

# Preparation of Poly(Styrene-*b*-2-Hydroxyethyl acrylate) Block Copolymer Using Reverse Iodine Transfer Polymerization

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**ABSTRACT:** Reverse iodine transfer polymerizations (RITP) of 2-hydroxyethyl acrylate (HEA) were performed in *N,N*-dimethylformamide at 75°C using AIBN as initiator. Poly(2-hydroxyethyl acrylate) (PHEA) with  $M_n = 3300$  g mol<sup>-1</sup> and  $M_w/M_n < 1.5$  were obtained. Homopolymerization of styrene in RITP was also carried out under similar conditions using toluene as solvent. The resulting iodopolystyrene (PS-I) with ( $M_n, SEC = 607$  g mol<sup>-1</sup>, polydispersity index (PDI) = 1.31) was used as a macroinitiator for the synthesis of amphiphilic block copolymers based on HEA with controlled well-defined structure. Poly(styrene-*b*-2-

hydroxyethyl acrylate) (PS-*b*-PHEA) with  $M_n = 13,000$  g mol<sup>-1</sup> and polydispersity index ( $M_w/M_n$ ) = 1.4 was obtained, copolymer composition was characterized using <sup>1</sup>H-NMR and FTIR, whereas SEC and gradient HPLC were used to confirm the formation of block copolymer and the living character of polymer chains. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** reverse iodine transfer polymerization; diblock copolymers; copolymerization; poly(styrene-*b*-2-hydroxyethyl acrylate)

## INTRODUCTION

Controlled/living free-radical polymerization LRP/CRP is one of the most effective routes to prepare well-defined polymers (predetermined molecular weight, narrow distribution, and tailored architectures).<sup>1</sup> The field of LRP/CRP has grown rapidly in the past decade.<sup>2</sup> A variety of well-controlled polymers have been successfully prepared by various CRP methods, including atom transfer radical polymerization (ATRP),<sup>3</sup> reversible addition-fragmentation chain transfer (RAFT),<sup>4</sup> and nitroxide-mediated polymerization (NMP).<sup>5</sup>

Reverse iodine transfer polymerization (RITP) has been also used to prepare well-defined polymers.<sup>6–8</sup> RITP is based on the use of molecular iodine (I<sub>2</sub>) as control agent. In RITP (Scheme 1), the radicals provided by the decomposed initiator react preferably with iodine or propagate with a few monomer units before reacting with iodine to form *in situ* the iodinated transfer agents (A-I and A-Mn-I, respectively).

Once all the iodine has been consumed, the core equilibrium of degenerative chain transfer between active and dormant chains takes place.<sup>8</sup>

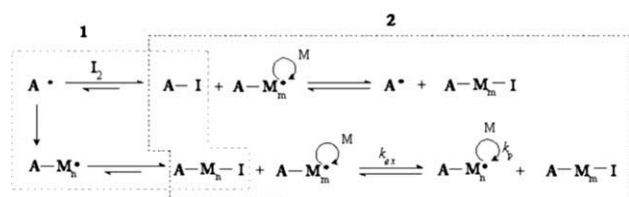
One molecule of iodine will control two polymer chains. So, in this process, the molecular weight of the polymer is controlled by the molar ratio between the quantity of monomer and twice the quantity of iodine initially added.

The advantages of RITP are that the transfer agent is generated *in situ* in the reaction medium, therefore in RITP the synthesis or storage of the transfer agents is not required.<sup>9</sup> Moreover, RITP is practically easier than other polymerization methods, as only molecular iodine needs to be added to the reaction to achieve control of the polymerization. RITP has already been successfully used to polymerize applied to a wide range of monomers such as acrylates,<sup>8</sup> styrene,<sup>10</sup> MMA,<sup>6</sup> and copolymers of vinylidene chloride and methyl acrylate.<sup>7</sup>

This study describes for the first time the use of RITP for the homopolymerization of 2-hydroxyethyl acrylate (HEA), and the subsequent copolymerization with styrene monomer to form block copolymers of poly(styrene-*b*-2-hydroxyethyl acrylate) (PS-*b*-PHEA). Poly(2-hydroxyethyl acrylate) (PHEA) is an acrylate polymer that is rubbery at room temperature. Because of its high affinity for water, it has been used in hydrophilic polymeric gel for applications such as agricultural, coating, and biomedical applications.<sup>11</sup>

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**Scheme 1** Simplified mechanism of reverse iodine transfer polymerization (RITP).

The synthesis of PHEA and subsequent amphiphilic block copolymers with well-defined structures has been reported using different CRP methods, such as ATRP<sup>12</sup> and NMRP.<sup>13</sup> For instance, HEA was polymerized by Coca et al.<sup>12</sup> using the ATRP method, the polymerization exhibited first-order kinetics and the number average molecular weights increased with conversion, whereas polydispersities remained low throughout the polymerization ( $M_w/M_n \sim 1.2$ ). Reactions were conducted in bulk and in 1 : 1 (v/v) aqueous solutions.

Muchlebach et al.<sup>14</sup> synthesized amphiphilic block copolymers by CRP. They reported the block copolymerization of butyl acrylate (BA) and 2-trimethylsilyloxyethyl acrylate by ATRP. Diblock and triblock copolymers with predefined block lengths and low polydispersities were obtained, when using methyl-2-bromopropionate as initiator and CuBr as catalyst. Hydrolysis of trimethylsilyl (TMS) groups led to block copolymers with (BA) and HEA units, which were characterized by size exclusion chromatography (SEC), nuclear magnetic resonance spectroscopy (NMR), and Fourier transform infrared spectroscopy (FTIR). Recently, NMP was also used to synthesize PHEA in bulk, in organic solvent (*N,N*-dimethylformamide), and controlled polymerization was obtained with polydispersity indices lower than 1.3. Amphiphilic block copolymers of poly(butyl acrylate) (PBA)-*b*-PHEA with different molecular weights and block composition were also studied.<sup>13</sup> Khutoryanski et al.<sup>15</sup> synthesized amphiphilic copolymers based on PHEA and P(vinyl butyl ether) via solution polymerization, and studied their interaction with poly (carboxylic acids).

To the best of our knowledge, there are only few articles reported on the preparation of block copolymers using RITP. Lacroix-Desmazes et al.<sup>8</sup> confirmed the living nature of RITP by preparation of a poly (methyl acrylate)-*b*-polystyrene block copolymer, where they used iodo-terminated poly(methyl acrylate) (PMA-I) as macroinitiator and added styrene as a second block. Tonnar et al.<sup>9</sup> successfully synthesized a poly(butyl acrylate-*b*-styrene) block copolymer in seeded emulsion polymerization using RITP, by using an iodo-terminated PBA-I as macroinitiator. Recently, Enriquez-Medrano et al.<sup>16</sup> used difunctional initiator to simplify the synthesis of triblock

copolymers of poly(styrene-butyl acrylate-styrene) by RITP in only two steps starting with the formation of the central block using 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethylhexane as a difunctional initiator and then resuming the polymerization to grow the external blocks in a second step.

Herein, we reports on the use of RITP to prepare PS-*b*-PHEA amphiphilic block copolymers. Iodo-terminated PS (PS-I) was synthesized first and then used as macroinitiator to grow the second PHEA block. This is the first report on the synthesis of this kind of diblock copolymers by such a straightforward controlled radical polymerization method, RITP. The successful formation of the block copolymer PS-*b*-HEA was confirmed by gel permeation chromatography (GPC) and further analyzed using HPLC in toluene/dimethylformamide (DMF) system. The reaction kinetic profile of the RITP process for styrene and HEA was also described here in more detail.

## EXPERIMENTAL

### Materials

Commercial HEA (HEA, Aldrich, 96%) contains impurities, such as ethylene glycol, acrylic acid, and ethylene glycol diacrylate. The presence of diacrylates leads to crosslinking, and acrylic acid may inhibit the polymerization. Therefore, the polymerization of unpurified or poorly purified monomer may be incomplete and/or slow or lead to insoluble solids. HEA was therefore purified by dissolving in water (25 vol %) and then washing the solution 10 times with hexane to extract diacrylates. The aqueous solution was then salted (200 g NaCl), and monomer was separated from aqueous phase by ether extraction (four times) to remove acrylic acid which remained in the water phase. Finally, magnesium sulfate (3 wt %) drying agent was used to remove traces of water before evaporation of the ether phase on a rotary evaporator. The purified monomer was distilled under vacuum immediately prior its use in polymerization. Stabilized styrene monomer was obtained from Aldrich. The stabilizer was removed by washing three times with a 3-wt % potassium hydroxide solution. The styrene was then purified by distillation under reduced pressure at 30°C. The initiator 2,2-azobis(isobutyronitrile) (AIBN) was obtained from Aldrich and recrystallized from methanol.

### Homopolymerization of HEA and styrene

In a typical procedure of HEA polymerization by the RITP process, HEA (6 g, 51.7 mmol), DMF (12 mL), AIBN (335 mg, 2.04 mmol), and iodine (304 mg, 1.20 mmol) were introduced in a Schlenk flask. After three freeze-thaw pump cycles, the flask was heated to 75°C in an oil bath. The polymerization was

conducted in the dark, under an argon atmosphere with magnetic stirring for 10 h. Samples for analysis purpose were continuously withdrawn from the reactor with a glass syringe through a septum and under positive nitrogen flushing.

The RITP of styrene was performed in a similar way at 75°C, except that the solvent used was toluene. Furthermore, in the case of styrene polymerization by RITP, a higher molecular weight was targeted. In a typical procedure, the stoichiometry used was: styrene (6 g, 57.6 mmol), toluene (12 mL) AIBN (0.0272 g, 0.17 mmol), and iodine (0.025 g, 0.1 mmol).

### Block copolymerization of HEA and styrene

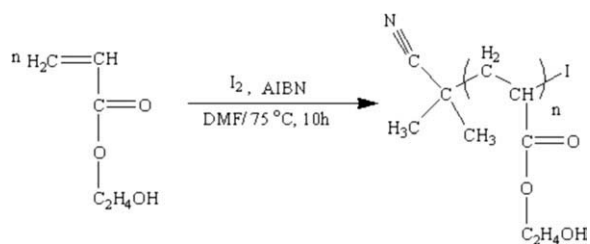
Block copolymers of PS-*b*-PHEA were prepared by the macroinitiator method. Iodo-polystyrene (PS-I) prepared according to procedure above, was used as macroinitiator (after removal of excess monomer from the first block). The macroinitiator was directly heated with HEA monomer at 75°C to afford the block copolymer. In a typical procedure, PS-I macroinitiator (1.6 g,  $1.23 \times 10^{-4}$  mol) was dissolved in DMF and mixed with HEA (1.3 g, 0.0112 mol) and AIBN (0.0001 g,  $6.02 \times 10^{-7}$  mol) in a Schlenk tube. After degassing by freeze-vacuum-thaw cycles, the polymerization was conducted in the dark with stirring at 75°C for 48 h. The resultant copolymer was then precipitated in a cold mixture of ethanol and diethyl ether, and then dried in a vacuum oven at 30°C for 3 days.

The block copolymer was characterized by the following techniques: <sup>1</sup>H-NMR, FTIR, SEC, and high-performance liquid chromatography (HPLC).

### Characterization

NMR analysis was performed at 20°C using a Varian VXR-unity 300 MHz. FTIR spectra were recorded with a Perkin-Elmer 1650 transform infrared spectrophotometer, using an average of 32 scans. SEC was performed using a Waters 600E system controller equipped with a Waters 610 fluid unit pump, a Waters 410 differential refractometer as detector, an a column set of PLgel 5 μm 50 × 7.5 mm and a PLgel 5 μm mixed-C 300 × 7.5 mm column. Measurements were carried out at 30°C, using tetrahydrofuran (THF) as eluent and a flow rate of 1 mL min<sup>-1</sup>.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) were recorded on a Voyager-DE STR (Applied Biosystems, Farmingham) equipped with a nitrogen 337 nm laser in the reflector mode, at 25 kV accelerating voltage and with delayed extraction. The matrix used was 2,5-dihydroxybenzoic acid (Aldrich) and potassium trifluoro acetate (KTFA; Aldrich) was used as the cationizing agent. For each analysis, the analyte sample was prepared by first making up the



**Scheme 2** Homopolymerization of HEA via RITP.

following concentration of the matrix, KTFA, and sample, in DMF, separately: 35 mg mL<sup>-1</sup> matrix; 5 mg mL<sup>-1</sup> KTFA; 1 mg mL<sup>-1</sup> sample, before mixing them in the ratio of 4 : 1 : 4 and hand spotting on the target plate. About 1000 laser shots were performed for each spectrum.

Separation of block copolymers by chemical composition in this study was performed using a dual pump HPLC comprising of the following units: Waters 2690 separation module (Alliance), Agilent 1100 series variable wavelength detector, PL-ELS 1000 detector. Data were recorded and processed using PSS WinGPC unity (Build 2019) software. The separation was done through a bare silica column [Nucleosil C18 5mm (250 × 4.6 mm<sup>2</sup>)] at 30°C. The samples were prepared in THF at a concentration of 5 mg mL<sup>-1</sup>.

## RESULTS AND DISCUSSION

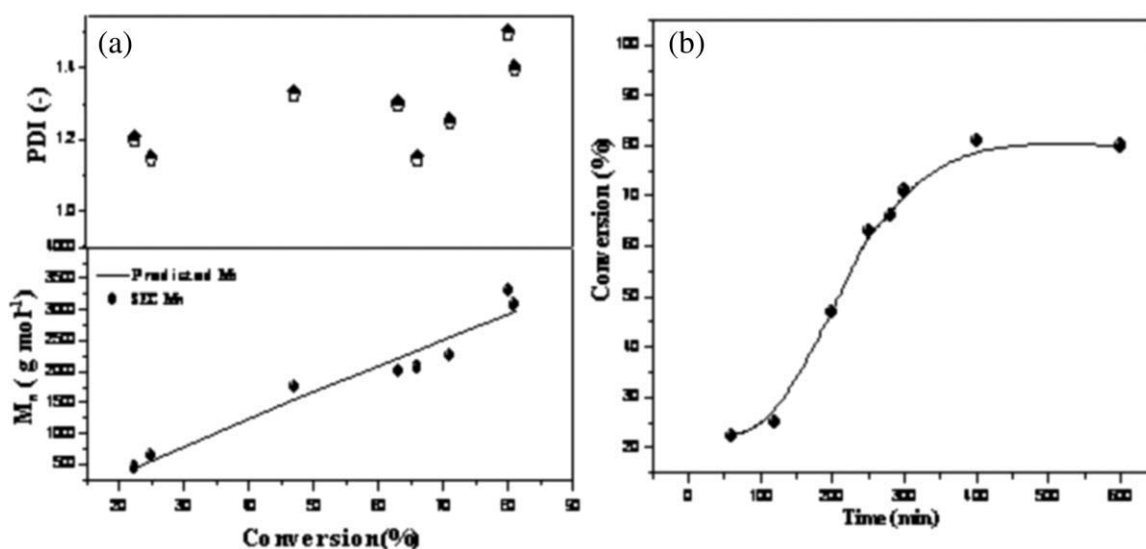
### Homopolymerization of HEA

Because of the insolubility of high molecular weight PHEA in common solvents, due to intermolecular hydrogen bonding,<sup>11</sup> only low molecular weights of PHEA were targeted. The homopolymerization of HEA in DMF proceeded with 80% conversion being achieved within 10 h  $M_n$  (SEC) = 3300 g mol<sup>-1</sup>,  $M_n$  (theor) = 2193 g mol<sup>-1</sup>, and polydispersity index (PDI) 1.5. Scheme 2 shows the homopolymerization of HEA by RITP.

HEA was polymerized in DMF so as to allow a relatively low viscosity and a good dissipation of the heat of the reaction.<sup>12</sup> DMF was also the selected solvent due to its ability to dissolve both the initiator and the monomer. Figure 1(a) shows that  $M_n$  increased linearly as a function of monomer conversion, indicating a constant number of growing chains throughout the polymerization, showing that the polymerization occurred in a controlled manner.<sup>17</sup>

The evolution of monomer conversion with time clearly shows that the RITP polymerization of HEA is relatively fast and the inhibition period took less than 2 h. This could be due to a slight accelerating effect of the polar solvent DMF.<sup>12</sup>

This is in agreement with the polymerization of HEA using ATRP in DMF, whereby a similar solvent effect was observed.<sup>11</sup> In the RITP process, during



**Figure 1** HEA polymerized by RITP: (a)  $M_n$  ( $_{exp}$ ),  $M_n$  ( $_{theory}$ ), and PDI versus conversion, and (b) conversion (%) versus time.

the inhibition period, the free radicals predominantly react with iodine to form *in situ* the reversible chain transfer agent. When all the iodine is consumed, at the end of the inhibition period, the degenerative transfer equilibrium takes place. The  $[initiator]/[I_2]$  ratio is the determining parameter controlling the duration of inhibition period.<sup>6,8</sup> the  $[initiator]/[I_2]$  ratio must be higher than 1.5 to achieve high yields of polymerization. Below 1.5 the polymerization yield has been reported to be generally low.<sup>6,8,9</sup> the theoretical inhibition time can be calculated by eq. (1)<sup>8</sup>:

$$\text{time}_{\text{(theoretical)}}^{\text{inhibition}} = \frac{-\ln\left(\frac{1-[I_2]_0}{f \cdot [AIBN]_0}\right)}{k_d} \quad (1)$$

where  $[I_2]_0$  and  $[AIBN]_0$  are initial concentrations of iodine and initiator, respectively,  $k_d$  is the decomposition rate constant of the initiator ( $k_d = 7.5 \times 10^{-5} \text{ s}^{-1}$  at  $75^\circ\text{C}$ ),<sup>18</sup> and  $f$  is the initiator efficiency ( $f = 0.7$  for AIBN) in DMF.<sup>19</sup> It was found that the experimental and theoretical inhibition times of RITP of HEA at  $75^\circ\text{C}$  are in fair agreement. This correlates well with findings obtained by Boyer et al.<sup>6</sup> who studied the RITP mechanism of methyl methacrylate (MMA). The consumption of monomer is very low until the concentration of molecular iodine becomes negligible, as the rate of reaction between radicals and iodine is much higher than the rate of propagation of the monomer. Hence, there is direct correlation between the inhibition period and the presence of free iodine in the reaction medium. Moreover, this inhibition period can be divided into two stages, the first stage being when the concentration of the A-I adduct builds up, and a second stage

corresponding to the formation of very short A- $M_n$ -I oligomers. Thus, all the iodine is consumed, whereas only few percent of HEA are being consumed during the inhibition period. However, it is worth mentioning that this behavior is not the same for all polymers prepared by RITP. A typical counter example is for the RITP-mediated polymerization of styrene, where the inhibited period is influenced by both concentrations of monomer and iodine due to the formation of styrene-iodine complex.<sup>20</sup>

The  $M_{n,SEC}$  was found to increase linearly as a function of the conversion, and the PDI remained below 1.5. The theoretical molecular weight was calculated according to the following equation<sup>8</sup>:

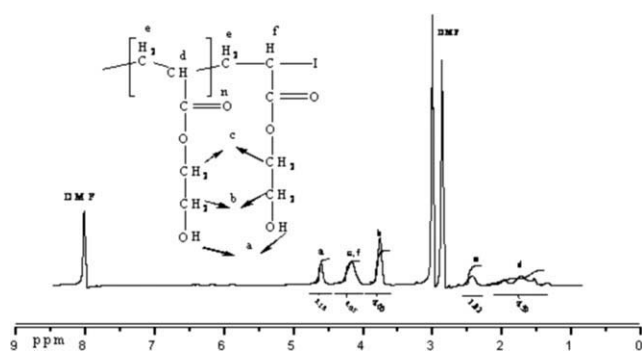
$$M_{n,theor} = \frac{m_{\text{mono}} \cdot C\%}{2n_{I_2}} + M_{A-I} \quad (2)$$

where  $m_{\text{mono}}$  is mass of monomer and  $C\%$  is conversion,  $n_{I_2}$  is the number of moles of iodine,  $M_{A-I}$  stand for molecular weight of A-I adduct, whereas A stands for the radical fragment from the initiator. The experimental  $M_n$  values measured via SEC were in good agreement with the theoretical  $M_n$  at low conversion. However, the deviation of experimental  $M_n$  from the prediction occurred at higher conversion, indicating a partial loss of control which could be due to the occurrence of chain transfer to polymer. However, overall RITP of HEA takes place in a controlled manner.

The  $^1\text{H-NMR}$  spectrum of PHEA purified by precipitation in cooled diethylether, is shown in Figure 2. Only traces of ethylenic protons were found at  $\sim 5.72$  and  $6.3$  ppm indicating the negligible residual of monomer.

The signal at  $4.8$  ppm comes from the resonance of the proton of the hydroxyl group (a), while the

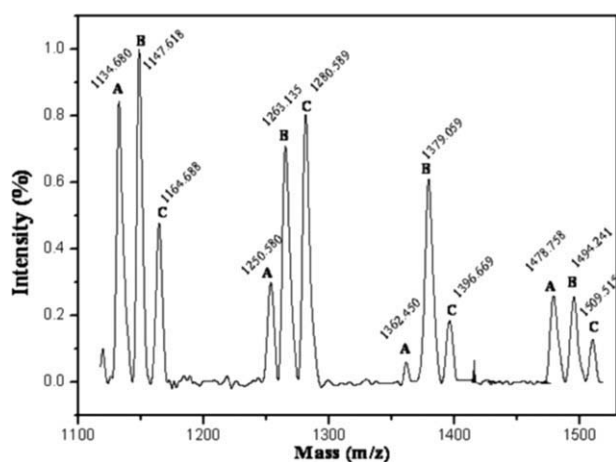




**Figure 2**  $^1\text{H-NMR}$  spectrum in  $\text{DMF-d}^7$  of PHEA polymerized in DMF by RITP.

signals at 4.07 and 3.7 ppm correspond to the  $\text{CH}_2$  protons of the hydroxyethyl group (c and b). The methine at  $\beta$  position from the iodo group (f) is expected to give a signal at 4.05 ppm. This is however overlapped with the resonance of methylene protons (c). A similar NMR spectrum of PHEA was also observed when prepared by ATRP, as reported by Coca et al.<sup>12</sup> They also found that the signal of the methine proton at the bromine end chain overlapped with the signal of the resonance of the methylene protons from the hydroxyethyl group. The PHEA structure was further analyzed using MALDI-TOF, which is a powerful analytical method to elucidate the structures of low to medium molecular weight polymers synthesized via CRP.<sup>21</sup>

Figure 3 shows a MALDI-TOF analysis of a low molecular weight PHEA prepared by RITP. Focusing on the zone  $m/z = 1100\text{--}1500$ , three different series (A, B, and C) are distinguished. The expected  $\text{A-M}_n\text{-I}$  structure cationized using  $\text{Na}^+$  appears at  $m/z = 1147.618$ , 1263.135, and 1379.059, with a strong intensity [as seen in the distributions (B)]. The distributions (C) at  $m/z = 1164.688$ , 1280.589, and 1396.669 can be attributed to the adsorption of PHEA with one water molecule, giving the structure  $\text{PHEA}(\text{H}_2\text{O})$ ,



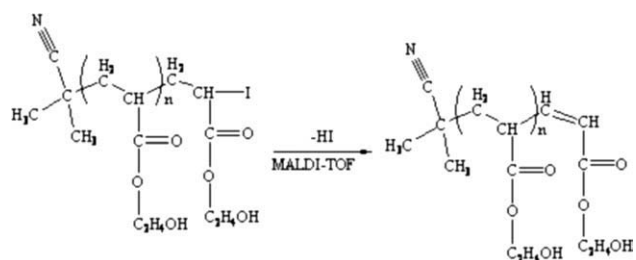
**Figure 3** MALDI-TOF spectrum of PHEA via RITP.

because this polymer has a high affinity for water. The complexation of water molecules in MALDI-TOF analysis of polymers has been reported by Ladaviere et al.<sup>22</sup> The distributions (A) at  $m/z = 1134.680$ , 1250.580, and 1362.450 could be due to elimination of HI from  $\text{A-M}_n\text{-I}$  polymer chains at high temperature ( $150^\circ\text{C}$ ) or during the MALDI-TOF analysis, resulting in an unsaturated chain end as shown in Scheme 3.

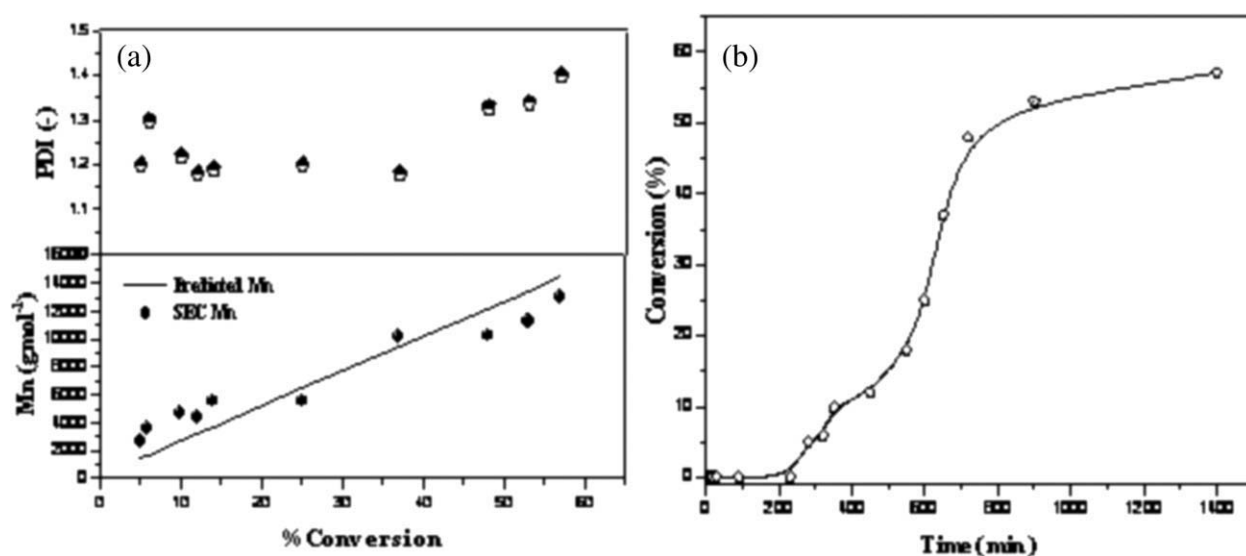
A similar elimination of hydrogen halide has been observed and reported for PHEA prepared via ATRP and terminated by bromine.<sup>12</sup> Nonaka et al.<sup>23</sup> prepared poly(methyl methacrylate) (PMMA) via ruthenium-mediated CRP. The polymer chains were terminated by chlorine, although the elimination of HCl from terminal chlorine was not observed during MALDI-TOF analysis, probably due to the higher stability of C–Cl covalent bond relative to C–Br or C–I. In summary,  $\text{A-M}_n\text{-I}$  was the major product in the sample, further confirming the relevance of the mechanism of RITP.

### Homopolymerization of styrene

Figure 4 shows the evaluation of  $M_n$  and PDI as a function of monomer conversion. The molar ratio of  $\text{AIBN}/\text{I}_2 = 1.4$ . The number average molecular weight  $M_n$  increased linearly with the conversion, and was found to correlate well with the theoretical  $M_{n, \text{predicted}}$ . The PDI remained in an acceptable range for reverse iodine transfer polymerization of styrene.<sup>20,24</sup> The plot of conversion as a function of time depicted in Figure 4(b) shows the presence of an inhibition period of about 3 h 49 min. These results corresponds well with the results of studies conducted by Tonnar et al.<sup>20</sup> who found in the early stages of styrene polymerization via RITP an inhibition period of about 4 h. This is shorter than the theoretical inhibition period, calculated by eq. (1) ( $k_d$  is  $0.00014285 \text{ s}^{-1}$  at  $80^\circ\text{C}$ ).<sup>18</sup> The calculated theoretical inhibition period is significantly longer (18 h) than the experimental inhibition time observed, which is not consistent with the observation made for RITP of HEA and other acrylates such as methyl acrylate<sup>8</sup> and methyl methacrylate.<sup>6</sup> Tonnar et al.<sup>20</sup> studied



**Scheme 3** Elimination reaction of PHEA during MALDI-TOF analysis.



**Figure 4** Styrene polymerized by RITP: (a)  $M_n$  (exp),  $M_n$  (theor) and PDI versus conversion and (b) conversion versus time.

the inhibition period for RITP of styrene and found that the only hypothesis that can explain the shorter inhibition than expected is due to the formation of styrene diiodide (Scheme 4). The formation of a charge transfer complex has also been reported as a possible reason for shorting the duration of the inhibition period.<sup>10</sup>

As the formation of styrene diiodide is reversible, iodine can be liberated after the end of observed inhibition period. The liberated iodine thus reacts immediately with radicals present in the reaction medium creating new transfer agents, this hypothesis accounts for the shorter inhibition period while keeping a good correlation between theoretical and experimental molecular weight.

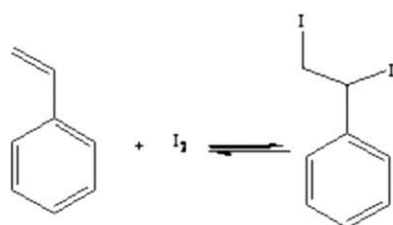
Clearly, the mechanism of RITP of styrene is a little bit more complicated than for HEA. The complexity of the RITP mechanism for styrene is due to the complexity of the chemistry between iodine and the styrene, whereby many different reactions can occur including addition of iodine onto the styrene double bond (yielding styrene diiodide),<sup>8</sup> iodine acting as initiator of cationic polymerization of styrene, formation of a charge transfer complex between iodine and styrene, or due to the ability of

iodine to form complexes with donor compounds such as benzene rings and derivatives.<sup>8</sup>

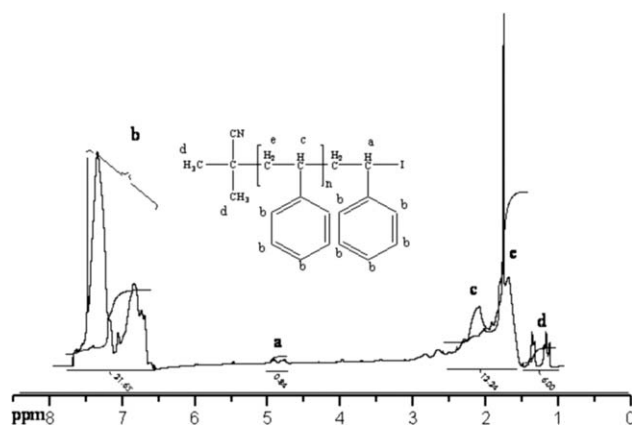
Notwithstanding the complicated mechanism of RITP polymerization of styrene, it remains a straightforward and simple technique to prepare polystyrene (PS) with a relatively well-defined structure.

Figure 5 shows a typical <sup>1</sup>H-NMR spectrum of a low molecular weight PS prepared via RITP. The signal at 4.5–4.8 ppm corresponds to the methine proton bearing the iodine chain end. This confirms the PS-I structure, which is consistent with that referenced in the literatures.<sup>25,26</sup> This also confirms the structure of the polymer according to the mechanism of RITP previously described in the introduction.

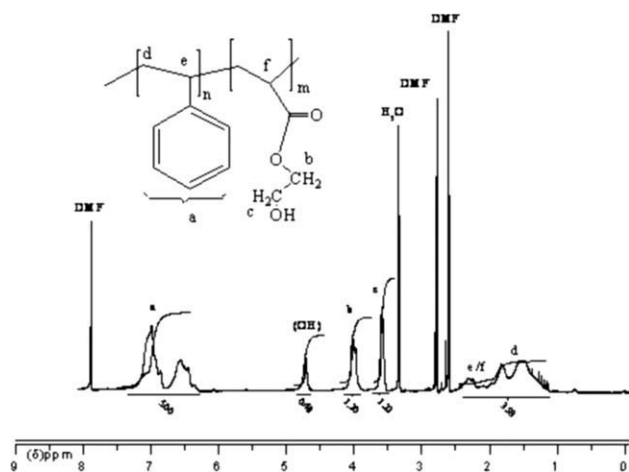
The protons *d* of the two methyl groups of the radical initiator (–C(CN)(CH<sub>3</sub>)<sub>2</sub>) appear at 1.20 ppm, peaks at 6.5–7.5 is corresponded to the aromatic protons, thus it is possible to calculate the molecular



**Scheme 4** Reversible addition of iodine onto styrene.



**Figure 5** <sup>1</sup>H-NMR spectrum in CDCl<sub>3</sub> of PS prepared by RITP.



**Figure 6**  $^1\text{H-NMR}$  spectrum in  $\text{DMF-}d^7$  of PS-*b*-PHEA prepared via RITP.

weight by  $^1\text{H-NMR}$  spectroscopy using the integral of the methine proton [Fig. 5(a)] at the iodine chain end (4.5–4.8) and the integral of aromatic protons in the polymer chain [Fig. 5(b)]. The results show that:  $M_{n, \text{theor}} = 700 \text{ g mol}^{-1}$ ,  $M_{n, \text{SEC}} = 607 \text{ g mol}^{-1}$ ,  $\text{PDI} = 1.31$  and  $M_{n, \text{NMR}} = 590 \text{ g mol}^{-1}$ . From  $^1\text{H-NMR}$ , it is also possible to evaluate the iodine functionality of chains  $F^{\text{iodine}}$  (i.e., the proportion of chains end-capped with iodine) using eq. (3).<sup>6</sup>

$$F^{\text{iodine}} = \frac{\int (-\text{CHI}^a-)}{\int \frac{(-\text{C}(\text{CN})(\text{CH}_2)_2)}{6}} \quad (3)$$

The iodine functionality determined by  $^1\text{H-NMR}$  is about 84%, indicating that most of the PS chains were end-capped with iodine. Thus PS-I prepared here was used as a macroinitiator to synthesize PS-*b*-PHEA block copolymer.

### Preparation of amphiphilic block copolymer

PS-*b*-PHEA was prepared using PS-I as a macroinitiator, and adding the second monomer (i.e., HEA). During the preparation of PS-I macroinitiator ( $M_n = 7.100 \text{ g mol}^{-1}$  and  $\text{PDI} = 1.5$ ), the conversion was kept below 50% to avoid loss of livingness by loss of iodine-capped ends, and the temperature was kept low ( $<40^\circ\text{C}$ ) when polymers were dried under vacuum.

The obtained block copolymer was characterized using  $^1\text{H-NMR}$  and FTIR spectroscopy. A typical  $^1\text{H-NMR}$  spectrum of PS-*b*-PHEA prepared via RITP is shown in Figure 6.

The signals at 6.50–7.30 ppm are related to the protons of the aromatic styrene groups. The strong signals at 3.55 and 4.05 ppm are ascribed to the methylene ( $-\text{CH}_2$ ) protons of the hydroxyethyl group (c and b) and the signal at 4.8 ppm

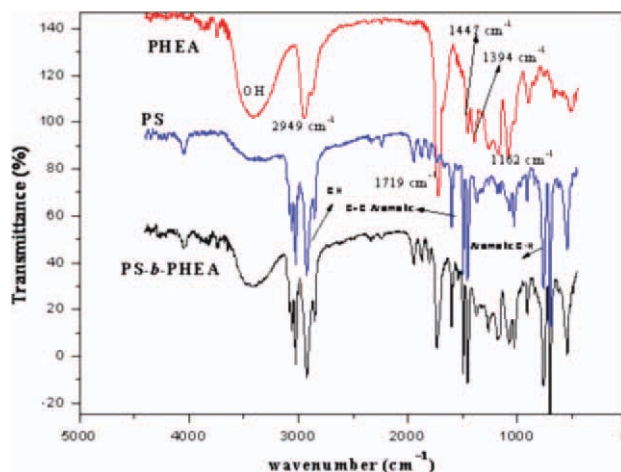
corresponds to the  $-\text{OH}$  of hydroxyethyl group. The presence of peaks belonging to styrene and HEA in the  $^1\text{H-NMR}$  spectrum indicated that copolymerization took place. However, it is worth mentioning that  $^1\text{H-NMR}$  does not allow differentiating between a blend containing two homopolymers from a copolymer containing both monomer units.

The methylene proton linked to iodine is expected to resonate at 4.05 ppm, which overlapped with the other  $-\text{CH}_2$  (b) from hydroxyethyl substitutes. The relative amounts of styrene and HEA monomer units incorporated into the copolymer were determined using  $^1\text{H-NMR}$ , by integration of specific peaks belonging to styrene (a) and HEA monomer units (b and c). The following equation was used:

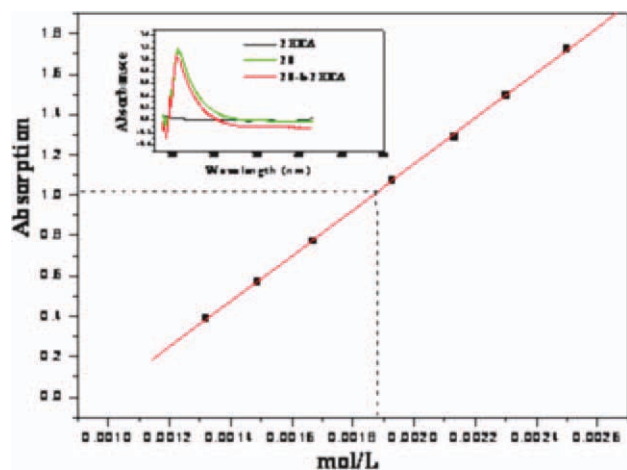
$$\text{PS}\% = \frac{\frac{\int a}{5}}{\frac{\int a}{5} + \frac{\int b+c}{4}} \times 100\% \quad (4)$$

where PS% is the percentage of PS in the copolymer, (a) and (b) and (c) are the integration of the peaks of styrene and HEA, respectively. PS-*b*-PHEA contained 62% styrene and 38% 2-hydroxyethyl acrylate, which in agreement with the theoretical ratio.

FTIR spectroscopy analysis of PHEA, PS, and PS-*b*-PHEA are shown in Figure 7. In the FTIR spectrum of PHEA a carbonyl band ( $\text{C}=\text{O}$  stretching) appeared at  $1719 \text{ cm}^{-1}$ , an aliphatic band ( $\text{C-H}$  stretching) was observed at  $2949 \text{ cm}^{-1}$  and an aliphatic ( $\text{C-H}$  bending) at  $1447 \text{ cm}^{-1}$ . The broad band at  $3500 \text{ cm}^{-1}$  corresponds to  $\text{O-H}$  stretching, and  $\text{O-H}$  bending can be seen at  $1394 \text{ cm}^{-1}$ . The ester group of the polymer ( $\text{C-O}$  stretching) shows bands in the FTIR spectrum at  $1162 \text{ cm}^{-1}$ . Bands belonging to ethylenic double bond at  $1633 \text{ cm}^{-1}$  had



**Figure 7** FTIR spectra of PS, PHEA, and PS-*b*-PHEA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8** Calibration curve for the determination of the percentage of styrene and HEA into PS-*b*-PHEA (the insert shows the UV/vis spectra of PS, PHEA, and PS-*b*-PHEA). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

completely disappeared; this FTIR spectrum of PHEA was found to be consistent with the literature.<sup>11</sup>

In the FTIR spectrum of PS the aromatic (C=C stretching) band appeared at 1602 cm<sup>-1</sup>, the aromatic (C-H) bands was observed at 740 cm<sup>-1</sup>, and aliphatic band (C-H stretching) appeared at 3024 cm<sup>-1</sup>. The FTIR spectrum of PS-*b*-PHEA exhibited all bands belonging to both blocks: HEA (i.e., C=O stretching at 1719 cm<sup>-1</sup>) and styrene aromatic ring (i.e., C=C stretching at 1602<sup>-1</sup> cm), giving an indication of the copolymerization of styrene HEA using the RITP method, the characteristic bands of double bonds disappeared in the spectrum of copolymer, for example, 1633 cm<sup>-1</sup> for HEA.<sup>11</sup> However, it is worth mentioning that FTIR spectroscopy does not allow differentiating between a blend containing two homopolymers from a copolymer containing both monomer units.

The copolymer was further characterized by UV-vis spectroscopy. The six-membered aromatic ring of the styrene monomer units were expected to absorb UV light in the region between 280 and 300 nm. The UV spectra of the PS, PHEA, and PS-*b*-PHEA are presented in Figure 8. UV analysis of the PS-*b*-PHEA showed that copolymer had strong absorption of UV light in the wavelength region where the styrene units absorb, whereas no absorption in this region was observed for PHEA.

A calibration curve was built from standard solutions of increasing concentration of PS in DMF, to determine the normal extinction coefficient of PS in DMF at a given wavelength of 255 nm. A plot of absorbance versus concentration of PS (in mol L<sup>-1</sup>) was constructed as shown in Figure 8. The linear relationship between concentration (C) (mol L<sup>-1</sup>) and

absorbance (*A*) shows that solutions of PS in DMF follow the Beer-Lambert law. From this calibration extinction coefficient ( $\epsilon$ ) can be determined via eq. (5):

$$A = \epsilon \cdot C \cdot b \quad (5)$$

where *A* absorbance,  $\epsilon$  is extinction coefficient (L mol<sup>-1</sup> cm<sup>-1</sup>), and *b* is the length of cuvette (cm).  $\epsilon$  was determined from the slope of linear curve in Figure 8 and was found to be 555 L mol<sup>-1</sup> cm<sup>-1</sup>.

Samples of a known mass of PS-*b*-PHEA were dissolved in DMF (concentration of 0.003 mol L<sup>-1</sup>) and its absorbance was measured. The actual apparent concentration in terms of PS units in the solution was calculated from the Beer-Lambert law and found to be equal to

$$C_{\text{PSunits}} = \frac{A}{\epsilon \cdot b} = \frac{1.04}{555 \times 1} = 0.00187 \text{ mol L}^{-1}$$

The amount of styrene units in the copolymer was about 62%, which was found to be in agreement with the copolymer composition determined via <sup>1</sup>H-NMR spectroscopy.

<sup>1</sup>H-NMR and FTIR spectroscopy results showed the presence of both species (i.e., PS segment and HEA segment) within the copolymer. However, these techniques again do not allow differentiating if the obtained product was indeed a pure block copolymer or a mixture of homopolymerization products, namely PS, PHEA, and PS-*b*-PHEA block copolymer.

### Block copolymer structure characterization

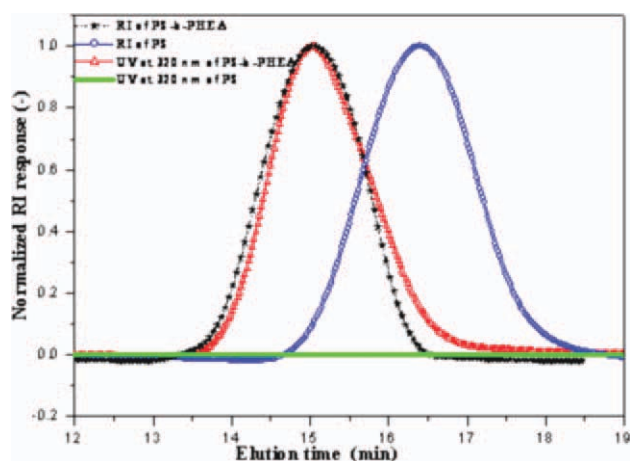
A combination of SEC and gradient HPLC characterization techniques were used to confirm the formation of block copolymer as well as the livingness of the PS-I macroinitiator. PS-*b*-PHEA block copolymers were prepared by sequential RITP polymerization of styrene followed by HEA. The macroinitiator PS-I was prepared first via RITP of styrene, until a conversion of 50% was reached. The resulting PS-I macroinitiator has a  $M_{n(\text{SEC})} = 7.100 \text{ g mol}^{-1}$  and PDI of 1.5. The theoretical molecular weight of the final block copolymer obtained was calculated using eq. (6).

$$M_{n,\text{theor}} = M_{n(1)} + \frac{m(2)}{n(1)} \times C_2 \quad (6)$$

where  $M_{n(1)}$  is the number average molecular weight of the first block (i.e., PS-I),  $m(2)$  is the mass of second monomer (i.e., HEA),  $n(1)$  is the number of moles of the macroinitiator, and  $C_2$  is the conversion of HEA.

The molecular weight of the block copolymer was found to increase monotonically with conversion, while the PDI decreased. The final molecular weight





**Figure 9** SEC traces of PS-*b*-PHEA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of block copolymer was found:  $M_{n,theo} = 11,305 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 13,000 \text{ g mol}^{-1}$ ,  $PDI = 1.4$ . Figure 9 shows an example of SEC traces of a block copolymer after extraction of unreacted monomer by dissolving in DMF and precipitating in mixture of cooled (methanol/diethylether).

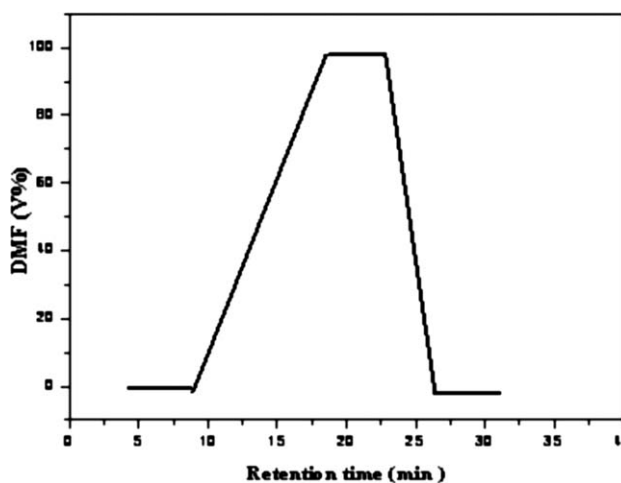
SEC instrument equipped with a dual detector system (RI and UV) was used to characterize the block copolymers. The UV detector was set up at a wavelength of 320 nm, which is the wavelength of absorption of C=O chromophore groups of the PHEA block only. It is noted that the entire molecular weight distribution shifts toward higher molecular weights compared to the macroinitiator, indicating that the molecular weight of the PS macroinitiator increased due to chain extension. This confirmed that most of the PS chains had a “living” character as they took part in the formation of the desired block copolymer. Moreover, the overlapping of the RI and UV signals proved that almost all polymer chains had integrated HEA monomer units. These results agree very well with those obtained by Lacroix-Desmazes et al.<sup>8</sup> who prepared a block copolymer of poly(methyl acrylate)-*b*-polystyrene via RITP and characterized the block copolymers using SEC with a dual detectors (refractive index and UV). They reported unimodal distribution with visible shift of the iodo terminated macroinitiator toward higher molecular weights. Tonnar et al.<sup>9</sup> also synthesized a block copolymer of poly(BuA)-*b*-poly(BuA-*co*-Sty) via RITP in aqueous phase, and observed similar results including the living character of the polymerization via RITP.

However, it is well known that block copolymers prepared by free-radical polymerization, using a monomer and a low molecular weight macroinitiator, may display heterogeneity in terms of both molecular mass and chemical composition.<sup>27,28</sup> Therefore, the characterization of these materials by

a single technique such as SEC can be inaccurate due to the effects of both the molecular mass and chemical composition on the specific hydrodynamic volume of each block.<sup>29,30</sup> Gradient elution HPLC, also known as gradient polymer elution chromatography (GPEC) is a good technique for separating copolymers based on their chemical composition.<sup>31</sup> A block copolymer may often in fact contain homopolymer, unreacted macroinitiator as well as copolymer. In this study, the GPEC separation of PS-*b*-PHEA was performed in toluene/DMF binary system. Linear gradients were used here, as shown in Figure 10. PS homopolymer is readily soluble in toluene and therefore unretained on the stationary phase. The block copolymer is however insoluble in the starting gradient composition. The retention process in the case of the PS-*b*-PHEA copolymer, using toluene/DMF system on silica relies on initial precipitation, followed by adsorption-retention after re-dissolution of the block copolymer in the solvent gradient.

Separation is a function of component polarity: here, PS is less polar than PHEA; therefore, the separation whereby PS elutes first is not due to the stationary phase but rather due to the solvent gradient. Indeed, the reverse stationary phase should already retain more PS than PHEA, PS is expected to elute first in a low polarity solvent (toluene), followed by PHEA. PS and PHEA homopolymer standards were used to identify their retention times in the elution profile. Figure 11 shows the retention times of these homopolymers under the selected conditions, PS was found to elute between 3 and 5 min, whereas PHEA eluted between 17 and 19 min.

Figure 12 shows the gradient HPLC chromatograph for a typical PS-*b*-PHEA copolymer. It shows that very good separation into three fractions was



**Figure 10** Gradient elution profile considered for separation of PS-*b*-PHEA block copolymer (stationary phase: Nucleosil 100 Si-5 $\mu\text{m}$ , eluent toluene/DMF).

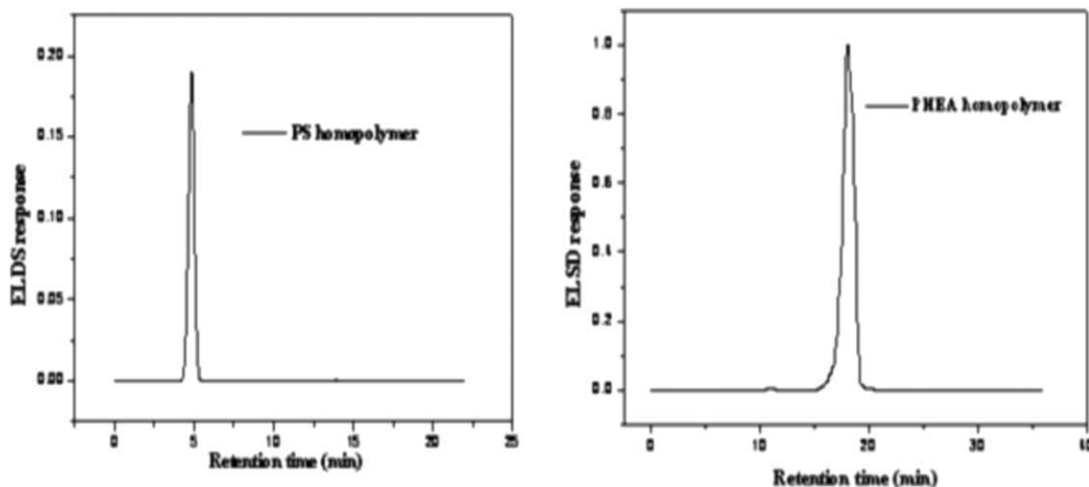


Figure 11 HPLC elution chromatogram of PS (left) and PHEA (right).

obtained. The assignment of the peaks was carried out by comparison of the chromatographic behavior of PS and PHEA homopolymer using a reversed phase column (Nucleosil CN 100 Å). The three elution peaks are assigned to sample constituents PS, PHEA, and PS-*b*-PHEA, respectively. PS homopolymer elutes first, followed by the block copolymer PS-*b*-PHEA and finally the homopolymer of PHEA elutes last.

The presence of PS homopolymer may be due to the presence of PS dead chains devoid of iodo end group at the beginning of the block copolymerization process. The presence of PHEA homopolymer is probably due to direct initiation of HEA in the presence of the free-radical initiator to form PHEA-I resulting from the reaction between this HEA radical and iodine arising from PS-I during the copolymerization reaction. As mentioned earlier, a very few

articles discussed the preparation of block copolymers via RITP<sup>8,9</sup> and the characterization of PS-*b*-PHEA copolymers by HPLC has not been reported before.

HPLC results proved that the block copolymerization between styrene and HEA by RITP was successful although small amount of PS and PHEA homopolymers were found.

## CONCLUSIONS

This study showed that controlled/living polymerization of styrene and HEA by RITP was successfully achieved. The reaction kinetic profile of the RITP process for styrene has however found to be different from HEA. The observed inhibition time was shorter for HEA than for styrene. The structure of polymers produced was analyzed by <sup>1</sup>H-NMR, FTIR, and MALDI-TOF and found to be in good agreement with the theoretical A-*M<sub>n</sub>*-I expected structure, showing that RITP can be used for the synthesis of functional PS-I and PHEA-I polymers with controlled molecular weights. Finally, from a PS-I and on addition of a second monomer, the amphiphilic block copolymer PS-*b*-PHEA was successfully synthesized, illustrating the living nature of the RITP process. The successful formation of the block copolymer PS-*b*-PHEA was confirmed by GPC and gradient HPLC.

These results demonstrate the potential of the RITP process for industrial development of controlled radical polymerization to synthesize block copolymers in a versatile cost and effective manner.

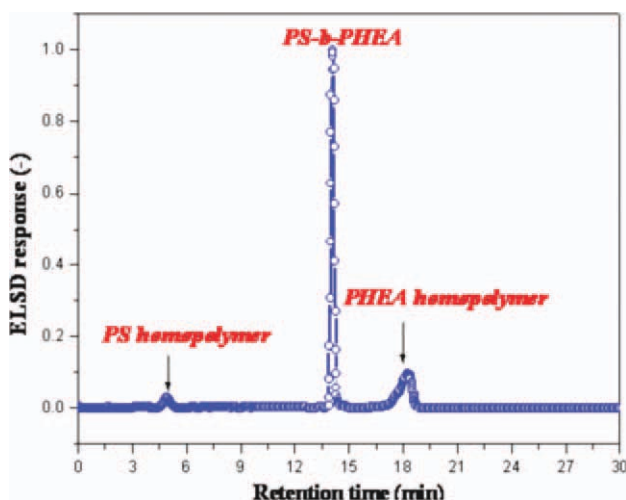


Figure 12 Gradient HPLC chromatogram of PS-*b*-PHEA block copolymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

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