Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Xiong, Lei , Wang, Rumin , Liang, Hongbo , Pang, Yu and Guan, Jing(2010) 'Synthesis and Characterization of Poly(methyl methacrylate)-*b*-Polystyrene/TiO_2 Nanocomposites Via Reversible Addition-Fragmentation Chain Transfer Polymerization', Journal of Macromolecular Science, Part A, 47: 9, 903 — 908

To link to this Article: DOI: 10.1080/10601325.2010.501306

URL: http://dx.doi.org/10.1080/10601325.2010.501306

Journal of Macromolecular Science, Part A: Pure and Applied Chemistry (2010) **47**, 903–908
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ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2010.501306

Synthesis and Characterization of Poly(methyl methacrylate)-*b*-Polystyrene/TiO_2 Nanocomposites Via Reversible Addition-Fragmentation Chain Transfer Polymerization

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Received March 2010, Accepted April 2010

A diblock copolymer, poly(methyl methacrylate)-*b*-polystyrene (PMMA-*b*-PS), was grafted onto the surface of nano-titania (nano-TiO_2) successfully via reversible addition-fragmentation chain transfer (RAFT) polymerization. The surface of TiO_2 nanoparticles was modified initially by attaching dithioester groups to the surface using silane coupling agent 3-(chloropropyl)triethoxy silane and sodium ethyl xanthate. The polymerization of methyl methacrylate and styrene were then initiated and propagated on the TiO_2 surface by RAFT polymerization. The resulting composite nanoparticles were characterized by means of XPS, FT-IR, ^{1}H NMR and TGA. The results confirmed the successful grafting of poly(methyl methacrylate) (PMMA) and diblock copolymer chains onto the surface of TiO_2. The amount of PMMA grafted onto the TiO_2 surface increased with the polymerization time. Moreover, the kinetic studies revealed that the $\ln([M]_0/[M])$, where $[M]_0$ is the initial and $[M]$ is the time dependent monomer concentrations, increased linearly with the polymerization time, indicating the living characteristics of the RAFT polymerization.

Keywords: TiO_2, RAFT polymerization, graft, composite nanoparticles, living characteristics

1 Introduction

Nano-TiO_2 is noted for its outstanding optical properties (1, 2), chemical stability (3), and environmental-friendliness (4) and has extensive applications in many fields, such as anticorrosion, self-cleaning coatings, gas sensors and photocatalysts (5–11). However, an inherent characteristic of nano-TiO_2 is that it tends to form aggregates when dispersed in common organic solvents and polymer matrices due to its extremely large specific surface area. This aggregation phenomenon often results in unsatisfactory effects and hinders the wide application of nano-TiO_2 in real products (12). Therefore, a tremendous amount of work had been done on the surface modification of nano-TiO_2 mainly to enhance their dispersive stability and reduce the tendency of aggregation (13–16).

Grafting polymer chains onto the surface of nanoparticles is one of the best ways to avoid aggregation. Based on this idea, a series of composites of nanoparticles with polymers have been prepared via several polymerization methods (17–22). Among these different methods, reversible addition-fragmentation chain transfer (RAFT) polymerization is the latest and the most applicable synthetic technique. The major advantages of this method include the control of molecular weight, narrow molecular weight distribution and a large number of monomers which can be polymerized (23, 24). In recent years, many reports of grafting polymers onto nanoparticles via RAFT polymerization have been published. Hua et al. (25) achieved the controlled graft modification of silica particles by using S-1-dodecyl-S′-(α', α'-dimethyl-α''-acetic acid)trithiocarbonate (DDACT) as a RAFT agent. The experimental results showed that the graft polymerization was well controlled by the RAFT process. Liu and Pan (26) designed a novel route to prepare RAFT agent, and grafted polystyrene (PS) onto silica nanoparticles via RAFT polymerization. Yang et al. (27)

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synthesized temperature-responsive carbon black nanoparticles by grafting poly(N-isopropylacrylamide) onto the surface of carbon black via RAFT polymerization. The resulting functionalized carbon black nanoparticles had good solubility in water. However, only a few papers in the literature have used the RAFT polymerization to graft polymers onto the TiO_2 nanoparticles (28).

In this paper, to prepare TiO_2-polymer nanocomposites, the RAFT agent was first immobilized on the surface of TiO_2, and then PMMA and PMMA-*b*-PS chains were grafted from these RAFT agents via RAFT polymerization. The resulting nanocomposites were characterized by Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). Additionally, the polymer cleaved from the nanocomposites was investigated by gel permeation chromatography (GPC) and ^1H nuclear magnetic resonance (NMR).

2 Experimental

2.1 Materials

$TiO_2$with an average diameter about 10∼100 nm were purchased from Zhoushan Nano-materials Co., Ltd. Styrene (St) and methyl methacrylate (MMA) used in this study were obtained from Shanghai Reagents Co., Ltd., and were distilled under reduced pressure to remove the inhibitor before polymerization. 2, 2′-azobisisobutyronitrile (AIBN) was obtained from Aldrich and was recrystallized with ethanol before use. The sodium ethyl xanthate and silane coupling agent 3-(chloropropyl)triethoxy silane (WD-30) were used as-received.

2.2 Synthesis of 3-(Chloropropyl)triethoxy Silane Functionalized Titania Nanoparticles (TiO_2-Cl)

In a typical experiment, 2 g of dried TiO_2, 20 mL of xylene and 0.6 mL of distilled water were added into a 100 mL three-necked flask, and the mixture was sonicated in a bath for 30 min. Then, 15 g of 3-(chloropropyl)triethoxy silane (WD-30) was added into the flask. The reaction mixture was then stirred at 80°C for 12 h. After cooling to room temperature, the product was vacuum filtered through a 0.22 μm millipore polycarbonate membrane and completely washed with toluene. The filtered product was then dried under vacuum at 40°C for 24 h.

2.3 Synthesis of Ethyl Xanthate Groups Functionalized Titania Nanoparticles (TiO_2-SC(S)OC_2H_5

Typically, 2 g of TiO_2-Cl, 1 g of sodium ethyl xanthate and 50 mL of anhydrous ethanol were added into a 100 mL flask, and the mixture was sonicated for 30 min. After that, the flask was immersed in an oil bath at 80°C for 12 h under an atmosphere of dry nitrogen. At the end of the reaction, the product was vacuum filtered through a 0.22 μm poly(tetrafluoroethylene) (PTFE) membrane, and the filter cake was washed with anhydrous ethanol three times. The RAFT agent functionalized TiO_2(TiO_2-SC(S)OC_2H_5) obtained was dried under vacuum at 40°C for 24 h.

2.4 Synthesis of TiO_2-PMMA

In this experiment, 50 mg of TiO_2-SC(S)OC_2H_5, 150 mg of MMA, and 0.2 mg of AIBN in 1 mL of DMF were added into a 10 mL dried flask. Then the flask was sealed under vacuum and placed in an oil bath at 90°C. The mixture was stirred for pre-scheduled hours. After polymerization, the viscosity had increased dramatically. The reaction mixture was diluted with tetrahydrofuran (THF) and vacuum filtered with a 0.22 μm PTFE membrane. To ensure the complete removal of the adhered and physically adsorbed polymer, the filtered mass was dispersed in THF, then filtered and washed with THF three times. The resulting product was redispersed in 10 mL of THF and subsequently precipitated by methanol (40 mL). The TiO_2-PMMA sample was obtained by drying overnight under vacuum at 40°C for 24 h.

2.5 Synthesis of TiO_2-PMMA-*b*-PS

Typically, 50 mg of TiO_2-PMMA, 150 mg of St and 0.2 mg of AIBN in 1 mL of DMF were added into a 10 mL dried flask. The flask was sealed under vacuum, placed in an oil bath at 90°C and the mixture stirred for 24 h. The reaction mixture was diluted with THF and vacuum filtered with a 0.22 μm PTFE membrane. The filtered mass was dispersed in THF, then filtered and washed with THF three times. The resulting filtered product was redispersed in 10 mL of THF and precipitated by the addition of methanol (40 mL). The TiO_2-PMMA-*b*-PS sample was obtained by drying overnight under vacuum at 40°C.

2.6 Cleavage of the Grafted Polymer from Modified TiO_2 Nanoparticles

In a typical procedure, 100 mg of the polymer grafted TiO_2 and 20 mL of THF were added into a polyethylene tube. Then, 1 ml of aqueous HF (49 wt%) was added into the tube. The reaction mixture was stirred at room temperature for overnight. The polymer was precipitated by adding the polymer solution into the methanol. The polymer obtained was dried under vacuum at 60°C for 24 h.

2.7 Measurements

Fourier transform infrared (FT-IR) spectra of the products were recorded on a Bruker 210 IR spectrometer at room temperature; the samples were ground with KBr and the mixture was then pressed into a pellet for IR measurement.

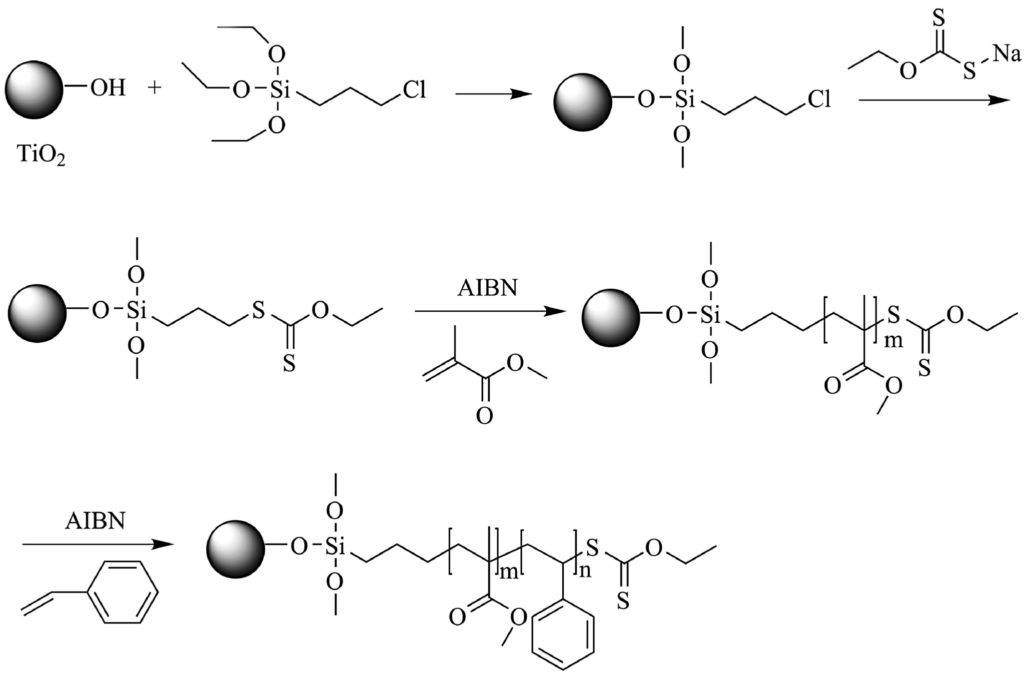

Fig. 1. Synthetic route of immobilizing the RAFT agent onto TiO_2 surface and surface RAFT polymerization from TiO_2.

X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB MK II system with Mg (Kâ) radiation. The ^1H nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker DMX 500 spectrometer, using $CDCl_3$ as a solvent. Thermal gravimetric analysis (TGA) was carried out on a Shimadzu TG-50 instrument with a heating rate of 20°C/min under nitrogen atmosphere, from 25°C to 700°C. The polymer molecular weights (*Mn*) and polydispersity (PDI) were determined at 40°C on a Waters 2414 gel permeation chromatograph (GPC) instrument equipped with microstyragel columns. Polystyrene standards were used for calibration, and THF was used as an eluent at a flow rate of 1 mL/min.

3 Results and Discussion

As described in the introduction, RAFT polymerization is a simple method to achieve living and controlled radical polymerization; it is activated by radicals generated from a traditional initiator. Figure 1 outlines the strategy used for immobilizing the RAFT agent on the surface of TiO_2nanoparticles, and then the functionalized TiO_2 nanoparticles was used as reacting sites for polymerization of methyl methacrylate and styrene.

3.1 Immobilization of RAFT Agent onto the TiO_2 Surface

The whole process of immobilizing the RAFT agent on $TiO_2$was verified by TGA, XPS and FT-IR. Figure 2 shows the TGA curves of TiO_2 nanoparticles, TiO_2-Cl and TiO_2-$SC(S)OC_2H_5$. A weight loss of 10.4% for the TiO_2 nanoparticles may be assigned to the weight loss of hydroxyl groups or absorbed gases on the TiO_2nanoparticles. The weight loss of the TiO_2-Cl was approximately 13.5% between 25°C and 700°C; thus, the content of the coupling agent grafted onto the TiO_2 was about 3.1 wt%. The TiO_2-$SC(S)OC_2H_5$had about a 17.2% weight loss in the same temperature zone. Thus, the weight of RAFT agent on the surface of TiO_2 was 3.7 wt%, which can be concluded based on the RAFT agent group's density being 0.44 mmol/g. There are about 9 sulfur atoms per 100 titanium atoms.

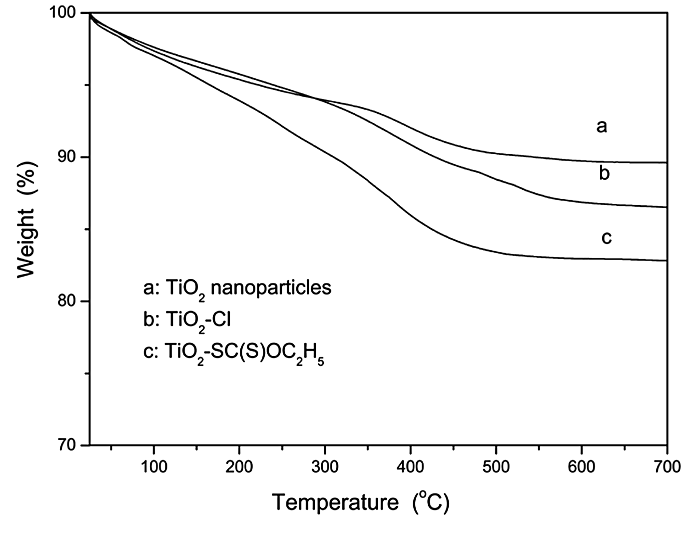

Fig. 2. TGA curves of TiO_2nanoparticles, TiO_2-Cl and TiO_2-$SC(S)OC_2H_5$.

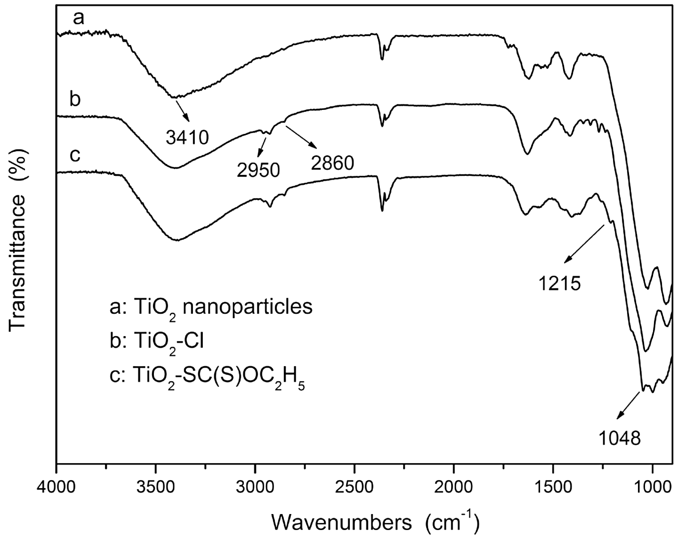

Fig. 3. FT-IR spectra of TiO_2 nanoparticles, TiO_2-Cl and TiO_2-SC(S)OC_2H_5.

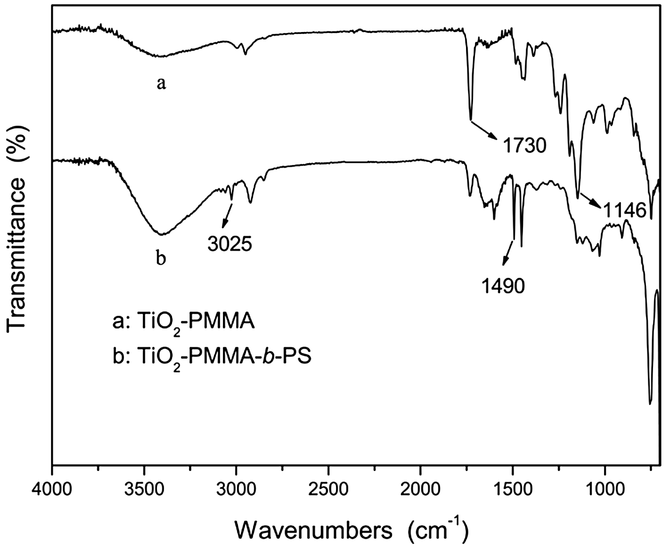

Fig. 5. FT-IR spectra of TiO_2-PMMA and TiO_2-PMMA-*b*-PS.

Figure 3 shows the FT-IR spectra of TiO_2 nanoparticles, TiO_2-Cl, and TiO_2-SC(S)OC_2H_5. The FT-IR spectrum of TiO_2 nanoparticles (Figure 3, curve a) shows an obvious absorption peak around 3410 cm^{-1}, due to the stretching vibration of –OH groups. Figure 3, curve b shows the sample of TiO_2-Cl; characteristic absorptions at 2860 cm^{-1} and 2950 $cm^{-1}$are assigned to -CH_2- groups of the coupling agent. Figure 3, curve c shows the spectrum of TiO_2-SC(S)OC_2H_5. The two characteristic absorptions at 1048 cm^{-1} and 1215 cm^{-1} are assigned to the stretching vibrations of C=S and C-O, respectively.

XPS was used to further characterize the TiO_2-SC(S)OC_2H_5. Figure 4 shows XPS spectrum of TiO_2-SC(S)OC_2H_5. The peaks at 530.3, 458.1, 285.2, 163.8 and 101.9 eV are attributed to O, Ti, C, S and Si elements, respectively. The content of elements on surface of TiO_2-SC(S)OC_2H_5 was calculated from the area of each element. The mol content of S was about 10.1% with respect to titanium, which is close to the result obtained from TGA. TGA, XPS and FT-IR results prove that the RAFT agent was successfully grafted onto the surface of TiO_2.

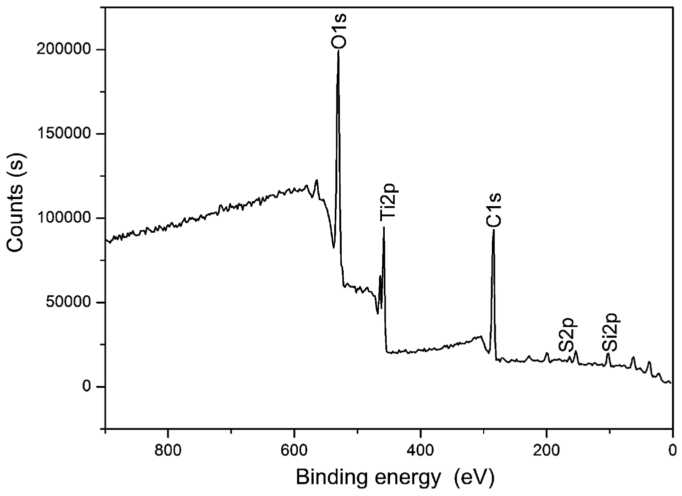

Fig. 4. XPS spectrum of TiO_2-SC(S)OC_2H_5.

3.2 Structure Analysis of the Hybrid Material

The chemical structure of the polymer grafted onto the surface of TiO_2 was characterized by ^{1}H-NMR and FT-IR spectra. Figure 5 shows the FT-IR spectra of TiO_2-PMMA and TiO_2-PMMA-*b*-PS. In the FT-IR spectrum of TiO_2-PMMA (Fig. 5, curve a), characteristic absorption peaks at 1730 cm^{-1} and 1146 cm^{-1} are assigned to C=O and C-O stretching, respectively. Figure 5, curve b shows the spectrum of TiO_2-PMMA-*b*-PS; the absorption peaks at 3025 $cm^{-1}$and 1490 $cm^{-1}$are the characteristic absorption bands of PS. The FT-IR data confirm the presence of PMMA and PMMA-*b*-PS on the TiO_2 surface.

Figure 6 shows the structural formula and the ^{1}H-NMR spectrum of the diblock polymer (PMMA-*b*-PS) cleaved from the surface of TiO_2. The peaks around 1.0~2.4 ppm are assigned to the hydrogen species associated with the backbone of the grafted PMMA-*b*-PS chain. The peak at 3.7 ppm, assigned to methyl protons of the ester unit, and the peaks around 6.3~7.2 ppm, assigned to the phenyl protons of PS, were also found in the spectrum. The ^{1}H-NMR analysis further suggests that the synthesis of TiO_2-PMMA-*b*-PS was successful.

3.3 Organic Content of the Hybrid Material

The relative amounts of PMMA and PMMA-*b*-PS on TiO_2were determined from TGA. Figure 7 shows the TGA curves of the TiO_2-PMMA and TiO_2-PMMA-*b*-PS.

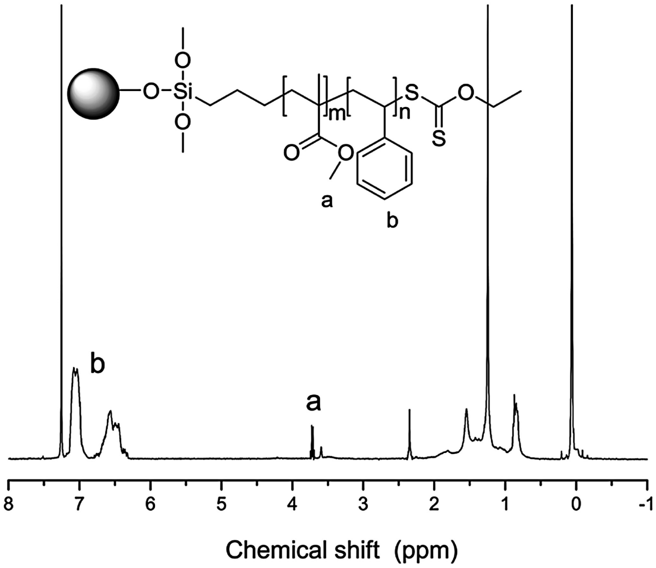

Fig. 6. ^{1}H-NMR spectrum of PMMA-*b*-PS cleaved from TiO_2-PMMA-*b*-PS in $CDCl_3$.

There are three stages for the weight loss of TiO_2-PMMA. The first region is below 280°C. The weight loss can be assigned to the loss of free hydroxyl groups condensed on the surface of TiO_2. The rapid weight reduction in the second region (280 ~ 430°C) can be attributed to the decomposition of PMMA. The third region (430 ~ 700°C) only shows a small weight loss which is likely due to the further decomposition of the residual PMMA segments. For the samples of TiO_2-PMMA, the polymer content increased from 29.8 wt% to 49.1 wt% when the polymerization time increased from 6 h to 24 h, which indicates that the amount of PMMA grafted onto the surface of TiO_2 increased with the polymerization time.

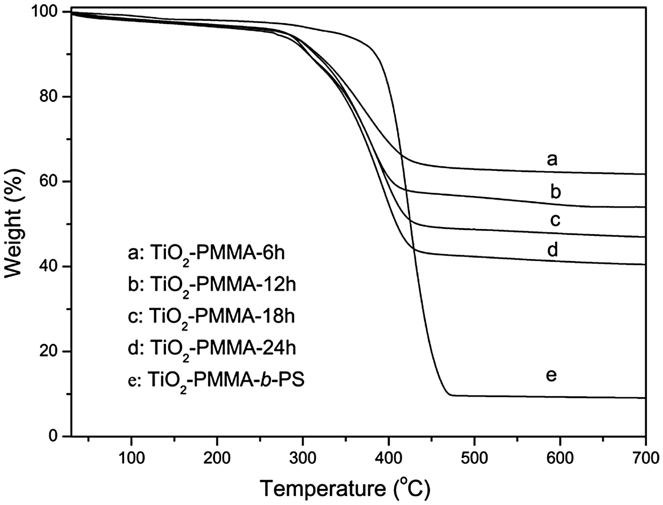

Fig. 7. TGA curves of TiO_2-PMMA-6h, TiO_2-PMMA-12 h, TiO_2-PMMA-18 h, TiO_2-PMMA-24 h and TiO_2-PMMA-*b*-PS.

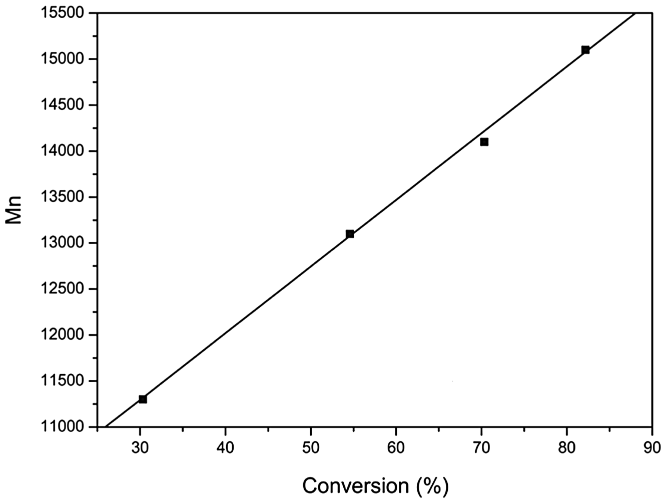

Fig. 8. Relationship between the monomer conversion and the molecular weight curve.

The TGA curve of TiO_2-PMMA-*b*-PS (using TiO_2-PMMA-6 h as macroinitiator) was similar with that of the TiO_2-PMMA, but the onset temperature of the second region (320°C) was at a higher temperature and the final residue was smaller than that of TiO_2-PMMA. According to the TGA results, the polymer content of TiO_2-PMMA-*b*-PS was 80.5 wt%. Discounting the polymer content of TiO_2-PMMA-6h (29.8 wt%), the PS grafted on TiO_2-PMMA was approximately 50.7 wt%. It can be concluded that the PS was grafted on the TiO_2-PMMA macroinitiator and the polymerization was a living process.

3.4 Control of the RAFT Polymerization

In order to determine the living characteristics of the RAFT polymerization, the polymers grafted on the surface of TiO_2

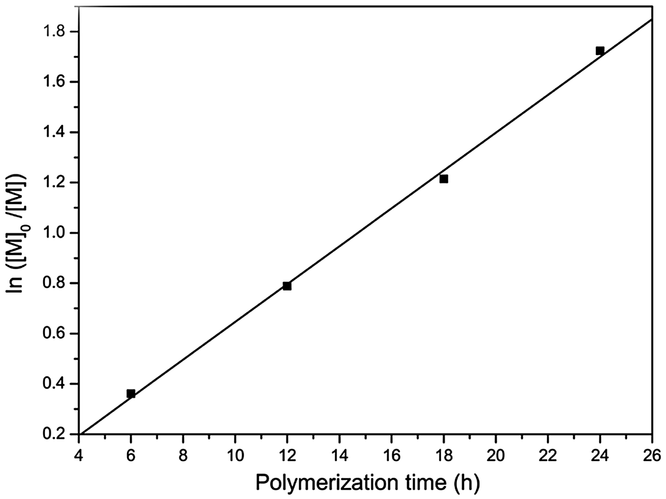

Fig. 9. Kinetic plots of $\ln([M]_0/[M])$ vs. polymerization time for RAFT polymerization MMA.

Table 1. Molecular weight and PDI of cleaved polymer at different polymerization times and content of grafted polymer

Sample	*Mn (g/mol)*	*Mw (g/mol)*	*PDI*[a]	*Conversion (%)*	*Polymer content (%)*[b]
TiO_2-PMMA-6h	11300	14000	1.24	30.32	27.8
TiO_2-PMMA-12h	13100	16800	1.28	54.58	35.5
TiO_2-PMMA-18h	14100	17200	1.22	70.31	42.6
TiO_2-PMMA-24h	15100	17500	1.16	82.16	49.1
TiO_2-PMMA-*b*-PS[c]	16200	24000	1.48	—	80.5

[a] PDI: molecular weight distribution calculated from *Mw/Mn.*

[b] Polymer content: the fraction of grafted polymer calculated from TGA data.

[c] TiO_2-PMMA-*b*-PS: using TiO_2-PMMA-6h as macroinitiator.

were cleaved. The GPC results and monomer conversion are presented in Table 1. It can be seen that the molecular weight and monomer conversion increased directly with the polymerization time, and the PDIs were relatively low. These results are obvious evidence for RAFT polymerization.

The monomer conversion vs. the molecular weight curve was plotted to further verify the living characteristics of the RAFT process (as shown in Fig. 8). The molecular weight exhibits a linear relationship with the monomer conversion, indicating that the active species was constant in the RAFT polymerization process.

The kinetic plots of $\ln([M]_0/[M])$ vs. polymerization time are shown in Figure 9. It shows that the $\ln([M]_0/[M])$ increased linearly with the polymerization time. This result demonstrates that the polymerization had nearly first-order kinetics of monomer consumption.

4 Conclusions

In this work, poly(methyl methacrylate)-*b*-polystyrene (PMMA-*b*-PS)/TiO_2 hybrid materials were prepared via RAFT polymerization. FT-IR, XPS and TGA results confirmed that the RAFT agent was immobilized on the TiO_2 surface. The successful synthesis of polymer chains grafted onto the surface of TiO_2 nanoparticles was determined by FT-IR and ^{1}H-NMR studies. Furthermore, TGA and GPC analyses of the resulting nanocomposites showed that the TiO_2-PMMA could be used as macroinitiators for further RAFT polymerization of styrene and the polymerization was a living and controlled process. This easy approach to prepare functionalized TiO_2 by RAFT polymerization is promising to open up a new method and explore a wider way for the fabrication and application of more TiO_2-polymer nanocomposites.

Acknowledgements

The authors are grateful for the financial support by the Science Foundation of Nanchang Hangkong University (ZC200801146) and the Youth Foundation of Jiangxi Educational Committee (GJJ10180).

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