Exfoliated Poly (styrene-*co*-methylstyrene) Grafted-Polyaniline/Layered Double Hydroxide Nanocomposite Synthesized by Solvent Blending Method

Mojtaba Abbasian

Laboratory of Polymer, Faculty of Chemistry, Payame Noor University, Tabriz, Iran

ABSTRACT: Well defined poly (styrene-*co*-methylstyrene) grafted polyaniline/organo-modified MgAl layered double hydroxide (LDH) was produced through solution intercalation method. After LDH nanoparticles were modified by the anion exchange reaction of MgAl (Cl) LDH with sodium dodecyl benzene sulfonate, Poly (styrene-*co*-methylstyrene) copolymers were synthesized by "living" free radical polymerization and then brominated with *N*-bromosuccinimide. Afterwards, 1,4-phenylenediamine was linked to brominated copolymers and prepared functionalized copolymer with amine. Poly (St-*co*-MSt)-*g*-PANI, has been synthesized by adding solution of ammonium persulfate and *p*-toluenesufonic acid in DMSO solvent. Finally, Poly (styrene-*co*-methylstyrene) *grafted*-Polyaniline/LDH nanocomposites were prepared by solution intercalation method. Characterization of these well-defined nanocomposites included FT-IR, gel permeation chromatography, thermogravimetric analysis, differential scanning calorimeter, transmission electron microscopy, and X-ray diffraction. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2573–2582, 2011

Key words: graft copolymer; poly (styrene-*co*-methylstyrene); poly aniline; LFRP; LDH; nanocomposite

INTRODUCTION

Polyaniline (PANI) is unique among conducting polymers in that its electrical properties could be reversibly controlled both by charge transfer doping and by protonation, which makes it a potential material for applications as chemical and biological sensors, actuators, microelectronic devices, etc.[1,2] However, the insolubility in common solvent, low processability and poor mechanical properties of PANI has obstructed its potential applications. To fulfill the industrial demand, several strategies have been developed to overcome such problems. For instance, the preparation of conventional thermoplastic-electroconductive polymer composites is a successful approach to achieve unique properties and applications of the resultant materials.[3,4] The development of PANI/metal nanoparticle composite with synergistic chemical and physical properties has received great attention world wide from both academic and industrial point of view.[5] It was reported that the nanoparticles themselves could act as conductive junctions between the PANI chains that resulted in an increase of the electrical conductance of the composites.[6] The electrical conductivity of such composites might also depend upon the molecular structure of the conductive polymer matrix (i.e., crystallinity). In recent years, there has been considerable interest in polymer/layered inorganic hybrids as nanocomposites due to their novel mechanical, thermal, optical, and physicochemical properties, which are rarely present in the pure polymer or conventional (microscale) composites.[7] The layered inorganic materials mainly include silicate clay minerals, manganese oxides, molybdenum sulfide, titanates, layered phosphates, and layered double hydroxides (LDHs). The LDH systems have much less studied because of the strong interlayer electrostatic interactions, small gallery space, and hydrophilic property of LDH.[8] LDHs have stronger interactions between the layers than silicates due to the higher charge density in the crystal structures, which hinders the exfoliation of the LDH nanolayers and the intercalation of the polymer chains.[9] Accordingly, the intercalation of LDHs involves the organic modification of the LDHs to expand the basal spacing and/or inorganic modification of the polymers to graft anions onto the polymers or monomers.

Polymer grafting reactions onto silicate clay minerals have been studied extensively to tailor the surface properties for desired applications,[10] such as chiral separation,[11] and protein adsorption.[12] At the

same time, great progress has been made in controlled/living free radical polymerizations in the past few decades, such as living free radical nitroxide-mediated polymerization (NMP),[13–15] atom transfer radical polymerization (ATRP)[16–18] and reversible addition-fragmentation chain transfer (RAFT)[19] process. Several publications describe ways to functionalize the solid surfaces with well-defined polymers with controlled molecular weight and narrow polydispersity. Using ATRP technique, El Harrak et al.[20] performed the graft polymerization of styrene onto silica beads in dimethylacetamide, Zhang et al.[21] reported that surface-initiated ATRP of methyl methacrylate and 2-hydroxyethyl methacrylate was carried out separately on spherical silica gel at ambient temperature, and Fu et al.[22] prepared conductive hollow nanospheres of poly(4-vinylaniline *graft*-polyaniline) via surface-initiated ATRP of 4-vinylaniline and oxidative graft copolymerization of aniline.

Conducting polymers, namely polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), and others, are promising materials for practical application because of their high electrical conductivity and environmental stability. Attempts have been made to intercalate these conducting polymers into clay layers with the goal of forming hybrid materials with good electrical conductivity for new applications.

In this work, we report a facile approach for the preparation of Exfoliated Poly (styrene-co-methylstyrene) grafted- Polyaniline/LDH nanocomposite by solvent blending and living free radical polymerization methods. First, Poly styrene-copolymer-Polymethyl styrene [poly (St-co-MSt)] was synthesized via nitroxide mediated living radical polymerization (NMRP) technique and then *N*-bromosuccinimide (NBS) was used as a brominating agent to obtain of copolymer with bromine. Then 1,4-phenylenediamine was linked to brominated poly (St-co-MSt) and a functionalized copolymer poly (St-co-MSt)-NH₂ was prepared. Poly (St-co-MSt)-g-PANI, has been synthesized by adding solution of ammonium persulfate and *p*-toluenesufonic acid (tosic acid) in DMSO solvent. The poly (St-co-MSt)-g-PANI/MgAl-LDH nanocomposite prepared by solution intercalation method in Xylene as a solvent.

EXPERIMENTAL

Materials

Styrene and Methylstyrene purchased from Merck and distilled under a reduced pressure before used. NBS was purchased from Merck (Frankfurt, Germany) a purified by recrystallization in water at 70°C. From Aldrich, 2,2′-Azo bis isobutyronitrile

(AIBN) was purchased and recrystallized in ethanol at 50°C. TEMPO (2, 2, 6, 6-tetramethylpiperidinyloxy) was prepared by the method reported from our research group previously.[13–15] Aniline (Merck) was dried with NaOH and fractionally distillated under reduced pressure sodium or CaH₂. Ammonium persulfate (APS) (Merck) was recrystallized at room temperature from EtOH/water. MgCl₂.6H₂O, AlCl₃.6H₂O, NaOH, and sodium dodecyl benzene sulfate (SDBS) were supplied by Merck and used without further purification. All other reagents were purified according to the literature.

Instrumentation

FT-IR spectra were recorded using Shimadzu FT-IR-8101*M*. The samples were prepared by grinding the dry powders with KBr and compressing the mixture to form disks. The disks were stored in a desicator to avoid moisture absorption. Spectra were recorded at room temperature. ¹H-NMR spectra were recorded on FT-NMR (400 MHz) Brucker in CDCl₃. The molecular weight of polymer was obtained with a maxima 820 GPC analysis instrument using polystyrene (10^6, 10^5, 10^4 A⁰) calibration standard with a THF mobile phase at a flow rate of 1 mL/min and column temperature at 30°C. The thermal properties of (PSt-co-PMSt), (PSt-co-PMSt)-g-PANI, and (PSt-co-PMSt)-g-PANI/LDH nanocomposite measurement were performed with a thermogravimetric analysis, TGA-PL (England). Sample of about 10 mg were heated from 25–600°C at rate of 10°C min⁻¹ under nitrogen flow. Differential Scanning Calorimeter (DSC) analyses were carried out using a NETZSCH (Germany)—200 F3 Maia DSC. The sample was first heated to 200°C and kept for 5 min to eliminate the heat history. The sample was then cooled down at a rate of 10°C/min. The sample was then reheated to 200°C at a rate of 10°C/min. The entire test was performed under nitrogen purging at rate of 50 mL min⁻¹. XRD spectra were obtained using a Siemens D 5000, X-ray generator (CuK$_\alpha$ radiation with $\lambda = 1.5406$ E) with a 2θ scan range of 2–80° at room temperature. The dispersion state and layered structure of the LDH were observed by using a VEGA//TESCAN, KX5000 Scan electron microscopy (SEM).

Synthesis of poly (St-*co*-MSt) via NMRP

Ten milliliter of styrene and methyl styrene monomers (50/50 v/v), 0.15 g (0.6 mmol) benzyl peroxide and 0.14 g (90 mmol L⁻¹) TEMPO was placed in ampoule degassed with several freeze-pump-thaw cycles, and sealed off under vacuum and placed in an oil bath at 95°C for 4 h. Then temperature increased to 130°C for another 12 h. The products were diluted with THF and the copolymer was
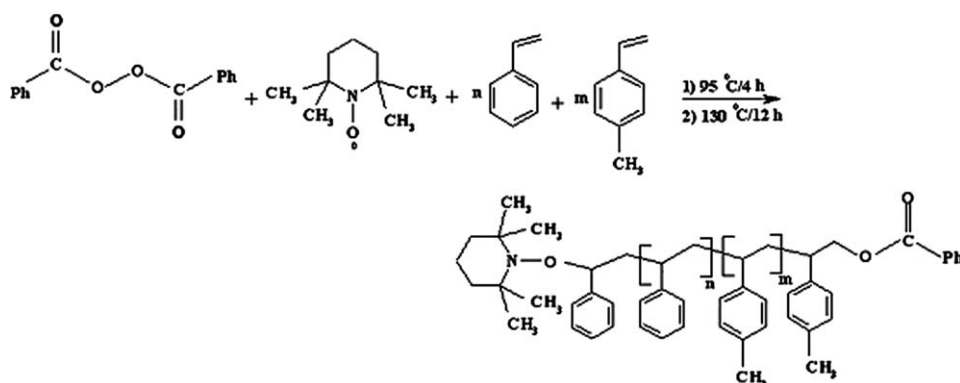
Scheme 1 Synthesis of poly (St-*co*-MSt) via NMRP.

recovered by filtration in ice methanol. This product was dried overnight in vacuum at room temperature (Scheme 1).

Synthesis of poly (St-*co*-MSt)-Br

The bromination reactions were carried out in ground-glass stoppered flasks fitted with dropping funnel and a reflux condenser. Thirty-four millimol of NBS and 21 mmol AIBN was dissolved in 10 mL dried CCl_4 and were added under argon to a stirred solution CCl_4 (30 mL) of poly (styrene-*co*-methyl styrene) (0.3 g). The mixture was stirred for 2 h at 70 temperatures and then precipitated into ice methanol. The resulting product was dissolved in THF, re-precipitated into methanol, washed with methanol, and finally dried overnight under vacuum (Scheme 2). Yield: 0.35 g (white powder). FT-IR (KBr, Cm^{-1}): 3075 (aromatic protons of toluene), 1608 (—C—C— aromatic protons), 1476 (—CH_3 of methyl styrene). ^{1}H-NMR ($CDCl_3$, ppm): 7.55–7.70 (aromatic protons), 4.15–4.25 ppm (—CH_2Br protons of methyl styrene).
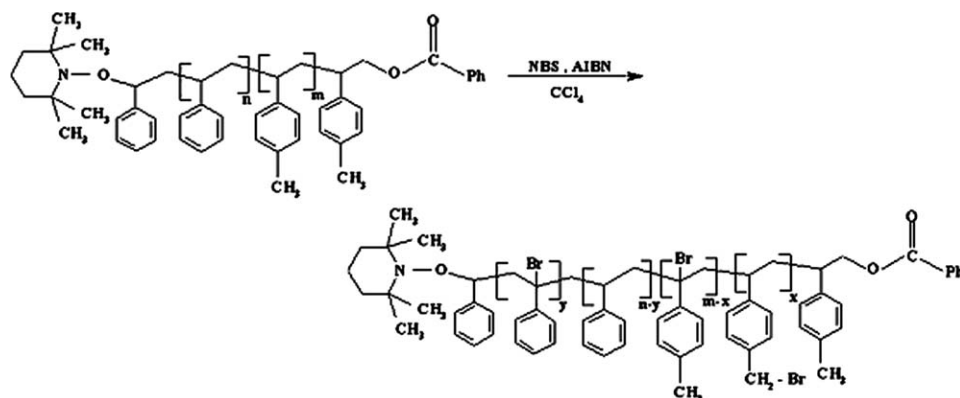
Synthesis of poly (St-*co*-MSt)-NH2

One gram of (0.01 mol) 1,4-phenylendiamine, 2 g anhydrous pulverized sodium carbonate, and 2 mL

pyridine were added to a 50 mL solution (DMF/CH_2Cl_2; 50/50 v/v) of 2 g poly (St-*co*-MSt)-Br in a 250 mL round-bottomed flask with a magnetic stirring bar. After refluxing at 75°C for 4 h, the reaction mixture was filtered and precipitated into ice methanol, and the product was washed with methanol and dried under vacuum in over night (Scheme 3).Yield: 2.5 g (white powder). FT-IR (KBr, Cm^{-1}): 3075 (aromatic protons of styrene), 1608 (—C—C— aromatic protons), 1476 (—CH_3 of methyl styrene), 3447 cm^{-1} and 1647 cm^{-1} (*N*—H stretching and bending vibration).

Preparation of poly (St-*co*-MSt)-*g*-polyaniline

Poly (St-*co*-MSt)-NH_2 (0.5 g) was completely dissolved in 30 mL DMSO. One gram of aniline (10 mmol) and 0.5 g (3 mmol) *p*-toluensufonic acid were added to the solution, and the mixture was vigorously stirred and temperature was reduced to 5°C. In a separate container, 2 g (8.77 mmol) $(NH_4)_2S_2O_8$ (ammonium peroxy disulfate) was dissolved in 10 mL tosic acid solution. The oxidant solution was slowly added at a rate of 5 mL/min to the mixture. The mixture was stirred for about 4 h, the polymer solution filtered into ice methanol. Then the product was washed successively by distilled water and

Scheme 2 Synthesis of poly (St-*co*-MSt)-Br.
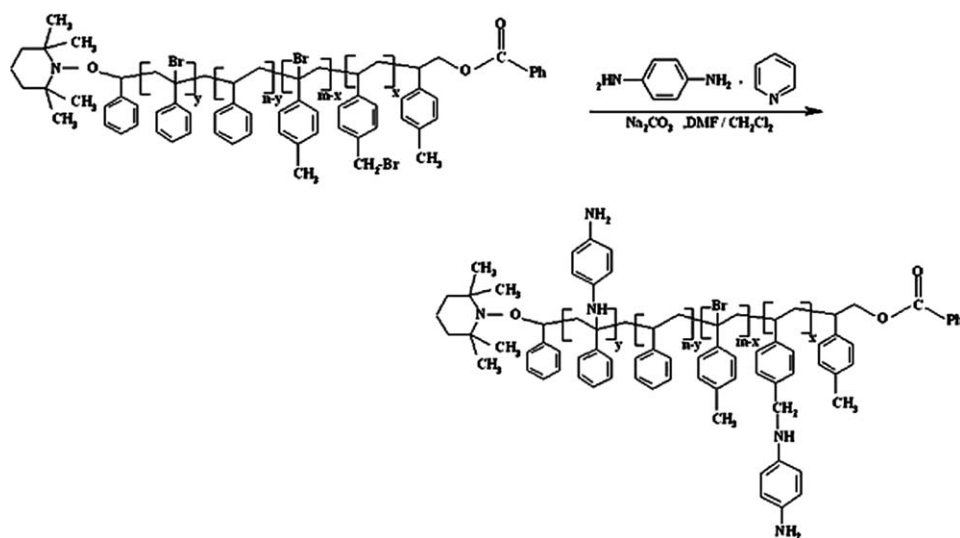
Scheme 3 Synthesis of poly (St-*co*-MSt)-NH$_2$.

methanol and dried at 50°C for 24 h. The precipitate was filtered, added to Toluene solvent to remove the Polyaniline from poly (styrene-*co*-methylstyrene)-*g*-polyaniline. Polyaniline is not soluble in toluene. The polymer solution was filtered into ice methanol and dried. The crude product was added to cyclohexane, and refluxed to remove the residual amount of ungrafted polymer (Scheme 4).
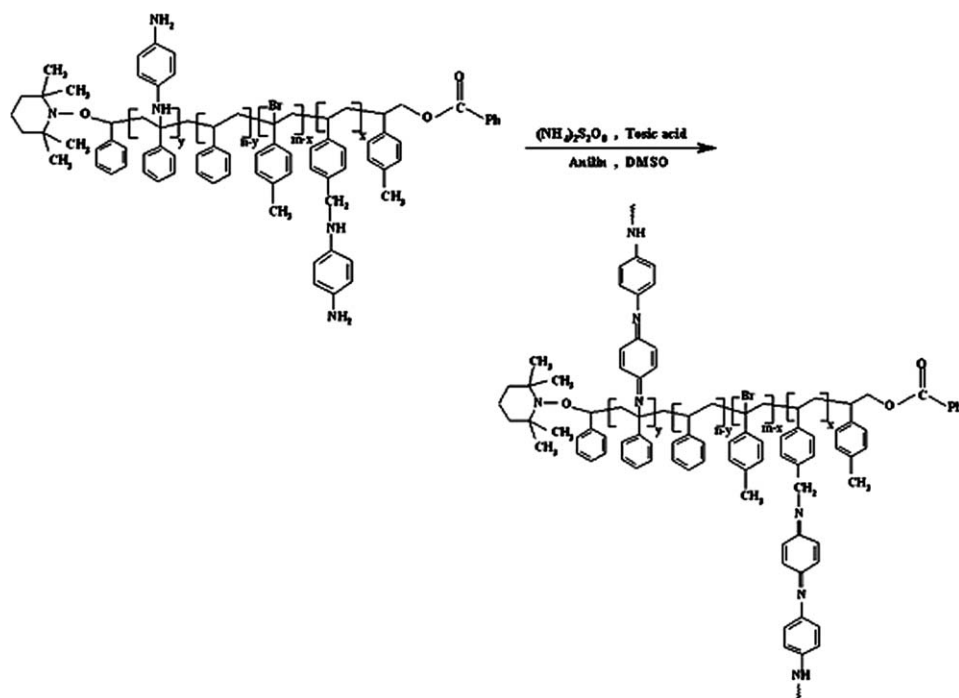
Preparation of Mg Al (Cl)

A mixed solution (3 : 1) of magnesium chloride (0.75M) and aluminum chloride (0.25M) was slowly

pumped into 150 mL decarbonated water under flowing N$_2$ with vigorous stirring at a constant pH of 8.0 ± 0.2 adjusted by simultaneous drop-wise addition of 0.5M NaOH solution. The resulting gels were treated in a microwave irradiation for 8 h operating at 2.45 GHz. Maximum power was 600W. The solids were recovered by decantation and washed several times with distilled water and filtration.

Preparation of surfactant-modified MgAl-LDH

The surfactant- modified MgAl-LDH was obtained by the anion exchange reaction of 1.0 g MgAl (Cl)

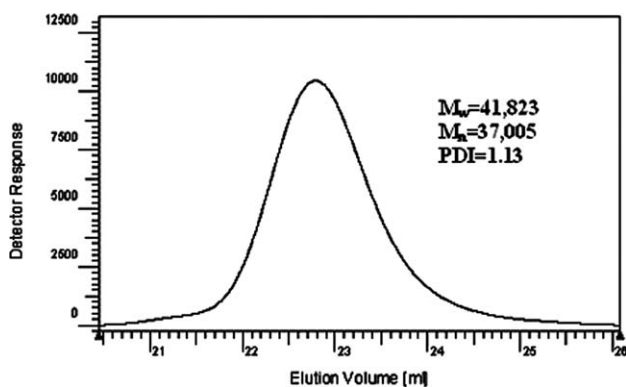**Scheme 4** Preparation of poly (styrene-*co*-methylstyrene)-*g*-polyaniline.

Figure 1 GPC chromatogram of the poly (styrene-*co*-methylstyrene).

with 100 mL 0.1M SDBS at 60°C. For this aim, 1.0 g MgAl (Cl) was dispersed into 150 mL decarbonated water by ultrasonic vibration for 20 min. Then 100 mL (0.1M) SDBS was slowly pumped into suspension, then the obtained slurry was stirred vigorously with a magnetic pellet for 24 h at 60°C. After this time, the solids were recovered by decantation and washed several times with distilled water and filtration.

Preparation of poly (St-*co*-MSt)-*g*-PANI/LDH nanocomposite

The poly (St-*co*-MSt)-*g*-PANI/MgAl LDH nanocomposite was prepared by the solution intercalation method. A desired amount (0.05 g) of MgAl (SDBS) was first refluxed in 100 mL Xylene for 24 h under flowing N$_2$. Then 1.0 g poly (St-*co*-MSt)-*g*-PANI was added into the MgAl (SDBS) suspension. After stirring for 3 h at 70°C, the mixture was poured into large amount of ice methanol for rapid precipitation. The precipitate was filtered and dried at 60°C under vacuum for 2 days.

RESULTS AND DISCUSSION

Synthesis of poly (St-*co*-MSt) by living polymerization

Living polymerization is characterized by a linear increase of the molecular weight with conversion and reaction time, and a narrow molecular weight distribution as evidenced by a polydispersity index (PDI = M_w/M_n) approaching 1.[23] Figure 1 represents the GPC chromatogram of the copolymer whose molecular weight distribution measured by GPC is 1.13. The single peak of the GPC chromatogram of the product indicated that the product could not be the blend of poly styrene (PSt) homopolymer and PMSt homopolymer; if so, the GPC chromatogram should appear as two peaks, one for the PSt homopolymer and the other for the PMSt homopolymer.

Synthesis of poly (St-*co*-MSt)-Br

The GPC trace of the poly (St-*co*-MSt) and poly (St-*co*-MSt)-Br (M_n = 37,567; M_w = 45,456; PDI = 1.21) was unimodal and showed no tailing or broadening of molecular-weight distribution, thus confirming that no crosslinking or chain scission occurred during the bromination procedures. Figure 2 shows the FT-IR spectra of the poly (styrene-*co*-methyl styrene) and brominated copolymer. The FT-IR spectra of poly (St-*co*-MSt) shows the characteristic absorption bands due to stretching vibration of C—H (3100–2850 cm^{-1}), weak aromatic overtone and combination bands in the 2100–1670 cm^{-1} region, C=C stretching vibrations (1606 and 1485 cm^{-1}), —CH$_2$ bending vibrations (1445–1372 cm^{-1}), and γ(C—H) in the aromatic ring (768 and 709 cm^{-1}). Figure 2(b) exhibit additional absorption band at 557 cm^{-1} attributed to C—Br group.

The ^{1}H-NMR of poly (St-*co*-MSt) and poly (St-*co*-MSt)-Br obtained by bromination of copolymer are shown in Figure 3. The ^{1}H-NMR spectra of poly (St-*co*-MSt) shows the resonance at about 2.28, 1.86, and 1.43 ppm are assigned to the —CH$_3$, —CH, and —CH$_2$ unite in copolymer respectively, and resonances at about 6.13–7.38 ppm are assigned to aromatic protons [Fig. 3(a)]. After bromination, the ^{1}H-NMR spectra shows the resonances at about 4.14–4.57 ppm assigned to the —CH$_2$Br group in brominated copolymer [Fig. 3(b)].

To calculate the extent of bromination for poly (St-*co*-MSt) of a particular extent of bromination the following method was adopted. Let poly (St-*co*-MSt)$_m$-[poly (St-*co*-MSt)-Br]$_n$ represent the brominated poly
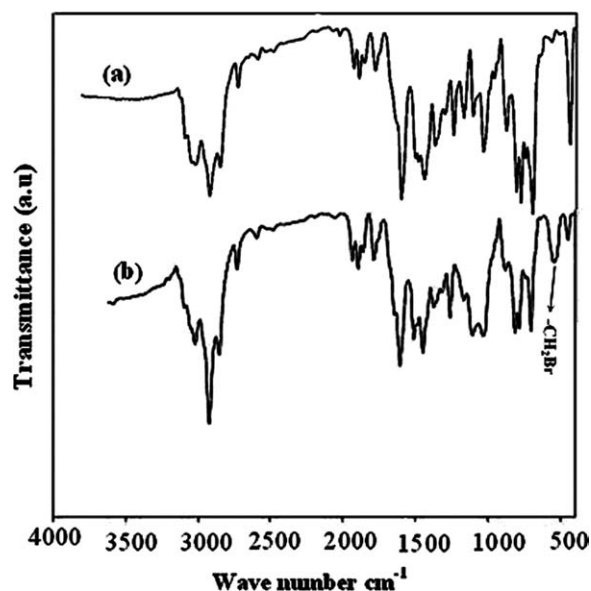

Figure 2 FT-IR spectra of poly (St-*co*-MSt) (a) and poly (St-*co*-MSt)-Br (b).

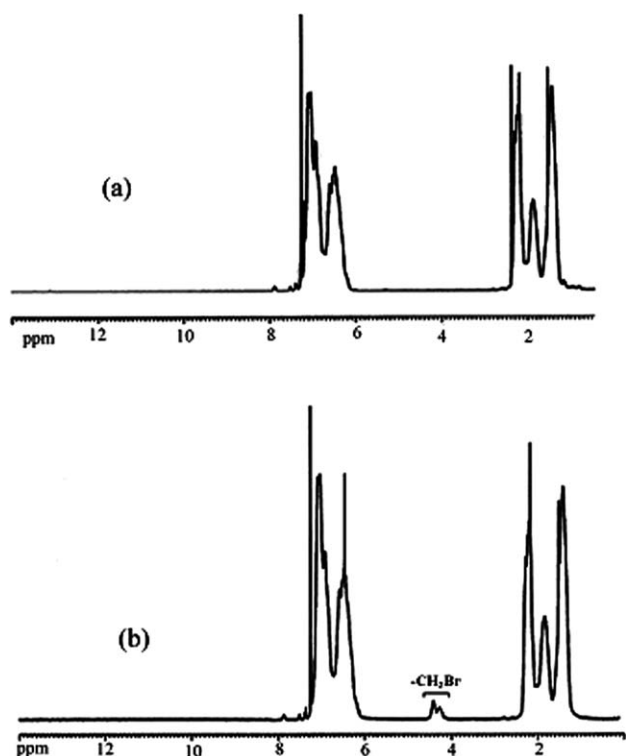**Figure 3** ^{1}H-NMR spectras of poly (St-co-MSt) (a) and poly (St-co-MSt)-Br (b).

styrene-methylstyrene copolymer. The mol % bromination is given by $n/(m + n) \times 100$. The area under the aliphatic region is given by $9n + 5m$ and the area under the aromatic region is given by $9n + 9m$. In Figure 3 solving the simultaneous equation with the integrated areas, it can be seen that $9n + 5m = 145.73$ and $9n + 9m = 154.1$ and therefore $n = 2$ and $m = 15.11$. Therefore the extent of bromination is $2/17.11 \times 100 = 11.68\%$.

Synthesis of poly (St-co-MSt)-NH$_2$

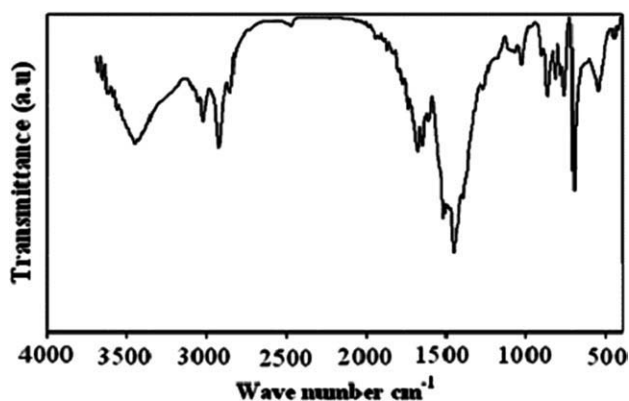Figure 4 shows the FT-IR spectra of the functionalized poly (styrene-co-methyl styrene) copolymer

Figure 4 FT-IR spectra of the poly (St-co-MSt)-NH$_2$.

TABLE I
Compositions of the (PSt-co-PMSt)-g-PANI Copolymers

| Polymer | Compositions | | |
	C%	H%	N%
polyaniline	76.1	4.6	14.2
(PSt-co-PMSt)-g-PANI	61.0	4.7	34.3
	Degree of grafting = 33/24%		

[poly (St-co-MSt)-NH$_2$]. The FT-IR spectra shows the absorption band at 2852–2923 Cm^{-1} and 3025 Cm^{-1} is attributed to ─CH aliphatic and aromatic stretching bond respectively. The stretching band around 1025 cm^{-1} is due to the C─N and the bands at 3447 cm^{-1} and 1647 cm^{-1} are attributed to N─H stretching and bending vibration, respectively.

Preparation of poly (St-co-MSt)-g-PANI

The elemental analysis was carried out to know about the composition of the copolymers with various elements such as C, H, and N present in the polymer matrix. Table I shows the compositions of the poly (St-co-MSt)-g-PANI. As shown in Table I, the degree of grafting is 33/24%.

Figure 5 shows the FT-IR spectra of the PANI (a) and poly (St-co-MSt)-g-PANI (b). The FT-IR spectra of PANI shows the C=N in the quinoidal units which appears at 1585 cm^{-1}, the benzenoid stretches at 1485 cm^{-1}, and the N-H stretches at 3470 cm^{-1}.

The FT-IR spectra of poly (St-co-MSt)-g-PANI shows characteristic absorption band of polyaniline, the C=N in the quinoidal units which appears at
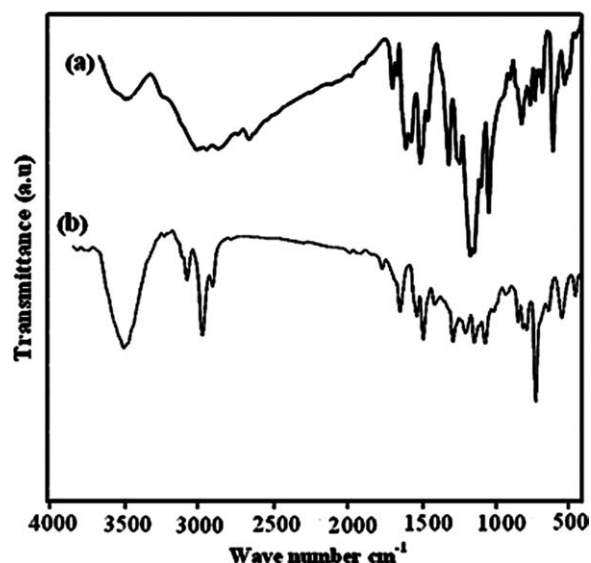

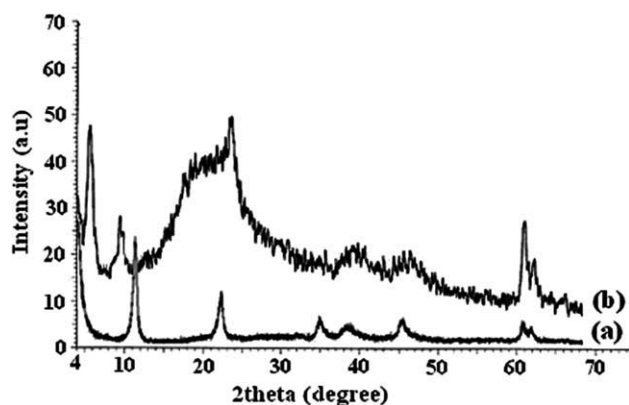**Figure 5** FT-IR spectra of the PANI (a) and poly (St-co-MSt)-g-PANI (b).

Figure 6 XRD patterns of Mg Al (Cl) (a) and MgAl (SDBS) (b).

1601 cm^{-1}, the benzenoid stretching band at 1498 cm^{-1}, the N—H stretches at 3512 cm^{-1}, and the aromatic C—H stretches at 3123 cm^{-1} were observed. The absorption peak at 1153 cm^{-1} is characteristic of electron-like absorption of the N = Q = N vibration (where Q denotes the quinoid ring) and characteristic peaks at 2921 and 2853 cm^{-1}, are attributed to aliphatic C—H stretching's.

Characterization of Mg Al (Cl) and surfactant-modified MgAl (Sdbs)

The XRD patterns of MgAl (Cl) and surfactant-modified MgAl (SDBS) are shown in Figure 6. The XRD pattern of Mg Al (Cl) [Fig. 6(a)] can be indexed in a hexagonal lattice with an *R*-3m rhombohedral symmetry, commonly used for the description of the LDH structure. Refined cell parameters are $a = 3.048$ A° ($= 2 \times d_{110}$) and $c = 23.41$ A° ($= 3 \times d_{003}$). The basal spacing of MgAl (Cl) sample is 0.78 nm. The average crystallite size D, calculated using the Debye-Sherrer formula $D = K\lambda/(\beta\cos\theta)$ was roughly about 21 nm. The basal spacing of MgAl (SDBS) sample increases to 1.92 nm from 0.78 nm of the MgAl (Cl) sample after the Cl^{-} ion in the MgAl (Cl) sample exchanged by SDBS, which indicates that the SDBS anions have been intercalated in the MgAl-LDH layers.

The morphologies of MgAl (Cl) and MgAl (SDBS) are show in Figure 7. The SEM images of MgAl (Cl) (a_1, a_2) show sheet like structures for nanoparticles. This will give small surface area. The morphologies of MgAl (SDBS) (b_1, b_2) showed homogenously distributed particles giving a relatively large surface
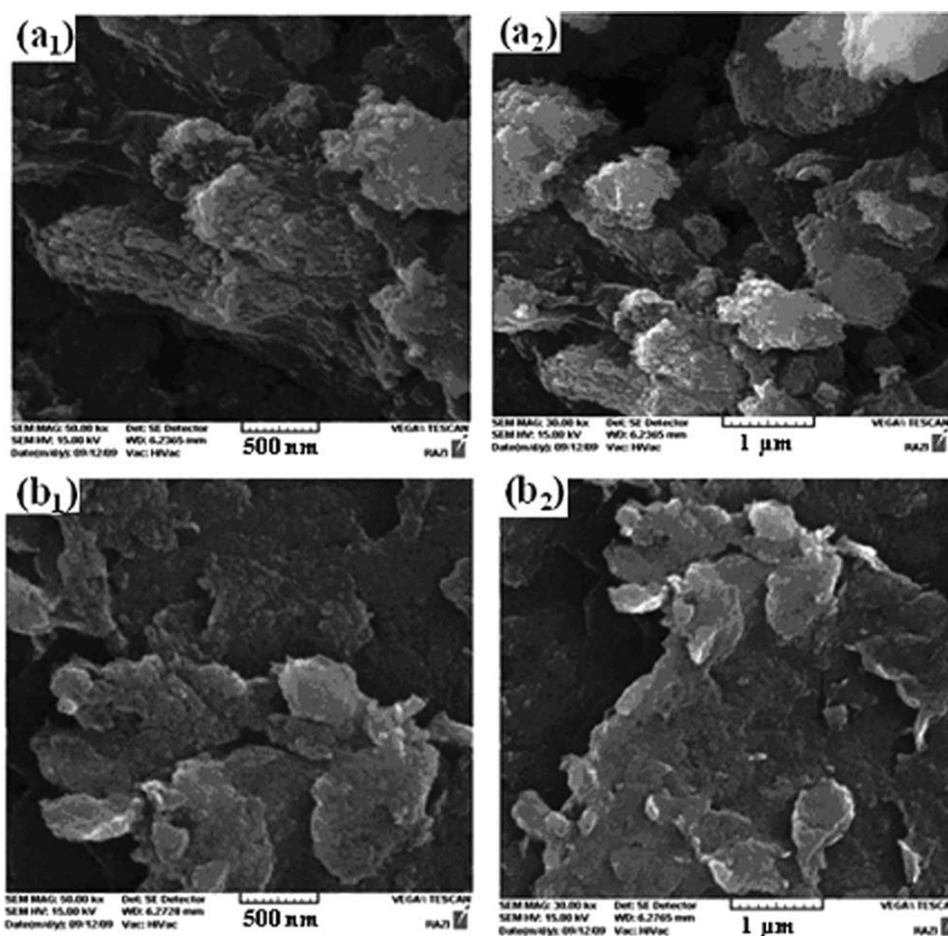

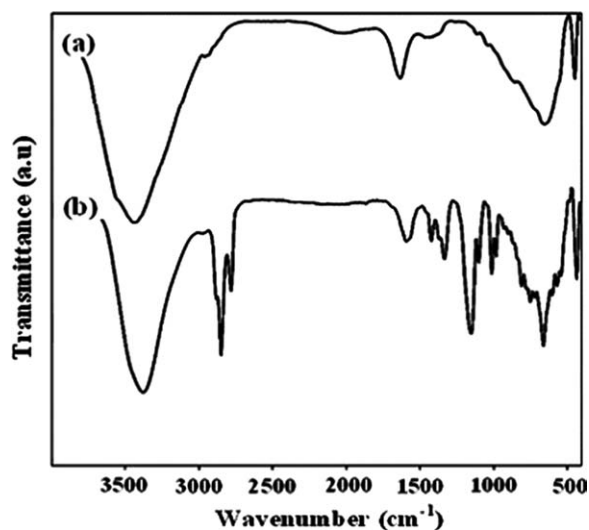**Figure 7** SEM images of MgAl (Cl) (a_1, a_2) and MgAl (SDBS) (b_1, b_2) at different magnifications.

Figure 8 FT-IR spectra of MgAl (Cl)-LDH (a) and MgAl (SDBS)-LDH (b).

Figure 9 XRD patterns of (PSt-*co*-PMSt)-*g*-PANI/MgAl (LDH) nanocomposite.

area. This is very important for preparation of polymeric nanocomposite.

The FT-IR spectra of MgAl (Cl) and MgAl (SDBS) are shown in Figure 8. The MgAl (Cl) sample has a broad adsorption band at around 3445 cm^{-1} due to O—H stretching of hydroxyl groups of LDH. The corresponding δ (H—OH) vibration appears at about 1632 cm^{-1}. The lattice vibration bands from the M—O and O—M—O (M = Mg, Al) groups appear in the 400–800 cm^{-1} region. Intercalation of SDBS instead of Cl$^-$ ions can be confirmed by the C—H stretching vibration at 2856, 2925, and 2958 cm^{-1} and the stretching vibration of sulfate group at 1041 cm^{-1}.
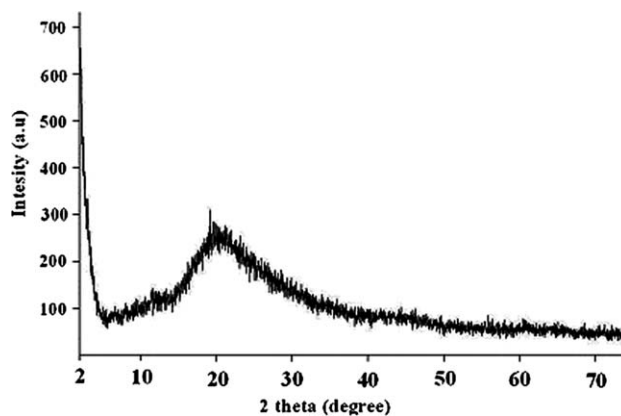
Structural characterization of exfoliated poly (St-*co*-MSt)-*g*-PANI/MgAl (LDH) nanocomposite

X-ray diffraction (XRD) provides information on the changes of the inter layer spacing of the LDH upon the formation of a nanocomposite. The formation of an intercalated structure should result in a decrease in 2θ, indicating an increase in the *d*-spacing; the formation of an exfoliated structure. The XRD patterns of poly (St-*co*-MSt)-*g*-PANI/MgAl (LDH) nanocomposite and neat polystyrene in the range of 2θ = 2°–75° were shown in Figure 9. The XRD patterns shown clearly in poly (St-*co*-MSt)-*g*-PANI/MgAl-LDH sample with 5 wt % MgAl-LDH loading, which indicates that the MgAl-LDH layers have been much exfoliated in the poly (St-*co*-MSt)-*g*-PANI matrix. The existence of the peak at 2-theta = 20 is related to neat polystyrene.
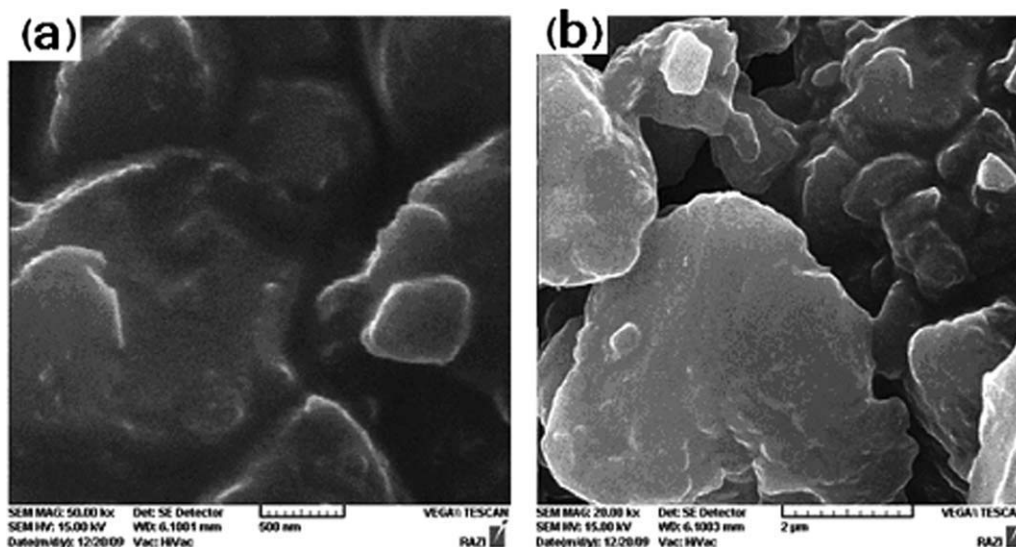

Figure 10 SEM images of (PSt-*co*-PMSt)-*g*-PANi/MgAl (LDH) nanocomposite.
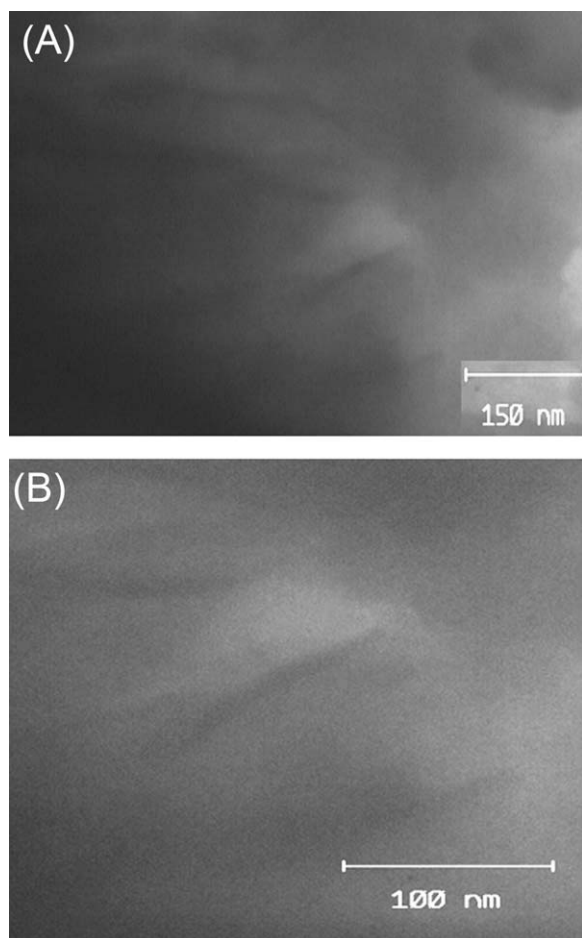
Figure 11 TEM images of the nanocomposites.

SEM characterization of nanocomposite

The SEM micrograph of MgAl (Cl) (Fig. 7) exhibits clusters of fine clay particles. Upon surfactant modification, MgAl (Cl) shows a dramatic improvement in the morphology of the LDH particles. The SEM micrograph of MgAl (SDBS) (Fig. 7) reveals a rough granular morphology showing large loosely packed fused grains forming fluffy agglomerates while SEM micrograph of poly (St-*co*-MSt)-*g*-PANi/MgAl (LDH) nanocomposite (Fig. 10) reveals MgAl (LDH) well dispersed in the polymeric matrix.

Figure 11 reveals that the nanocomposites were in the much exfoliated state. The dark lines indicate the montmorillonite layers with a thickness of about 1 nm. In Figure 11(a,b), nano-sized montmorillonite aggregates could be detected in varying degrees, which might be attributed to intercalated or partially exfoliated structures. This observation is consistent with the XRD results. If the silicates are dispersed randomly and homogeneously in the polymer matrix, the interface area is enormous and pronounced interaction can be expected. (Fig. 11)

Glass transition of poly (St-*co*-MSt)-*g*-PANI and poly (St-*co*-MSt)-*g*-PANI/LDH nanocomposite

Figure 12(a–c) shows the DSC thermogram of poly (St-*co*-MSt), poly (St-*co*-MSt)-*g*-PANI, and poly (St-*co*-MSt)-*g*-PANI/LDH nanocomposit respectively. The poly (St-*co*-MSt) exhibits an enthalpy peak approximately at 80°C, corresponding to the glass transition temperature (T_g). The enthalpy peaks seen at 81°C in Figure 12(b) has been attributed to the evaporation of any residual water and solvent. A strong exothermic peak appears at 315°C that indicates the degradation of this copolymer. The transition observed at 175°C can be designed as the T_g. Figure 12(c) exhibits an exothermic peak at 265°C corresponding to the degradation of copolymer. The transition appears at 189°C can be attributed to the glass transition of this sample. Polystyrene chains bonded to
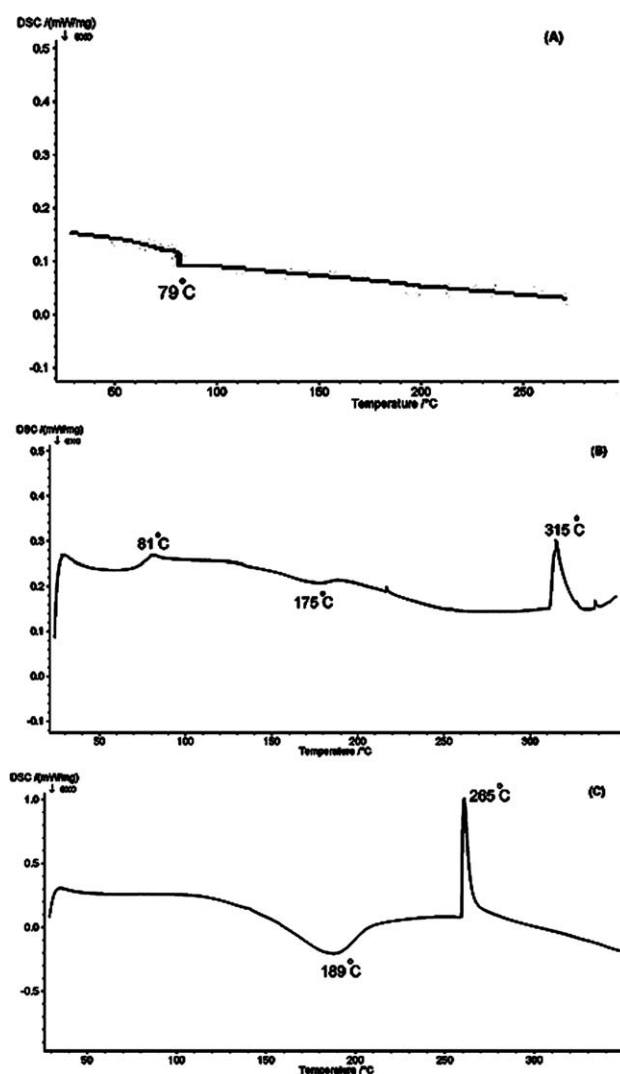

Figure 12 DSC traces of the (PSt-*co*-PMSt) (a), (PSt-*co*-PMSt)-*g*-PANI (b), and (PSt-*co*-PMSt)-*g*-PANI/LDH nanocomposite (c).
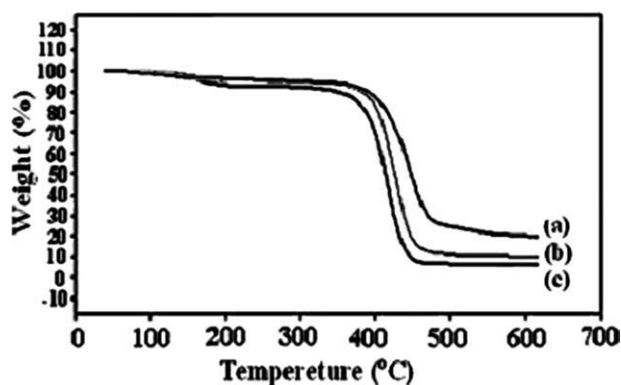
Figure 13 TGA curves of poly (St-*co*-MSt)-*g*-PANi/LDH nanocomposite (a), poly (St-*co*-MSt)-*g*-PANI (b), and poly (St-*co*-MSt) (c).

the backbone of PANi lead to more flexibility in copolymer structure and cause to the degradation at lower temperatures. The thermogram also confirms the absence of any melting (T_m) for all of the samples.

Thermal stability of poly (St-*co*-MSt)-*g*-PANI/ OMMT nanocomposite

Characteristic TGA curves of poly (St-*co*-MSt), poly (St-*co*-MSt)-*g*-PANI and poly (St-*co*-MSt)-*g*-PANI/ LDH nanocomposite is shown in Figure 13. TGA results indicate improvement of the thermal stability for poly (St-*co*-MSt)-*g*-PANI compared to poly (St-*co*-MSt) copolymer and higher thermal stability for poly (St-*co*-MSt)-*g*-PANI/LDH nanocomposite (5 wt % LDH) compared to neat poly (St-*co*-MSt)-*g*-PANI.

CONCLUSIONS

Poly (St-*co*-MSt)-*g*-PANI/LDH nanocomposite was synthesized through solution intercalation method. The growing of aniline onto functionalized Poly (St-*co*-MSt) copolymer has enhanced its solubility, processability, and changed its properties. The structure of obtained copolymer and terpolymer were investigated by ^{1}H-NMR, GPC and FT-IR spectroscopy. The exfoliating structure of nanocomposite was probed by XRD, transmission electron microscopy (TEM), and SEM. The thermal stability and T_g of poly (St-*co*-MSt)-*g*-PANI/MgAl-LDH nanocomposite

improved observably in comparison with pure terpolymer. The unique properties of the nanocomposites result from the strong interactions between the LDH structural layers and the polymeric chains.

References

1. Zheng, J.; Li, G.; Ma, X.; Wang, Y.; Wu, G.; Cheng, Y. Sens Actuators B 2008, 133, 374.
2. Tang, Q.; Wu, J.; Sun, H.; Fan, S.; Hu, D.; Lin, J. Carbohydr Polym 2008, 73, 473.
3. Jiang, J.; Li, L.; Zhu, M. React Funct Polym 2008, 68, 57.
4. Chuang, F. Y.; Yang, S. M. J Colloid Interface Sci 2008, 320, 194.
5. Neelgund, G. M.; Hrehorova, E.; Joyce, M.; Bliznyuk, V. Polym Int 2008, 57, 1083.
6. Castillo-Castro, T. D.; Larios-Rodriguez, E.; Molina-Arenas, Z.; Castillo-Ortega, M. M.; Tanori, J. Compos Part A: Appl Sci Manuf 2007, 38, 107.
7. Celik, M.; Onal, M. J Polym Res 2007, 14, 313.
8. Leroux, F.; Basse, J. P. Chem Mater 2001, 13, 3507.
9. Chen, W.; Qu, B. J. J Mater Chem 2004, 14, 1705.
10. Spange, S. Prog Polym Sci 2000, 25, 781.
11. Ling, F.; Brahmachary, E.; Xu, M.; Svec, F.; Frechet, J M. J. J Sep Sci 2003, 26, 1337.
12. Yoshioka, H.; Mikami, M.; Nakai, T.; Mori, Y. Polym Adv Technol 1995, 6, 418.
13. Bani, F.; Abbasian, M.; Afshar Taromi, F.; Entezami, A. Iranian Polym J 2004, 13, 513.
14. Abbasian, M.; Namazi, H.; Entezami, A. Polym Adv Technol 2004, 15, 606.
15. Abbasian, M.; Entezami, A. A. Polym Adv Technol 2007, 18, 306.
16. Abbasian, M.; Rahmani, S.; Mohammadi, R.; Entezami, A. J Appl Polym Sci 2007, 104, 611.
17. Abbasian, M.; Entezami, A. A. Iranian Polym J 2006, 15, 395.
18. Tizpar, S.; Abbasian, M.; Afshar Taromi, F.; Entezami, A. J Appl Polym Sci 2006, 100, 2619.
19. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559.
20. Harrak, A. El.; Carrot, G.; Oberdisse, J.; Eychenne-Baron, C.; Boue, F. Macromolecules 2004, 37, 6376.
21. Zhang, K.; Li, H.; Zhang, H.; Zhao, S.; Wang, D.; Wang, J. Mater Chem Phys 2006, 96, 477.
22. Fu, G. D.; Zhao, J. P.; Sun, Y. M.; Kang, E. T.; Neoh, K. G. Macromolecules 2007, 40, 2271.
23. Moad, G.; Rizzardo, E.; Thang, S. H. Aus J Chem 2005, 58, 379.