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Synthesis through ATRP and Characterization of hydrophobic polystyrene-*block*-polyethylene glycol-*block*-polystyrene tri-block copolymer: A simple laboratory approach

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ABSTRACT

Simple laboratory synthesis of poly (styrene)-*block*-poly (ethylene glycol)-*block*-poly(styrene) (PS-PEG-PS) tri-block copolymer (TBC) using versatile atom transfer radical polymerization (ATRP) technique is reported. *Chloro*- and *Bromo*-PEG macroinitiators were synthesized by the transformation of the end group of PEG through 2-chloro or bromo propionyl chloride which was subsequently used in the preparation of symmetrical TBC of PS-PEG-PS under ATRP conditions using styrene as monomers. The PEG-macroinitiators and synthesized TBC were characterized by FT-IR and ¹H-NMR spectroscopy. The average molecular weight and molecular weight distributions of the TBC were obtained using GPC analysis. The experimental results showed that the polymerization was controlled/living with the PDI=1.4. The thermal behaviour and compositional properties of the TBC were studied using TGA. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Block copolymers;
PEG-macroinitiator;
ATRP;
Styrene.

INTRODUCTION

Block copolymers are of considerable interest for various applications, such as emulsifiers, dispersion stabilizers, compatibilizers, biological materials, phase transfer catalysts, and water-absorbing elastomers^[1-4]. Molecular design of block copolymers with well-defined architectures is a very important area of research now a days^[5]. Traditionally, block copolymers with pre-determined number-average molecular weight (M_n) and low polydispersity indices (PDI) are always synthesized by anionic, cationic, and group-transfer polymerization methods; however, these polymerization methods can

be successfully carried out only under strictly controlled conditions^[6]. TBCs of poly (styrene) (PS) and poly (ethylene oxide/ethylene glycol) (PEG) with the block sequence (PS)_m-(PEG)_n-(PS)_m are nonionic amphiphilic molecules, which are both surface-active and able to form micelles in aqueous/organic solvents. They are commercially synthesized in a variety of molecular weights and PS/PEG ratios. Thus, TBCs of PS-PEG-PS represents an important class of polymeric surfactants and are used in various industries, viz., pharmaceutical, coal and petroleum, agricultural and fine chemicals^[7,8].

ATRP can overcome many of the limitations of other

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living polymerization reactions (only a small number of monomers can be used, the reactions are sensitive to moisture, and two or more monomers cannot be randomly copolymerized) and provide a technique to maximize the potential of living polymerizations^[9]. The control of the polymerization afforded by ATRP is a result of the formation of radicals that can grow, but are reversibly deactivated to form dormant species^[10,11]. Re-activation of the dormant species allows the polymer chains to grow again, only to be deactivated later. Such a process results in a polymer chain that slowly, but steadily, grows and has a well-defined end group (for ATRP that end group is usually an alkyl halide)^[12,13]. Although other controlled radical polymerization systems have been reported by various groups^[14,15], ATRP remains the most powerful, versatile, simple, and inexpensive technique. ATRP produces polymers with very low polydispersities and provides extensive control of molecular architecture using a wide range of monomers. A variety of gradient, block and graft copolymers with novel compositions, macromolecular architectures and functional end groups have been prepared^[16-18]. The ATRP technique has been used to synthesize well-defined polymers with molecular weights ranging from 1000 to 100,000 g/mol. However, termination and other side reactions also occur, and they become more prominent as the molecular weight of the polymer increases^[11,19].

Researcher groups like Cheng, S. et al.^[20], Batsberg et al.^[1,21] and Yuan et al.^[22] were also reported the synthesis of PS-PEG-PS copolymer via ATRP and studied the micellar behavior of such amphiphilic triblock copolymers. The performance of copolymer materials depends on structurally related parameters, such as molecular weight distribution, chemical nature of the end-groups, random or block nature of copolymer, and balance between hydrophobic and hydrophilic segments. Synthesis of PS-PEG-PS triblock copolymers is not a new thing actually, but present situation, attention is always given towards the synthesis and applications of water soluble TBCs of PS-PEG-PS, where one may hope to have micelles in thermodynamic equilibrium. Our group would be interested in the synthesis of well-defined hydrophobic/water insoluble TBCs of PS-PEG-PS which just give the minor effect of ethereal oxygen of PEG block that may be the future useful material for

many electrical applications.

In this context, we report the synthesis of new hydrophobic PS-PEG-PS triblock copolymer with novel physical properties with reasonable molecular weight and low polydispersity *via* ATRP technology and, using poly (ethylene glycol) with a C-Cl or C-Br-end-group macroinitiators. The structure and molecular characteristics of this synthesized PS-PEG-PS triblock copolymer were studied by FT-IR, ¹H-NMR, TGA, and GPC. The compatibility and the potential morphological behaviour of this PS-PEG-PS ternary block system are under our investigation

EXPERIMENTAL SECTION

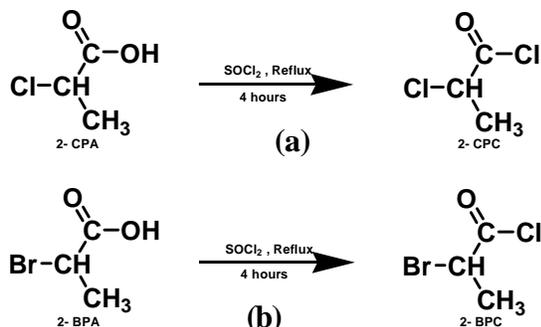
Materials

Monomer styrene was purchased from commercial sources and purified by passing through a column filled with Al₂O₃ to removal of inhibitors, then washed with 5% NaOH, and finally neutralize with ion free water. Purified styrene was stored over molecular sieves in glass bottle until used. Polyethylene glycol with molecular weight of 1500 g/mol was product of Sigma-Aldrich. Bipyridine (Bipy) and 4-dimethyl amino pyridine (4-DMAP) were of Loba Chemie of AnalaR grade. The CuCl was freshly prepared by reducing CuSO₄.5H₂O with sodium bisulphate NaHSO₃ and HCl. Other reagents used in synthesis like hexane, diethyl ether, thionyl chloride, ethanol and THF are of Merck products and used without further purification.

Synthesis of 2-Chloro propionyl chloride/2-Bromo propionyl chloride

30 mL(0.413 mol) of redistilled thionyl chloride was placed in a 250 mL three-neck RBF equipped with a reflux condenser arranged on magnetic stirrer. 15 mL(0.175 mol) 2-CPA was added cautiously dropwise with the help of dropping funnel during the course of 30-40 minutes and the mixture was stirred and reflux for the 4 hrs. to ensure all the acid (-COOH) was converted into acid chloride(-COCl). Rearranged the apparatus for the distillation and collect the crude acid chloride boiling between 80-115°C. Finally, redistilled from a flask provided with a short fractionating column and collect the 2-CPC at 100-113°C. The yield was 80% (14 mL). Similarly 2-BPC was synthesized by

taking 2-BPA in place of 2-chloro propionic acid and adopting the above same procedure. Both the compounds were utilized in the synthesis of PEG-macroinitiator consisting C-Cl and C-Br end group.



Scheme 1 : Synthesis of (a) 2-CPC & (b) 2-BPC

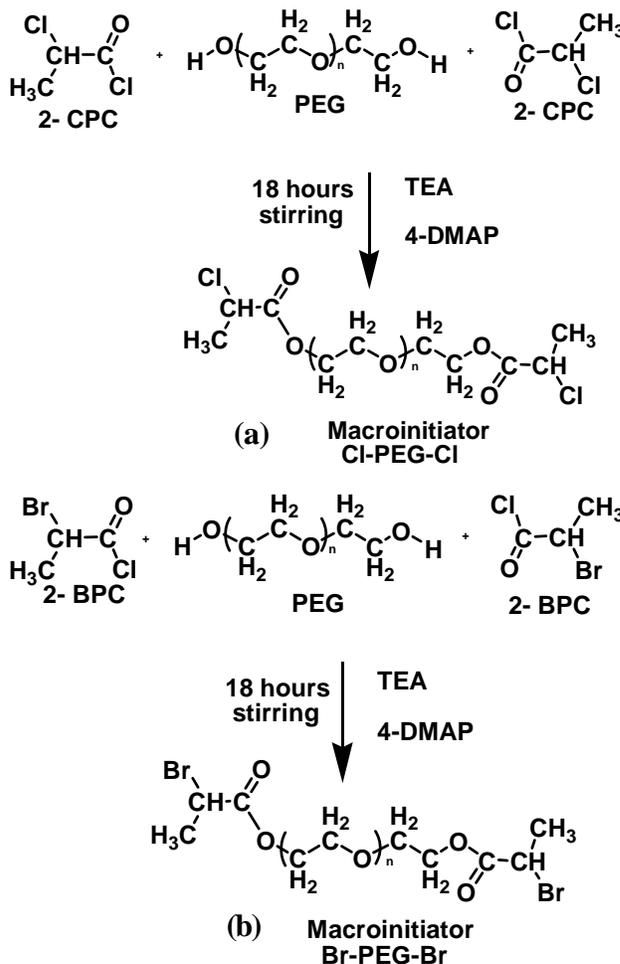
Synthesis of poly (ethylene glycol)-Macroinitiators

The PEG-macroinitiators were synthesized through 2-chloro or bromo propionyl chloride as shown in scheme 2a and 2b. In a 100 mL two neck RBF, 2.4 gm (19.8 mmol) 4-dimethyl amino pyridine (4-DMAP) was dissolved into 20 mL dichloromethane (DCM) and 1.84 mL (0.0132 mmol) triethylamine (TEA) was added. The mixture was vigorously stirred for 1 hr under the N_2 atm. in ice bath maintaining the temperature $0^\circ C$. After 1hr, 1.2 mL (16.5 mmol) 2-CPC mixed with 5 mL DCM was injected with syringe. When the yellowish dispersed solution was obtained, the solution of 10 gm (6.6 mmol) PEG dissolved in 20 mL DCM was added dropwise with the help of dropping funnel and stirring was continued for the further 18 hrs. The macroinitiator was precipitated by adding large excess of diethyl ether in ice bath. The macroinitiator was isolated by filtration and washed with diethyl ether. After recrystallization from dry ethanol, the product was again washed with diethyl ether and then dried under vacuum for a day. The final product, a white crystalline powder was stored under a nitrogen atmosphere.

Synthesis of PS-PEG-PS Triblock copolymer by ATRP

The TBC of PS-PEG-PS was synthesized through ATRP using the above synthesized macroinitiators and styrene as monomer by bulk polymerization procedure. In a 150 mL RBF were placed macroinitiator, ligand bipyridyl and catalyst CuX in a 1:2:6 ratios and the mix-

ture degassed by a freeze-pump-thaw technique three times. After 30 minutes 10 mL (87.22 mmol) monomer styrene was added with help of canula. The reaction was allowed to proceed under stirring at $110^\circ C$ for 20 hrs. The polymer product was recovered through column chromatography with alumina and was purified by the precipitation into hexen.



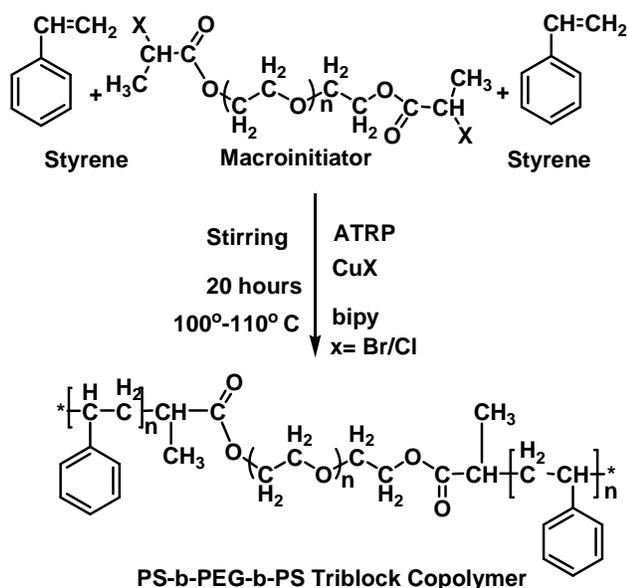
Scheme 2 : Synthesis route of (a) C- Cl end group and (b) C-Br end group with PEG-macroinitiator

Measurements

Fourier transform infrared (FT-IR) spectra of the all compounds were recorded on Shimadzu-8400S spectrophotometer by KBr pellet method. The spectra were obtained over the frequency range $4000-400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} and 30 scan. The proton nuclear magnetic resonance (1H -NMR) spectra of block copolymer made on Bruker Avance II 400 NMR spectrometer operated at 400 MHz using TMS as an internal standard, and the $CDCl_3$ solvent provided the deu-

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terium lock frequency at 25°C from SAIF, Chandigarh. Thermal gravimetry analysis (TGA) was conducted for the degradation pattern of the synthesized polymer was done on Shimadzu (TGA-50) at a heating rate of 10°C/min. The apparent M_n , apparent M_w , and molecular weight distribution of the triblock copolymer were determined by gel permeation chromatography using a PL-GPC 200 gel permeation chromatography instrument of, with one refractive index detector and two PL gel-mixed-B 10 μ m columns (300 \times 7.5 mm), operated with THF as the eluent at 35°C. The chromatograms were calibrated with PS standards.



Scheme 3 : The synthesis route of PS-PEG-PS triblock copolymer *via* ATRP

RESULTS AND DISCUSSION

In the synthesis of PS-PEG-PS triblock copolymer, initially 2-CPC and 2-BPC were synthesized from their respective carboxylic acids. The FT-IR spectra of synthesized acid chloride derivatives along with respective, carboxylic acids were shown in Figure 1.

Both the acids clearly shows the broad band ranging from 3200-3500 cm^{-1} depicted the -OH stretching band due to the carboxylic acid functional group, beside that in the spectrum of their corresponding acid chlorides does not shows these broad spectrums. It indicates the substitution of -OH group by -Cl group during the reaction with used thionyl chloride. These

acid chloride derivatives further used to prepared PEG-Macroinitiator consisting -Cl and -Br terminal groups.

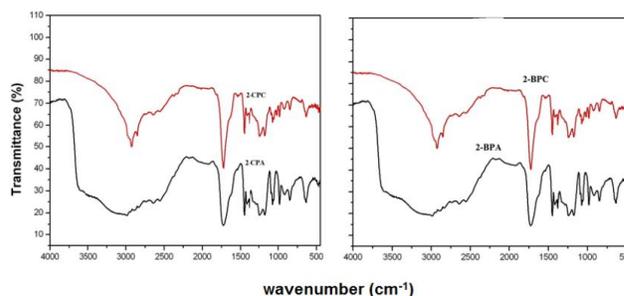


Figure 1 : The FT-IR spectrum of 2-CPC/2-BPC initiator alongwith respective acids

The FT-IR spectra of the PEG-Macroinitiator of chlorine & bromine based are shown in Figure 2. The spectrum of Cl-PEG-Cl Macroinitiator [Figure 2(A)] clearly shows that the broad absorbance band of -OH group was completely disappeared and the presence of characteristic absorbance band of -C=O band at 1760 cm^{-1} indicates the covalent combination of 2-CPC and PEG-1500. Similar observation also observed in the case of Br-PEG-Cl Macroinitiator [Figure 2(B)].

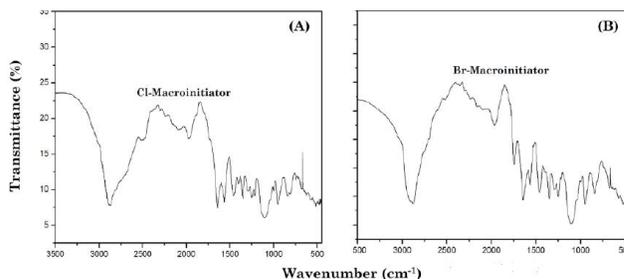


Figure 2 : FTIR spectrum of (A) Cl-PEG-Cl and (B) Cl-PEG-Br macroinitiators

Both the telechelic Cl-PEG-Cl and Br-PEG-Br macroinitiators were used to initiate ATRP of styrene in bulk and in solution for formation of TBC of PS-PEG-PS. The product purification was carried out by extraction with cyclohexane (for PS) and water (for PEG macroinitiators). Figure 3 shows the comparison FTIR spectra of PEG, Cl-PEG-Cl Macroinitiator and PS-PEG-PS triblock copolymer. The spectrum of PS-PEG-PS triblock copolymer shows the presence of typical absorbance of PEG and aromatic absorbance of styrene both.

Figure 4 represents the $^1\text{H-NMR}$ spectra of triblock copolymer, PS-PEG-PS by bulk polymerization initiated by Cl-PEG-Cl macroinitiator. A single peak at 3.64 δ ppm existed in both the MI and TBC for the methyl-

ene group ($-\text{CH}_2-$) of PEG, but for the triblock copolymer, two peaks at 6.5 δ ppm and 7.1 δ ppm appeared for phenyl ring protons. Both the IR spectra and the $^1\text{H-NMR}$ spectra confirmed the coexistence of the polystyrene chain and the polyethylene glycol chain in the macromolecular structure^[24].

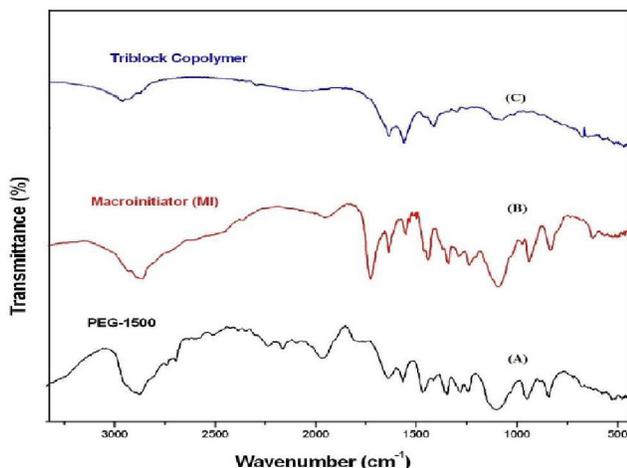


Figure 3 : FTIR spectrum of the PEG, Cl-PEG-Cl MI & TBC

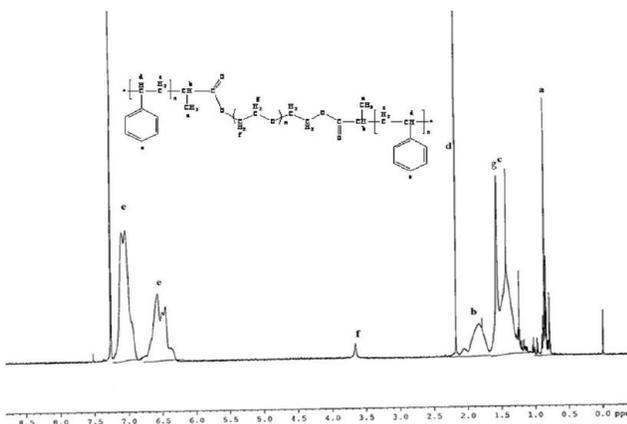


Figure 4 : The $^1\text{H-NMR}$ spectra of triblock copolymer, PS-PEG-PS

$^1\text{H-NMR}$: 1) 0.9 δ ppm for the methyl proton of propyl group, 2) 1.2 δ ppm for the methylene proton of styrene, 3) 1.9 δ ppm for the methyn proton of propyl group, 4) 2.1 δ ppm for the methyn proton of styrene 5), 3.7 δ ppm for the methylene protons of PEG and 6) 6.5 δ and 7.1 δ ppm for the phenyl ring protons.

To determine the thermal stability of the polymer the thermal gravimetric analysis was conducted. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties^[25]. Figure 5 shows the TGA curve of obtained from TBC of PS-PEG-PS. The

thermogram indicates the starting of thermal degradation of TBP undergoes at 301 $^\circ\text{C}$ and with a total mass loss of 100.0%. TGA results in the temperature region below the onset of degradation. At about 68 $^\circ\text{C}$, the TBP starts to evolve the small amount of moisture, which is clearly found to be 3%.

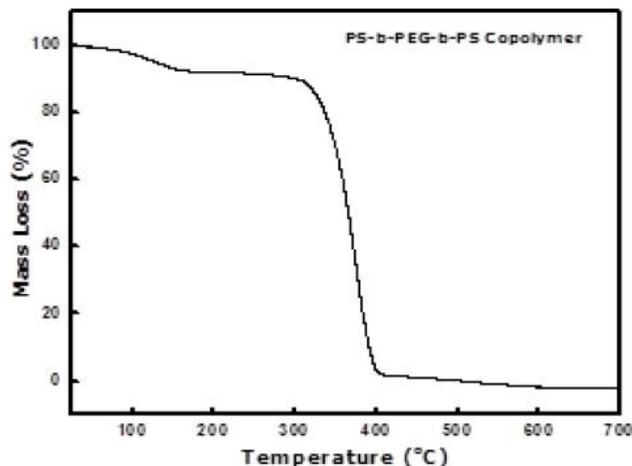


Figure 5 : TGA curve of triblock PS-PEG-PS copolymer

The GPC curve of triblock copolymer obtained in bulk is presented in Figure.6. The single peak of the GPC curve of the products at 4.940 indicated that the product could not be the blend of PS-homopolymer and PEG-homopolymer; if so, the GPC curves should appear as two peaks. Data indicates the involvement of essentially all PEG macroinitiator chains in initiating the ATRP of styrene. The Number Average (M_n) = 176171, Weight Average (M_w) = 247765 and Polydispersity (M_w/M_n) = 1.4 for TBC of PS-PEG-PS are also obtained from the GPC measurements. The synthesized polymer have narrow polydispersity (M_w/M_n) values 1.4, which further indicates a high efficiency of the

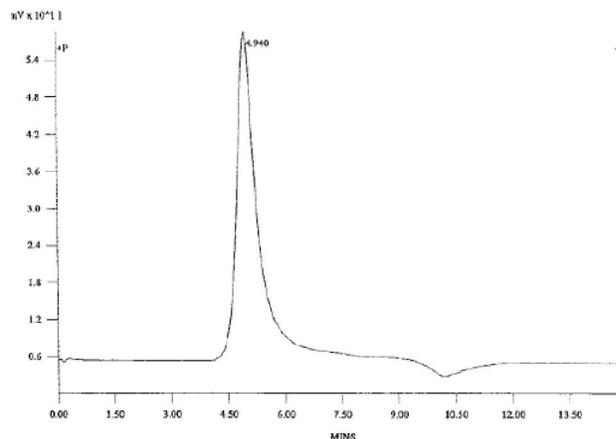


Figure 6 : The GPC of triblock PS-PEG-PS copolymer

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macroinitiators and a low degree of uncontrolled polymerizations generated by side reaction particularly thermal polymerization.

CONCLUSIONS

It has been shown those 2-chloro (or bromo) propionates PEG-macroinitiators are active in ATRP of styrene. Hydrophobic TBC of PS-PEG-PS with controlled structure was effectively synthesized and well characterized, which have not been obtained previously by direct polymerization from a macroinitiators. The good control over the molecular weight distribution was obtained *via* ATRP conditions. Clear understanding of the laboratory approach was reported and it was concluded that compared to other “living” radical system, ATRP represents a simple, inexpensive, and more general method for controlled radical polymerization. The compatibility and the potential morphological behavior of this PS-PEG-PS ternary block system will be key for future electrical applications.

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