

Preparation of Polystyrene/MMT Nanocomposite Through *In Situ* RAFT Polymerization by New Chain Transfer Agent Derived from Bisphenol A

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ABSTRACT: Reversible addition-fragmentation chain transfer (RAFT) polymerization was performed in the presence of a new RAFT agent based on bisphenol A and modified clays and successfully prepared polystyrene/MMT nanocomposite. The structure of RAFT agent was investigated by Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance spectroscopy (^1H NMR). The polymer had well-defined molecular weight and narrow polydispersity obtained by gel permeation chromatography (GPC). The morphology of polystyrene/MMT nanocomposite was investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) and was found to be exfoliated. Thermal stability of pure polystyrene and polystyrene/MMT synthesized via RAFT polymerization was also investigated and showed better thermal stability for nanocomposite. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Various different living and controlled/living polymerization methods were used in the production of well-dispersed silicate layers, including, atom transfer radical polymerization (ATRP),^{1,2} nitroxide-mediated polymerization (NMP),^{3,4} and reversible addition-fragmentation chain transfer (RAFT)^{5–8} polymerization. Using these methods, synthesis of polymers with controlled molecular weight and narrow polydispersity index has been successful.

Among these methods, RAFT process is an attractive for production of new materials with different properties. The main reason for high performance RAFT polymerization is first, it doesn't need to metal catalysts and second it can be done in various ranges of reaction conditions like temperature and solvent and also a wide range of monomers with functional groups and without functional groups (e.g., OH, NR₂, COOH, CONR₂) have been polymerized via this polymerization method.⁹ This is a kind of polymerization which reacts by reversible addition-fragmentation chain transfer in the presence of dithiocarbonyl compounds.¹⁰ When xanthates were used in dithiocarbonyl compounds, this process is known as macromolecular architecture design by interchange of xanthates (MADIX).^{11,12} By choosing a suitable R and Z groups, RAFT agent [ZC = S(SR)], can be use successfully, for synthesis of

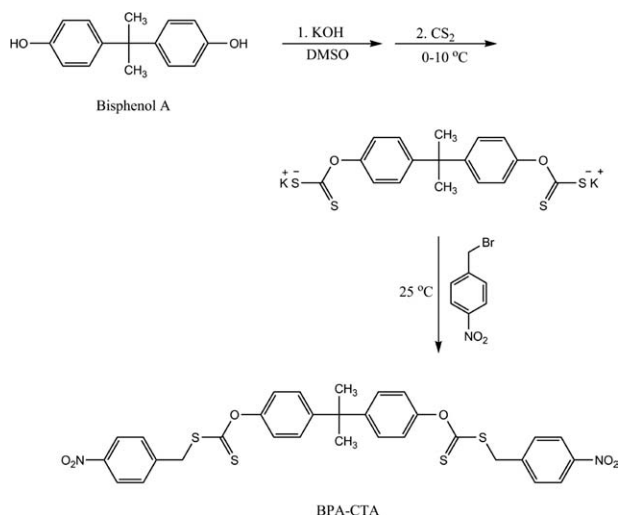
polymers with narrow polydispersity index and predetermined molecular weight.¹³

One of the best ways for preparation of nanocomposites is *in situ* polymerization which was done via different mechanisms especially conventional free radical polymerization. However, this conventional free radical has disadvantages like broad polydispersity index which was affected on physical and mechanical properties of resulted polymer.¹⁴

The improved properties of polymeric nanocomposites, requires simultaneous modification of polymer matrix properties (molecular weight and polydispersity index) and how the distribution of particles are dispersed within the matrix. Recently, to resolve restrictions of conventional free radical polymerization, the RAFT polymerization has been used for preparation of nanocomposites.¹⁵

Polymer clay nanocomposites (PCNs) due to improvements in the properties of polymeric materials without harmful effects, has many applications.¹⁶ Because of the strong dependence of morphology with molecular weight, polydispersity, and degree of polymerization, the living radical polymerization methods are used for preparing polymer nanocomposites.¹⁷

Here, a new RAFT agent was synthesized starting from Bisphenol A (BPA) that have well controlled molecular weight and



Scheme 1. Synthetic route for RAFT agent derived from bisphenol A.

narrow polydispersity and it was used for polymerization of styrene and making its nanocomposite with montmorillonite. Techniques such as FT-IR, GPC, XRD, TGA, and TEM have been used to study progress of the polymerizations and the morphology of the nanocomposite.

EXPERIMENTAL SECTION

Materials and Instruments

All solvents, monomer (styrene), and other chemicals were purchased from Merck-Chemical at the highest purity available unless otherwise stated. Styrene (99%), was purified by washing with an aqueous solution of NaOH (5 wt %) to remove the inhibitor, followed by distilled water until the washings were neutral to litmus, dried by anhydrous MgSO_4 and fractionally distilled under vacuum. 2,2'-Azobis(isobutyronitrile) (AIBN, 97%) was purified by recrystallization from methanol and dried at room temperature in a vacuum oven and finally, stored at -15°C . dimethylsulfoxide (DMSO), dimethylformamide (DMF) and carbon disulfide were dried over molecular sieves (4 Å) before use. Bisphenol A (BPA) and 4-nitrobenzyl bromide were

used as received. Modified clay was cloisite 30B and was purchased from Special Chem.

Characterization

FTIR spectra were recorded on a JASCO FTIR-6300 spectrometer by using KBr pellets. ^1H NMR spectra were recorded on Bruker 300 MHz spectrometer. Thermogravimetric analysis (TGA), differential thermogravimetry (DTG) were performed on a SETARAM labsys TG system conducted over the temperature range from 25 to 600°C with a programmed temperature increment of $15^\circ\text{C min}^{-1}$ under N_2 atmosphere. Differential scanning calorimetry (DSC) was performed on a SETARAM labsys TG system and for measurement of the glass transition temperature (T_g) of the PS and PS/MMT, about 5–10 mg samples in an aluminum holder were heated from 25 to 600°C under nitrogen atmosphere at a heating rate of $15^\circ\text{C min}^{-1}$. All samples were dried under vacuum at 40°C for 24 h prior to DSC measurements. Molecular weights were determined using Knauer gel permeation chromatography (GPC) equipped with Smartine Pump 1000, a differential refractive index (DRI) detector (Smartin Ri 2300) and PL Gel 10 μm column. THF was used as solvent with flow rate of 1 mL min^{-1} at room temperature. GPC was calibrated with standard polystyrene with polydispersity index of 1.09. X-ray diffractions were performed on Bruker D8 AVANCE instrument and X-ray generator (Cu K α radiation with $\lambda = 1.5406 \text{ \AA}$) with a 2θ scan range of 1.4° – 10° at room temperature. Transmission electron microscopy (TEM) was performed on PHILIPS C120 (100 kV).

Synthesis of RAFT Agent Derived from Bisphenol A (BPA-CTA)

In a two-necked round bottomed flask equipped with dropping funnel, a solution of bisphenol A (1 g, 4.38 mmol) in DMSO (8 mL) was prepared. Then an aqueous solution of KOH (0.74 g, 13.2 mmol, 1 : 3 eq) was added and stirred for 4 h at room temperature. The temperature was then decreased to 0 – 10°C and an excess of carbon disulfide (1 : 20 eq) was added to this solution using dropping funnel. The reaction mixture was stirred at room temperature for 3 h and then 4-nitrobenzyl bromide (2.81 g, 13 mmol) was added slowly. The final mixture was stirred at room temperature for 10 h and the resulted

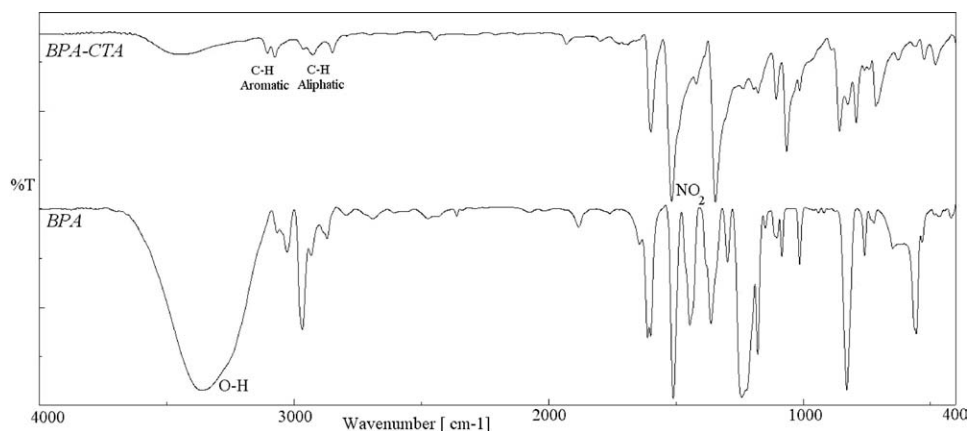


Figure 1. Compared FTIR spectrum of bisphenol A (BPA) and its RAFT agent (BPA-CTA).

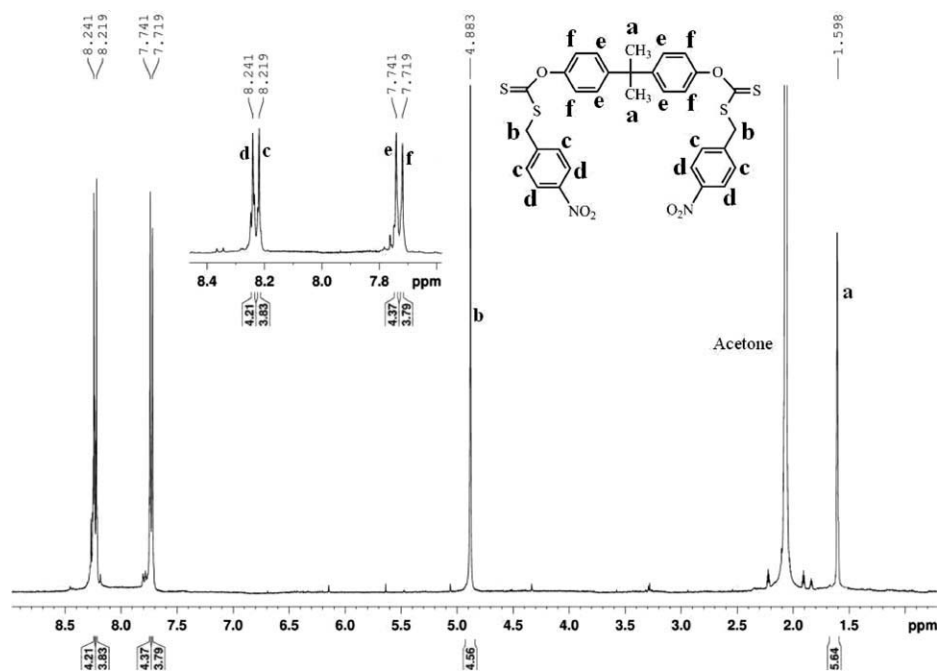


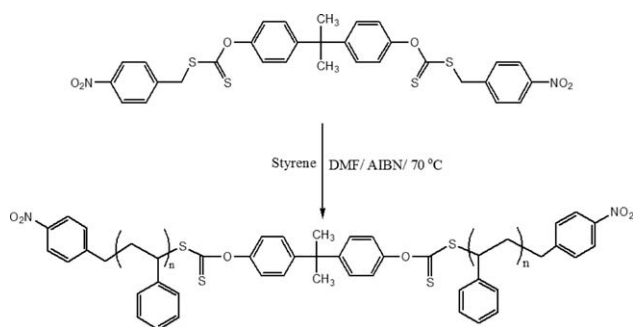
Figure 2. ^1H NMR spectrum of RAFT agent (BPA-CTA) in acetone- d_6 .

precipitate was washed with water, and recrystallized in methanol. (Yield: 78%).

^1H NMR (Acetone- d_6 , ppm): 8.24–8.21 (m, aromatic, 8H), 7.74–7.71 (m, aromatic, 8H), 4.88(s, 4H, $-\text{CH}_2-$), 1.59 (s, 6H, $-\text{CH}_3$)

Synthesis of RAFT Agent Derived from Hydroquinone (CTA2)

In a two-necked round bottomed flask equipped with dropping funnel, a solution of hydroquinone (0.48 g, 4.38 mmol) in DMSO (5 mL) was prepared. Then an aqueous solution of KOH (0.74 g, 13.2 mmol, 1 : 3 eq) was added and stirred for 4 h at room temperature. The temperature was then decreased to 0–10°C and an excess of carbon disulfide (1 : 20 eq) was added to this solution using dropping funnel. The reaction mixture was stirred at room temperature for 3 h and then 4-nitro benzyl bromide (2.81 g, 13 mmol) was added slowly. The final mixture was stirred at room temperature for 10 h and the resulted precipitate was washed with water, and recrystallized in methanol. (Yield: 80%).



Scheme 2. Synthetic route for synthesis of polystyrene using RAFT agent.

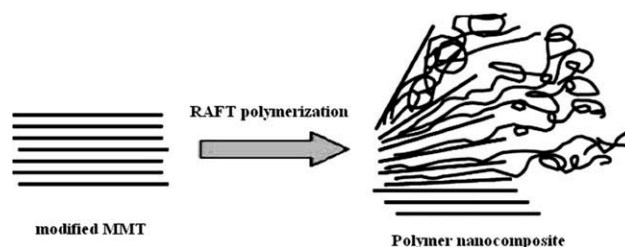
^1H NMR (Acetone- d_6 , ppm): 8.31–7.72 (m, aromatic, 12H), 4.92(s, 4H, $-\text{CH}_2-$).

Synthesis of Polystyrene Using RAFT Polymerization

In a round bottomed flask (25 mL), a solution of BPA-CTA (RAFT agent, 0.02 g, 3.07×10^{-2} mmol) in DMF (6 mL) was prepared. Then AIBN (0.002 g, 1.22×10^{-2} mmol) and freshly distilled styrene monomer (1.92 g, 18.42 mmol) were added and nitrogen was purged into this solution for 15 min. The mixture was stirred in an oil bath at 70°C for 12 h. The polymerization was stopped by cooling in ice-bath and the resulted polymer was precipitated in methanol and after washing with methanol, it was dried in a vacuum oven at 60°C for 12 h. monomer conversion was measured gravimetrically (0.76).

Preparation of Polystyrene/Clay Nanocomposite through *In Situ* RAFT Polymerization (PS/MMT)

In a round bottomed flask (25 mL), freshly distilled styrene monomer (1.92 g, 18.42 mmol) and modified montmorillonite, MMT, (0.096 g, 5 wt % monomer) were mixed for 24 h to complete swelling of the clay in monomer. Then a homogeneous mixture was obtained using ultrasonication for 2 h. A



Scheme 3. Preparation of Polymer-clay nanocomposites through *in situ* RAFT polymerization.

Table I. RAFT Polymerization of Styrene at Absent and Also at Presence of Different Amounts of RAFT Agent

| Polymer | $[M]_0/[RAFT]_0$ | Conv (%) | M_n (g mol ⁻¹) | PDI |
|---------|------------------|----------|------------------------------|-----|
| PS | - | 91 | 151,000 | 3.1 |
| PS-CTA | 300 | 84 | 26,900 | 1.6 |
| PS-CTA | 600 | 76 | 44,000 | 1.3 |

solution of RAFT agent (either BPA-CTA or CTA2, 3.07×10^{-2} mmol) and AIBN (0.002 g, 1.22×10^{-2} mmol) in DMF (6 mL) was added to the mixture and to remove oxygen, nitrogen was purged into the solution for 15 min. The mixture was then stirred in an oil bath at 70°C for 12 h. The resulted polymer was precipitated in methanol, washed with methanol and at the same time methanol was evaporated and the composite was vacuum dried at 60°C for 12 h. monomer conversion was measured gravimetrically (~ 0.78).

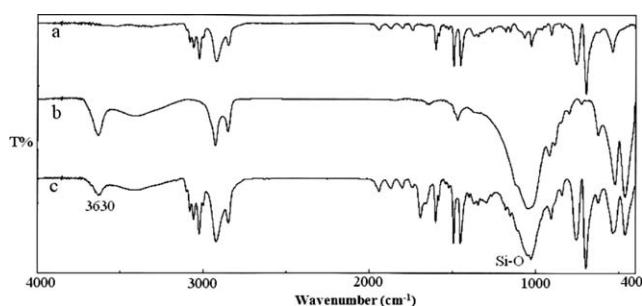
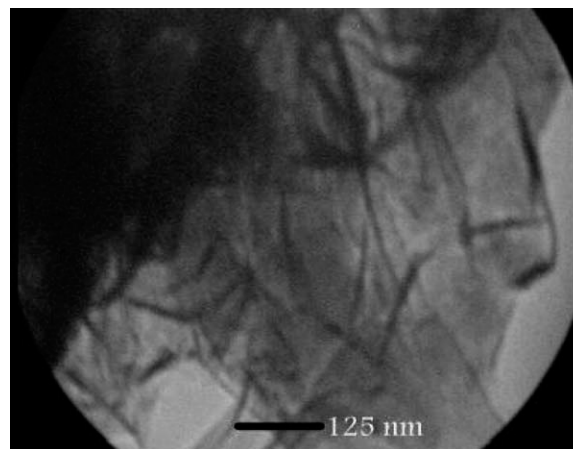
The other two polymer clay nanocomposites, PS/MMT(CTA2) and PMMA/MMT (BPA-CTA), were prepared according to reported procedure in Preparation of Polystyrene/Clay Nanocomposite through *In Situ* RAFT Polymerization (PS/MMT) section.

RESULTS AND DISCUSSION

Because of factors like simple synthetic route, low cost and having two functional for synthesizing high molecular weight polymers, a RAFT agent, BPA-CTA, was introduced and synthesized from reaction of bisphenol A, carbon dioxide and 4-nitrobenzyl bromide, with 78% yield in DMSO according to Scheme 1.

Because of sensitivity of the compounds to hydrolysis and also need a medium to dissolve the salt intermediates, BPA-O⁻K⁺ and BPA-OCS₂⁻K⁺, DMSO was pickup as solvent.

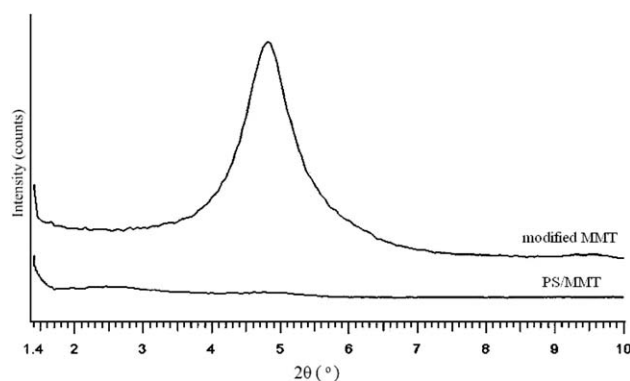
Comparison of FTIR spectrums of BPA and BPA-CTA (Figure 1) shows that a broad peak at 3400 cm⁻¹ related to hydroxyl groups in BPA was completely disappeared in BPA-CTA and also two sharp peaks at 1345 and 1550 cm⁻¹ are related to NO₂ groups was formed in BPA-CTA spectrum. The melting point of BPA is 158°C while for BPA-CTA, is 86°C which was because of decreasing hydrogen bonding in this compound. ¹H NMR spectrum of this compound shows peaks at 8.24–8.21 ppm and 7.74–7.71 ppm for aromatic protons, 4.88 ppm for benzyl protons and 1.59 ppm for methyl groups (Figure 2).

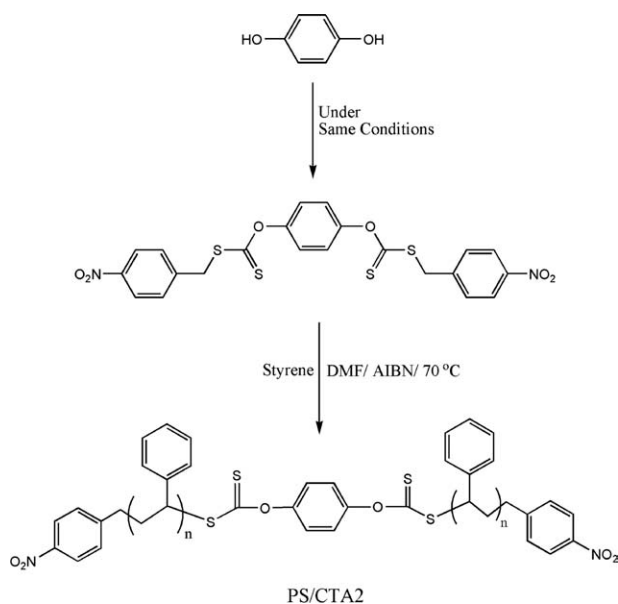
**Figure 3.** FTIR spectrum of (a) synthesized polystyrene using BPA-CTA; (b) modified MMT; (c) Polystyrene/MMT nanocomposite.**Figure 4.** Transmission electron micrograph of the PS/MMT nanocomposite.

This synthesized RAFT agent, BPA-CTA, was then used for synthesis of polystyrene and also polystyrene/MMT nanocomposite (Schemes 2 and 3). First a reaction between styrene monomer and BPA-CTA in the presence of AIBN as initiator was done and the resulted polymer was characterized by FTIR spectroscopy and GPC analysis.

To obtain the effect of RAFT agent in polymerization reaction, three different reactions was designed, according to Table I. First the polymer was synthesized without RAFT agent with PDI of 3.1 which is regular for noncontrolled polymerization. Next step two different amounts of RAFT agent were used and from GPC analysis, it was shown that RAFT polymerization has been controlled successfully the molecular weight and molecular weight distribution when the ratio of $[M]_0/[RAFT]_0$ was 600. The polydispersity (M_w/M_n) of polystyrene prepared through RAFT process was 1.3 which indicates a narrow molecular weight distribution. The number-average molecular weight for this compound was about 44,000 g mol⁻¹.

Then, according to optimized conditions obtained from above polymerization reaction, an *in situ* reaction between styrene monomer, MMT, RAFT agent, and AIBN was done and the resulted nanocomposite was obtained and characterized using FT-IR, XRD, and TEM.

**Figure 5.** Compared XRD spectra of modified MMT and exfoliated polystyrene/MMT nanocomposite.

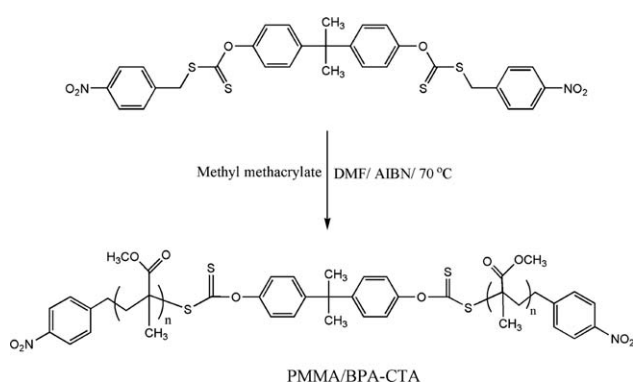


Scheme 4. Synthetic route for RAFT agent derived from hydroquinone.

Figure 3 shows the FT-IR spectra of synthesized PS using RAFT process (a), modified MMT (b) and PS/MMT nanocomposite prepared through *in situ* RAFT polymerization (c). The FT-IR spectra of pure PS shows the characteristic absorption bands due to stretching vibration of C–H ($3060\text{--}2850\text{ cm}^{-1}$), weak aromatic overtone ($1940\text{--}1700\text{ cm}^{-1}$), intense C=C stretching vibration ($1600\text{--}1490\text{ cm}^{-1}$) and two sharp peaks at $755\text{--}695\text{ cm}^{-1}$ are related to monosubstituted aromatic rings of polystyrene.

FT-IR spectrum of PS/MMT nanocomposite shows the combination from modified MMT and polystyrene those obvious two important peaks, one at 3630 cm^{-1} which was related to structural hydroxyl groups stretch in the clay and the other is at 1047 cm^{-1} which was related to strong Si–O stretching bond.

The structure of the PS/MMT nanocomposite containing 5 wt % modified MMT was confirmed by TEM photograph, as shown in Figure 4. The MMT layers are randomly dispersed in polystyrene matrix by styrene monomers and further exfoliation during *in situ* RAFT polymerization. The exfoliated or interca-



Scheme 5. Synthetic route for synthesis of polymethyl methacrylate using BPA-CTA RAFT agent.

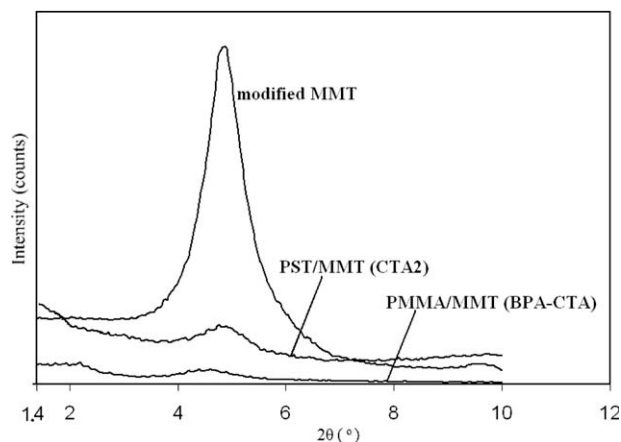


Figure 6. Compared XRD spectra of modified MMT, PS/MMT (CTA2) and PMMA/MMT (BPA-CTA) nanocomposites.

lated structure is mainly created by the pressure exerted on the clay sheets by the growing polymer chains within the interlayer space. Here, because of structure of RAFT agent (two functional and flexible) which makes polymers with larger chain lengths, this pressure is more and the percentage of exfoliation is high.

Because TEM imaging gives a picture of only a very small portion of sample, the exfoliated morphology was further confirmed by X-ray diffraction. However, TEM imaging seems to favor the exfoliated hypothesis, as no regularly oriented clay particles were observed.

XRD analysis is a powerful tool for investigating the crystal structure of polymer–clay nanocomposites (PCNs). XRD investigations on morphology of modified MMT and polystyrene/MMT nanocomposite show that polystyrene diffuses in clay layers. There is no characteristic MMT peak in the XRD pattern for polystyrene/MMT nanocomposite containing 5 wt %

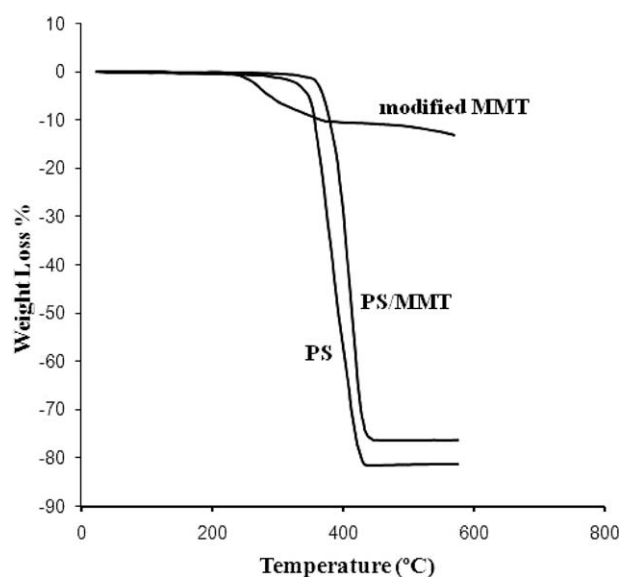


Figure 7. TGA curves of, pure PS; modified MMT and PS/MMT nanocomposite obtained at a heating rate of $15^{\circ}\text{C min}^{-1}$ in nitrogen.

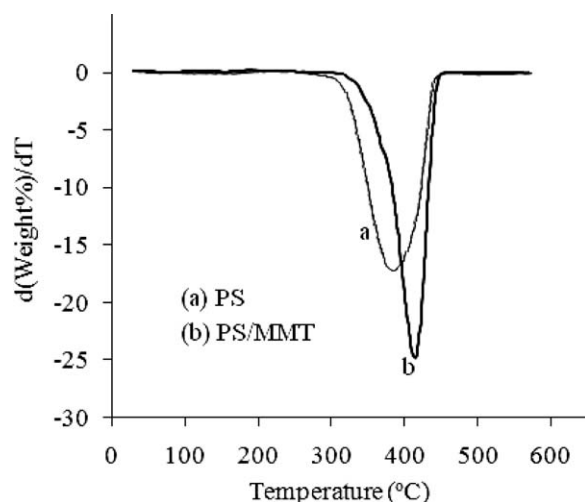
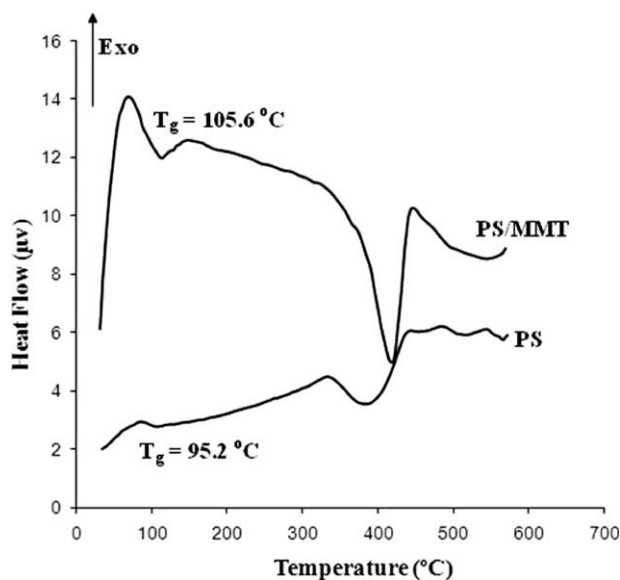
Table II. Thermal Data of Polystyrene and Polystyrene/MMT Nanocomposite

| Polymer | $T_{5\%}$ decomp. (°C) | $T_{10\%}$ decomp. (°C) | $T_{50\%}$ decomp. (°C) | Remaining % | T_g (°C) |
|-----------------|------------------------------|-------------------------------|-------------------------------|----------------|---------------|
| Polystyrene | 345 | 356 | 391 | 19 | 95.2 |
| Polystyrene/MMT | 365 | 381 | 437 | 24 | 105.6 |

modified MMT prepared through *in situ* RAFT polymerization. This result indicates the exfoliation of MMT into nanolayers in the polystyrene matrix (Figure 5).

To obtain more information about this reaction, two parallel experiments were done. One was polymerization of styrene in the presence of modified MMT using a RAFT agent derived from hydroquinone (CTA2, a new two functional RAFT agent, Scheme 4) and the other was polymerization of methyl methacrylate in the presence of modified MMT using BPA-CTA (Scheme 5). According to Figure 6, a morphology of exfoliated-intercalated was obtained for PS/MMT using CTA2 as RAFT agent and for PMMA/MMT a morphology of rather exfoliated was obtained using BPA-CTA as RAFT agent. These experiments confirmed the structure of BPA-CTA is causing exfoliation of PS/MMT.

The thermal stability of synthesized PS and PS/MMT nanocomposite was investigated by thermogravimetric analysis (TGA). The TGA weight loss curves for PS and PS/MMT prepared via RAFT polymerization are shown in Figure 7. The PS nanocomposite had higher thermal stability when compared with the corresponding pure polymer. The peak degradation temperature of PS/MMT is increased. The enhancement of thermal stability is due to incorporation of the layered silicates into the polymer network, and the restriction of thermal motion of PS chains in the gallery. The temperatures at which 5, 10, and 50% weight loss occurred by decomposition were compared between controlled PS and PS/MMT using similar RAFT agent (BPA-CTA).

**Figure 8.** DTG curves of pure PS and PS/MMT nanocomposite obtained at a heating rate of $15^{\circ}\text{C min}^{-1}$ in nitrogen.**Figure 9.** DSC curves of, pure PS and PS/MMT nanocomposite.

In all cases the temperatures of decomposition were in the presence of clay clearly improved the thermal stability of controlled polystyrene. Table II shows the remaining amount of 600°C and the amount of polymer degradation at $T_{5\%}$, $T_{10\%}$, and $T_{50\%}$.

DTG curves shows the temperatures at maximum mass loss rate for the PS and PS/MMT prepared through RAFT polymerization (Figure 8).

DSC thermograms of the pure PS and PS/MMT are shown in Figure 9. The pure PS exhibits a heat flow peak at $\sim 95.2^{\circ}\text{C}$ which is related to the glass transition temperature (T_g) of PS, while its value has increased to PS/MMT and is $\sim 105.6^{\circ}\text{C}$. Its value has increased due to reduce the segmental motions of the polymer chains and this can be ascribed to the confinement of the exfoliated polymer chains within the layered silicates of modified MMT.^{18,19}

CONCLUSION

Polystyrene produced via RAFT process with chain transfer agent based on bisphenol A (BPA) had well-defined molecular weight and narrow polydispersity. The morphology of PS/MMT was found to be exfoliated through *in situ* RAFT polymerization by dispersing modified clay in styrene monomers. According to the XRD and TEM analysis, complete spread of MMT layers in polystyrene matrix and its exfoliated structure of PS/MMT nanocomposite are justified. Also, the thermal stability of PS/MMT nanocomposite compared with pure PS has improved. These results indicate that RAFT polymerization has ability to produce of the polymer nanocomposites with an exfoliated structure. The fact that exfoliated structure was obtained is in line with the accepted model, was polymerization within the clay galleries generates pressure on the clay platelets from the growing chains, eventually leading to the exfoliated structure. In the present system, in addition to good compatibility between the modified clay and styrene monomer, the bifunctionality and structure of RAFT agent is a most driving force

for make exfoliation structure. This is due to make polymers with larger chain lengths.

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