer such as surface modification of nanoparticles with, titanate and silane coupling agents [35-37], modification by chemisorption of small molecules [26,38] and modification by the adsorption of polymers [39]. In addition to, polymer chains have been attached chemically to the inorganic nanoparticles. In this respect, "grafting from" and "grafting to" methods have been proposed. The "grafting from" approach relies on the immobilization of initiators for the controlled/living radical polymerization (CRP) of various monomers, followed by the chain growth from the surface and formation of polymer brush of possible high grafting density [40–42]. Currently, to the best of our knowledge, most of the reported approaches to prepare organicinorganic nanocomposites involve living radical polymerizations. Hojjati and Charpentier who used the relatively new technique of RAFT polymerization, to polymerized methylmeta crylate from TiO₂ nanoparticles [43], Zhao and his coworkers functionalized multiwalled carbon nanotubes via nitroxide-mediated radical polymerization [44], and by applying ATRP, Liu and Wang, grew polymer chains of hydroethyl acrylate from ZnO nanoparticles [45].

For the first time, synthesis and characterization of poly (4styrene-graft-4-vinylpyridine)/TiO₂ chloromethyl [(PCMS-g-P4VP)/TiO₂] nanocomposite via nitroxide-mediated radical polymerization (NMRP) are reported. Firstly, TiO₂ nanoparticles were modified by MPS coupling agent. Thereafter, 4-chloromethyl styrene monomers were added to carry out copolymerization with vinyl groups on the MPS-modified TiO₂ by free radical initiator AIBN in solution medium. Afterward, 1-hydroxy-2,2,6,6tetramethyl-1-piperidinyloxy (TEMPO-OH) was coupled with poly (4-chloromethyl styrene)/TiO₂ nanocomposite by a substitution nucleophilic reaction in N,N-dimethylformamide (DMF) as the solvent. The controlled graft copolymerization of 4-vinylpyridine was initiated by PCMS/TiO₂ carrying TEMPO groups as a macroinitiators.

2. Experimental

2.1. Materials

Titanium dioxide (P_{25} , Degussa AG, Frankfurt, Germany), average primary particle size 21 nm and specific surface area (BET) 50+/-15 m²/g. 4-Chloromethyl styrene and 4-vinylpyridine monomers from Merck (Darmstadt, Germany) were distilled under a reduced pressure before use. TEMPO was prepared in our laboratory [8,11]. Natrium-L(+)-ascorbate and 3-(trimethoxysilyl) propylmethacrylate (MPS), were obtained from Merck and used without further purification. 2, 2'-Azobis (isobutyronitrile) (AIBN) from Merck, crystallized in ethanol at 50 °C before use. Toluene, (Merck) was dried by refluxing over sodium and distilled under argon prior to use. All other reagents were purchased from Merck and purified according to the standard methods.

2.2. Modification of TiO₂ nanoparticles with MPS coupling agent

The process started with dispersing of certain amount (1.5 g) of TiO_2 nanoparticles in ethanol (100 ml) as the solvent under 20 min ultrasonication, into which distilled water (0.6 g), ammonia (25wt.%, 0.4 g), and the coupling agent MPS (1.5 g) were added. The dispersed solution was then transferred to a 250 ml round bottom flask equipped with a condenser and a magnetic stirrer under bubbling argon gas. The solution temperature was maintained at 70 °C under stirring for 8 h. The particles were recovered by centrifugation at 6000 rpm for 10 min. The particles were then redissolved in ethanol and reprecipitated by centrifugation which was repeated until the solution was clear. The solid product was dried overnight under vacuum at room temperature.

2.3. Encapsulation of modified TiO_2 nanoparticles by poly (4choloromethyl styrene) via in situ free radical polymerization

The free radical polymerization of 4-choloromethyl styrene monomers from the MPS-modified TiO₂ was accomplished by the followed procedure:

MPS-TiO₂ (0.5 g), AIBN (0.05 g) and 4-choloromethyl styrene monomers (3.0 g, 21.6 mmol) were mixed into a 100 ml flask containing 20 ml toluene. The mixture was irradiated with ultrasonic vibrations for 15 min, bubbling with argon gas. Thereafter, the mixture was refluxed into an oil bath maintained at a temperature of 65 °C and stirred with electromagnetic stirring for 12 h under argon protection to complete the polymerization. The product recovered by filtration in large amount of methanol. To ensure that no ungrafted polymer remained in the product, the particles were redissolved in toluene and reprecipitated by centrifugation at 6000 rpm for 10 min, with this process repeated until the solution was clear (Yield: 0.81 g). For preparation of pure poly (4choloromethyl styrene) the polymer was cleaved from TiO₂ nanoparticles, through the refluxing, for about 24 h under acidic conditions (Scheme 1).

2.4. Preparation of TEMPO-OH by reduction of TEMPO

TEMPO (0.25 g, 1.6 mmol) was suspended in a solution of sodium ascorbate (0.525 g, 5.3 mmol) in water (5 ml) and shaken vigorously until it was completely decolorized (\sim 30 min). The resulting suspension was extracted with ether. Afterward, the ether extracts was washed with water and brine, dried (using Na₂SO₄), and evaporated under reduced pressure to produce a crude product (Scheme 2).

2.5. Synthesis of PCMS-TEMPO/TiO₂ macroinitiator

In a tree-neck round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer, 0.10 g (0.65 mmol) of TEMPO-OH was dissolved in anhydrous *N*,*N*-dimethylformamide (DMF) (3 ml) and added under N_2 atmosphere to 30 mg (1.3 mmol) hexane washed NaH (from 60% suspension in oil).



Scheme 1. Encapsulation of modified nano-TiO₂ by PCMS via in situ free radical polymerization.



Scheme 2. Preparation of TEMPO-OH by reduction of TEMPO.

The mixture was stirred for 30 min. In a separate container, 1 g of poly (4-chloromethyl styrene)/TiO₂ was dissolved in 5 ml DMF and was slowly added to the mixture under N₂ atmosphere and refluxed for 24 h at room temperature. The reaction was terminated by pouring the content of the flask into a large amount of methanol. The white solid was filtered, washed with methanol and dried in vacuum (Scheme 3).

2.6. Nitroxide-mediated living radical polymerization of 4-vinylpyridine onto PCMS-TEMPO/TiO₂ macroinitiator

In a typical experiment, a dry ampoule was charged with toluene (10 ml), 4-vinylpyridine monomers (3.0 g, 28.5 mmol), and PCMS-TEMPO/TiO₂ macroinitiator (0.5 g). Thereafter, the ampoule was sealed and three cycles of freeze-pump-thaw were performed to remove oxygen. After which the reaction mixture was heated at 130 °C and maintained at this temperature for 12 h. The reaction was terminated by pouring the content of the ampoule into a large amount of methanol. To remove the ungrafted poly (4-vinylpyridine) from the crude product, the powder was extracted with DMF in a Soxhlet apparatus for 24 h. The precipitated polymer was filtered, washed several times with DMF, and dried under vacuum (Yield: 0.68 g), (Scheme 4).

2.7. Characterization

Fourier-transform infrared (FTIR) spectra of the samples were obtained on a Shimadzu 8101M FTIR (Shimadzu, Kyoto, Japan). The

samples were prepared by grinding the dry powders with KBr and compressing the mixture into disks. The disks were stored in a desiccator to avoid moisture absorption. The spectra were recorded at room temperature. ¹H nuclear magnetic resonance (NMR) spectra were obtained at 25 °C using an FT-NMR (400 MHz) Brucker spectrometer (Brucker, Ettlingen, Germany). The sample for ¹H NMR spectroscopy was prepared by dissolving about 10 mg of products in 5 ml of deuterated chloroform. Transmission electron microscopy (TEM) was performed using a Philips EM208 microscope (Phillips, Eindhoven, Netherlands) with a 100 kV accelerating voltage. The thermal properties of the nanocomposites were obtained with a TGA-PL STA 1640 (Polymer Laboratories, Shropshire, UK). About 10 mg of the sample was heated between 25 and 600 °C at a rate of 10 °C min⁻¹ under flowing nitrogen. Differential scanning calorimetry analyses were performed with a NETZSCH (Selb, Germany)-DSC 200 F3 Maia. The sample was first heated to 200 °C and then allowed to cool for 5 min to eliminate the thermal history. Thereafter, the sample was reheated to 200 °C at a rate of 10 °C min⁻¹. The entire test was performed under nitrogen purging at a flow rate of 50 ml min⁻¹. Ultraviolet–visible (UV–Vis) spectra of the samples were measured using a Shimadzu 1601 PC, UV-Vis spectrophotometer (Shimadzu, Kyoto, Japan) in the wavelength range 300-800 nm.

3. Results and discussion

3.1. Modification of TiO₂ nanoparticles with coupling agent MPS

The functional silanes have been widely used for the surface modification of metal oxides. To get evidence that coupling agent MPS was chemically bonded to TiO_2 nanoparticles, FTIR spectroscopy investigation was firstly used to identify the qualitative composition of modified TiO_2 . The FTIR spectra of coupling agent MPS (a), raw TiO_2 (b) and MPS-modified TiO_2 (c) are shown in Fig. 1. The FTIR spectra of the coupling agent MPS shows the characteristic



Scheme 3. Synthesis of PCMS-TEMPO/TiO₂ macroinitiator.



Scheme 4. Nitroxide-mediated living radical polymerization of 4-vinylpyridine onto PCMS-TEMPO/TiO2 macroinitiator.

absorption bands due to stretching vibration of C–H in the 2944–2843 cm⁻¹ region, the band around 1719 cm⁻¹ is due to stretching vibration of C=O and the band around 1637 cm⁻¹ is due to stretching vibration of C=C which can act as the functional site for the further copolymerization [35].

The Ti–O–Si transmittance peak at 1068 cm⁻¹ and C=O vibration band at 1708 cm⁻¹ are found for the MPS-modified TiO₂ (Fig. 1-c). In addition grafting of coupling agent MPS onto TiO₂ surface with covalent chemical bonding can be confirmed by the –CH stretching vibration at 2925–2874 cm⁻¹ region. The bands around 1634 cm⁻¹ and3385 cm⁻¹ are due to the hydroxyl groups on the surface of TiO₂ nanoparticles. The shift of the C=O vibration band from 1719 to 1708 cm⁻¹ is due to the formation of the hydroxyl group on the surface of TiO₂ nanoparticles [46].

The TiO₂ nanoparticles both before and after modification was studied by organic phase/water partitioning experiments. As one would expect after modification by an organic group, nano-TiO₂'s hydrophilicity changes. A photograph of vials containing equal volumes of chloroform and water, and equal masses of unmodified titania and modified titania are shown in Fig. 2. The modified titania (Fig. 2-b) exhibited good dispersion in organic phase (chloroform), while unmodified TiO₂ (Fig. 2-a) one partitioned into the water phase, indicating the success of the incorporation of the MPS coupling agent to the titania surface.

3.2. Encapsulation of modified TiO₂ nanoparticles by poly (4-chloromethyl styrene)

The methacrylate group of the MPS can further react with 4chloromethyl styrene monomers via free radical polymerization, forming a polymer shell chemically bonded to the inorganic TiO_2 core. Fig. 3 shows the FTIR spectra of free poly (4-chloromethyl styrene) and the TiO₂ nanoparticles encapsulated by PCMS. It is found that the TiO₂ nanoparticle encapsulated by PCMS is characterized by the C–H aromatic stretching vibration at 3050 and 3021 cm⁻¹, the C–H aliphatic stretching vibration at 2923 and 2852 cm⁻¹, the phenyl ring stretching vibration at 1445, 1511 and 1610 cm⁻¹, the ring in phase C–H stretching vibration at 1020 cm⁻¹, and the ring out of-plane bend at 681 cm⁻¹, where the typical absorption bands for PCMS are clearly seen, indicating the existence of PCMS on the particle surface.

3.3. Synthesis of PCMS-TEMPO/TiO₂ macroinitiator

At first in order to produce the active sites on PCMS/TiO₂ nanocomposite, TEMPO was added to PCMS/TiO₂. So, TEMPO-OH reacts with PCMS/TiO₂ to give the PCMS-TEMPO/TiO₂ macroinitiator. The ¹H NMR spectra of PCMS/TiO₂ nanocomposite indicate the chemical shifts at 1.13–2.34 and 6.17–7.35 ppm represent the aliphatic (a) and aromatic (c) protons respectively, and the chemical shifts at 4.16–4.67 ppm shows the $-CH_2Cl$ protons (b) in this product. Comparison with the ¹H NMR spectrum of PCMS/TiO₂ the ¹H NMR spectrum of PCMS-TEMPO/TiO₂ macroinitiator indicates the additional chemical shifts of CH_2 –O (d) and methyl groups (e) of TEMPO molecules at 3.34–3.48 and 0.76–1.06 ppm respectively [47,48]. The ¹H NMR spectra showed that the functional groups of the TEMPO were coupled with PCMS/TiO₂ nanocomposite, thus the NMRP reaction has been occurring (Fig. 4).

3.4. Preparation of poly (4-chloromethyl styrene-grft-4vinylpyridine)/TiO₂ nanocomposite

Poly (4-vinylpyridine) is a pH-sensitive polymer which is soluble in water when the pH value is below 4.7 and becomes insoluble when the pH is high (>4.7). Therefore, block or graft



Fig. 1. FTIR spectra of coupling agent MPS (a), raw TiO₂ (b) and MPS-modified TiO₂ (c).

copolymers of P4VP could respond to pH values in water solution and self-assemble to form different supramolecular structures. Additionally, the complexing properties of the P4VP, e.g., toward metallic salts, make it act as an interesting multidentate ligand for the preparation of block or graft copolymers/nanoparticle mixtures [16–18]. Thus, we choose P4VP as the building blocks of the shell.

The thermal homolytic scission of the C–O bond of the aminoxy moiety of the PCMS-TEMPO/TiO₂ macroinitiator takes place at 130 °C and causes the radical polymerization of 4-vinylpyridine to yield the controlled graft copolymerization. The bond dissociation is considered to be reversible [11]. To successfully carry out this copolymerization, it was necessary to perform this reaction at this temperature any spontaneous thermal polymerization and it was necessary to perform that at this reaction condition, the polymerization is living and controlled. For comparison, the blank experiments proceed in the absence of TEMPO onto PCMS/TiO₂ was also included. In this condition, no homo poly (4-vinylpyridine) was formed in the absence of macroinitiator under the identical NMRP conditions. This suggests that the possibility of the formation of homopolymer in the grafting reaction can be excluded in this study and it performed that the polymerization is living.

Fig. 5 shows the FTIR spectra of (PCMS-g-P4VP)/TiO₂ (a) and PCMS/TiO₂ (b) nanocomposites. The FTIR spectra of (PCMS-g-P4VP)/TiO₂ nanocomposite is basically the same due to strong absorption by (PCMS-g-P4VP) and weak absorption of TiO₂.



Fig. 2. The photographs were taken after the samples were placed in the bottles and ultrasonicated for 10 min; the concentration was ca. 0.5 mg/ml. In the bottles, the upper layer is water and the lower layer is chloroform phase. The unmodified TiO_2 is well dispersed in the water phase (a), while the modified TiO_2 is suspended in the organic phase (b).

Compared with that of PCMS/TiO₂, new peaks at 1360 and 1636 cm⁻¹ attributed to pyridine groups in the FTIR spectrum of (PCMS-g-P4VP)/TiO₂ nanocomposite were observed [16,49]. The band around 3414 cm⁻¹ is due to the hydroxyl groups in the TiO₂ nanparticles.

The chemical structure of the (PCMS-g-P4VP)/TiO₂ nanocomposite was further examined by ¹H NMR spectroscopy. In the ¹H NMR spectrum of the (PCMS-g-P4VP)/TiO₂ (Fig. 6), the signals due to the aromatic protons (c) and the pyridine ring protons (g) were observed at 6.04–7.15 and 8.08–8.43 ppm, respectively



Fig. 3. FTIR spectra of free PCMS (a) and PCMS/TiO₂ nanocomposite (b).



Fig. 4. ¹H NMR spectra of PCMS/TiO₂ nanocomposite and PCMS-TEMPO/TiO₂ macroinitiator.

[17,50]. Furthermore, the living graft copolymerization of 4-vinylpyridine onto $PCMS/TiO_2$ is characterized by the functional groups of the TEMPO at the end of poly (4-vinylpyridine) chains. The functional group of the TEMPO appears with characteristic

signals of CH–O and methyl groups (e) at 3.46 and 0.75–1.02 ppm respectively. The ¹H NMR spectra show that the functional groups of the TEMPO were retained at the end of poly (4-vinylpyridine) chains, which provides strong evidence that the NMRP reaction



Fig. 5. FTIR spectra of (PCMS-g-P4VP)/TiO₂ (a) and PCMS/TiO₂ (b) nanocomposites.



Fig. 6. ¹H NMR spectra of (PCMS-g-P4VP)/TiO₂ nanocomposite.

Table 1

Grafting parameters for PCMS/TiO₂ and (PCMS-g-P4VP)/TiO₂ nanocomposites.

Samples	Mass of	Weight	Grafting	Grafting
	Grafting (W _g)	Gain (%WG)	Efficiency (%GE)	Yield (%G)
PCMS/TiO ₂	0.81	8.8	23.1	38.2
(PCMS-g-P4VP)/TiO ₂	0.68	5.1	17.4	26.5



Fig. 7. UV–Vis spectra of PCMS/TiO₂ nanocomposite (a), (PCMS-g-P4VP)/TiO₂ nanocomposite (b) and PCMS (c).

occurred. These data were confirmed the successful synthesis of the (PCMS-g-P4VP)/TiO₂ nanocomposite via nitroxide-mediated radical polymerization.

The grafting parameters such as grafting yield, grafting efficiency, and weight gain were calculated, based on gravimetric measurements, according to the following equations: grafting yield (%G) = $(W_g - W_0)/W_g \times 100$; grafting efficiency (%GE) = $W_g/(W_m + W_0) \times 100$; weight Gain (%WG) = $(W_g - W_0)/(W_m + W_0) \times 100$; where W_g is the mass of the grafting copolymer, W_0 is the mass of initiator (MPS-TiO₂ or PCMS-TEMPO/TiO₂), and W_m is the mass of the monomer taken for the reaction. The grafting parameters for PCMS/TiO₂ and (PCMS-g-P4VP)/TiO₂ nanocomposites were calculated and summarized in Table 1.

3.5. Optical properties

The samples for UV–Vis spectroscopy were prepared by addition of same amount of the obtained nanocomposites into boiled DMF solutions. Films with relatively uniform thickness were obtained on the sidewall of a quartz glass after solvent evaporation. The UV–Vis spectra of PCMS/TiO₂ nanocomposite, (PCMS-g-P4VP)/ TiO₂ nanocomposite and pure PCMS are shown in Fig. 7. Their absorbance at wavelengths 400 nm (A₄₀₀) and 300 nm (A₃₀₀) were

Table 2	
Absorbance at wavelengths 400 nm (A_{400}) and 300 nm (A_{300}) .	

Samples	$A_{300} (nm)$	
PCMS	0.210	0.052
PCMS/TiO ₂	1.315	0.414
(PCMS-g-P4VP)/TiO ₂	0.908	0.381



Fig. 8. DSC traces of the PCMS (a), PCMS/TiO₂ (b) and (PCMS-g-P4VP)/TiO₂ (c).



Fig. 9. TGA curves of the TiO₂ (a), MPS-modified TiO₂ (b), PCMS/TiO₂ (c), (PCMS-g-P4VP)/TiO₂ (d) and PCMS (e).

recorded and are summarized in Table 2. Small values of absorbance at the visible and UV region were observed for PCMS, which is reasonable transparency but has no function of filtering out UV light. However, relatively strong absorbance in the UV region and small absorbance at the visible region, which also means a typical optical property of the combination of visual transparency and UV filters close to the visual wavelengths, were observed for the (PCMS-g-P4VP)/TiO₂ nanocomposite. The scattering is remarkably enhanced in the UV range for PCMS/TiO₂ compared to scattering in the (PCMS-g-P4VP)/TiO₂ sample. The range of UV wavelengths is often subdivided into UV-A (380–315 nm), UV-B (315–280 nm), and UV-C (280–10 nm). Thus, PCMS/TiO₂ and (PCMS-g-P4VP)/TiO₂ nanocomposites can be applied to block the UV-A radiation.

3.6. Thermal property study

Thermal behaviors of the obtained nanocomposites were investigated by differential scanning calorimetry (DSC) and

Table 3	
Weight changes of the samples from TG	A.

Samples	Initial wt. (%)	Residual wt. (%)	Grafted MPS (%)	Grafted PCMS (%)	Grafted P4VP (%)
TiO ₂	100	99.32	_		_
PCMS	100	8.68	-	_	-
MPS-TiO ₂	100	95.02	4.3	_	-
PCMS/TiO ₂	100	56.74	4.3	38.28	_
$(PCMS-g-P4VP)/TiO_2$	100	30.17	4.3	38.28	26.57

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Fig. 10. TEM micrographs of raw TiO₂ nanoparticles (a), TiO₂ nanoparticles encapsulated by PCMS (b) and (PCMS-g-P4VP)/TiO₂ (c).

thermogravimetric analysis (TGA). Fig. 8 shows the DSC traces of the PCMS (a), PCMS/TiO₂ (b) and (PCMS-g-P4VP)/TiO₂ (c). The PCMS is non-crystalline and therefore does not exhibit any crystallization or melting transitions. Fig. 8(a) exhibits an endothermic peak approximately at 81 °C, corresponding to the glass transition temperature of PCMS. In Fig. 8(b) the transition observed at 106 °C can be designed as the glass transition temperature of PCMS/TiO₂

nanocomposite. The DSC traces of (PCMS-*g*-P4VP)/TiO₂ nanocomposite (Fig. 8c) shows a strong endothermic peak at 310 °C, corresponding to the degradation of the poly (4-vinylpyridine) chains. For the (PCMS-*g*-P4VP)/TiO₂ nanocomposite, the T_g is too weak to measure, or it is suppressed due to the confinements of polymer chains (especially P4VP due to its hydrophilichydrophobic balance) by the TiO₂ nanoparticles. In this Figure the



Fig. 11. The photographs were taken after the samples were placed in the bottles and ultrasonicated for 10 min; the concentration was ca. 1 mg/ml. Photograph of samples: PCMS/TiO₂ in toluene (a), PCMS/TiO₂ in DMF (b), (PCMS-g-P4VP)/TiO₂ in toluene (c) and (PCMS-g-P4VP)/TiO₂ in DMF (d).

weak transition observed at 119 °C can be designed as the glass transition temperature of (PCMS-g-P4VP)/TiO₂ nanocomposite. Strong interfacial bonding between the modified TiO₂ nanoparticles and polymer chains leads to an increase of the glass transition temperature of nanocomposites by impeding the chain flexibility.

Characteristic TGA curves of the TiO₂ (a), MPS-modified TiO₂ (b), PCMS/TiO₂ (c), (PCMS-g-P4VP)/TiO₂ (d) and PCMS (e) are shown in Fig. 9. TGA results indicate improvement of the thermal stability for PCMS/TiO₂ compared to neat PCMS. According to the Fig. 9(c), we can draw the conclusion that the weight-loss around 450 °C in the TGA curve of PCMS/TiO₂ is a result of the decomposition of PCMS chains covalently attached to TiO₂ nanoparticles. Higher decomposition temperature of PCMS/TiO₂ (450 °C) compared with pure PCMS (420 °C), indicated that no polymers adsorbed noncovalently onto the surface of TiO₂ nanoparticles. In comparison with the TGA curve of PCMS/TiO₂, a new weight-loss region around 320 °C was observed, which corresponded to the decomposition of the poly (4vinylpyridine) in the TGA curve of (PCMS-g-P4VP)/TiO₂. Moreover, according to Fig. 9(d), we can conclude that the weight-loss of the (PCMS-g-P4VP)/TiO₂ nanocomposite between 150 and 280 °C is accelerated, followed by the early degradation of the TEMPO molecules at the end of poly (4-vinylpyridine) chains [44]. The weight percent of grafted modifier, grafted PCMS and grafted P4VP are calculated from the TGA curves and summarized in Table 3.

3.7. Transmission electron microscopy

Direct and clear evidence of the PCMS and (PCMS-g-P4VP) chemically bonded to TiO₂ nanoparticles were demonstrated not only from TGA and FTIR spectroscopy but also from transmission electron microscopy images. TEM images of the raw TiO₂ nanoparticles (a), TiO₂ nanoparticles encapsulated by PCMS (b) and (PCMS-g-P4VP)/TiO₂ nanocomposite (c) are shown in Fig. 10. Fig. 10(a) shows the TEM image of the raw TiO_2 nanoparticles consisting of agglomerated spherical particles. It is clearly demonstrated in Fig. 10(b and c) that the PCMS and (PCMS-g-P4VP) shell is formed on the particle surface. The polymer shell can be seen with less contrast. Since the free PCMS and (PCMS-g-P4VP) has been separated from the bonded PCMS and (PCMS-g-P4VP), Fig. 10 suggests that PCMS and (PCMS-g-P4VP) shells are formed on TiO₂ nanoparticles. However, some agglomeration of TiO₂ nanoparticles still exists, although the generally excellent separation of TiO₂ nanoparticles is attributed to the growing of PCMS and (PCMS-g-P4VP) chains which separates the previously agglomerated TiO₂ nanoparticles.

3.8. Dispersibility test

On the basis of the evidence mentioned previously, the conclusion could be drawn that PCMS-TEMPO/TiO₂ macroinitiator could initiates "living" free radical polymerization of 4vinylpyridine monomers to yield the controlled graft copolymer. The photographs of PCMS/TiO₂ and (PCMS-g-P4VP)/TiO₂ nanocomposites in toluene and DMF solvents are shown in Fig. 11. A homogeneous solutions of PCMS/TiO₂ in toluene (Fig. 11a) and DMF (Fig. 11b) solvents were a visual indication of the existence of TiO_2 nanoparticles in the solutions. Here the solutions represent a good dispersion of PCMS/TiO₂ to form stable systems. After the copolymerization, the dispersibility of (PCMS-g-P4VP)/TiO₂ in toluene had changed (Fig. 11c). The (PCMS-g-P4VP)/TiO2 nanocomposite became dispersible in toluene, which was a bad solvent for poly (4vinylpyridine), whereas PCMS/TiO₂ could disperse in it very well. The (PCMS-g-P4VP)/TiO₂ nanocomposite shows a homogeneous solution in DMF solvent (Fig. 11d). Here the solution represents a good dispersion of (PCMS-g-P4VP)/TiO₂ to form a stable system. The change in the dispersibility was additional evidence showing that (PCMS-g-P4VP)/TiO₂ was obtained. In other words, the dispersibility of polymer grafted TiO₂ was a reflection of the solubility of the polymer attached, so the polymer change from PCMS to (PCMS-g-P4VP) affected the dispersibility of TiO₂.

4. Conclusions

Poly (4-chloromethyl styrene)/TiO₂ nanocomposite was synthesized by in situ free radical polymerizing of 4-chloromethyl styrene monomers in the presence of 3-(trimethoxysilyl) propylmethacrylate (MPS) modified nano-TiO₂. Thereafter, TEMPOterminated poly (4-chloromethyl styrene)/TiO₂ macroinitiator (PCMS-TEMPO/TiO₂) was prepared by reacting of PCMS/TiO₂ with sodium 4-oxy-TEMPO derived from TEMPO-OH. Macroinitiator PCMS-TEMPO/TiO₂ could initiates "living" free radical polymerization of 4-vinylpyridine monomers to yield the controlled graft copolymer [(PCMS-g-P4VP)/TiO₂]. TGA results indicated that no polymers adsorbed noncovalently onto the surface of TiO₂ nanoparticles. Also FTIR spectroscopy and TEM images investigation provided direct and clear evidence for the presence of PCMS and (PCMS-g-P4VP) shell on nano-TiO₂ core particles. Significantly, the obtained nanocomposites showed a strong absorption of UV light in the wavelength range of 300-400 nm. Thus, the prepared nanocomposites could be used to block the UV radiation in the mentioned wavelength range. The PCMS/TiO₂ that was obtained was easily dispersed in organic solvents such as toluene to give a stable suspension. Yet, when the PCMS layer was changed to a (PCMS-g-P4VP) layer, the dispersibility of the sample changed. In other words, NMRP technique could be used as a powerful tool to modify TiO₂ nanoparticles into useful materials.

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