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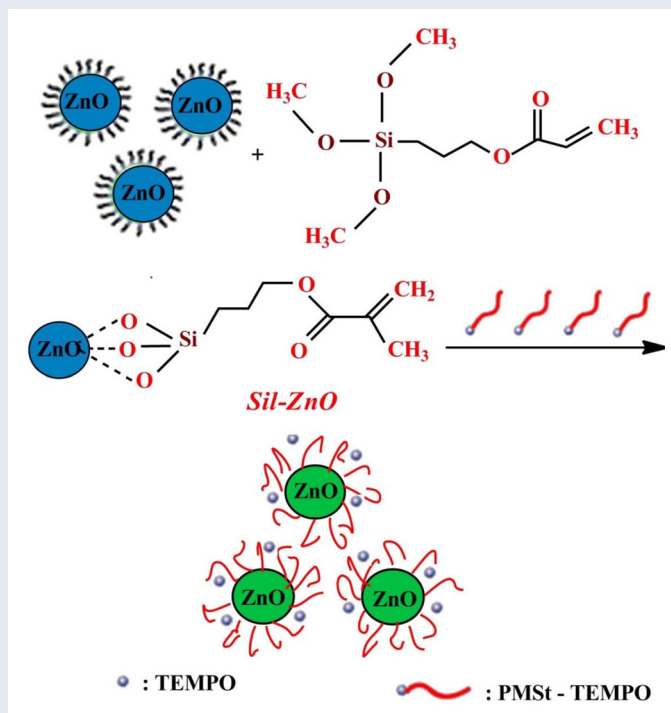
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ABSTRACT

A nanocomposite composed of ZnO and poly (methyl styrene-co-chloro methyl styrene) P (MSt-co-CMSt) by *in situ* polymerization method were prepared successfully. For this purpose, firstly, the zinc oxide surface was treated with 3-(trimethoxysilyl) propyl methacrylate (TMSPMA), a silane coupling agent, and following that this functionalization nano-ZnO particle was reacted with PMSt to prepare PMSt-grafted TMSPMA-ZnO. The resulting PMSt-grafted TMSPMA-ZnO was brominated with N-bromosuccinimide and coupled with 1-hydroxy-2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO-OH) to produce an NMRP macroinitiator (PMSt-TEMPO/nano-ZnO). The well-controlled graft polymerization of 4-chloromethyl styrene (CMSt) with macroinitiators were carried out to produce nanoparticles based-ZnO (PMSt-co-PCMSt)/zinc oxide nanocomposite). Properties, crystal structure, and the morphology of (PMSt-co-PCMSt)/zinc oxide nanocomposite was studied using ¹H-NMR, FT-IR, XRD, TGA, DSC, TEM, and UV-Vis spectroscopy. The results of FT-IR investigation and observations of TEM images represented clear and strong evidence for the preparation of PMSt and PMSt-co-PCMSt with spherical morphology of ZnO nanoparticles. The synthesized nanocomposites can be utilized a compound to attenuate the UV irradiation in the range of pointed wavelength.

GRAPHICAL ABSTRACT



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KEYWORDS

Chloromethyl styrene; graft copolymer; methyl styrene; TEMPO; ZnO nanoparticles

1. Introduction

In the last decades, nanometer-sized based-on inorganic particles nanocomposites, which represent extraordinary chemical, mechanical and physical properties, have received much significance and have been used in different areas such as semiconductor technology, preparation of the catalyst, chemistry-based photoelectron, plastic and rubber, beauty products and coating.^[1] These mentioned nanoparticles, show thermal particularity, optical, mechanical, electrical features with the adaptability to create films.^[2] Recently, much consideration has been dedicated on zinc oxide (ZnO) as one of the most versatile nanoparticles-based inorganic compounds. ZnO has some considerable properties such as weak dielectric constant, unique chemical stability, high catalysis activity, good luminescent transitions, infrared absorption, and intensive ultraviolet.^[3] Thus, ZnO based on nanomaterials could be potentially applied as gas sensors, catalysts, visitants, semiconductors, piezoelectric apparatuses, bactericide and antibacterial, field-radiation exhibitions and UV shielding.^[4] However, the application of ZnO- based nanomaterials might be prevented due to their excellent propensity of agglomeration, which is derived from a high ratio of surface area toward volume. Newly, many investigations have been done to modification of the surface ZnO nanomaterials.^[5] The process of polymeric adsorption on the ZnO nanomaterials surface might be a valuable and alternative process.^[6] For better dispersion of nanomaterials in the matrix of polymer, the surface modification ZnO nanoparticles by organic materials is essential. Typically, there are two methods for modification of surface nanoparticles based inorganic compounds.^[7] One method is carried out using a reaction with small molecules or surface absorption, for example, the surfactant $C_{18}H_{37}-(OCH_2CH_2-)_{10}-OH$, the stearic acid, etc..^[8,9] Polymer grafting on the surface of nanoparticles by covalently linked to the hydroxyl functional groups is another method.^[10,11] Furthermore, many regards chemically have been focused on the polymer chains. In this regard, “grafting to” and “grafting from” approaches have been offered. The “grafting from” method is attributed to the immobilized initiators in the controlled/radical polymerization of different monomers, chased by the development of the polymer chain from the surface is possible to make of polymer brushes with feasible excellent grafting density.

In the past decades, many researchers have encountered fast growth in the field of controlled free- radical polymerization (CFRP) to produce polymers based on tailor-form with foresighted molecular weights.^[12,13] Various approach has been introduced to attain this feature: Atom transfer radical polymerization (ATRP)^[14–16] Reversible addition-fragmentation process (RAFT)^[17] and nitroxide- mediated radical polymerization (NMRP).^[18–20] The nitroxide-mediated radical polymerization approach is a controlled/living radical method that provides the synthesis of graft and star copolymers with well-defined structures under favorable conditions. These polymerization approaches are belonged to use of the stable nitroxide radicals, such as (TEMPO) and well-accepted radical initiators, such as (B.P.O). A superiority of nitroxide-mediated radical polymerization approach is

the synthesis of graft copolymers compared to other copolymerization methods such as anionic polymerization. And also, the terminative groups in the mediated radical polymerization approach are in stable condition at room temperature and previous polymer materials could be isolated, kept, and utilized as required. In addition, in anionic polymerization, accurate conditions for polymerizations are needed.^[21]

Compared to other graft copolymerization's, an advantage of nitroxide-mediated radical polymerization is that in the preparation of grafted copolymers, the terminal groups are stable in air at room temperature, and pre-polymers can be isolated, stored, and utilized as needed and in this type of polymerization, precise polymerizations conditions are required. In addition to, monomers such as styrene and methyl styrene can be polymerizing facile by this polymerization.

At present, to the best of our science, most proposed methods for the synthesis of nanocomposite based on organic polymers involve living radical polymerizations. In order to polymerizing MMA from TiO_2 nanoparticles, Charpentier and Hojjati have represented the relatively novel method of RAFT polymerization.^[22] Zhao and his workmates used nitroxide-mediated radical polymerization for functionalization of multi-wall carbon nanotubes (MWCNTs),^[23] Wang and Liu using ATRP approach for growing of polymer chains of 2-Hydroxyethyl Acrylate (2-HEA) from ZnO nanoparticles.^[24]

Here in, a method alternative for synthesizing and characterization of poly [methylstyrene-co-chloromethyl styrene]/zinc oxide nanocomposite by using NMRP is confirmed successfully. Firstly, nano-ZnO particles were prepared and treated with TMSMA (coupling agent) to obtain vinyl groups on the surface of nanoparticles. Then, MSt monomers were polymerized and attached onto nanoparticles in the presence of 2-azobisisobutyronitrile (AIBN) as initiator. Afterward, synthesized TEMPO-OH was coupled with brominated modified ZnO nanoparticles and 4-(chloromethyl) styrene by a substitution nucleophilic reaction to obtain an NMRP macroinitiator. The controlled graft polymerization of CMSt was initiated by PMSt/nano-ZnO particles carrying TEMPO groups to obtain poly (MSt-co-CMSt) zinc oxide nanocomposite.

2. Experimental

2.1. Materials

The monomers of methyl styrene (MSt) and 4-Chloromethyl styrene (CMSt) were acquired from Merck (Germany, Darmstadt), then distilled under a reduced pressure before utilization. TEMPO was synthesized by our research group in a laboratory.^[25,26]

Synthesize of nano-ZnO particles by a precipitation method similar to that introduced by Fu et al was performed.^[27] 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) and Sodium-L (+)-ascorbate were provided from Merck and used without refining. N-bromosuccinimide (NBS) was bought from Merck and was purged by

recrystallization in water at 80 °C. AIBN (Azobisisobutyronitrile) crystallized in ethanol at 60 °C before use and was acquired from Merck. Toluene and (N, N-dimethylformamide) DMF (Merck, Darmstadt, Germany) after reflux over sodium were dried and distilled before use under argon. α -Chloro phenyl acetyl chloride was utilized as received. All other chemical materials commercially and of analytic grade are accessible according to standard methods.

2.2. Characterization

Specimens were first produced by investigating Fourier-Transform Infrared (FTIR) spectroscopy on a device S-8400FTIR- SHIMADZU model in the wavenumber of 400–4000 cm^{-1} . The specimens have compressed mixture into the form pellets and obtained by minifying the dry powders with potassium bromide. In order to desist from dampness absorption, the pellets were kept in a desiccator. $^1\text{H-NMR}$ spectrum (Proton Nuclear Magnetic Resonance) (Ettlingen, Germany, Bruker) was provided at 25 °C employing an FT-NMR spectrometer (400 MHz) apparatus. The specimen for investigation of $^1\text{H NMR}$ was synthesized by dissolving about 10 mg of produced specimens in 5 ml of CHCl_3 (deuterated chloroform). The spectra of XRD (X-ray diffraction) (Germany, Siemens) were provided by Siemens D 5000, X-ray producer (Cu K_α radiation with $\lambda = 1.5606 \text{ \AA}$) with a 2θ scan range of 2 to 80° at room temperature. TEM (Transmission Electron Microscopy) (Phillips, Netherlands, Eindhoven) was carried out using a Philips CM10 microscope with a 100 kV accelerating voltage. The thermal properties of the resulted nanocomposites were achieved with a TGA-PL STA 1640 (Polymer Laboratories, Shropshire, UK) devices. About 10 mg of the samples was agitated between 25 and 600 °C at a rating of 10 °C min^{-1} under flowing N_2 . The DSC analysis (differential scanning calorimetry) with NETZSCH (Germany, Selb)-DSC 200 F3 Maia was accomplished. The specimen was first agitated to 200 °C and then cooled for 5 min to eliminate the thermal history. Accordingly, the specimen was re-agitated to 200 °C at a rating of 10 °C min^{-1} . The entire experiment was performed under flow N_2 at a rating of 50 $\text{ml}\cdot\text{min}^{-1}$. UV-Vis (Ultraviolet-Visible) (Shimadzu 1601 PC) spectra of the specimens was investigated using a UV-Vis spectrophotometer device in the wavelength range 300–800 nm.

2.3. Preparation of ZnO surface nanoparticles with (TMSPMA, coupling agent)

The grafted TMSPMA in ethanol condition according to relevant reference was accomplished.^[28] (R = 70%).

2.4. Attaching of poly (methyl styrene) (PMSt) on the surface of Nano-ZnO particle

A 100 ml round-bottomed glass comprising 20 ml ethanol was saturated with coupling agent (TMSPMA-grafted-ZnO nanoparticle) (0.2 g), AIBN (160 mg), and MSt monomers (12 ml). The mixture was subjected to radiation with

ultrasonic shakings for about 15 min. Following that, the mixture was refluxed in an oil bath and kept at 70 °C under flowing argon. The solution was stirred 24 hr in this condition with electromagnetic stirring to complete the polymerization process. The product was recovered by purification in a great deal cold methanol. So as to ensure that ungrafted polymer methyl styrene was eliminated from the resulting product, the particles were re-dissolved in toluene, reprecipitated and centrifuged at 6000 rpm. This work was repeated until the solution was visible. (Weight of product: 0.42 g, Yield: 4.2, R = 32%). Finally, the polymer was refluxed for about 24 h under acidic conditions and was utilized to preparation of parent PMSt and separated from ZnO nanoparticles

2.5. Bromination of poly (methyl styrene)-grafted ZnO-TMSPMA

A 250 ml round-bottomed flask equipped with a magnetic stirring bar was charged with N-bromosuccinimide (NBS, 0.22 g), AIBN (0.03 g), a suspension of PMSt (0.5 g) and CCl_4 (40 ml). The mixture was refluxed at 90 °C for 3 hr. After which, the reaction mixture was purged and washed several times with acetone. To obtain precipitate, the reaction mixture was washed with cold methanol and dried overnight under a vacuum oven for 24 hr to afford brominated poly methyl styrene (PMSt-Br). Bromine represents active positions for substitution of TEMPO on the polymer (R = 17%).

2.6. Reduction of TEMPO to 1-hydroxy-2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO-OH)

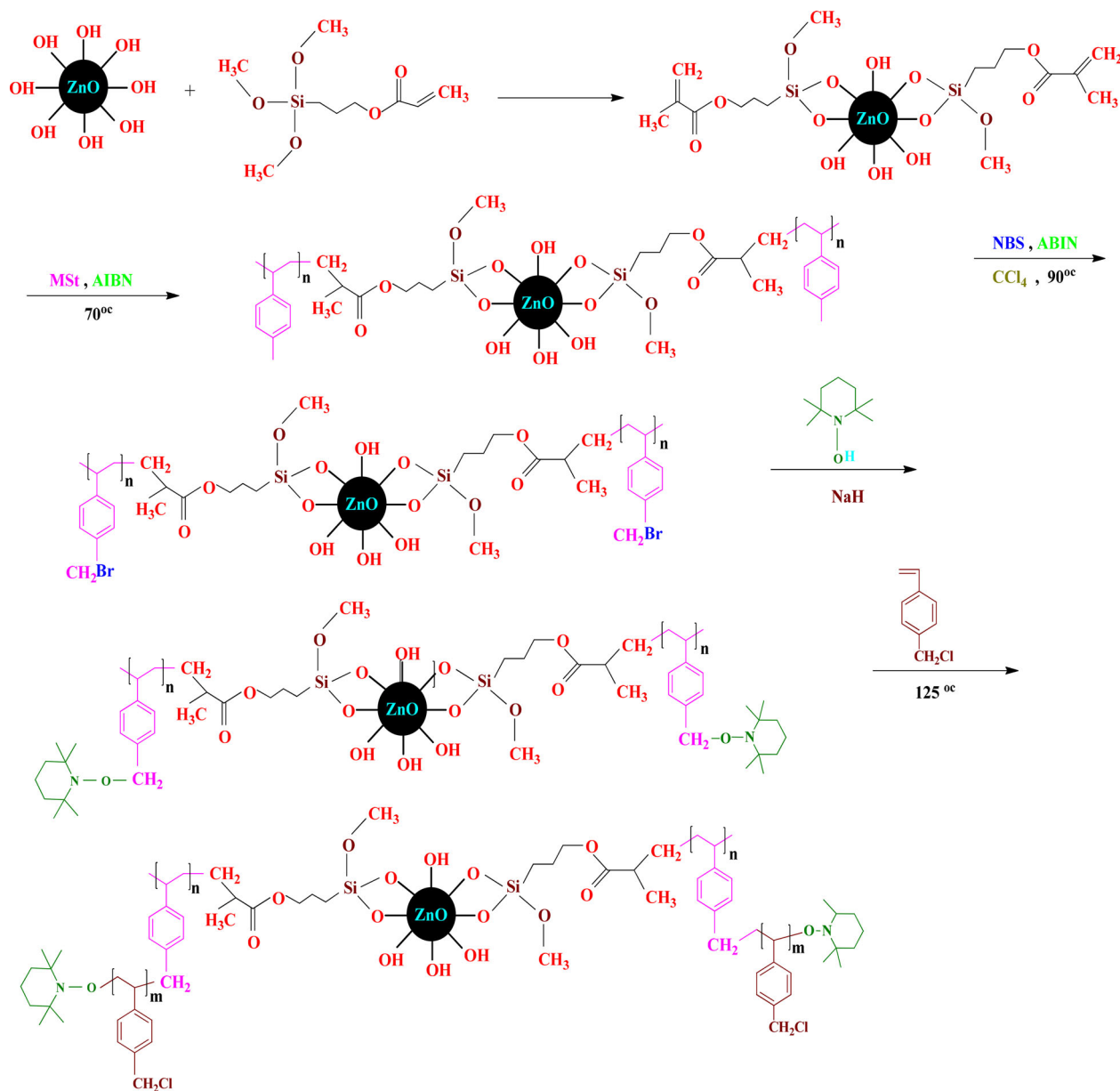
Reduction of TEMPO to 1-hydroxy-2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO-OH) was accomplished according to relevant reference^[25,28] (R = 67%).

2.7. Synthesis of PMSt-TEMPO/ZnO macroinitiator

In a 150 ml three-neck round-bottom flask fitted with a flux condenser, gas inlet/outlet, dropping funnel, and a magnetic stirrer was saturated with TEMPO-OH (0.10 g, 0.65 mmol), dissolved in 30 ml anhydrous DMF and 30 mg (1.3 mmol) hexane washed NaH (from 60% suspension in oil) under flowing N_2 . The mixture was stirred for 30 min. In a separate container, 1 gr of PMSt-grafted ZnO-TMSPMA was dissolved in DMF (50 ml) and slowly added to the mixture under flowing N_2 , after refluxing for 24 hr at room temperature. The reaction was terminated by pouring the flask content into a great deal of ice methanol. The white solid was filtered, washed with ice methanol, and dried in a vacuum oven.^[28] (R = 23%).

2.8. Graft polymerization of CMSt onto PMSt-TEMPO/ZnO macroinitiator

To a solution of macroinitiator, PMSt-TEMPO (200 mg) in anisole (5 ml) was added CMSt monomer (6 ml). Then the



Scheme 1. The overall strategy for Graft polymerization of 4-(chloromethyl) styrene to modified ZnO nanoparticles by NMRP.

solution was degassed, sealed off under argon flow, and temperature was increased up to 125 °C to begin polymerization near TEMPO. After 15 hr, the reaction mixture was precipitated into ice methanol, and the produced powder was dried under a vacuum oven at room temperature. To the investigation of ZnO nanoparticle's effects on T_g and thermal properties of the graft copolymer, we prepared a sample of new graft copolymer with ZnO content (10 w %), by solution mixing as labeled CMSt-10. At this stage, the obtained graft copolymer (about 1 w% ZnO content) was dissolved in toluene, then 9 w% nano-ZnO was added to the polymer solution and exposed under ultrasonic radiation. Finally, the polymer nanocomposite was obtained by precipitation in cold methanol. In a simple examination, a dry flask was charged with anisole (5 ml), CMSt monomers (3 ml), and PMSt-TEMPO/ZnO macroinitiator (200 mg). The flask was then sealed, and three freeze-pump-thaw cycles were

performed to eliminate oxygen. The reaction mixture was then heated to 130 °C and kept at this temperature for 12 h. The reaction was completed by plunging the contents of the flask in some methanol. To remove the un-grafted PCMSt from the crude product, the powder was extracted with DMF in a Soxhlet apparatus for about 24 hr. The resulting precipitated polymer material was filtered, washed with DMF, and dried under vacuum (Yield: 0.48 g, R= 3%), (Scheme 1).

In a facile method, a dry ampoule was saturated with anisole (6 mL), brominated poly (methyl styrene)-grafted ZnO-TMSPMA (200 mg) and Chloro methyl styrene monomers (3 mL). To eliminate oxygen, the ampoule was sealed and three cycles of freeze-pump-thaw were performed. Afterward, the reaction mixture at 120 °C was agitated and kept at this temperature for about 12 h. The reaction was completed by pouring the content of the ampoule into a

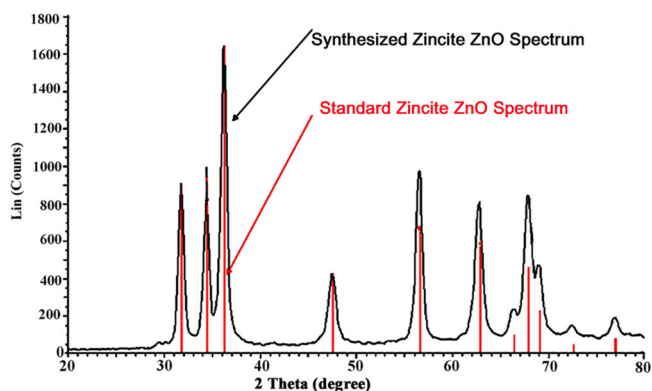


Figure 1. X-ray diffraction spectra of synthesized and standard bare ZnO nanoparticles.

great deal of ice methanol. In this condition, we indicate that no polymer was achieved.^[28]

3. Results and discussion

3.1. Preparation of ZnO nanoparticles

Patterns were performed on a diffractometer with Cu K α radiation. The average size of resulted crystallite (D in nm) of ZnO nanoparticles was determined from XRD patterns of the ZnO nanoparticles. According to the Debye Scherrer equation is given in equation (1):

$$D = k \lambda / \beta \cos \theta \quad (1)$$

Where k is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.154 nm, β is the full width at half maximum intensity (FWHM), and θ is the diffraction angle ($^{\circ}$). The average particles sizes of prepared ZnO are about 23 nm. The XRD spectrums of nano-ZnO particles, are the characteristic bands sequences shown in Figure 1, which comply with the standard zincite phase of ZnO (International Center for Diffraction Data, JCPDS 5-0664, and Straight lines in Figure 1).

3.2. Modification of ZnO nanoparticles with coupling agent (3-aminopropyl triethoxysilane)

Silane functional groups have been extensively applied for the treatment of zinc oxides surface. To get verify that the coupling agent (TMSPMA) was chemically grafted onto ZnO nanoparticles, FTIR examination was first utilized to definite the characterization and formation of TMSPMA modified ZnO^[29,30].

3.3. Attaching of modified ZnO nanoparticles onto 3-aminopropyl triethoxysilane

The group of methacrylates exciting in TMSPMA could react with MSt monomers and making a polymer that chemically attached to the inorganic ZnO core. Figure 2 displays the FT-IR spectrum of free PMSt (a), PMSt-grafted ZnO-TMSPMA (b), Brominated PMSt (c). The FT-IR spectrum of PMSt shows the characteristic absorption peaks

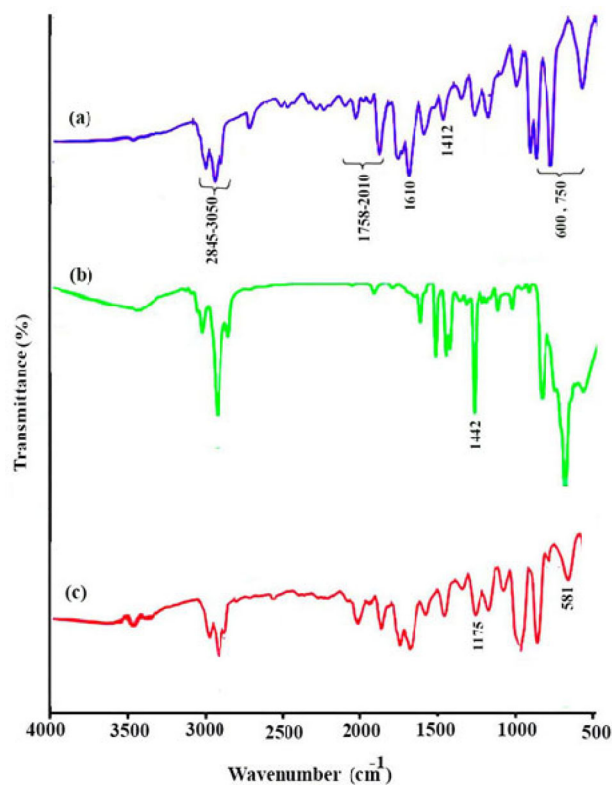


Figure 2. FT-IR spectra of free PMSt (a), Attaching of modified ZnO nanoparticles by onto poly (methylstyrene) (b) Brominated modified ZnO nanoparticles that attached by onto polymethylstyrene (c).

owing to stretch vibration of C-H at 2845-3050 cm^{-1} , combination peak and weak aromatic connotation in the 2010-1758 cm^{-1} , C=C stretch vibrations at 1610 and 1412 cm^{-1} , CH₂ bending vibrations at 1442 cm^{-1} , γ (C-H) in the aromatic ring at 600 and 750 cm^{-1} and CH₂-Br bending vibrations at 1175 cm^{-1} . The additional absorption peak at 581 cm^{-1} was attributed to the C-Br group in Brominated PMSt.

3.4. Synthesis of PMSt-TEMPO/nano-ZnO macroinitiator

At first glance, TEMPO was added onto brominated PMSt-grafted modified ZnO nanoparticles to obtain the acting positions. The prepared brominated PMSt-grafted modified ZnO nanoparticles, PMSt-TEMPO/nano-ZnO macroinitiator, and (PMSt-co-PCMSt)/ZnO nanocomposite specimens were demonstrated using ¹H NMR spectra as shown in Figure 3. The ¹H-NMR spectrum of brominated PMSt-grafted modified ZnO nanoparticles, display the chemical shifts at 1.12-2.36 and 6.14-7.32 ppm demonstrate the aliphatic and aromatic protons respectively, and the chemical shifts at 4.11-4.25 ppm displays the -CH₂Br protons in the obtained product. In comparison with the ¹H NMR spectra of PMSt/PMSt-grafted modified ZnO nanoparticles and PMSt-TEMPO/ZnO macroinitiator in Figure 3(b), displays the excess chemical shifts of CH₂ and CH₂-O groups of TEMPO molecules at 3.76-3.91 and 0.76-1.06 ppm respectively.^[31] Thus, ¹H-NMR spectra indicated evidence of TEMPO functional groups which, was coupled with brominated PMSt/PMSt-grafted modified ZnO nanoparticles. In

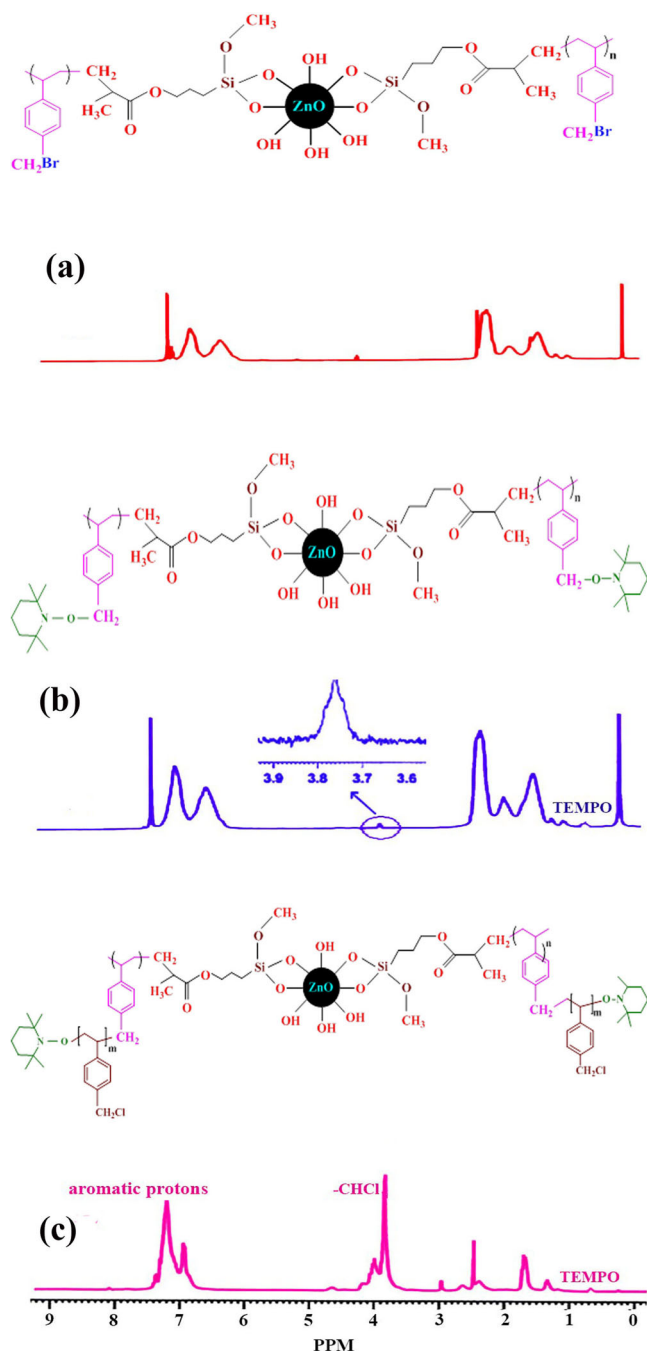


Figure 3. ¹H NMR spectra of (a) Brominated modified ZnO nanoparticles that attached by onto polymethylstyrene (b) TEMPO-PMSt/ZnO and (c) (PMSt-g-PCMSt)/ZnO.

the ¹H-NMR spectra of the (PMSt-g-PCMSt)/ZnO nanocomposite **Figure 3(c)**, the signals owing to the chloromethyl group's protons and aromatic protons were seen at 3.62-4.24 and 6.24-7.18 ppm, respectively. In addition, the graft polymerization of CMSt onto PMSt/nano-ZnO is identified by the functional TEMPO groups at the ending of PCMSt side chains. The functional TEMPO group was revealed with particular signals of CH₂ groups and -CH-O-N- at 0.75-1.02 and 3.46 ppm, respectively. ¹H NMR spectrum indicates that the functionalization of TEMPO groups was maintained at the end of the PCMSt chains, which provides clear evidence that the NMRP reaction and preparation of the (PMSt-co-

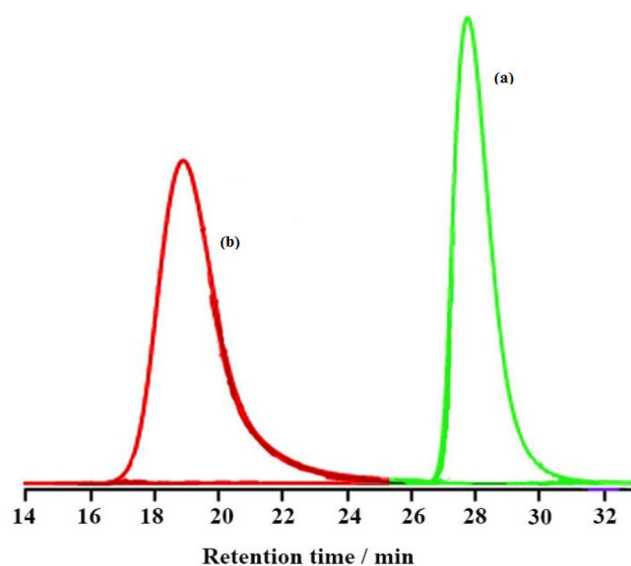


Figure 4. GPC trace of (a) bulk PMSt in the presence of TEMPO and (b) (PMSt-g-PCMSt)/ZnO nanocomposite.

PCMSt)/ZnO nanocomposite by radical polymerization with nitroxide-mediators were successfully confirmed.

3.5. Study on the controllability of the grafting polymerization

GPC patterns of the PMSt-TEMPO/ZnO macroinitiator and (PMSt-g-PCMSt)/ZnO nanocomposite are shown in **Figure 4**. GPC results show the molecular weight improved with monomer conversion from high to medium mode; after that, it inclined from the direct line. The index of polydispersity is various from 1.4 to 1.6 during the graft polymerization process. As a result, the livingness is not as good as normal homogeneous TEMPO mediated radical polymerization. These reasons can be considered (a) the ability to move of stable nitroxyl radical on the nano-ZnO surface was weak and could not trap propagating radicals in an effectual mode, (b) some amount of the prepared nitroxyl radical on the surface polymer was protected by the grafted polymer chains and for this reason, did not participate in reversible trapping of propagating radicals, (c) small amount of the propagating radical added to sp² carbon to make C-C bond between ZnO surface and polymer chain, as introduced by Schaffer and workmates.^[32]

3.6. Optical properties study

The specimens for UV-Vis spectroscopy were synthesized by the increasing of the favorable amount of the produced nanocomposites into boiling DMF as a solution. Films with partly monotone thickness were provided after solvent vaporization on the sidewall of quartz glass. UV-Vis spectrum of ZnO nanoparticles (bare ZnO) (a), TMSPMA modified ZnO nanoparticles (b) and PMSt-grafted ZnO-TMSPMA are appeared (c) in **Figure 5**. TMSPMA modified ZnO nanoparticles, and PMSt-grafted ZnO-TMSPMA has absorption band in the region of UV (<400 nm) as the bare

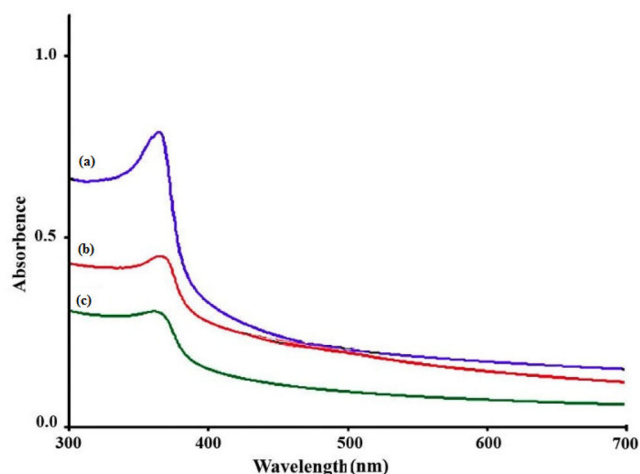


Figure 5. UV-Vis spectrum of (a) ZnO nanoparticles (bare ZnO), (b) TMSpMA modified ZnO and (c) Attaching of modified ZnO nanoparticles by onto poly (methylstyrene).

nano-ZnO particles. It is well-confirmed that they would have a unique ability to hold strong lights and excellent adaptability with industrial high-application polymers.

3.7. Thermal property study

Since, DSC and TGA are thermoanalytical techniques, they can be used in thermal degradation and behaviors of the prepared nanocomposites. Figure 6 displays the DSC curves of PMSt (a), PCMSt-grafted modified ZnO (b) and (PMSt-g-PCMSt)/ZnO nanocomposite (c). Since, PMSt is amorphous, any crystallization or melting transitions do not exhibit. Thus, DSC curves of PMSt illustrate an endothermic peak approximately at 78 °C, attributable to the transition glass temperature (T_g) of PMSt. In Figure 6(b), the transition detected at 110 °C could be attributed to T_g of PMSt-grafted modified ZnO. T_g for (PMSt-g-PCMSt)/ZnO nanocomposite is too poor to measurement, or it is repressed owing to the restriction of polymer chains (by ZnO nanoparticles) Figure 6(c). Also, the poor transition shown at 58 °C can correspond to T_g of (PMSt-g-PCMSt)/ZnO nanocomposite. Strong interfacial grafting between the polymer chains and TMSpMA modified ZnO led to an enhancement in T_g of nanocomposites by suppressing the chain flexibility. But in the (PMSt-g-PCMSt)/ZnO nanocomposite, poly (chloromethyl styrene) chains were caused that the nanocomposite crystals to move toward the amorphous system.

Characteristic TGA traces of the bare ZnO (a), TMSpMA modified ZnO (b), PMSt-grafted modified ZnO (c), (PMSt-g-PCMSt)/ZnO nanocomposite (d) and free PMSt (e) are appeared in Figure 7. The TGA result demonstrates an improvement in the thermal stability of PMSt- modified ZnO compared to bare PMSt. In the TGA trace of PMSt-grafted modified ZnO Figure 7(c), from the weight-loss around 410 °C can be concluded that the decomposition of PMSt chains is covalently connected to nano-ZnO nanoparticles. The sifting the decomposition of PMSt-grafted modified ZnO (410 °C) compared to bare PMSt (390 °C), displayed that no polymers adsorbed no-covalently onto the

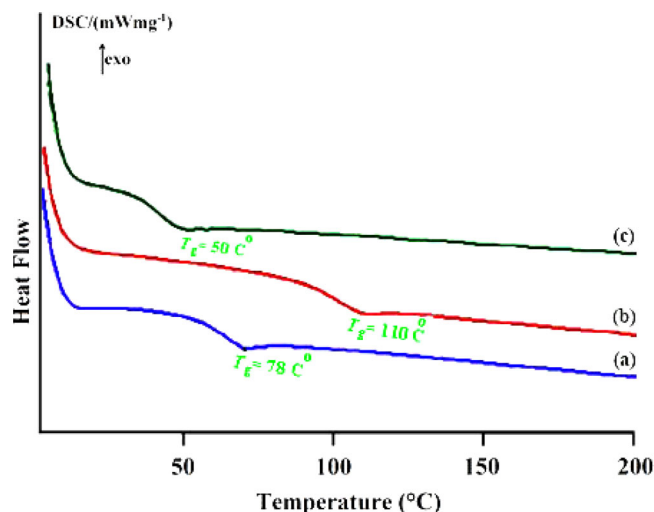


Figure 6. DSC diagram of (a) free PMSt, (b) Attaching of modified ZnO nanoparticles by onto poly (methylstyrene) and (c) (PMSt-co-PCMSt)/ZnO anocomposite.

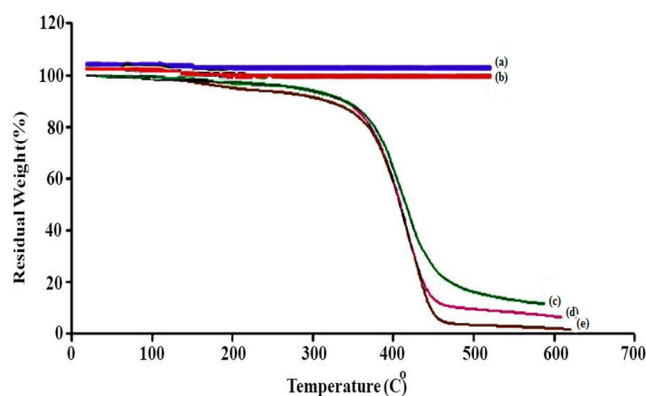


Figure 7. TGA diagram of (a) bare ZnO, (b) TMSpMA modified ZnO, (c) Attaching of modified ZnO nanoparticles by onto poly (methylstyrene) (d) P (MSt-co-CMSt)/ZnO nanocomposite and (e) free PMSt.

surface of nano-ZnO particles. In the TGA curve of (PMSt-g-PCMSt)/ZnO nanocomposite Figure 7 (d), a novel weight-loss area near 300 °C was seen, which belonged to the PCMSt decomposition in (PMSt-g-PCMSt)/ZnO nanocomposite. In addition, according to Figure 7 (d), it can be concluded that the weight-loss of the (PMSt-g-PCMSt)/ZnO nanocomposite is increased, chased by the primary degradation of the TEMPO iniferter molecules at the ending of PCMSt chains.

3.8. SEM and TEM study

The morphologies of prepared ZnO nanoparticles (a), synthesized PMSt-grafted modified ZnO (b), and (PMSt-g-PCMSt)/ZnO nanocomposite (c) were detected by SEM and TEM in Figure 8. Bare ZnO nanoparticles display the morphology of rough and sheet-like. Furthermore, certain particles have the propensity to accumulate Figure 8(a). Figure 8(b and c) shows the ZnO nanoparticles after polymerization with MSt and CMSt. These images display that after polymerization, the surface topography of ZnO nanoparticles have been changed and their diameter is

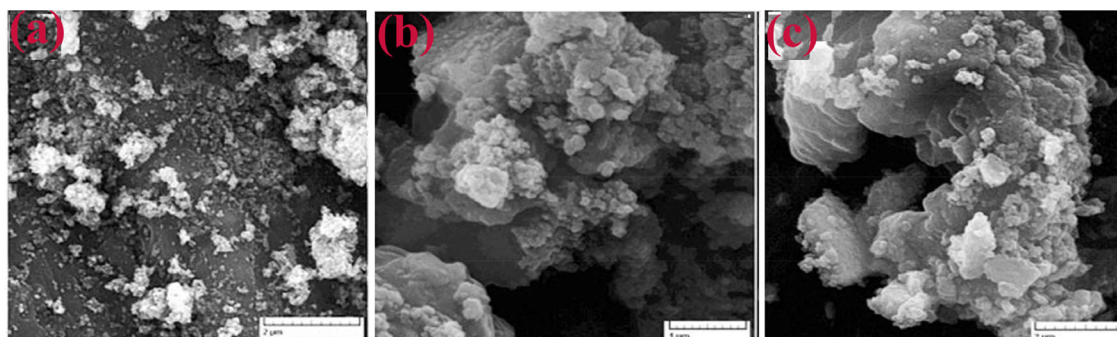


Figure 8. SEM images of (a) bare ZnO, (b) Attaching of modified ZnO nanoparticles by onto poly (methylstyrene) and (c) (PMSt-co-PCMSt)/ZnO nanocomposite.

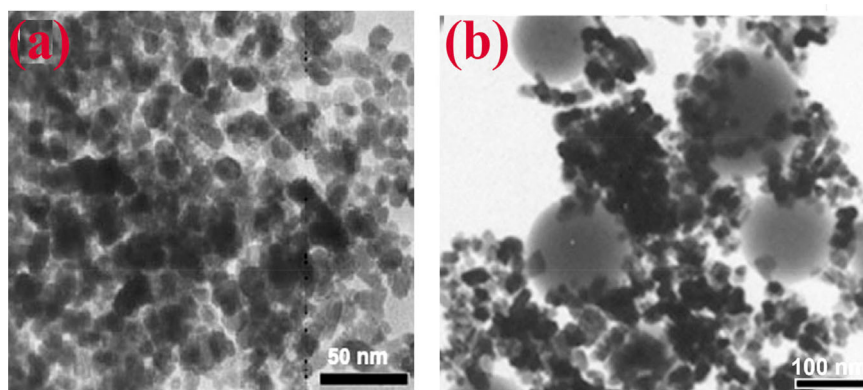


Figure 9. TEM images of (a) bare ZnO nanoparticles and (b) (PMSt-co-PCMSt)/ZnO nanocomposite.

approximately 60 nm. Also, the growth of active branched PCMS grafts can be clearly seen from Figure 8(b and c). These images exhibit a uniform growth of nanoparticles and also obviously illustrates that the particles are spherical and the particle size decreases with increasing MSt and CMSt. These correspond to the polymer chains that can expand from the NMRP coupling agent, which was grafted to the surface of ZnO.

On the other hand, TEM images of the bare nano-ZnO particles and (PMSt-g-PCMSt)/ZnO nanocomposite are shown in Figure 9. It is obvious from many references that the nano-ZnO particles illustrate spherical morphology. Due to the large particular surface area and unique surface energy, a certain number of nanoparticles accumulate. The accumulation occurred maybe during the method of drying. To ensure that whether or not the polymer was enclosed on the surface of nano-ZnO particles, the composited particles were detected by TEM. As seen from Figure 9, the dark and inconspicuous parts in the micrographs illustrate ZnO nanoparticle and PMSt polymer, respectively. It is obvious that the ZnO nanoparticle was embedded into the graft polymer. The nano-ZnO particle is disordered and too small to confirm that there is just one nano-ZnO particle in a composited microsphere and their average particle size is approximately 60 nm. Figure 9 (a and b) illustrates that accumulation was diminished, and nanoparticles distribution was developed. Furthermore, it can be concluded that around the nano-ZnO particles, there spheroidal some of shads, indicating the existence of the grafted polymer. As a result, (PMSt-g-PCMSt)/ZnO nanocomposite displayed that nano-ZnO particles were well distributed in the polymer matrix (Figure 9 (b)).

4. Conclusions

(PMSt-g-PCMSt)/ZnO nanocomposite was prepared by free radical polymerization of various monomers in the presence of 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) modified nano-ZnO. Afterward, TEMPO terminated poly (methyl styrene)/ZnO macroinitiator (PMSt-TEMPO/ZnO) was prepared by reacting brominated PMSt/ZnO with sodium 4-oxy-TEMPO derived from TEMPO-OH. Macroinitiator PMSt-TEMPO/ZnO could initiate “living” free radical polymerization of CMS monomers to produce the controlled graft copolymer [(PMSt-g-PCMSt)/ZnO]. TGA results showed that no polymer was adsorbed noncovalently on the surface of ZnO nanoparticles. FTIR spectroscopy and TEM images study also represented clear and direct evidence for the presence of (PMSt-g-PCMSt) as a spherical onto nano-ZnO particles. Significantly, the obtained nanocomposites showed strong UV light absorption in the range of 300-400 nm. Therefore, the prepared nanocomposites can be used as compounds to attenuate (scatter and, or absorb) UV rays in the related wavelength range. Finally, the NMRP technique can be used as a tool to modify ZnO nanoparticles into useful nanomaterials.

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