Synthesis and characterization of magnetic and fluorescent styrene co-polymer nanofiber

Sugirtharaj Luna Eunice,[1] Balakrishnan Meenarathi,[2] Shanmugavel Palanikumar,[2] Ramasamy Anbarasan[2]

[1]Department of Chemistry, Kamaraj College of Engineering and Technology, Virudhunagar 626 001, Tamilnadu, India
[2]Department of Polymer Technology, Kamaraj College of Engineering and Technology, Virudhunagar 626 001, Tamilnadu, India
Correspondence to: R. Anbarasan (E-mail: anbu_may3@yahoo.co.in)

ABSTRACT: Fluorescent and magnetic poly(styrene) (PS) based random co-polymer nanofiber was synthesized in a controlled manner via chemical polymerization in three steps. A fluorescent and magnetic nanohybrid {Fe_3O_4/Congored (CR)} was separately prepared and chemically grafted onto the epichlorohydrin (ECH) units of the random co-polymer. Characterizations of the above synthesized polymers were done with the help of Fourier transform infrared (FTIR) spectroscopy, UV–visible spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, fluorescence emission spectroscopy, field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM) measurement, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC) like analytical techniques. The FESEM results indicated that after the grafting of nanohybrid onto the random co-polymer backbone, the polymer exhibited a nanofiber like morphology. Due to the surface functionalization and encapsulation reactions, the magnetic moment value of the nanohybrid and its nanocomposites were found to be reduced. Synthesis and characterization of magnetic and fluorescent random co-polymer based nanofiber is the primary target of the present investigation and its application is extended to the catalysis field. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42796.

INTRODUCTION

Electro spinning is one of the methods available for the preparation of fiber from the polymer solution with uniaxial stretching. Among the thermoplastic polymers, poly(styrene) (PS) plays a vital role in domestic application.[1,2] In 2004, Zhang et al.[3] synthesized PS nanofiber through reverse micelles, gas, antisolvent and ultrasound techniques. PS nanofiber formation via electro spinning process was explained in the literature.[4] Cellulose nanowhiskers loaded PS nanofiber by electro spinning was reported by Rojas et al.[5] PS nanofiber for cation exchange purpose was studied by An and co-workers.[6] Effect of humidity and molecular weight of PS on the electro spinning process was thoroughly studied.[7] Other authors also studied about the electro spinning of PS.[8–10] After a thorough literature survey we found that a special attention was given to PS fiber formation by electro spinning process. The aim of the present investigation is synthesis of PS fiber by a simple chemical route.

Co-polymerization is one of the techniques which allow a beneficial balance in the properties by combining the best characteristics of the constituents with relative ease. Specifically, PECH with pendant chlorine atom offers more advantage particularly towards the further grafting reaction. For example, in 2009, Lee et al.[11] synthesized poly (oxy ethylene methacrylate) grafted PECH via ATRP method. Co-polymerization of styrene and MMA with PECH was reported in the literature.[12] Block co-polymer of starch with PECH in alkaline medium was reported in the literature.[13,14] Callau and co-workers[15] reported about the graft co-polymerization of ECH with biphenyl carboxylate groups. By thorough literature survey, we find few reports available with the random and block co-polymers of ECH. In the present investigation we are going to report the Acrylic acid (AA) initiated ring opening polymerization (ROP) of ECH followed by the synthesis of random co-polymer with styrene. To the best of our knowledge, this type of report is not available in the literature so far.

Additional Supporting Information may be found in the online version of this article.

The surface functionalized ferrite offers extensive application in the field of chemistry, particularly in bio-medicinal chemistry. In 2008, Wu and research team reviewed the surface functionalization of magnetic iron oxide nanoparticles.[16] Functionalized silica decorated superparamagnetic Fe_3O_4 nanocrystals for biological applications were synthesised.[17] In 2014, Palanikumar et al.[18] reported about the folic acid functionalized Fe_3O_4 for the sedimentation of starch molecules. Meenarathi and coworkers[19] synthesized acid fuschin functionalized Fe_3O_4 for the ROP of ε-caprolactone (CL). Amino acid functionalized ferrite magnetic polymer adsorbent was reported in the year 2010.[20] While going through the literature, we could not find any report based on the CR functionalized Fe_3O_4. In the present investigation, the CR dye functionalized Fe_3O_4 was successfully synthesized and characterized.

Till date one lakh dyes are available in the market among which 10% of the dyes are disposed into the natural environment as dye stuff waste. This leads to environmental pollution and hence restriction in the utilization of dyes. The dye molecules are used as a bio-probe in the bio-medical field for a long time. Among the dyes, an azo type CR dye is very useful in the bio-medical field.[21] The bio-medical applications of CR dye was explained by other research team also.[22–25] Few reports are available for the synthesis of CR functionalized Fe_3O_4 in the literature. This urged us to do the present investigation. The novelty of the present investigation is synthesis of Fe_3O_4 dispersed CR grafted PECH random co-polymer by a simple chemical route to produce a magnetic and fluorescent PS nanofiber.

In the present investigation 1D PS nanofiber was synthesized via co-polymerization followed by grafting reaction by a simple chemical reaction. The novelty of the present investigation is the synthesis of PS nanofiber with magnetic and fluorescent activity via an eco-friendly and inexpensive chemical method.

EXPERIMENTAL

Materials
Epichlorohydrin (ECH, Aldrich chemicals, India), phthalic anhydride (PAH, Nice chemicals, India), peroxy disulphate (PDS, Nice chemicals), congored dye (CR, Nice chemicals), styrene (Aldrich chemicals), Acrylicacid (AA, Aldrich chemicals) and sodium lauryl sulphate (SLS, Nice chemicals) were purchased and used as received. Ferrite (Fe_3O_4) nanoparticles were prepared by using ferric chloride ($FeCl_3$, Nice chemicals), sodium hydroxide pellet (NaOH, Nice chemicals) and ferrous sulphate ($FeSO_4$, Nice chemicals). Styrene was purified using NaOH solution. All other chemicals were received and used without any further purification. Solutions were made using double distilled (DD) water. Tetrahydrofuran (THF, CDH chemicals, India) was used as a solvent for the dissolution of the polymer.

### Preparation of CR/Ferrite Grafted Random Co-polymer
The synthesis of the random co-polymer involves a three step process and is given in Scheme 1. In the first step, poly(ECH), (PECH) was synthesised by using AA, as an initiator for the ROP of ECH.[26] In the second step, AA-PECH-PS was synthesized by using PDS as a free radical initiator through emulsion

polymerization method. The random co-polymer obtained in the second step was structurally modified by using Fe_3O_4/CR nanohybrid as mentioned in the third step.

5 mL of ECH monomer was taken in a two way necked 100 mL round bottomed flask (RBF). The two-way neck was used for N_2 inlet and outlet respectively. 2 mL of AA initiator was charged into the RBF and stirred well for 5 min. The ROP of ECH was initiated by the addition of AA in the presence of 0.10 g PAH as a co-monomer via emulsion polymerization method and this produces a random co-polymer. The ROP of ECH was carried out at 45°C for 6 h under nitrogen atmosphere with vigorous stirring. After the completion of the reaction the contents were repeatedly washed with DD water. At the end of washing, the contents were evaporated to dryness at 110°C over night. The water molecules and the unreacted ECH units were evaporated. This viscous product formed is known as PECH.

In the second stage, 5 g of homopolymer and 15 mL styrene was added under vigorous stirring conditions. Once the solution becomes completely miscible, 1 g SLS and 0.50 g PDS were added under N_2 atmosphere with vigorous stirring conditions. After 4 h of stirring, the contents were washed with 25 mL DD water for three times to remove all the unreacted ECH or SLS. Finally, the contents were transferred to a petri dish for drying at 110°C for 6 h. Thus obtained powder is a random co-polymer, poly(AA-ECH-PS).

To prepare the fluorescent co-polymer, 1 g of random co-polymer was dissolved in 25 mL THF solvent and transferred into a 50 mL RBF. Required amount of Fe_3O_4/CR nanohybrid was charged in the RBF and stirred well. The fluorescent random co-polymer was prepared under five different concentrations. The concentration of the nanohybrid was varied between 0.10 and 0.50 g. 0.10 g NaOH in 5 mL DD water was added to the RBF and the system was heated to 45°C for 6 h. During the course of the reaction, the chlorine atom of ECH unit reacted with the amino group of CR dye and 1 mole of HCl was removed. The amino group of CR dye was bound with the Fe_3O_4 surface whereas the —SO_3Na group remained as such. The amino or imino group of CR interacts with the Cl atom of the co-polymer in an alkaline medium. The surface binding nature of the amino group towards the Fe_3O_4 surface was well explained in our earlier publications. At the end of the reaction time, the contents were transferred into a 500 mL beaker and kept on a magnetic bar. The unreacted dye and random co-polymer was stayed on the liquid medium whereas the nanohybrid grafted random co-polymer was settled down due to the magnetic and gravitational forces. The top layer was removed with the help of a pipette without disturbing the settled materials. Further, the settled material was washed well with DD water for three times and kept on a magnetic bar to completely remove the unreacted dye molecules. The complete removal of dye from the nanohybrid grafted random co-polymer was confirmed by the UV-visible spectroscopy. By such a method nanohybrid grafted random co-polymer was purified. Then the contents were dried at 110°C for 6 h. Thus obtained dark brown colored powder is the nanohybrid modified random co-polymer. It is stored in a zipper lock cover and characterized further.
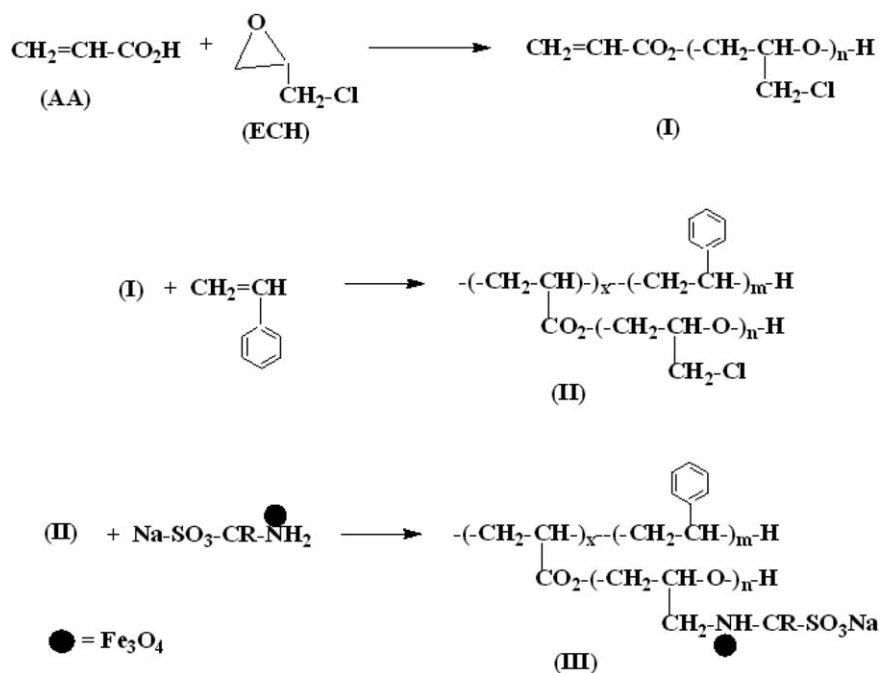
Scheme 1. Synthesis of poly(AA-PECH-g-CR/Fe$_3$O$_4$)-co-PSty.

Characterization

The random co-polymer sample was dissolved in CHCl$_3$ solvent and subjected to fluorescence emission measurement from 350 to 700 nm by using Elico SL174, India Instrument. A Waters 2690 GPC instrument was used to determine the M_w of the polymer samples using THF as an eluent at room temperature at the flow rate of 1 mL min^{-1} against PS standard. Field emission scanning electron microscopy (FESEM) was used to examine the morphological behavior of the polymer with the help of FESEM – Hitachi S4800 Japan, instrument. Magnetic measurements (VSM) were carried out with a superconducting quantum interference device magnetometer (Lakesore-7410-VSM, USA) with magnetic fields up to 7 T at 32°C. Thermogravimetric analysis (TGA) analysis was performed under air purge at the heating rate of 10°C/min by using SDT 2960 simultaneous TGA and differential scanning calorimetry (DSC) Analyzer, TA instruments. Fourier transform infrared (FTIR) spectra for the samples were recorded with the help of Shimadzu 8400 S, Japan instrument by KBr pelletization method from 400 to 4000 cm^{-1}. Three milligram sample was ground with 200 mg of spectral grade KBr and made into a disc under the pressure of 7 tons. Jasco V-570 instrument was used for UV–visible spectrum measurements. 2 mg of sample was dissolved in 10 mL of THF under ultrasonic irradiation for 10 min and subjected to UV–visible spectral measurements. ^{1}H-NMR (500 MHz) spectra were obtained using an nuclear magnetic resonance (NMR) apparatus (Varian, Unity Inova-500 NMR) at room temperature in dueterated DMSO solvent. DSC was measured by using Universal V4.4A TA Instruments under nitrogen atmosphere at the heating rate of 10 K/min from room temperature to 373 K. The second heating scan of the sample was considered in order to delete the previous thermal history of the sample. The surface morphology of the sample was scanned by scanning electron microscopy (SEM, JSM 6300, JEOL model)

instrument. The samples were lyophilized on glass slides and then coated with gold.

RESULTS AND DISCUSSION

The main aim of the present investigation is to increase the application of the random co-polymer in various science and engineering field, particularly in bio-medical field as a bio-probing agent. The random co-polymer is characterized by various analytical methods.

Figure 1(a) shows the FTIR spectrum of the random co-polymer. A broad peak around 3400 cm^{-1} is due to the ─OH stretching of the PECH units. The aromatic ─CH symmetric and anti-symmetric stretching was observed at 2853 cm^{-1} and 2924 cm^{-1} respectively. The aliphatic ─CH stretching is observed at 3029 cm^{-1} and 3069 cm^{-1}. The carbonyl stretching of the AA segment appears at 1706 cm^{-1}.[27–31] A broad peak at 1021 cm^{-1} is responsible for the C─O─C ether linkage of PECH structure. The aromatic C─H bending vibrations are observed at 697, 747, and 826 cm^{-1}. The aromatic bending vibrations arises from the styrene segments. The chloride ion stretching can be seen at 538 cm^{-1} which appears from the ECH units. Figure 1(b–f) indicates the FTIR spectrum of nano-hybrid grafted random co-polymer. Here also the above said peaks were observed. While increasing the concentration of the nanohybrid some of the peaks disappeared. For example, the chloride ion stretching from the ECH units disappeared due to the chemical grafting of the amino group of CR. Similarly the C═O stretching of the AA units disappeared. A new peak is observed at 877 cm^{-1} due to the C─H out of plane bending vibration from the CR units. A twin peak at 553 cm^{-1} is ascribed to the Fe─O (M─O) stretching of ferrite.[32] Thus the
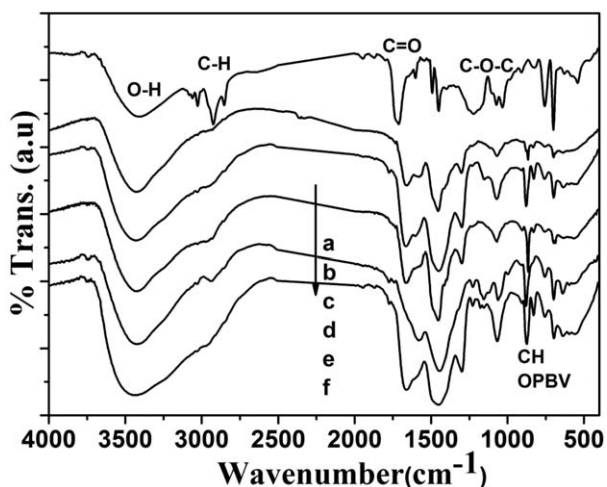
Figure 1. FTIR spectrum of nanohybrid grafted random co-polymer at the weight of (a) 0g, (b) 0.10g, (c) 0.20g, (d) 0.30g, (e) 0.40g, (f) 0.50g.

FTIR spectrum confirms the chemical grafting of the nanohybrid onto the random co-polymer backbone.

The chemical grafting of the nanohybrid onto the random backbone is confirmed by ^{1}H-NMR spectroscopy. Figure 2(a) indicates the ^{1}H-NMR spectrum of the random co-polymer before structural modification. This spectrum shows one strong aromatic peak from 6.3 to 7.6 ppm due to the aromatic protons from the styrene unit. Figure 2(b) indicates the ^{1}H-NMR spectrum of the nanohybrid grafted random co-polymer. In this spectrum mainly we have concentrated on aromatic protons only. In this case we can see three different aromatic protons, i.e., aromatic protons from styrene units, tri substituted naphthalene

units and para-disubstituted biphenyl segments. These three distinct aromatic protons are indicated in the spectrum [Figure 2(b)]. The aromatic protons from styrene units appeared at 7.1 to 7.3 ppm. The tri substituted naphthyl aromatic protons appeared at 6.8 to 6.9 and 7.4 ppm.[28] The aromatic protons from diphenyl rings appeared at 6.6 ppm. Appearance of many aromatic protons confirms the chemical grafting of the nanohybrid onto the random co-polymer backbone.

The UV–visible spectrum gives an idea about the electronic transitions involved in the system. Figure 3(a) indicates the UV-visible spectrum of the ferrite-CR nanohybrid system. The nanohybrid system exhibits a strong absorbance peak at 499.2 nm. The nanohybrid after the chemical grafting reaction with the random co-polymer is shown in Figure 3(b–f). After the chemical grafting the absorbance peak was red shifted to 518.6nm. In 2014, Kohila et al.[33] explained the UV-visible spectrum of CR before and after grafting with silk fiber. The present results coincide with their report. It is very interesting to note that while increasing the concentrations of the nanohybrid the peak absorbance value proportionally increased. In order to find out the order of the chemical grafting reaction a log-log plot for the (weight of nanohybrid) Vs absorbance was made [Figure 3(g)]. The plot was found to be a straight line with a slope value of 1.10 which indicates the first order chemical grafting reaction with respect to the weight of the nanohybrid. The slope value confirms that one mole of the nanohybrid is required to modify one mole of ECH unit. During the structural modification one mole of HCl is removed which confirms the 1 : 1 participation of both the random co-polymer and the nanohybrid.

The fluorescent property of the dye molecule increases its application particularly in bio-medical field as a bio-probe material.
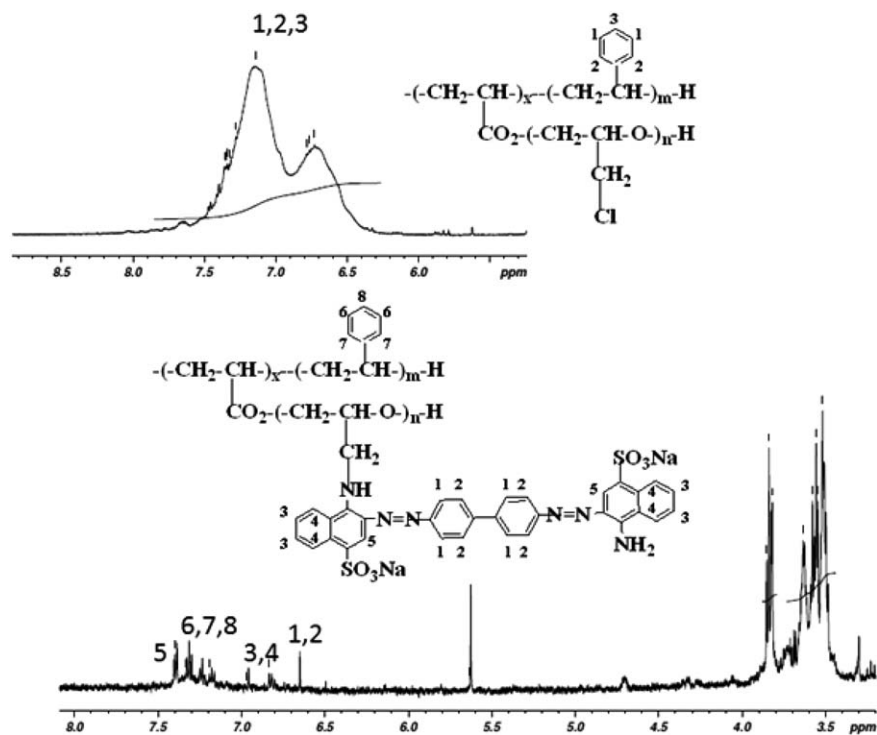

Figure 2. ^{1}H-NMR spectrum of (a) random co-polymer, (b) 0.3g nanohybrid grafted random co-polymer.
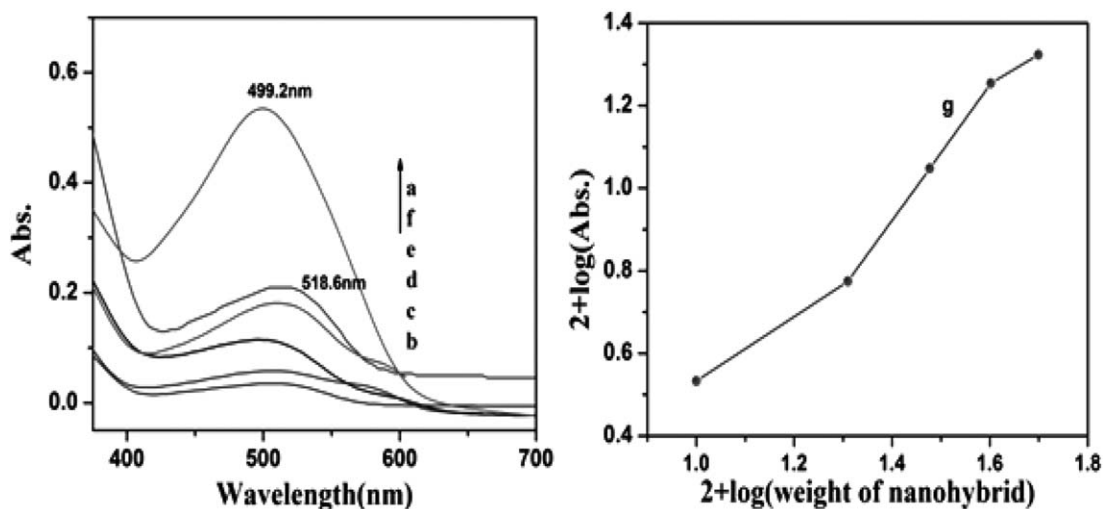
Figure 3. UV–visible spectrum of (a) nanohybrid, nanohybrid grafted random co-polymer at the weight of (b) 0.10g, (c) 0.20g, (d) 0.30g, (e) 0.40g, (f) 0.50 g, (g) plot of log(weight of nanohybrid) vs. log(abs.).

The fluorescence emission spectrum of the nanohybrid is given in Figure 4(a). The emission peak is observed at 523.9 nm.[33] After the chemical grafting reaction, the emission peak was blue shifted to 511.6 nm due to the decrease in surface plasamon resonance effect. This is also due to the decrease in size of the ferrite nanoparticles. Figure 4(b–f) indicates that while increasing the concentration of the nanohybrid system, the fluorescence emission intensity (FEI) is also proportionally increased. While increasing the concentration of the nanohybrid, the CR units are introduced or chemically grafted with the random co-polymer backbone. In order to find the order of the chemical grafting reaction, the plot of log(weight of the nanohybrid) Vs log(FEI) [Figure 4(g)] was made and the plot obtained was a straight line. The slope of the straight line was noted as 0.95 which confirms the first order chemical grafting of the nanohybrid onto the random co-polymer. This indicates that one mole of the nanohybrid is required to modify one mole of the random co-polymer backbone.

The surface morphology of the random co-polymer before and after the structural modification with the nanohybrid is shown in Figure 5. Figure 5(a) shows the image of the random co-polymer before the chemical grafting reaction with the size of less than 50 nm. The appearance of the nanoparticle is due to the presence of ferrite. Figure 5(b) indicates the FESEM image of 0.3g nanohybrid grafted random co-polymer. Here, surprisingly one can see a 1-D nanofiber. The breadth of the fiber was determined as 42 nm with a length of several micrometers. The nanosized ferrite is also dispersed on the random co-polymer structure. The plus point of the present investigation is the synthesis of fluorescent nano co-PS fiber. So far, the fiber form of PS is not reported by any simple chemical method, to the best of our knowledge. In 2014, Shaer and co-workers[8] reported the synthesis of fluorescent and magnetic PS fiber through the electro spinning method. When compared with the literature, the present investigation yielded an economically cheaper methodology for the synthesis of nanosized PS fiber.
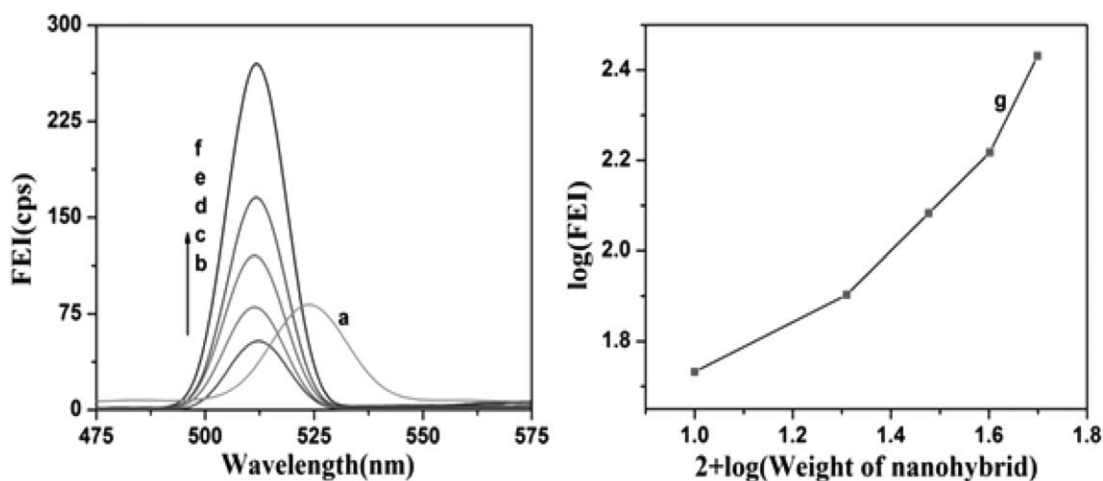

Figure 4. Fluorescence emission spectrum of (a) nanohybrid, nanohybrid grafted random co-polymer at the weight of (b) 0.10g, (c) 0.20g, (d) 0.30g, (e) 0.40g, (f) 0.50g, (g) plot of log (weight of nanohybrid) vs. log(FEI).
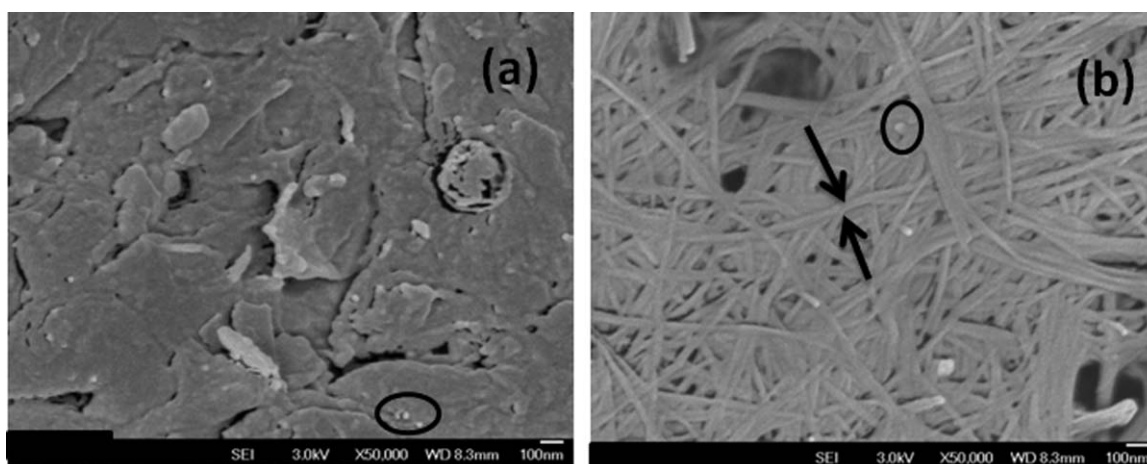
Figure 5. FESEM image of (a) random co-polymer, (b) random co-polymer grafted with 0.30 g nanohybrid.

The surface morphology of the random co-polymer after grafting reaction is indicated in Figure 6. In Figure 6(a) the circled area indicates fiber forming nature of PS. Thus the SEM results support the FESEM results. Figure 6(b) represents the SEM image of the random co-polymer after the surface modification process. After the chemical grafting reaction the spherical form of PS is distorted and appearance of two different regions, the hard (PS) segments and the soft (PECH) segments are shown in Figure 6(b).

One more advantage of the present investigation is the magnetic behavior of the random co-polymer due to the presence of nano ferrite. The magnetization value of the ferrite before and after functionalization reaction is shown in Figure 7(a,b) respectively. The magnetization values were determined as 55 and 50.4 emu/g respectively. The decrease in magnetization value is due to the surface adsorption or functionalization reaction.[18] The nanohybrid after the chemical grafting with the random co-polymer [Figure 7(c)] exhibits the magnetization value of 21.98 emu/g. The sudden drop in magnetization value can be explained on the basis of encapsulation effect, i.e., ferrite sphere

is surrounded by the random co-polymer chains. In other words one can say that the voids or the empty spaces present in the random co-polymer chains are filled with nano ferrite. While heating the nanohybrid above 45°C, the interaction between the metal oxide surface and capping agent were found to be broken. In the present investigation, the grafting of nanohybrid onto the random co-polymer backbone was carried out by emulsion method at 65°C for three h under N_2 atmosphere. At this experimental condition there is a chance for the breaking of interaction between the metal oxide and the capping agent. As a result, the metal oxides were dispersed on the polymer matrix. Due to the coil like structure of the polymer chain the ferrites were tightly engaged by the random co-polymer chains. As a result of the steric and compression effect, the magnetization values were reduced.

The gel permeation chromatography (GPC) analysis explains the molecular weight of the synthesized co-polymer. The molecular weight of the co-polymer was determined in terms of M_w, M_n, and polydispersity (PD) values as 1.32×10^5 g/mol, $6.99 \times$
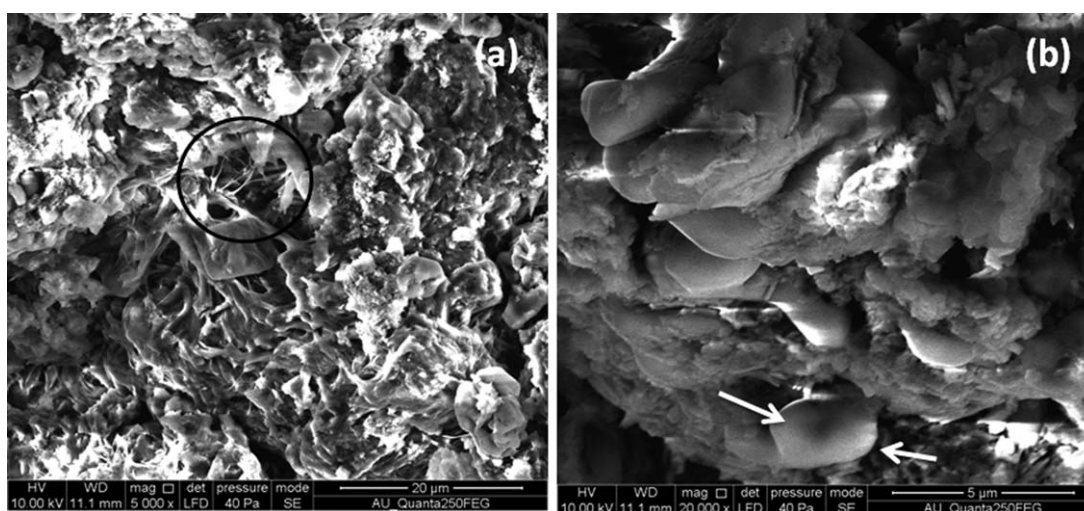

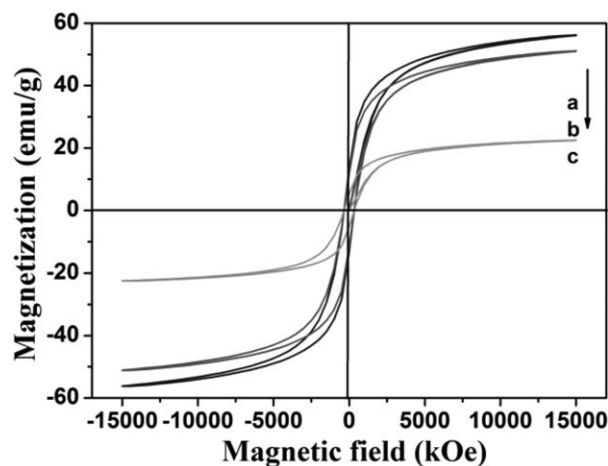**Figure 6.** SEM image of (a,b) 0.30 g nanohybrid grafted random co-polymer.

Figure 7. VSM loop of (a) Fe₃O₄, (b) Fe₃O₄/CR nanohybrid, (c) random co-polymer grafted with 0.30 g nanohybrid.

Figure 8. DSC thermogram of (a) random co-polymer, nanohybrid grafted random co-polymer at the weight of (b) 0.10g, (c) 0.20 g, (d) 0.30 g, (e) 0.40 g, (f) 0.50 g.

10^4 and 1.89, respectively. The PD value confirms the absence of cross linking or branching reaction during the synthesis of random co-polymer. The GPC data of 0.3 g nanohybrid grafted random co-polymer was also determined. The M_w, M_n, and PD values were determined as 1.39×10^5 g/mol, 7.59×10^4 and 1.84, respectively. The increase in M_n and M_w values confirms the chemical grafting of the nanohybrid on the random co-polymer backbone without any crosslinking.[34] Molecular weight is one of the important factors to form a fiber. This molecular weight was found to be enough to form a fiber.

In order to study the influence of the nanohybrid, the thermal transition of the random co-polymer was studied and reported in Figure 8. The DSC thermogram of the random co-polymer before the structural modification is shown in Figure 8(a). The thermogram did not show any transition. This confirms the amorphous nature of the random co-polymer. The random co-polymer after the structural modification with the nanohybrid is given in Figure 8(b–f). The thermogram exhibits one endothermic peak. The weight of the nanohybrid was varied between 0.1 and 0.5g. While increasing the concentration of the nanohybrid the T_g value of the random co-polymer is slightly shifted toward higher temperature. While increasing the % weight loading of the nanohybrid the area of the peak is also widened. The T_g was varied between 104 and 116°C. This infers that after the structural modification the crystallinity of the system was slightly increased. The crystalline nature is due to the aromatic CR dye. Moreover, the T_g is linearly increased with an increase in percentage weight loading of the nanohybrid. In 2011, Shinde et al.[35] explained the T_g of PS and its co-polymers as 85°C. In the present investigation the T_g value was highly increased. This is due to the chemical grafting of nanohybrid onto the random co-polymer backbone, i.e., the amino group of nanohybrid reacted with the Cl atom of PECH of random co-polymer.

In the TGA study, the thermal stability of the random co-polymer before and after the structural modification with the nanohybrid is given in Figure 9(a–f). Figure 9(a) represents the TGA thermogram of the random co-polymer with a three step
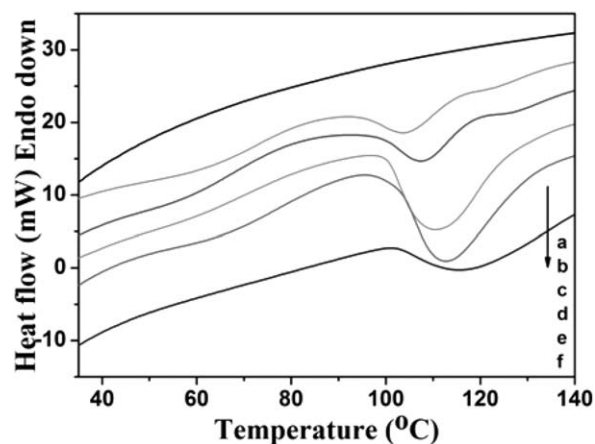
degradation process. The first minor weight loss before 350°C is associated with the breaking of bond between the propylene oxide units. The second major weight loss around 420°C is associated with the degradation of PS units.[35] The third minor weight loss around 527°C is ascribed to the evolution of CO_2 from the degradation of AA units. Above 575°C the system exhibits 3% weight residue remaining. The random co-polymer after the structural modification with the nanohybrid exhibits a two step degradation process [Figure9(b–f)]. Below 150°C the system exhibits one minor degradation step due to the removal of moisture, physisorbed and chemisorbed water molecules that are chemically bonded with the dye molecules. The second major weight loss around 375°C can be explained on the basis of degradation of PS backbone. Above 575°C the system exhibits 52% weight residue remained [Figure 9(f)]. It was found that while increasing the percentage weight loading of the nanohybrid the % weight residue above 575°C is increased. This confirms the thermal stability of the magnetic, fluorescent and styrene co-polymer nanofiber system.
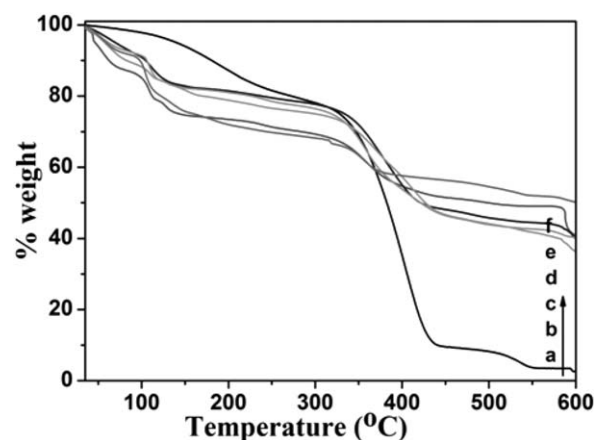

Figure 9. TGA thermogram of (a) random co-polymer, nanohybrid grafted random co-polymer at the weight of (b) 0.10 g, (c) 0.20 g, (d) 0.30 g, (e) 0.40 g, (f) 0.50 g.

The term eco-friendly includes the bio-compatible, bio-degradable and economically cheaper method of preparation. Due to the presence of ether linkage present in the PECH segments the random co-polymer is bio-compatible and bio-degradable one. Generally, for the preparation of PS fiber, electro spinning method is used. In the present investigation, a simple chemical method is used for the preparation of PS fiber. The prepared polymer itself is in fiber form. The important point noted here is the PS fiber prepared by the simple chemical reaction is obtained in nanoform. During the chemical grafting reaction, the CR dye molecules were relieved from the ferrite nanoparticles surface and dispersed uniformly on the random co-polymer surface. Now the free amino group from CR dye is interacted with the Cl atom of ECH units and forms a stable sigma bond between them. This leads to the magnetic and fluorescent polymer. Hence, in the present investigation, a nanosized fiber, magnetic, fluorescent and eco-friendly random co-polymer was synthesized successfully.

The random co-polymer forgot to show any fiber formation, but after the chemical grafting with nanohybrid, nanosized fiber formation was observed without any compromise in the thermal properties of PS. In the present investigation, the water insoluble bulky sized styrene units behaved like a hard segment whereas the ECH units behaved like a soft segments. After the chemical grafting with the nanohybrid, the random co-polymer followed certain stereo-regularity. The influence of nano ferrite is also a considerable one during the fiber formation through the surface catalytic effect. Hence, the present investigation leads to the formation of a simple eco-friendly, magnetic and fluorescent PS co-polymer nanofiber formation.

CONCLUSIONS

From the above study, the niche points are presented here as conclusion. The emulsion polymerization method was adopted for the synthesis of random co-polymer. The disappearance of C=O stretching at 1720 cm^{-1} in the FTIR spectrum and appearance of new peaks around 7.5 ppm in the ^{1}H-NMR spectrum confirmed the chemical grafting of nanohybrid onto the random co-polymer backbone. A red shift in the UV–visible spectrum declared the structural modification of random co-polymer by the nanohybrid. While increasing the weight of nanohybrid, the FEI was proportionally increased and followed the first order grafting reaction. The nanosized fiber formation was confirmed by the FESEM image followed by the SEM images. The magnetization value of nanohybrid (50.5 emu/g) and random co-polymer nanocomposite (21.9 emu/g) were found to be lower than that of the pristine ferrite (55 emu/g). The increase in M_w confirmed the chemical grafting of nanohybrid onto the random co-polymer backbone. While increasing the weight of nanohybrid both the T_g and % weight residue remained above 550°C were increased linearly. This type of material is very much useful in the bio-medical field as a bio-imaging agent.

REFERENCES

1. Ferrandiz Mas, V.; Bond, T.; Alcocel, E. G.; Cheeseman, C. R. *Const. Build. Mater.* **2014**, *61*, 285.

2. Tang, W. C.; Cui, H. Z.; Wu, M. *Const. Build. Mater.* **2014**, *51*, 338.

3. Zhang, J.; Liu, Z.; Han, B.; Jiang, T; Wu, W.; Chen, J.; Li, Z.; Liu, D. *J. Phys. Chem. B* **2004**, *108*, 2200.

4. Bafekrpour, E.; Rarhizkar, M.; Fang, J.; Wang, X.; Lin, T. *Int. J. Adv. Engg. Appl.* **2012**, *5*, 1.

5. Rojas, O. J.; Montero, G. A.; Habibi, Y. *J. Appl. Polym. Sci.* **2009**, *113*, 927.

6. An, H. W.; Shin, C. *J. Adv. Comp. Inform.* **2006**, *10*, 1.

7. Casper, C. L.; Stephens, J. S.; Tassi, N. G.; Chase, D. B.; Rabolt, J. F. *Macromolecules* **2004**, *37*, 573.

8. Schaer, M.; Crittin, M.; Kasmi, L.; Pierzchala, K.; Calberone, C.; Fink, A.; Sienkiewicz, A. *Fibers* **2014**, *2*, 75.

9. Liu, W.; Huang, C.; Jin, X. *Nanoscale Res. Lett.* **2014**, *9*, 350.

10. Fashandi, H.; Karmi, M. *Polymer* **2012**, *5*, 5832.

11. Le, K. J.; Rark, J. T.; Koh, H.; Min, B. R.; Kim, J. H. *Ionics* **2009**, *I5*, 163.

12. Tasdelan, M. A.; Yogci, Y.; Biedron, T.; Kubisa., P. *Polym. Bull.* **2007**, *58*, 653.

13. Simkovic, I.; Laszlo, J. A.; Thompson, A. *Carbohydr. Polym.* **1996**, *30*, 25.

14. Simkovic, I.; LaszloJ, A. *J. Appl. Polym. Sci.* **1997**, *64*, 2561.

15. Callau, S.; Reina, L.; Mantecon, A. *Macromolecules* **1999**, *32*, 7790.

16. Wu, W.; He, Q.; Jiang, C. *Nanoscale Res. Lett.* **2008**, *3*, 397.

17. He, Y. P.; Wang, S. Q.; Li, C. R.; Zou, B. S. *J. Phys. D. Appl. Phys.* **2005**, *38*, 1342.

18. Palanikumar, S.; Kannammal, L.; Meenarathi, B.; Anbarasan, R. *Int. Nano Lett.* **2014**, *4*, 104.

19. Meenarathi, B.; Kannammal, L.; Palanikumar, S.; Anbarasan, R. *Mater. Res. Exp.* **2014**, *1*, 1.

20. Zhau, Y. G.; Sheng, H. Y.; Pan, S. D.; Hu, M. Q.; Xia, Q. H. *J. Mater. Sci.* **2010**, *45*, 5291.

21. Satyren, S. D.; Hamilton, R. L.; Styren, G. C.; Klunk, W. E. *J. Histochem. Cytochem.* **2000**, *48*, 1223.

22. Crystal, A. S.; Giasson, B. I.; Crowe, A.; Lee, V. M.; Kung, M. P.; Zhuang, Z. P.; Trojanowski, J. Q. *J. Neurochem.* **2003**, *86*, 1359.

23. Hudson, S. A.; Ecroyd, H.; Kee, T. W.; Carver, J. A. *FEBS J* **2009**, *276*, 5760.

24. Rybarska, J.; Pielearska, B.; Roterman, I. *Folia Histochem. Cytobiol.* **2004**, *U*(2), 101.

25. Gultek, A. *Turk. J. Chem.* **2010**, *3*, 437.

26. Ferrahi, M. I.; Benedda, M.; Benyoucef, A.; Belbachir, M. *Bioint. Res. Appl. Chem.* **2012**, *2*, 243.

27. Chen, H. H.; Anbarasan, R.; Kuo, L. S.; Chen, P. H. *Mater. Chem. Phys.* **2011**, *126*, 584.

28. Meenarathi, B.; Chen, H. H.; Chen, P. H.; Anbarasan, R. *J. Polym. Res.* **2013**, *20*, 18.

29. Meenarathi, B.; Palanikumar, S.; Kannammal, L.; Anbarasan, R. *Spectrochim. Acta Part A* **2015**, *135*, 93.

30. Meenarathi, B.; Anbarasan, R. *Int. J. Sci. Res. Eng. Technol.* **2014**, *1*, 15.

31. Chen, H. H.; Anbarasan, R.; Kuo, L. S.; Chen, P. H. *J. Mater. Sci.* **2011**, *46*, 1796.

32. Palanikumar, S.; Siva, P.; Meenarathi, B.; Kannammal, L.; Anbarasan, R. *Int. J. Biol. Macromol.* **2014**, *67*, 91.

33. Kohila, V.; Sribala, M. G.; Kannammal, L.; Meenarathi, B.; Dhanalakshmi, T.; Anbarasan, R. *Ind. J. Fiber Text. Res.* **2014**, *39*, 172.

34. Luna Eunice, S.; Meenarathi, B.; Palanikumar, S.; Anbarasan, R. *Iran. Polym. J.* **2015**, *24*, 651.

35. Shinde, V. S.; Girme, M. R.; Pawar, V. U. *Ind. J. Chem.* **2011**, *50A*, 781.