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Evaluation of the Confinement Effect of Nanoclay on the Kinetics of Styrene Atom Transfer Radical Polymerization

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ABSTRACT: The grafting through method was employed to study the effect of nanoclay confinement on the atom transfer radical polymerization (ATRP) of styrene. An ammonium salt containing a double bond on its structure was used as a clay modifier. Employing ATRP to polymerize styrene in the presence of modified montmorillonite resulted in a finely well-defined polystyrene nanocomposite. The gas chromatography (GC) results showed the linear increase of $\ln(M_0/M)$ versus time, which indicated the controlled behavior of the polymerization. Another confirmation of the living nature of the polymerization was the linear increase of molecular weight against monomer conversion concluded from the gel permeation chromatography (GPC) data. Nanoclay exerted acceleration on the polymerization of free polystyrene chains. The polydispersity

indexes of polymer chains increased by the addition of nanoclay. In the case of clay-attached polystyrene chains, number and weight-average molecular weights were lower than that of freely dispersed polystyrene chains. The polydispersity index of the clay-attached chains was higher in respect to the freely dispersed polystyrene chains. The living nature of polymer chains was more elucidated by Fourier transform infrared spectroscopy (FTIR). Exfoliation of the clay layers in the polymer matrix of polystyrene nanocomposite containing the lowest amount of nanoclay has proven by Transmission Electron Microscopy (TEM). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 409–417, 2012

Key words: nanolayers; atom transfer radical polymerization (ATRP); polystyrene; kinetics

INTRODUCTION

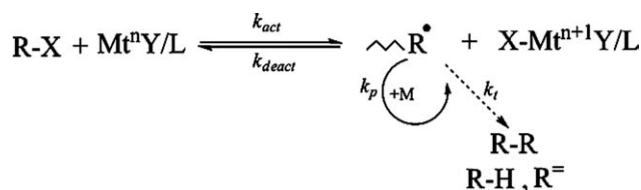
Controlled radical polymerization (CRP) techniques are robust methods for synthesizing polymers with targeted molecular weight, narrow molecular weight distribution, and well-defined topology.¹ In this context, nitroxide-mediated polymerization,² reversible addition-fragmentation chain transfer polymerization (RAFT),³ and atom transfer radical polymerization (ATRP)⁴ have extensively been studied. Some advantages of ATRP over other CRP systems including the applicability to a wide variety of monomers and systems of polymerization,⁵ the simplicity of the reaction setup and conditions (low temperature and pressure), and its less sensitivity to impurities⁶ have made it an interesting field of study. ATRP can be employed not only to synthesize homopolymers but also to prepare various kinds of functional (chain end functionality or functionality on the backbone),

gradient, graft, branched, star, and brush (co)polymer structures.

Mechanistically, CRP is based upon the existence of an equilibrium reaction which swiftly switches growing chains between active and dormant states. Consequently, the instantaneous concentration of free radicals is lessened and therefore the bimolecular irreversible termination reactions are suppressed.⁵ Atom transfer radical polymerization uses a transition metal complex as its catalyst in the equilibrium process. Transition metal complex, or the activator, ($M^{n+}Y/L$) is responsible for homogeneous cleavage of alkyl halide bond ($R-X$) through a reversible redox process. As a result, it undergoes the inner-sphere electron oxidation with the abstraction of a radically transferable atom (X) from the dormant species (P_nX). The growing radicals (R^*) react reversibly with the transitional metal in the higher oxidation state, or the deactivator ($X-M^{n+1}Y/L$), to form dormant species. This equilibrium is conducted with the rate constants of k_{act} and k_{deact} for the activation and deactivation reactions respectively. When k_{deact} is much larger than k_{act} ($k_{deact} \gg k_{act}$) and the rate of initiation is much more than the rate of propagation, the probability of bimolecular termination reactions is reduced and the polymerization resembles a living system (Scheme 1).⁷ In this scheme, k_t

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Scheme 1 Reversible Equilibrium in ATRP Reaction.

and k_p represent the termination and propagation rate constants, respectively. Also, $R-R$, $R^=$, and RH stand for the dead chains resulted from the combination of radicals, disproportionation between growing radicals, and the abstraction of a hydrogen atom by a growing radical.

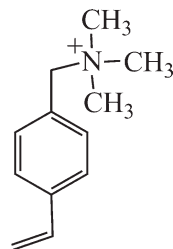
The radical concentration reduces by decreasing the activation rate constant of an ATRP reaction. Consequently, the polymerization rate in the case of atom transfer radical polymerization is lower than the conventional radical polymerization. Polar mediums and additives with polar functional groups such as phenols, carboxylic acids, and water increase the polymerization rate in an ATRP reaction.^{8–11}

Recently, the capability of ATRP to synthesize surface-initiated polymer chains has been reported frequently. To this end, substrates with different geometries have been employed.^{12–15} Functionalization of the substrates by ATRP initiator groups is the most frequently used route to synthesize polymer brushes the physical and chemical properties of which could be precisely adjusted through the monomer chemistry, molecular weight, and its distribution, and the architecture of the polymer chains.

In the past few years, nanoclay, because of its higher thermal and mechanical properties, has frequently been added into polymer matrices. Because there are polar bonds on the layers of nanoclay, the polymerization rate of various monomers can be affected in the presence of nanoclay. A review of related literature indicates that there are some attempts at the kinetics study of polymerization in the presence of nanoclay layers. Kim et al. reported that using nanoclay in the emulsion polymerization of styrene resulted in an increase in the molecular weight and a reduction in the polydispersity index of polystyrene chains.¹⁶ Similar results have been obtained by Lee and Jang in the free radical polymerization of methyl methacrylate in the presence of nanoclay layers in emulsion.¹⁷ Modified nanolayers of saponite have been employed in the miniemulsion polymerization of styrene by Tong and Deng and a reduction in the molecular weight and an increase in the polydispersity index of polystyrene chains were observed.¹⁸ Datta et al. reported the effect of nanoclay and its swelling time in monomer on the kinetics of atom transfer radical polymerization of butylacrylate.¹⁹ They found that molecular weight of

resulted polymer chains increased by increasing the clay content and its swelling time in monomer. According to their results, an interaction between the carboxylic groups of butylacrylate and the hydroxyl groups on nanoclay surface brings about such an acceleration rate. The grafting from method was employed by Behling et al. to graft polymer chains on clay layers.²⁰ They studied the effect of grafting density of ATRP initiator on the kinetics of polymerization and reported that the proximity of initiator groups attached to the clay layers and the transitional metal catalyst increase the probability of activating macroinitiators and thereby increasing the rate of polymerization. The effect of the addition of Cloisite 30B on the atom transfer radical polymerization kinetics of styrene has also been studied by this group; an increase in the polymerization rate and polydispersity index of polystyrene chains was reported.²¹ Salem and Shipp reported that grafted polystyrene chains obtained by “grafting through” RAFT polymerization and free polystyrene chains synthesized in the same condition are not so different in kinetics terms.²²

In the present research, we take the advantages of the ATRP method to study the differences in the kinetics of tethered and free chains using modified montmorillonite as a planar filler. The ATRP process was applied to the mixture of monomer and modified montmorillonite, which was ion-exchanged by a special chemical with the structure given in Scheme 2. In our well-tuned process, polystyrene chains were partially attached to the clay by a grafting-through process. Thus, a mixture of clay-attached and -free polystyrene chains was obtained. By now, there has been reported no study on the effect of clay confinement on the kinetics of styrene atom transfer radical polymerization. In some cases, the rate enhancement of nanoclay in the polymerization of free polymer chains has been reported¹⁹; conversely, in some other cases, the hindrance effect of nanoclay has been observed.²³ Thus, there are not any clear reports on the effect of nanoclay on the kinetics of ATRP. In this study, there is a combination of free and clay-attached polymer chains in the synthesized nanocomposite matrix. We have tried to



Scheme 2 Structure of nanoclay modifier used in this study.

solve the reported contradictions of nanoclay effect on the kinetics of ATRP by reporting the different effects of nanoclay on the propagation of clay-attached and free polymer chains.

The study on the effect of clay addition on the rate constant of propagation and termination reactions and consequently on the properties of the synthesized polymer is currently ongoing in our group. Monte Carlo simulation method is also utilized for the confirmation of our results.

EXPERIMENTAL

Materials

Styrene (Aldrich, 99%) was passed through an alumina-filled column, dried over calcium hydride, and distilled under reduced pressure (60°C, 40 mm Hg). Montmorillonite [Southern clay product, cation exchange value (CEC) of 92 meq/100 g] was stirred in de-ionized water for a day, and then was separated by centrifugation, filtered, dried, and finally stored in vacuum oven (50°C, 40 mm Hg). Copper(I) bromide (CuBr, Aldrich, 98%) was washed with glacial acetic acid, filtered, and finally washed with ethanol; it was dried in vacuum oven (50°C, 40 mm Hg) and then stored in a nitrogen atmosphere. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), ethyl α -bromoisobutyrate (EBiB, Aldrich, 97%), anisole (Aldrich, 99%), vinylbenzyltrimethylammonium chloride (Aldrich, 99%), xylene (Sigma-Aldrich, 99%), and neutral aluminum oxide (Aldrich) were used as received.

Preparation of organophilic montmorillonite

The quaternary alkyl ammonium cation with a double bound at the end of its backbone was employed as a pristine clay modifier. The amount of intercalating agent used for the cation-exchange reaction is as goes along²⁴:

$$\text{CEC value of clay per } 100 \text{ g} \times \text{clay content (g)} \times 1.2 \\ = (X/M_w) \times 1 \times 1000$$

where *X* represents the quantity of clay modifier in grams, *M_w* is the molecular weight of the intercalating agent, and the constant of 1.2 refers to using excess amount of intercalating agent. For all the preparations, a suspension of 4.5 g of Na-MMT with a CEC value of 92 mEq/100 g in 200 mL of distilled water was stirred in a round-bottom flask over 5 h. During the same time, in another flask, 1.05 g of intercalating agent and 200 mL ethanol were stirred for 5 h. The modifier solution in ethanol was added dropwise to the clay suspension. After the solution was stirred overnight, the white precipitated part

was filtered, washed with 80/20 (v/v) methanol/water mixture several times until no chloride ion could be detected by an AgNO₃ solution. The product dried in vacuum in 60°C overnight and the yield was 92%.

Preparation of polystyrene/modified montmorillonite nanocomposite

The ATRP polymerizations were performed in a 250 mL lab reactor, which was placed in an oil bath thermostated at the desired temperature. A number of batch polymerizations were run at 110°C in a solution medium and with the molar ratio of 140 : 1 : 1 : 1 for [St] : [EBiB] : [CuBr] : [PMDETA], giving a theoretical polymer molecular weight of 14,776 g mol⁻¹ at 100% conversion by including molecular weight of the initiator (195.05 g mol⁻¹). The reactor was degassed and back-filled with nitrogen gas three times, and then left under N₂. The batch experiments were run by adding deoxygenated monomer (styrene, 32.256 mL, 0.28 mol), modified montmorillonite, catalyst (CuBr, 0.287 g, 0.002 mol), ligand (PMDETA, 0.417 mL, 0.002 mol), xylene as a diluents (10 mL), and 0.5 mL of deoxygenated anisole as an internal standard to the reactor and then increasing the reaction temperature to 110°C (within about 15 min). The solution turned light green as the CuBr/PMDETA complex formed. Finally, after the majority of the metal complex had formed, initiator (EBiB, 0.293 mL, 0.002 mol) was added to the system to start the styrene ATRP. A sample was taken before the reaction started and used as a comparison reference for the samples later taken at the different stages of the reaction so as to measure the monomer conversion.

Separation of attached and unattached polymer chains

The polymer samples were dissolved in THF. By high-speed ultracentrifugation and then passing the solution through a 0.2 μ m filter, the unattached polymer chains were separated from the anchored ones after passing through the filter pores.²⁵ The tethered chains were cleaved from the layers by a reverse cation exchange procedure: Nanocomposite (2 g), 125 mL of THF/Methanol (4/1, v/v) solution, and LiBr (0.1 g) were refluxed in a 150 mL round-bottom flask equipped with a condenser and stirring bar for 6 h. The cleaved polystyrene samples were obtained after centrifugation. The solution was poured into methanol (500 mL) to precipitate the polymer chains.²⁶ The separated chains were also passed through a neutral aluminum oxide column to remove catalyst particles. Finally, the cleaved and free polymer chains were dried in a vacuum oven at 65°C.

TABLE I
Designation of the Samples

| Nanocomposite designation | Method of preparation | Proportion of clay (wt %) | The time of monomer and clay dispersion (h) | Nanoclay designation | Type of montmorillonite | Modifier content per gram of nanoclay (g) |
|---------------------------|-----------------------|---------------------------|---|----------------------|-------------------------|---|
| PS | ATRP | 0 | – | MMT | Pristine | 0 |
| PSNA240 | <i>In situ</i> ATRP | 2 | 40 | M-MMT0.5 | Modified | 0.115 |
| PSNA440 | <i>In situ</i> ATRP | 4 | 40 | M-MMT1 | Modified | 0.23 |
| PSNA840 | <i>In situ</i> ATRP | 8 | 40 | M-MMT1.5 | Modified | 0.345 |

Designation of the samples is based on the content of nanoclay and its dispersion time in the monomer prior to the polymerization. For instance, PSNA240 represents the sample with 2% of nanoclay and 40 h dispersion time.

The designation of the nanocomposites and various modes of their preparation along with the content of nanoclay and also various types of nanoclay with their modifier content are summarized in Table I.

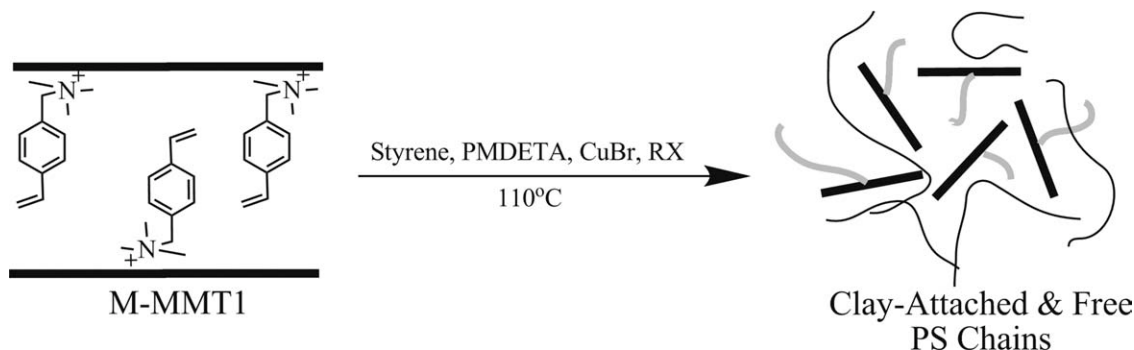
Gas chromatography (GC) is a simple and highly sensitive characterization method and does not require removal of the metal catalyst particles. GC was performed on an Agilent-6890N with a split/splitless injector and flame ionization detector (FID), using a 60 m HP-INNOWAX capillary column for the separation. The GC temperature profile included an initial steady heating at 60°C for 10 min and a 10°C/min ramp from 60 to 160°C. The samples were also diluted with acetone. The ratio of monomer to anisole at different stages of the reaction was measured by GC to calculate monomer conversion throughout the reaction. The average molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) technique. A Waters 2000 ALLIANCE with a set of three columns of pore sizes of 10000, 1000, and 500 Å was utilized to determine polymer average molecular weights and polydispersity index (PDI). THF was used as the eluent at a flow rate of 1.0 mL/min, and the calibration was carried out using low polydispersity polystyrene standards. For the GPC measurements, catalyst particles were removed by pass-

ing the polymer solutions through a neutral aluminum oxide column. The FTIR spectra were recorded on a Bomem FTIR spectrophotometer, within a range of 400–4400 cm^{-1} using a resolution of 4 cm^{-1} . An average of 32 scans has been reported for each sample. The cell path length was kept constant during all the experiments. The samples were prepared on a KBr pellet in vacuum desiccators under a pressure of 0.01 Torr. The transfer electron microscope, Philips EM 208, with an accelerating voltage of 200 kV was employed to study the morphology of the nanocomposites; the samples of 70 nm thickness were prepared by Reichert-ultramicrotome (type OMU 3).

RESULTS AND DISCUSSION

Intercalated nanoclay with an intercalating agent, which has a double bond, M-MMT1, was used in nanocomposite preparation through *in situ* atom transfer radical polymerization, as demonstrated in Scheme 3. This type of clay surface modifier is used to evaluate the confinement effect of nanoclay in the propagation of polymer chains during the polymerization. Additionally, this modifier makes the surface of nanoclay hydrophobe enough to easy diffusion of styrene molecules into the gallery of clay platelets. Also, because of the similarity in the molecular structure of the modifier and styrene molecules, modifier molecules make the clay platelets more compatible with the monomer molecules.

Figure 1 represents the kinetic plot for the polymerization of styrene in all the nanocomposites and



Scheme 3 Preparation of polystyrene nanocomposite.

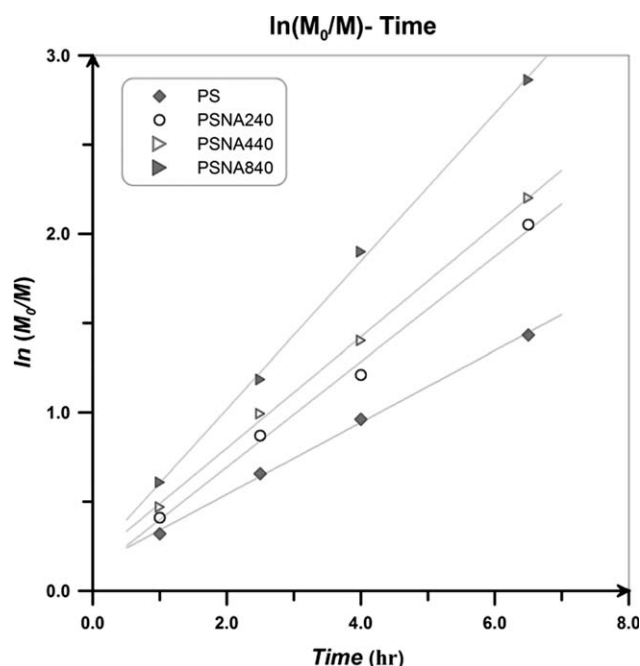


Figure 1 Kinetic plot with respect to the reaction time.

neat polystyrene. As it is clear, $\ln(M_0/M)$ increases linearly with reaction time, which states a constant radical concentration in the polymerization medium. Also, side reactions of chain termination are almost eliminated.⁷ According to the results, the rate of the polymerization increases with the addition of nanoclay. According to the results, the most remarkable rise in the rate of monomer conversion is seen in the PSNA840 polymerization. Consequently, the added nanolayer has a catalytic effect on the polymerization rate. This rate enhancement effect may be a consequence of the interaction between Al-OH groups of the nanoclay surface and the phenyl rings of styrene. Such an acceleration in the rate of polymerization with nanoclay loading was also observed in styrene *in situ* free radical polymerization^{16,27–29} and some other monomer (like butylacrylate) *in situ* atom transfer radical polymerizations.^{19,29} On the other hand, as demonstrated by Datta et al.,³⁰ in the case of surface-initiated polymerizations, in which the initiator is anchored to the clay layers, the polymerization rate reduction may occur. In such systems, the aggregated clay layers deactivate the initiator moieties trapped between the platelets. Consequently, a fall in the portion of species capable of initiating new chains causes a reduction in the rate of monomer consumption.

As previously mentioned, the slope of semilogarithmic plot is an indication of polymerization rate which can be derived from Eq. (1)³¹:

$$\ln(M_0/M) = \frac{k_p K_{\text{ATRP}} [P_n - X] [\text{Cu}^{\text{I}}]}{\text{Cu}^{\text{II}}} t = k_{\text{app}} t \quad (1)$$

where M_0 and M denote the monomer concentration at the beginning of the reaction and at the time t , respectively. K_{ATRP} , k_p , and k_{app} are ATRP equilibrium constant, propagation rate constant, and apparent rate constant, respectively. $[P_n - X]$, $[\text{Cu}^{\text{I}}]$, and $[\text{Cu}^{\text{II}}]$ stand for the concentration of dormant species, transition metal in the lower oxidation state, and transition metal in the higher oxidation state, respectively. In regard with the constant concentration of macro-radicals in ATRP ($10^{-8} \text{ mol L}^{-1}$), the k_{app} values of the neat polystyrene and its nanocomposites can be derived from the slope of semilogarithmic plots; the results are summarized in Table II. As interpreted from Table II, by increasing nanoclay loading, the value of k_{app} rises. The addition of 4 wt % nanoclay noticeably increases the polymerization rate. This considerable increment in the polymerization rate can be observed from a rise in the slope of the semilogarithmic kinetic plot and from an increase in the values of k_{app} of polymerization. This value increases by 12.3% for the PSNA440 sample in comparison with the neat polystyrene sample. The sample PSN840 experiences a considerable increment in the quantity of apparent polymerization rate in comparison with the reference sample, i.e., the neat polystyrene ($\sim 22.9\%$).

Figure 2 displays the polymer chain characterizations of the resultant samples in terms of number and weight average molecular weights and polydispersity indexes of free and attached polymer chains; the details derived from the GPC traces are also summarized in Table III. The GPC traces of all the samples display monomodal peaks corresponding to the molecular weight values predetermined by the molar ratio of monomer to initiator. There is a shoulder in the molecular weight distributions at high molecular weight tail, which is attributed to radical coupling.^{32,33} As it is clear, the more the clay content, the more intensified the mentioned peak. Such a deviation from the living feature of ATRP is on account of the acceleration effect of nanoclay on the rate of polymerization. Induction of polarity into the reaction medium by clay particles, to some extent, could also be a possible factor in increasing polymerization rate. Theoretical molecular weight is acquired from Eq. (2) using the experimentally obtained conversion data:

TABLE II
Variation of k_{app} as a Function of Clay Content

| Sample designation | k_{app} (10^{-5} s^{-1}) | Increase of apparent rate constant | |
|--------------------|---|------------------------------------|----------------------------|
| | | In respect to PS | In respect to prior sample |
| PS | 19.7 | — | — |
| PSNA240 | 27.2 | 7.5 | 7.5 |
| PSNA440 | 32.0 | 12.3 | 4.8 |
| PSNA840 | 42.6 | 22.9 | 10.6 |

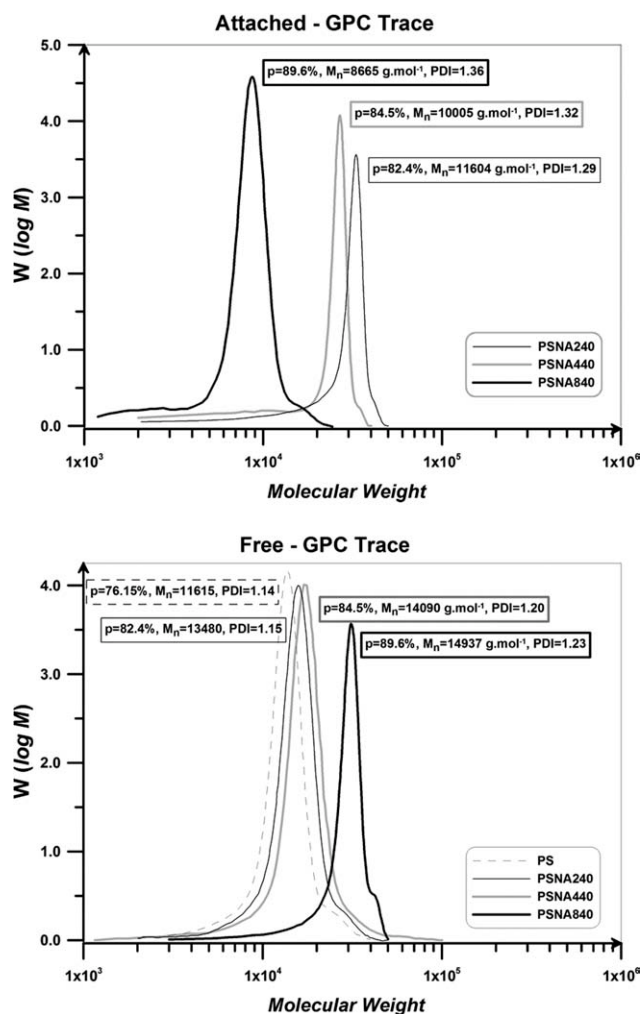


Figure 2 GPC traces of PS macroinitiator and nanocomposites prepared via ATRP.

$$M_n^{\text{Theo}} = \frac{[M]_0}{[I]_0} \times p \times M_0 \quad (2)$$

where $[M]_0$ and $[I]_0$ are the initial concentration of monomer and initiator, respectively. Conversion is denoted by p and the symbol for the molecular weight of monomer is M_0 , which in the case of styrene monomer is $104.15 \text{ g mol}^{-1}$.

As it can be seen in Table III, a good correlation is exhibited between the theoretical and experimental molecular weight of free polymer chains, which affirms the controlled nature of the polymerization system. However, the molecular weight of the extracted free polymer chains from the nanocomposite samples is a bit higher than the one calculated by theoretical relation presented by Eq. (2); this demonstrates that nanoclay exerts a rate increasing effect on the polymerization of free polystyrene chains. This effect is attributed to the partially polarizing effect of the nanoclay on the reaction medium and thereby its acceleration effect on the polymerization rate. As reported previously, polar solvents (especially hydroxyl containing ones like water, phenol, and carboxylic acids) exert a rate acceleration effect on the polymerization systems for rising radical activation rate and reducing radical recombination rate.^{10,11,34–36} Pendant hydroxyl groups and oxygen containing groups of clay layers could possibly cause a polarity change into the reaction medium. Additionally, from a recent research, it is evident that a negatively charged surface could absorb and gather positively charged catalyst (Cu ions at our work) and consequently enhances the chain growth rate.³⁷ The accelerating effect of nanoclay on polymerization rate was also reported in other works.^{19,29} The polydispersity index of polymer chains increases by the addition of nanoclay, as given in Table III. The addition of nanoclay, which acts as an impurity in the polymerization system, causes the molecular weight distribution of the resultant polymers to broaden; PDI increases from 1.14 to 1.23 by an 8 wt % loading of nanoclay. The number and weight average molecular weights of the clay-attached polystyrene chains are lower than that of the freely dispersed polystyrene chains. For instance, number average molecular weight of the free chains in PSNA440 is $14,090 \text{ g mol}^{-1}$, whereas a molecular weight of $10,005 \text{ g mol}^{-1}$ is obtained for the similar clay-attached chains. It is also evident that polydispersity index of the attached chains is higher in respect to the free polystyrene chains. The low inter-layer space of nanoclay layers restricts the diffusion of dormant species into the distance between

TABLE III
MWs and PDI of Resultant Polymer Samples Resulted from GPC Trace

| Sample designation | Reaction time (min) | Conversion (%) | M_n (g mol ⁻¹) | | | M_w (g mol ⁻¹) | | PDI | |
|--------------------|---------------------|----------------|------------------------------|-----------------|--------|------------------------------|-----------------|-----------------|-------------|
| | | | Exp. | | | Exp. | | Attached chains | Free chains |
| | | | Free chains | Attached chains | Theo. | Free chains | Attached chains | | |
| PS | 270 | 76.15 | – | 11,615 | 11,251 | – | 13,242 | – | 1.14 |
| PSNA240 | 270 | 82.4 | 11,604 | 13,480 | 12,175 | 14,969 | 15,502 | 1.29 | 1.15 |
| PSNA440 | 270 | 84.5 | 10,005 | 14,090 | 12,485 | 13,239 | 16,908 | 1.32 | 1.20 |
| PSNA840 | 270 | 89.6 | 8,665 | 14,937 | 13,239 | 11,784 | 18,373 | 1.36 | 1.23 |

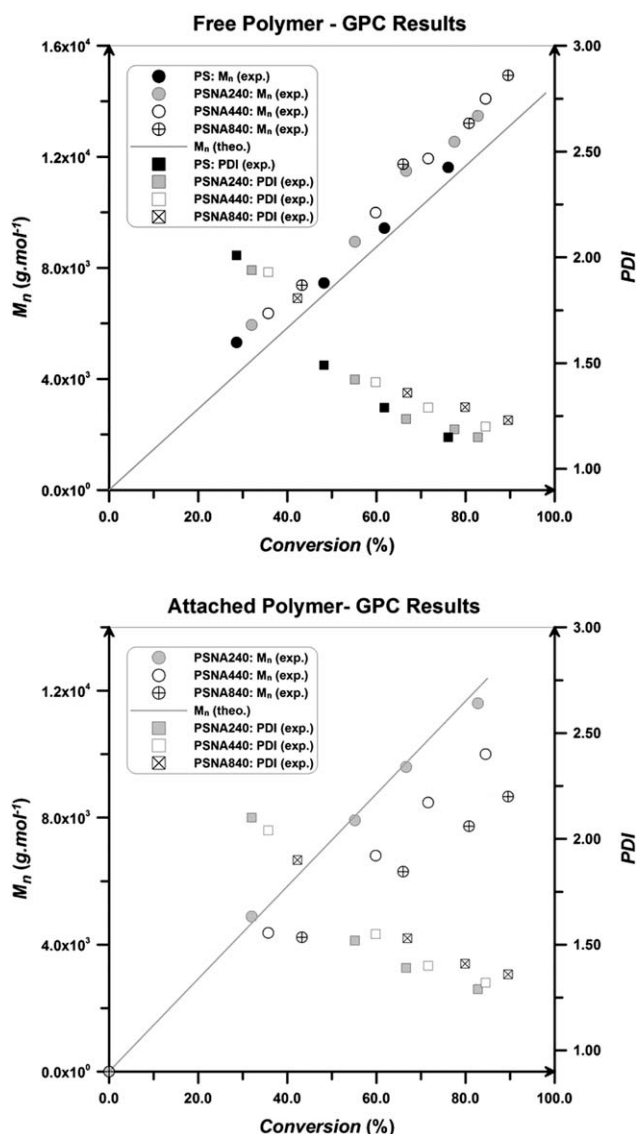


Figure 3 Molecular weights and polydispersity indexes of extracted polymer chains as a function of conversion.

nanolayers; consequently, mainly small molecules of alkyl halide can diffuse into and attach onto the clay layers. Thus, to propagate an attached polystyrene chain, it is necessary that monomer diffuse into the interlayer spacing. Because the diffusion of monomer into the mentioned confined region is a slow process, the molecular weight of polymer chains propagated from the clay layers would be lower than that of the unattached free polystyrene chains. The low activity of clay-attached polymer chains would be another reason to slow down the activation and thereby lowering the molecular weight of attached polymer chains. The high value of PDI of attached polymer chains can be ascribed to the competition of attached polymer chains for the absorption of monomer molecules, which can hardly diffuse into the interlayer spacing.²⁹ Additionally, nanoclay is an impurity in the polymerization me-

dium; hence, it causes the molecular weight distribution of extracted polymers to broaden. Also, cleaved PS chains still carry a quaternary ammonium unit, which tend to interact with the GPC column material, and thus in a decreased molecular weight and a broader apparent molecular weight distribution.²⁶ A large difference between the experimental and theoretical molecular weight of attached polymers demonstrates the confined propagation of polystyrene chains attached to clay layers for the hindrance effect of small interlayer spacing. Shorter chains are better able to diffuse between clay platelets; thus, there is an accumulation of short chains near the clay platelets and this can mainly affects the molecular weight of the attached chains.

The GPC results of the attached and free polymer chains extracted from PSNA240, PSNA440, and PSNA840 at different time intervals and monomer conversions are displayed in Figure 3. The molecular

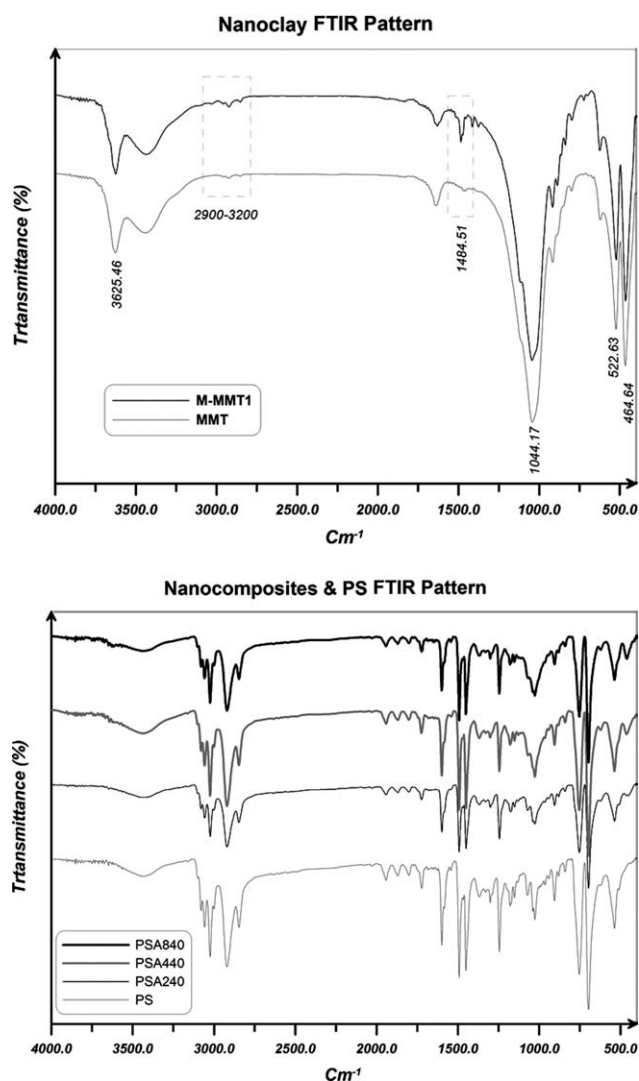


Figure 4 FTIR spectra of the neat polystyrene and prepared nanocomposites.

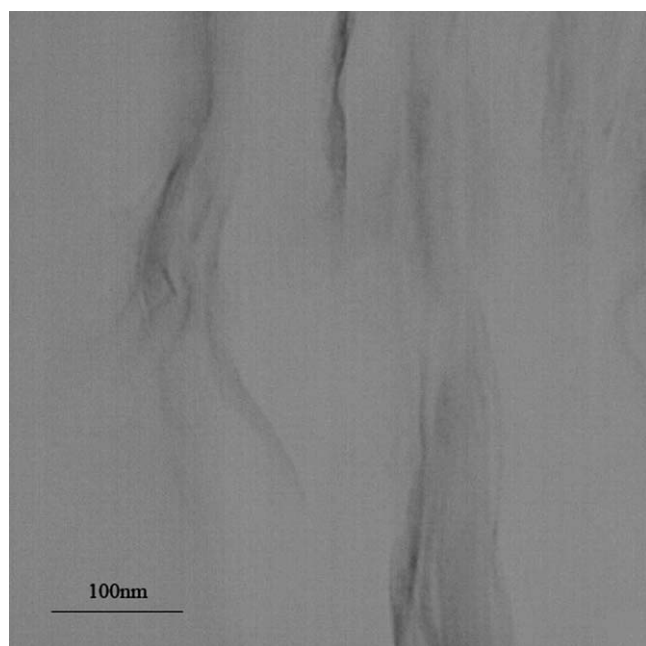


Figure 5 TEM Images of PSNA240.

weights increase linearly with monomer conversion, while polydispersity index drops as expected for controlled/living radical polymerizations. In the case of free polymer chains, the experimental results are in a good relation with the theoretical molecular weight, demonstrating a well-controlled polymerization. As the line graphs elaborate, the experimental number-average molecular weights of PSNA440 and PSNA840 further deviate from the theoretical prediction as compared with the M_n of the PSNA240 sample, which clarifies the effect of nanoclay on the polymerization kinetics. Samples with a higher molecular weight and broader molecular weight distribution are obtained by PSNA440 and PSNA840 rather than the PSNA240 at similar time intervals during the reaction. All the samples experience narrow molecular weight distributions and polydispersity index decreases as the reaction proceeds, which is attributed to the higher homogeneity of the chain length of polymers. As previously mentioned, the attached polymer chains have smaller molecular weights and larger polydispersity index in comparison with the free polymer chains and by adding clay content, the concentration of modifier double bond is increased which can be resulted in higher portion of attached chains and higher molecular weight free chains at the end of the reaction.

The IR spectra of M-MMT1 presented in Figure 4(A) reveals that some wavelengths of characteristic bonds are varied in comparison with the neat montmorillonite. This shows that the replacement of modifier molecules with sodium ions between the clay layers is carried out successfully. The spectra of M-MMT1 shows a characteristic bond of 1484.51

cm^{-1} which is attributed to the C=C bond of modifier in the interlayer spacing of the modified nanoclay.

IR spectra of the neat polystyrene and its nanocomposites were studied to evaluate the interaction between the nanoclay and the polymer matrix [Fig. 4(B)]. Through this, the affirmation of nanoclay effect on the polymerization kinetics could also be investigated. The spectrum of nanoclay shows a characteristic bond of 3625 cm^{-1} which, in the clay-dispersed nanocomposites, is shifted to higher wave numbers around 3630 cm^{-1} ; this indicates the interaction of phenyl groups of the polystyrene with the hydroxyl groups of nanoclay. This interaction in the case of ATRP reactions causes a catalytic effect on the polymerization rate. Additionally, the characteristic wave number of Al—O bond in M-MMT1, 464 cm^{-1} , shifts to smaller values in the nanocomposite samples ($\sim 457 \text{ cm}^{-1}$); this is also a consequence of nanoclay and phenyl group interaction that could possibly have a positive effect on the polymerization rate. It is worth to mention that residual water in the clay, characteristic bond at 3420 cm^{-1} , could also increase the polymerization rate.¹¹ A characteristic bond is also seen at the wave number of 757 cm^{-1} corresponding to C—Br bond. Therefore, the chain end functionality of polystyrene synthesized via ATRP could be easily demonstrated by FTIR technique. As a result of the mentioned functionality of polystyrene chains, synthesis of block, star, and graft copolymers could be possible too. The characteristic wave number of the peaks of nanoclay increase in the nanocomposite samples by increasing the clay loading, as interpreted from the spectra.

TEM image displayed in Figure 5 is used to investigate the clay platelets delamination and dispersion in the matrix of the polystyrene nanocomposites. The TEM results show the exfoliation of clay layers in the polymer matrix of the polystyrene nanocomposite with 2 wt % of nanoclay (PSNA240). The exfoliated clay platelets are specified by the tactoids in the TEM image.

CONCLUSIONS

To study the confinement effect of nanoclay platelets on the kinetics of atom transfer radical polymerization, polystyrene, and its nanocomposites with different clay loadings were synthesized by ATRP. The controlled nature of ATRP made it easy to synthesize tailor-made nanocomposites with a predictable degree of polymerization. $\ln(M_0/M)$ increases linearly with reaction time in *in situ* ATRP systems. By adding nanoclay, the value of k_{app} and thereby the polymerization rate rises. The GPC trace of all the samples displays a monomodal peak. There is a shoulder in GPC trace, which is attributed to radical

coupling. Intensity of the shoulder is more intensified by the addition of clay content. There is a good correlation between the theoretical and experimental molecular weight of free polymer chains, which affirms the controlled nature of the polymerization system. However, nanoclay exerts an accelerating effect on the polymerization of free polystyrene chains. The polydispersity index of polymer chains increases by the addition of nanoclay. The number and weight average molecular weights of the clay-attached polystyrene chains are lower than that of the freely dispersed polystyrene chains. The polydispersity index of the attached chains is larger in respect to the free polystyrene chains. The IR spectrum of M-MMT1 shows a characteristic bond of 1484.51 cm^{-1} which is attributed to the C=C bond of modifier in the interlayer spacing of modified nanoclay. The spectrum of nanoclay shows some characteristic bonds which are shifted to different wave numbers in the clay-dispersed nanocomposites; this indicates the interaction of phenyl groups of the polystyrene with the hydroxyl groups of nanoclay and could possibly have a positive effect on the polymerization rate. The chain end functionality of polystyrene synthesized via ATRP could also be easily demonstrated by FTIR technique. TEM results show the exfoliation of the clay layers in the polymer matrix of polystyrene nanocomposite containing the lowest amount of nanoclay (PSNA240).

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