Nitroxide-Mediated Radical Polymerization of Styrene Initiated from the Surface of Titanium Oxide Nanoparticles

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INTRODUCTION

Recently, many researchers have attempted to utilize controlled/living polymerization methods for the preparation of nanocomposite polymers with well-defined structures. Controlled/living radical polymerization (CLRP) enables synthesis of polymers with narrow molecular weight distributions (MWDs), predetermined molecular weights and various complex architectures. The past few years have witnessed a rapid development in the field of controlled radical polymerization for synthesizing tailor made polymers with well-defined architecture and predictable molecular weights [1]. A number of techniques have been explored to achieve this control: atom transfer radical polymerization (ATRP) [2-9], nitroxide-mediated radical polymerization (NMRP) [10-15], and reversible addition fragmentation process (RAFT) [16]. Nitroxide-mediated radical polymerization method is a controlled free radical methodology, which allows the synthesis 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). In this type of process, the propagating species (Pn°) reacts with a stable radical (X°) as seen in Fig. 1. The resulting dormant species (Pn-X) can then reversibly cleave to regenerate the free radicals once again. Once Pn° forms it can then react with a monomer, M, and propagate further. The most commonly used stable radicals have been nitroxides, especially 2, 2, 6, 6-tetramethyl tetramethylpiperidinyl-1-oxy (TEMPO).

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ABSTRACT
Titanium dioxide (TiO₂) nanoparticles, with an average size of about 45 nm, were encapsulated by polystyrene using in situ nitroxide mediated radical polymerization in the presence of 3-aminopropyl triethoxy silane as a coupling agent and 2, 2, 6, 6-tetramethylpiperidinyl-1-oxy as a initiator. First, the initiator for nitroxide mediated radical polymerization was covalently bonded onto the surface of Titanium dioxide nanoparticles through our novel method. For this purpose, the surface of TiO₂ nanoparticle was treated with 3-aminopropyl triethoxy silane, a silane coupling agent, and then these functionalized nanoparticles was reacted with ±-chloro phenyl acetyl chloride. The chlorine groups were converted to nitroxide mediated groups by coupling with 1-hydroxy-2, 2, 6, 6-tetramethyl piperidine. These modified TiO₂ nanoparticles were then dispersed in styrene monomers to carry out the in situ free radical polymerization.

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anionic polymerization, stringent polymerizations conditions are required [17].

In recent years, polymer encapsulated submicron inorganic particles have attracted increasing because of their exceptional properties and use in technological applications [18-21]. Titanium dioxide (TiO$_2$) is one of the most important pigments and fillers used for a variety of scientific endeavors such as a dye in conjugated polymers for photo electrochemical [22] or photoconductive agents [23] a photo catalyst in a photodegradable TiO2-polystyrene nanocomposite films [24] and semiconductor electrodes in photo electrochemical cells [25]. However, it is difficult to disperse inorganic nanoparticles in non-polar polymers due to the incompatibility at the inter phase 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 [27-30]. Many efforts have been taken to overcome this problem and to enhance the fillermatrix interaction, such as ultrasonic irradiation, which has been explored for dispersion of SiO$_2$, TiO$_2$, and Al$_2$O$_3$ 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 [28-30], modification by chemisorptions of small molecules [19,31] and modification by the adsorption of polymers [32]. 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 [33-35]. Currently, to the best of our knowledge, most of the reported approaches to prepare organic inorganic nanocomposites involve living radical polymerizations. Hojjati and Carpenters who used the relatively new technique of RAFT polymerization, to polymerized methyl metacrylate from TiO$_2$ nanoparticles [36], Zhao and his coworkers functionalized multi walled carbon nano tubes via nitrooxide-mediated radical polymerization [37], and by applying ATRP, Liu and Wang, grew polymer chains of hydroethyl acrylate from ZnO nanoparticles [38].

For the first time, synthesis and characterization of Poly styrene/TiO$_2$ nanocomposite via nitrooxide-mediated radical polymerization (NMRP) are reported. Firstly, TiO$_2$ nanoparticles were modified by 3-aminopropyl triethoxy silane coupling agent. Thereafter, these functionalization nanoparticles were reacted with α-chloro phenyl acetyl chloride. The chlorine groups were converted to nitrooxide mediated groups by coupling with 1-hydroxy-2, 2, 6, 6-tetramethy-piperidine (TEMPO-OH). These modified TiO$_2$ nanoparticles were then dispersed in styrene (St) monomers to carry out the in situ free radical polymerization by TEMPO iniferter.

**Fig. 1.** Mechanism for nitrooxide-mediated polymerization

**MATERIALSAND METHODS**

Titanium oxide (Degussa P25) dried at 150°C in inert atmosphere. 3-aminopropyl triethoxy silane (APTES) was provided by Merck Co. and used without further purification. Toluene and Tetrahydrofuran (THF) (Merck, Germany) were dried by refluxing over sodium and distilled under argon prior to use. Dimethyl formamide (DMF) dried over CaH$_2$ and distilled before use. Triethylamine (TEA) was dried with molecular sieves and then distilled. α-Chloro phenyl acetyl chloride was used as received. Styrene (Merck) was dried with CaH$_2$ and distilled before use. TEMPO was prepared in our laboratory in Tabriz Payame Noor University. Triethylamine (TEA) was dried with molecular sieves and then distilled. α-Chloro phenyl acetyl chloride was used as received. Styrene (Merck) was dried with CaH$_2$ and distilled before use. TEMPO was prepared in our laboratory in Tabriz Payame Noor University [10-15]. Sodium ascorbate was provided by Aldrich Co. and
Grafting of polymerization initiating agent to modified TiO$_2$ nanoparticles

The amino functionalized nanoparticle surfaces were immersed in anhydrous THF (6 mL). After this dispersion, triethylamine (0.5 mL) and $\alpha$-chloro phenyl acetyl chloride (0.5 mL) were added. The reaction was allowed to proceed overnight with moderate agitation. The functionalized Titanium oxide surfaces were then purified by multiple washings with THF and dichloromethane and dried in vacuum at room temperature.(3).

Reduction of TEMPO to 1-hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMPO-OH)

Reduction of TEMPO to 1-hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMPO-OH) was carried out. For this purpose TEMPO (0.2 gr) was suspended in a solution of sodium ascorbate (1 gr) in water (13 ml) and shaken vigorously until it was completely decolorized (0.5 h). The resulting suspension was extracted with ether. Afterwards, the ether extracts were washed with water and brine, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to give a crude product (4).

Synthesis of TEMPO/modified-TiO$_2$ macro-initiator

In a two-neck round-bottom flask equipped with condenser, gas inlet/outlet, and a magnetic stirrer, 0.20 g of TEMPO-OH was dissolved in anhydrous N,N-dimethyl formamide (DMF) (30 ml) and under argon atmosphere 18 mg of NaH was added. The mixture was stirred for 30 min. Then 0.4 g of acetyl chloride-grafted TiO$_2$ nanoparticles was slowly added to the mixture under argon atmosphere and the mixture was stirred for 18 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 (Fig5).
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Graft Polymerization of styrene onto the TEMPO/modified TiO$_2$ with NMRP

For preparation nano composites, 0.2 g of nanoparticles containing TEMPO initiator and 11 ml freshly distilled styrene monomer was stirred under argon gas flow and 125 °C, then a white viscous solution was obtained after 40 hours. The viscous solution was dissolved in tetrahydrofuran and was precipitated with acidified methanol. For remove homopolymers from nanocomposites, the product were extracted with cyclohexane in Soxhlet extraction apparatus for 10 hours and then dried at room temperature.

RESULTS AND DISCUSSION

Modification of TiO$_2$ nano-particle with coupling agent APTES and grafting the polymerization initiator

The functional silanes have been widely used for the surface modification of metal oxides. To get evidence that coupling agent APTES was chemically bonded to TiO$_2$ nano-particle, FT-IR spectroscopy investigation was initially used to identify the qualitative composition of modified TiO$_2$. The FT-IR spectra of TiO$_2$ (a), APTES-grafted TiO$_2$ (b) and the macroinitiator (acetyl chloride grafted TiO$_2$-APTES)(c) are shown in Fig. 7. FT-IR spectra of TiO$_2$ sample shows that this inorganic material is non reactive because there is no functional group on its surface. The introduction of APTES to the surface of nanoparticles (NPs) is confirmed by the bands at 1108 and 1029 cm$^{-1}$ assigned to the Si–O–C stretching vibrations and 900 cm$^{-1}$ assigned to the Ti–O–Si. The broad band at 3300 cm$^{-1}$ is referred to the N–H stretching vibration. The presence of the anchored propyl group is confirmed by C–H stretching vibrations that appear at 2860-2923 cm$^{-1}$. Reaction of APTES-grafted TiO$_2$ with chlorophenyl acetylchloride produces macroinitiator in which the presence of APTES moiety is asserted with the peak at 2929 cm$^{-1}$ is assigned to propyl groups and peak at 1625 cm$^{-1}$ is assigned to the stretching vibrations of the C=O group.

Synthesis of TEMPO/modified-TiO$_2$ macro-initiator

For synthesis TEMPO/modified-TiO$_2$ macro-initiator, first the TEMPO initiator was synthesized and then TEMPO was reduction to TEMPO-OH, then the TEMPO/modified-TiO$_2$ macro-initiator were synthesized. 8 shows the TEMPO (a), TEMPO-OH(b) and TEMPO/modified-TiO$_2$ macro-initiator (c). In TEMPO spectrum, absorption band in the region 978 cm$^{-1}$ is assigned to the stretching vibrations of N-O, and stretching vibrations of C-H (aliphatic) bands has appeared in the region 2984 cm$^{-1}$. After the reduction of TEMPO to 1-hydroxy-2,2,6,6-tetramethyl piperidine (TEMPO-OH), the peak in 3407 cm$^{-1}$ represent OH group. Stretching vibrations of CH$_3$ group is appears in 2975 and 2933 cm$^{-1}$, and also bending vibrations of CH$_3$ groups are visible in 1380 cm$^{-1}$. After
Encapsulation of modified TiO$_2$ nano-particle by polystyrene

Fig. 8 (d) shows the FT-IR spectra of TiO$_2$ nanoparticles encapsulated by polystyrene. The peak at 1490 and 1660 cm$^{-1}$ is assigned to the stretching vibrations of the C-C from benzene ring and bending vibrations of the C-H from benzene ring were appears at 754 cm$^{-1}$ and also bending vibrations (offset) of the C-H from benzene ring were appears at 698 cm$^{-1}$. Stretching vibrations of the C-H from PS are appears between 2850-3026 cm$^{-1}$. Vibrations of the C-H from PS are appears between 2850-3026 cm$^{-1}$.

SEM characterization of nanocomposite

Scanning electron microscope (SEM) provides an actual image of the morphology of the nanocomposite. Fig. 9 shows the SEM image of the titanium oxide nanoparticles (a) and PS-TiO$_2$ nanocomposite (b). TiO$_2$ nanoparticles show the spherical morphology and most of the particles have tendency to aggregate, and the average particle size is about 39 nm. Fig 9(b) shows SEM images of PS-TiO$_2$ nanocomposite. In these images, a sheet of polymer is created. In addition, the polymers exist as a piece, this indicates that the polymerization has begun separately of each particle and dispersion is better.
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 Thermal property study

DSC measurements
Thermal behaviors of the obtained nano-composites were investigated by differential scanning calorimetric (DSC) and thermo gravimetric analysis (TGA). Fig. 10 shows the DSC traces of the PS-TiO$_2$ nano-composite. Polystyrene is non-crystalline and therefore does not exhibit any crystallization or melting transitions. Polystyrene exhibits an endothermic peak approximately at 83 °C, corresponding to the glass transition temperature. In Fig. 10, the endothermic peak seen at 76 °C has been attributed to the evaporation of any residual water and solvent. The DSC measurements indicate that the PS-TiO$_2$ nanocomposites have only one endothermic step based on glass transition temperatures (Tg) at 121 °C. The former Tg temperature is higher than that of the PS (83 °C). Perhaps in the PS/TiO$_2$ nanocomposites, the TiO$_2$ nanoparticles disperse homogeneously in the polystyrene matrix. Strong interfacial bonding between the modified TiO$_2$ nanoparticles and polymer chains leads to an increase of glass transition temperature of nano-composite by impeding the chain flexibility.

Thermal stability of PS/TiO$_2$ nanocomposite
The thermal degradation of the nanocomposites was studied using TGA. Fig. 11 presents TG curve obtained under nitrogen environment for PS/TiO$_2$ nanocomposites. TGA results indicate improvement of the thermal stability for PS/TiO$_2$ compared to neat polystyrene. According to Fig. 11 we can conclude that the weight-loss at 332 and 476 °C in the TGA curve of PS/TiO$_2$ is a result of polystyrene chains decomposition that was covalently attached to TiO$_2$ nano-particles. Higher decomposition temperature of PS/TiO$_2$ composites (332 °C) compared with pure PS (250 °C) indicated that no polymer was adsorbed noncovalently onto the surface of TiO$_2$ nanoparticles. It appears from these data (TG curves) that in inert atmosphere, the presence of TiO$_2$ nanoparticles have significant effect on the thermal degradation of PS.

3.6. Transmission electron microscopy
The transmission electron micrographs (TEM) of the bare TiO$_2$ nanoparticles(a) and PS grafted TiO$_2$ (b) are shown in Fig. 12. It is clear in Fig. 12(a) that the TiO$_2$
nanoparticles show spherical morphology. Due to the large specific surface area and high surface energy, some nanoparticles aggregate. The aggregation occurred probably during the process of drying. In order to check whether or not the polymer was encapsulated on the surface of nano-TiO$_2$, the composite particles were characterized by TEM. As is shown in Fig. 12(b), the black and translucent parts in the micrographs represent nano-TiO$_2$ and PS polymer, respectively. It was obviously revealed that nano-TiO$_2$ particle was embedded into the polymer. The nano-TiO$_2$ particle is too small and irregular to ensure that there is only one nano-TiO$_2$ particle in a composite and their diameter is about 45 nm. Fig. 12(b) shows that aggregation among TiO$_2$ nanoparticles was alleviated and dispersion was improved. Besides, one can also observe that around the TiO$_2$ nanoparticles there encircle some shadows, implying the existence of the grafted polymer layers.

CONCLUSION

Nano-TiO$_2$/Polystyrene nanocomposite had been prepared through nitroxide-mediated radical polymerization. For this purpose to reduce the aggregation among TiO$_2$ nanoparticles an effective surface modification method was proposed. Firstly, TiO$_2$-nanoparticles were modified by APTES coupling agent, then the amine groups from coupling agent reacted with the initiator. After purification, the modified particles were treated with TEMPO. Then polystyrene chains were grown from the functionalized nanoparticles surface in the presence of a TEMPO. After characterization, DSC results showed the increase glass transition temperature of composites compared to pure polymer. TGA results showed the increase thermal stability of composites than that of pure polymer. Scanning electron microscopy and transmission electron microscopy showed the growth of polymers on particle surfaces and core–shell hybrid structures for composites.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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