

# Synthesis and identification of polystyrene via conventional and controlled radical polymerization methods: Effect of temperature, initiator and transfer agent on molecular weight and reaction rate

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## ABSTRACT

Polystyrene (PSt) has been known as one of the important polymers with a wide range of applications. Ability to synthesize PSt with different but predictable molecular weights for various applications is very important in the laboratories and industries. In this study, using various simple and inexpensive techniques with only free radical mechanism, it was tried to synthesize PSt with different low ( $< 2 \times 10^4$  g mol<sup>-1</sup>) to high ( $> 10^5$  g mol<sup>-1</sup>) molecular weights. PSts with high and moderate molecular weights ( $2 \times 10^4$ - $10^5$  g mol<sup>-1</sup>) were synthesized using thermal and conventional free radical polymerizations, respectively. Reverse iodine transfer radical polymerization (RITP) was utilized to synthesize PSt with a low and controlled molecular weight. Conversion, molecular weight distribution and PSt structure were analyzed using <sup>1</sup>H-NMR spectroscopy and size exclusion chromatography (SEC), respectively. Moreover, ω-iodo poly(dimethylsiloxane), i.e. PDMS-I, was also used as a macrotransfer agent for ITP of styrene. Diblock copolymer of PDMS-b-PSt was characterized by <sup>1</sup>H-NMR and SEC analyses. **Polyolefins J (2019) 6: 85-94**

**Keywords:** Polystyrene; low to high molecular weights; thermal polymerization (TP); free-radical polymerization; (reverse) iodine transfer radical polymerization ((R)ITP)

## INTRODUCTION

Styrene is one of the few monomers which can be polymerized under free radical [1], cationic [2, 3], anionic [4, 5] and metal catalyzed conditions [6]. This is due to low polarity of the styrene molecule and resonance stabilization of the growing polystyryl species in the transition state. PSt is one of the polymers that is used in a wide variety of applications in laboratories [7], each of its application requires a specific molecular weight.

Many of monomers such as n-alkyl acrylates [8],

methacrylates [9], chloroprene, styrene [10-12], substituted styrenes [13] or styrene analogs can be polymerized thermally by means of self-initiation. Thermal polymerization (TP) of styrene is interesting from commercial viewpoints, because the rate of radical initiation is high enough at temperatures above 100°C. High molecular weight ( $M_n > 10^5$  g mol<sup>-1</sup>) and hence the polymer quality can be achieved via changing the temperature from 100 to 180°C [7, 14]. Low molecular weight could be obtained by increasing temperature to 200°C, however, concentration of the byproducts (mostly dicyclobutanes as well as cyclic trimers

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oligomers) produced in thermal polymerization was increased [14].

Conventional free radical polymerization (CFRP) is one of the most commonly used methods for producing a wide range of moderate to high molecular weight polymers with numerous properties suitable for industry [15, 16]. The most important reason for the commercial success of this kind of polymerization is the easy reaction conditions, such as the appropriate temperature range, insensitivity to moisture and no need to purify monomers, solvents, and so on. Radical polymerization is not affected by water and protonated impurities, and it is possible to carry out this kind of polymerization in bulk, solution, water suspension, dispersion and emulsion systems. However, there are several problems with using this method. For instance, full control of molecular weight, molecular weight distribution, end-group functionality, and in the case of copolymers, the distribution of chemical composition is not practical [17].

Over the last two decades, the introduction of controlled radical polymerization (CRP) has attracted more attentions in synthesis of the novel polymers [18-20]. Interest in CRP is due to this fact that it opens windows for the preparation of various polymers and copolymers (alternating, block, graft and gradient copolymers) with controlled characteristics of molecular weight and its distribution and functionality [18-21]. Among different CRP techniques, much attention has recently been attracted to using iodinated chain transfer agent (CTA) in the iodine transfer radical polymerization (ITP) [22-24] and especially molecular iodine [25-28] as in situ generator of CTA in the reverse ITP (RITP). ITP and RITP are rather low-cost methods which are applicable for various monomers and in both heterogeneous and homogeneous systems. Highly pure polymers can be synthesized using these methods.

Recently, copolymers of PSt and poly(dimethylsiloxane) (PDMS) have widely been investigated. In these copolymers, the unique properties of silicon and PSt are combined together. Combination of these two polymers opens a window to new types of materials with various industrial applications [29]. For example, PDMS-*b*-PSt copolymers can be utilized as thermoplastic elastomers, compatibilizers, and surfactants in polymer blends. Various polymerization techniques have been used to synthesize these copolymers. Among them, CRP has been widely studied. PSt-*b*-PDMS-PSt triblock copolymer latex was achieved using an

$\alpha,\omega$ -diiodopoly(dimethylsiloxane) (I-PDMS-I) as a macrotransfer agent (macro-CTA) in ITP of styrene [30].

Despite numerous works on this topic, less attention has been focused on the RITP of styrene in bulk medium. In addition, no effort has previously been done about the preparation of PSt with different molecular weights using simple and inexpensive procedures via only the radical mechanism. In this study, PSt with different low to high molecular weights was synthesized only by simple radical polymerization mechanism. To achieve this end, various simple methods were used. First, TP of styrene was carried out at 130°C to achieve high molecular weight PSts. Then, 2,2'-azobis(isobutyronitrile) (AIBN) was utilized at 70°C to obtain PSt with moderate molecular weights. Finally, molecular iodine was used as in situ chain transfer agent generator to synthesize low molecular weight PSts via RITP in the presence of AIBN in bulk at 70°C. In fact, this study suggests a simple and an inexpensive way to synthesize PSts with low to high molecular weights where only temperature, AIBN and molecular iodine are used as reaction variables. In addition, PDMS-*b*-PSt block copolymer was prepared via ITP at 80°C in bulk using an iodinated PDMS (PDMS-I), as a macrotransfer agent, and AIBN as a radical initiator. Produced PSts were characterized using <sup>1</sup>H-NMR and SEC.

## EXPERIMENTAL

### Materials

Styrene (Aldrich,  $\geq 99\%$ ) monomer was dried in the presence of calcium hydride (Merck) by magnetic stirring for 10 h, distilled under reduced pressure and then kept at -4°C. Monohydroxy functionalized-poly(dimethylsiloxane), (PDMS-OH with a number-average molecular weight ( $\overline{M}_n$ ) of 4670 g mol<sup>-1</sup>, a value reported by Aldrich Co.) was used as received. As an in situ CTA generator, I<sub>2</sub> molecule (Merck) was utilized as received. AIBN (Fluka,  $\geq 98\%$ ) as an initiator was used after recrystallization from methanol. 2-Bromopropionyl bromide (Aldrich, 97%), benzene, sodium iodide (NaI), sodium hydrogen carbonate, anhydrous magnesium sulfate, acetone, anhydrous tetrahydrofuran (THF), triethylamine (TEA), dichloromethane and diethyl ether all were obtained from Merck and were used without purification.

## Synthesis of PDMS-I

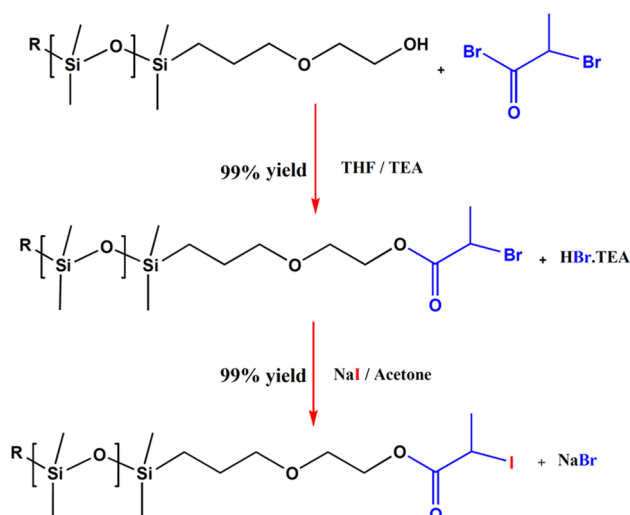
The synthesis and identification of  $\omega$ -iodo PDMS was performed according to the literature (Scheme 1) [31]. In the first step, PDMS-OH was substituted by 2-bromopropionyl bromide (98% yield). Then, brominated product was converted to iodinated one via refluxing in acetone using NaI (99% yield,  $\overline{M}_{n,SEC}$  = 5029 g mol<sup>-1</sup>, PDI = 1.23).

## Styrene Polymerization by TP and FRP

A required amount of styrene monomer was charged to the sealed glass tube equipped with a magnetic stirrer (Table 1, Exp. S1). Reaction mixture was deoxygenated by purging the N<sub>2</sub> into the tube for at least 30 min. Tube containing reaction mixture was then sealed with a rubber septum. The reaction was started in an oil bath at the desired temperature (120 and 130°C) under magnetic stirring. The reaction mixture was removed from the oil batch and reaction was stopped immediately via immersing in the water/ice batch. PSt was recovered by precipitation in methanol. PSt was then dried under reduced pressure at 60°C and subjected to SEC analysis. Conversion of monomer was determined via gravimetric method. It should be noted that bulk and solution FRP of styrene were performed with a procedure same as that used in TP expect that AIBN and benzene were used as initiator and solvent, respectively, and temperature of polymerization was set at 70°C. Corresponding experiments (Exps. S3-S5) are given in Table 1.

## RITP and ITP of Styrene

For bulk RITP of styrene, a given amount of styrene (20 mmol), I<sub>2</sub> (0.06 mmol) and AIBN (0.10 mmol)



**Scheme 1.** Synthesis of PDMS-Br and PDMS-I from PDMS-OH.

with concentration ratios of [Styrene]<sub>0</sub>: [I<sub>2</sub>]<sub>0</sub>: [AIBN]<sub>0</sub> equal to 200:0.6:1 was added to the experiment tube. The experiment tubes were degassed by purging N<sub>2</sub> into the tubes for about 30 min. The sealed experiment tubes were then subjected to an oil bath at a given temperature of 70 ± 0.1°C and reaction was performed in the dark under magnetic stirring. The tube was taken from the oil batch at the various times and polymerization was stopped immediately by immersing in the water/ice batch. Small amount of the hydroquinone inhibitor was added to a fraction of reaction mixture where it was used in the <sup>1</sup>H-NMR analysis. The remaining reaction mixture was precipitated in the excess methanol. Precipitated product was taken and then dried under reduced pressure at 60°C for at least 24 h. The dried product was subjected to SEC analysis. ITP of styrene

**Table 1.** Polymerization recipes as well as results obtained for polymerization of styrene with various methods.

EPX. No.	Method	Time (min)	T (°C)	[St] <sub>0</sub> /[AIBN]/[I <sub>2</sub> ] <sub>0</sub>	X (%) <sup>(a)</sup>	$\overline{M}_{n,th}$ (g/mole) <sup>(b)</sup>	$\overline{M}_{n,SEC}$ (g/mole) <sup>(c)</sup>	PDI <sup>c</sup>
S1	TP	205	120	200/0/0	31.30	-	300000	1.95
S2	TP	120	130	200/0/0	40.50	-	242700	1.73
S3	FRP	285	70	200/0.23/0	52.01	-	79400	2.14
S4	FRP	190	70	200/1/0	48.53	-	43700	2.18
S5	FRP	210	70	200/2/0	82.70	-	30400	2.31
S6 <sup>(d)</sup>	FRP	300	70	200/1/0	38.90	-	27290	1.87
S7-1	RITP	240	70	200/1/0.6	21.02	3840	4200	1.87
S7-2	RITP	420	70	200/1/0.6	67.07	11840	10750	1.63
S7-3	RITP	480	70	200/1/0.6	84.02	14780	13500	1.59
S7-4	RITP	1050	70	200/1/0.6	97.1	17050	18100	1.38

<sup>(a)</sup> Calculated gravimetrically in TP and FRP methods and from <sup>1</sup>H-NMR spectra and Eq. (1) in RITP method.

<sup>(b)</sup> Calculated theoretically by using Eq. (2).

<sup>(c)</sup> Obtained from SEC analysis.

<sup>(d)</sup> This experiment was performed in solution with molar ratio of [Styrene]<sub>0</sub>: [Benzene]<sub>0</sub> = 1:1.

was done with a procedure similar to RITP of styrene except instead of  $I_2$ , the PDMS-I was used as a macro-CTA at 80°C.

### Characterization

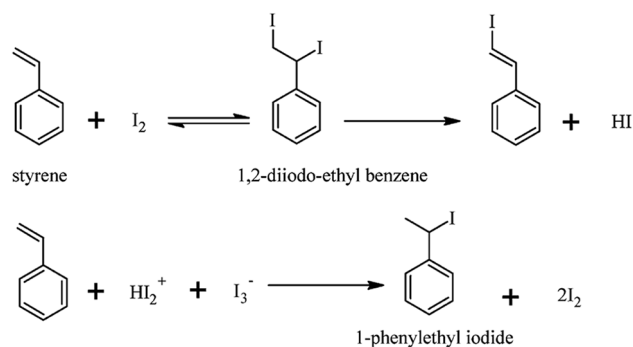
Conversion of the monomer was calculated from  $^1\text{H-NMR}$  spectra (500 MHz, Bruker Avance) recorded at room temperature using  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  solvent. Molecular weight distribution of the polymers was measured using an Agilent 1100 gel SEC with a refractive index (RI) detector and THF as the eluent at 25°C. Columns were calibrated using PSt standards with narrow polydispersity index (PDI) and molecular weights in the range of about  $10^3$ – $3 \times 10^6 \text{ g mol}^{-1}$  (see supporting information for calibration curve).

## RESULTS AND DISCUSSION

Table 1 shows various polymerization conditions as well as corresponding results obtained for polymerization of styrene. Thermal polymerization (TP) of styrene in bulk is a usual method for synthesis of PSt in the industrial scale [16]. PSt with a molecular weight as high as  $\bar{M}_n = 300000$  and  $242700 \text{ g mol}^{-1}$  (Exps. S1 and S2 in Table 1) was obtained using TP in the present work. In this method, high molecular weight was obtained at the beginning of reaction and with the progress of the reaction, it remained almost constant [11]. To synthesize PSts with decreased molecular weight, initiator concentration can be increased. There are two ways to do this, i.e. increasing the temperature of TP or charging external radical initiator to the reaction mixture. It is clear from Table 1 that the increase of the concentration of external initiator (AIBN) led to a decrease in molecular weight ( $\bar{M}_n = 79400$ ,  $43700$  and  $30400 \text{ g mol}^{-1}$  for Exps. S3–S5, respectively, in Table 1). Moreover, molecular weight in FRP was reduced by decreasing monomer concentration using solvent (Exp. S6, Table 1).

The chemistry between iodine ( $I_2$ ) and styrene is a very complex where various reactions can happen; for example, reversible addition of  $I_2$  onto styrene double bond which forms 1,2-diiodoethylbenzene, from which 1-phenylethyl iodide (1-PEI) is formed (Scheme 2) [32, 33].

RITP of styrene in bulk was performed at  $[\text{AIBN}]_0/[\text{I}_2]_0$  molar ratio of 1/0.6 at different times while molecular weights from  $3840$  to  $17050 \text{ g mol}^{-1}$  were tar-



**Scheme 2.** General mechanism for the formation of 1,2-diiodoethylbenzene and the subsequent formation of 1-phenylethyl iodide [33].

geted (Table 1). Figure 1 indicates  $^1\text{H-NMR}$  spectrum of the unreacted styrene along with the produced PSt at the conversions of 21.02 and 84.02 % (Exps. S7-1 and S7-3, respectively, in Table 1) for bulk RITP of styrene. All signals were assigned to the relevant protons (Figure 1) [33, 34]. AIBN ( $\delta = 1.45 \text{ ppm}$ ), the head ( $(\text{CH}_3)_2(\text{CN})\text{C}-$ ,  $\delta = 0.9 \text{ ppm}$  (Hd)) and terminal ( $-\text{CH}(\text{Ph})-\text{I}$ ,  $\delta = 4.1$ – $4.3 \text{ ppm}$  (Hg)) groups were assigned. Due to difference of reaction medium in bulk and solution polymerizations, this assignment of terminal group is slightly different from that reported in the literature [33, 34]. The conversion of styrene was calculated from  $^1\text{H-NMR}$  analysis of the mixture of reaction via Eq. (1) (Figure 1).

$$X = \frac{I_{(\text{Ar-H+a})} - 6I_{(\text{c})}}{I_{(\text{Ar-H+a})} - I_{(\text{c})}} \quad (1)$$

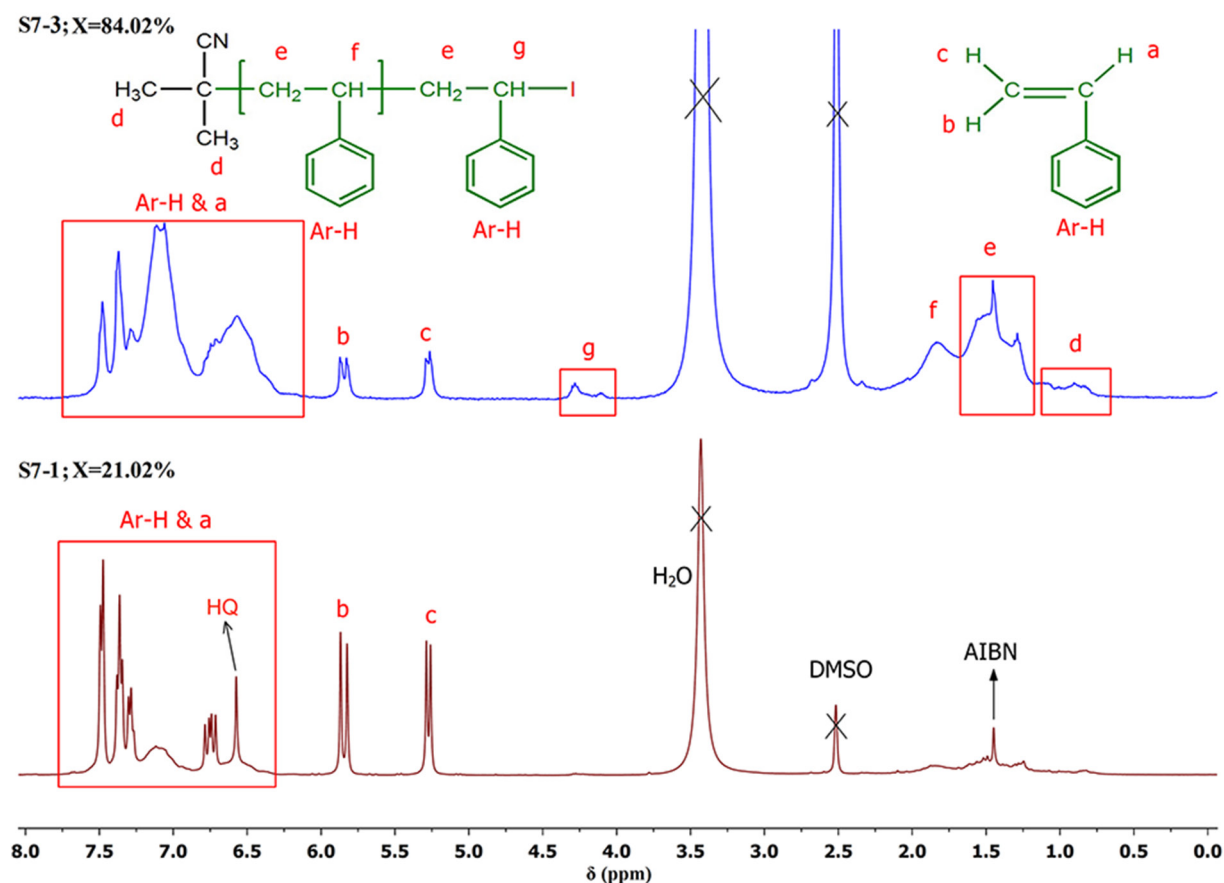
in which  $I_{(\text{Ar-H+a})}$  is sum of integrals of the aromatic (in both reacted and unreacted styrene) and methine (in the unreacted styrene protons) and  $I_{(\text{c})}$  is integral of the one of methylene protons in the unreacted styrene (Figure 1). Peak appeared at about 6.6 ppm was assigned to the aromatic protons of hydroquinone (HQ). Integral of this peak was considered in the calculation of styrene conversion.

Theoretical  $\bar{M}_n$  ( $\bar{M}_{n,\text{th}}$ ) (Table 1) can be calculated in the RITP of styrene via Eq. (2).

$$\bar{M}_{n,\text{th}} = \left( \frac{[\text{M}]_0 X \bar{M}_w}{2[\text{I}_2]_0} \right) + \bar{M}_{\text{A-I}} \quad (2)$$

in which  $[\text{M}]_0$ ,  $\bar{M}_w$  and  $X$  indicate initial concentration, molecular weight ( $104.15 \text{ g mol}^{-1}$ ) and conversion of the styrene, respectively.  $[\text{I}_2]_0$  indicates initial concentration of the molecular iodine.  $\bar{M}_{\text{A-I}}$  indicates molecular weight of the  $\alpha$ - and  $\omega$ -end groups of the polymer

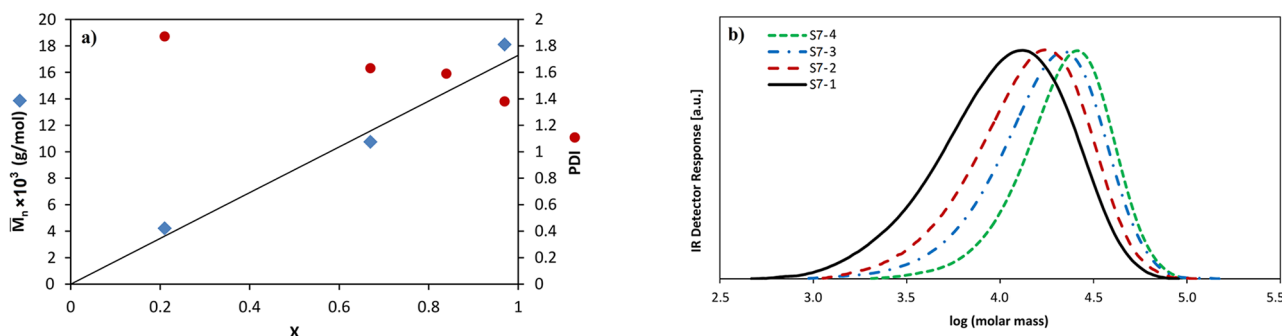




**Figure 1.**  $^1\text{H}$ -NMR spectrum of the monomer mixture and produced polymer after the styrene conversions of 21.02 and 84.02% for bulk RITP of styrene with  $[\text{Styrene}]_0:[\text{AIBN}]_0:[\text{I}_2]_0 = 100:1:0.6$  (see Exps. S7-1 and S7-3 in Table 1).

chain ( $M_{A-I} = 195 \text{ g mol}^{-1}$  in the current study) formed from AIBN-derived radical fragment ( $A = (\text{CH}_3)_2\text{CN}$ ) C-) and  $\text{I}_2$  molecule (-I). A good agreement between the theoretical and experimental was obtained (Table 1). Figure 2(a) shows versus conversion (Exps. S7-1 to S7-4). The corresponding SEC chromatograms are given in Figure 2(b). PDI of the synthesized PSt are in an acceptable range (1.38-1.87) for the CRPs. The relatively low PDI values can be attributed to the produc-

tion of 1-PEI during the induction period [24] as well as to the slow rate of the polymerization. The good control of the molecular weights suggests that the possible side reaction (formation of styrene diiodide) does not interfere with the RITP mechanism. In addition, it is clear from Figure 2 that molecular weight of the polymers increases linearly with the styrene conversion, indicating that irreversible chain transfer does



**Figure 2.** Change in number-average molecular weight as a function of conversion (a) and corresponding SEC chromatograms (b) for RITP of styrene at  $70^\circ\text{C}$  ( $[\text{Styrene}]_0:[\text{AIBN}]_0:[\text{I}_2]_0 = 100:1:0.6$ , see Exps. S7-1 to S7-4 in Table 1).

not noticeably occur in the course of polymerization, i.e. the polymerization proceed via controlled characteristics.

To better understand polymerization of the styrene by RITP, the polymerization kinetics was monitored by  $^1\text{H-NMR}$ . The evolution of  $\ln([M]_0/[M])$  as a function of time (Figure 3) showed the presence of an induction period. Change of color of the reaction mixture from brown to colorless due to the complete consumption of the  $\text{I}_2$  molecules is an indicator of the end of the induction period ( $t_{\text{inh,th}}$ ) [35] which can be followed visually. Experimental induction period (3 hr) is much shorter than the theoretical one (12 hr) calculated by Eq. (3). This can be attributed to the consumption of  $\text{I}_2$  via a reacting styrene with  $\text{I}_2$  (Scheme 2).

$$t_{\text{inh,th}} = \left( -\ln \left[ 1 - \frac{[\text{I}_2]_0}{f \times [\text{Initiator}]_0} \right] \right) / k_d \quad (3)$$

in which  $[\text{I}_2]_0$  and  $[\text{initiator}]_0$  show initial molar concentrations of the  $\text{I}_2$  and initiator (AIBN in the current study), respectively.  $k_d$  and  $f$  indicate the rate constant of the AIBN decomposition ( $k_d = 4.72 \times 10^{-5} \text{ s}^{-1}$  at  $70^\circ\text{C}$ ) [35] and AIBN efficiency ( $f = 0.7$ ) [36], respectively. Relationship between the  $\ln([M]_0/[M])$  versus time was linear up to high conversion ( $\approx 85\%$ ), showing that radical concentration is constant at the steady state and reaction rate is also dependent on the first order of the [styrene]. This is due to a fact that iodine radicals bring the propagating polymer chain into the “sleeping” state and thereby decrease the probability of irreversible chain termination and/or transfer.

By considering  $k_d$  and  $f$  values of AIBN at  $70^\circ\text{C}$  (38) and using Eq. (S2) given in the supporting information,  $k_p k_t^{-0.5}$  value for RITP of styrene at  $[\text{AIBN}]_0/[\text{I}_2]_0$

ratio of 1/0.6 (Exps. S5-1 to S5-4) was estimated from plots of  $\ln([M]_0/[M])$  versus  $(1 - \exp(-k_d \tau/2))$  (Figure 3) to be  $2.6 \times 10^{-2} \text{ L}^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$ .

### Syntheses and Identification of Halogenated PDMS

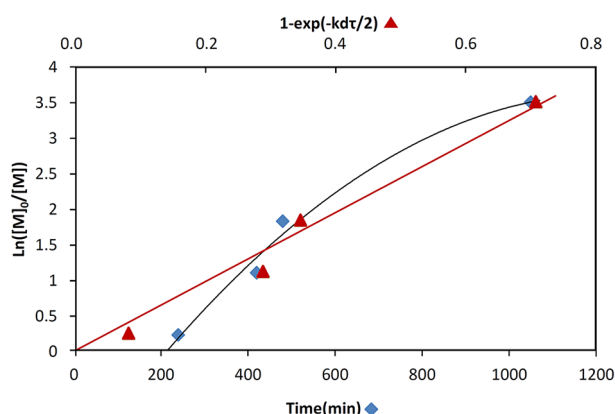
Prior to use, PDMS-OH was analyzed by SEC and  $^1\text{H-NMR}$ . Figure 4 shows typical  $^1\text{H-NMR}$  spectra of the PDMS-OH, PDMS-Br and PDMS-I. Additional peaks in the spectrum can also be observed, probably due to impurity in the PDMS-OH [37]. A broad peak was seen in the region of 1.6-1.8 ppm which may be related to unknown side product in the preparation of PDMS-OH (peaks assigned with \* indicate an impurity found in PDMS-OH, while that assigned with \*\* indicates unknown side product) [37, 38]. By considering the number of peaks appeared and ratio and integrals values, the structure shown in Figure 4 can be suggested [37]. Number-average polymerization degree ( $\overline{\text{DP}}_n$ ) and  $\overline{M}_n$  values of PDMS-OH and PDMS-I were determined by  $^1\text{H-NMR}$  analysis via Eqs. (4) and (5), respectively, and results are presented in Table 2.

$$\overline{\text{DP}}_n = \frac{I_G \text{ or } (I_{G''})}{3I_E \text{ or } (3I_{E''})} \quad (4)$$

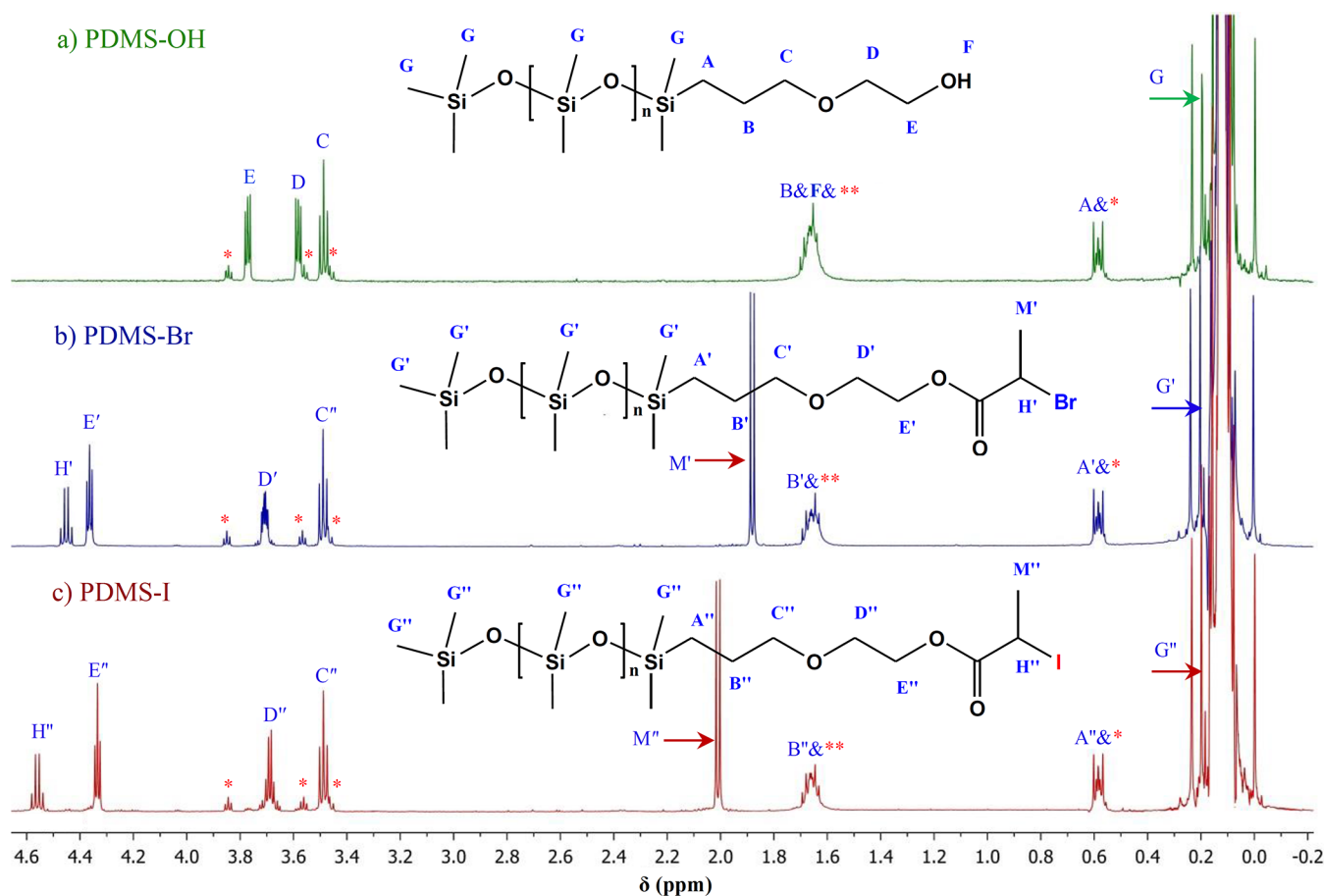
$$\overline{M}_n = (\overline{\text{DP}}_n \times M_{\text{ru}}) + M_{\text{end groups}} \quad (5)$$

in which  $I_G$  ( $I_{G''}$ ) and  $I_E$  ( $I_{E''}$ ) are integral of protons of G (or  $G''$ ) and E (or  $E''$ ), respectively.  $M_{\text{ru}}$  and  $M_{\text{end groups}}$  show molecular weights of the repeating unit and end groups, respectively.

The  $^1\text{H-NMR}$  spectra of PDMS-Br and PDMS-I are shown in Figure 4 (b and c). In comparison with PDMS-OH, quantitative shift of the peak at about 3.77 ppm (corresponding to  $-\text{CH}_2\text{-OH}$  methylene protons of  $\text{H}_E$ ), a new peak at about 4.36 ppm (corresponding to the  $-\text{CH}_2\text{-O-CO-}$  methylene protons of  $\text{H}_{E'}$ ) and appearance of doublet peak at about 1.89 ppm (corresponding to the  $-\text{CH}(\text{Br})(\text{CH}_3)$  methyl protons of  $\text{H}_{M'}$ ) and quartet peak at about 4.45 ppm (corresponding to the  $-\text{CH}(\text{Br})(\text{CH}_3)$  methine protons of  $\text{H}_{H'}$ ) in the spectrum of PDMS-Br (Figure 4(a)) confirm that reaction of the hydroxyl end groups of PDMS-OH and 2-bromopropionyl bromide is quantitative [30, 37, 39]. When PDMS-Br was iodinated, the peaks of the protons  $\text{H}_{M'}$  and  $\text{H}_{H'}$  were shifted to about 2.01 ppm ( $\text{H}_{M''}$ ) and 4.56 ppm ( $\text{H}_{H''}$ ), respectively, due to the iodine atom (Figure 4(c)) [30, 39]. Peaks intensity and chemical shift related to impurity protons have not changed by bromination and iodination of PDMS-OH,



**Figure 3.** Evolution of  $\ln([M]_0/[M])$  versus time (◆) and  $1 - \exp(-k_d \tau/2)$  (▲) for RITP of styrene at  $70^\circ\text{C}$  ( $[\text{Styrene}]_0/[\text{AIBN}]_0/[\text{I}_2]_0 = 100:1:0.6$ , see Exps. S7-1 to S7-4 in Table 1).



**Figure 4.**  $^1\text{H}$ -NMR spectra of the PDMS-OH (a), PDMS-Br (b), PDMS-I (c) and mixture of styrene and produced PDMS-b-PSt diblock copolymer after the styrene conversion of 88.10 % for bulk ITP of styrene with  $[\text{Styrene}]_0:[\text{PDMS-I}]_0:[\text{AIBN}]_0 = 100:0.54:0.46$  at  $80^\circ\text{C}$  (d) in  $\text{CDCl}_3$  solvent.

indicating that impure species are not reactive in the chemical modifications [37].

SEC showed three peaks in the PDMS-OH chromatogram in which two peaks with low molecular weight overlap with each other and third peak appears in high molecular weight (Figure 5) [37]. The  $\overline{M}_{n,\text{SEC}}$  was  $6273 \text{ g mol}^{-1}$  ( $\overline{\text{DP}}_n = 66.22$ ) and the PDI was obtained to be 1.95 (Table 2) [37]. After brominating

and iodinating PDMS-OH, the peak at high molecular weight was eliminated and the  $\overline{M}_{n,\text{SEC}}$  of PDMS-I was obtained to be  $5029 \text{ g mol}^{-1}$  ( $\overline{\text{DP}}_n = 66.04$ ,  $\text{PDI} = 1.3$ ). The molecular weight obtained by  $^1\text{H}$  NMR ( $\overline{M}_{n,\text{NMR}} = 5182 \text{ g mol}^{-1}$ ) is close to that obtained by SEC [37]. These results showed the presence of impurities in the commercial PDMS-OH.

**Table 2.** Results obtained from SEC and  $^1\text{H}$ -NMR analyses for PDMS-OH, PDMS-I macro-CTA and PDMS-b-PSt diblock copolymer.

EXP. No.	Time (min)	$X_{\text{I}}^{(a)}$ (%)	$\overline{M}_{n,\text{th}}$ (g/mole)	$\overline{M}_{n,\text{NMR}}$ (g/mole) <sup>(b)</sup>	$\overline{M}_{n,\text{SEC}}$ (g/mole) <sup>(c)</sup>	PDI <sup>(e)</sup>
PDMS-OH	-	-	4670 <sup>(d)</sup>	5013	6273	1.95
PDMS-I	-	-	4852 <sup>(e)</sup>	5182	5029	1.23
PDMS-b-PSt	120	88.10	18219 <sup>(f)</sup>	18030	17396	1.67

<sup>(a)</sup> Calculated from  $^1\text{H}$ -NMR spectra via Eq. (1).

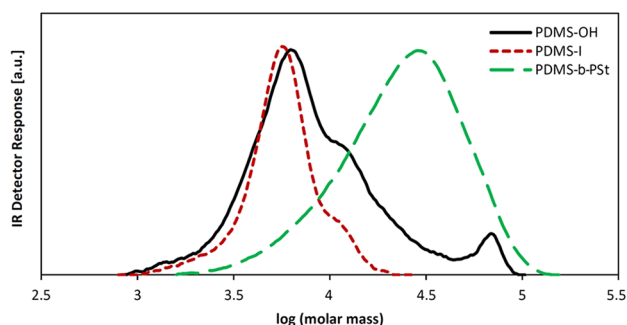
<sup>(b)</sup> Calculated from  $^1\text{H}$ -NMR spectra via Eqs. (5) and (6), respectively.

<sup>(c)</sup> Obtained from SEC analysis.

<sup>(d)</sup>  $\overline{M}_n$  value reported by the manufacturer.

<sup>(e)</sup> This value was calculated via  $\overline{M}_{n,\text{PDMS-I}} = \overline{M}_{n,\text{PDMS-I}} + 181.95$ .

<sup>(f)</sup>  $\overline{M}_{n,\text{th}} = \frac{[M]_0 X M_w}{[PDMS-I]_0 + [AIBN]_0 f(1 - e^{-k_d t})} + \overline{M}_{n,\text{PDMS-I}}$  in which  $[PDMS-I]_0$  indicates initial molar concentration of PDMS-I.  $k_d$  is the decomposition rate constant ( $k_d = 9.8 \times 10^{-5} \text{ s}^{-1}$  at  $80^\circ\text{C}$ ) of the AIBN initiator [35]. Other symbols have been defined in the previous sections.



**Figure 5.** SEC chromatograms of the PDMS-OH, PDMS-I macrotransfer agent and PDMS-b-PSt diblock copolymer.

### Synthesis of PDMS-b-PSt Diblock by Bulk ITP

Bulk polymerization of styrene via ITP was done using PDMS-I as a macro-CTA with molar ratios of  $[\text{Styrene}]_0 : [\text{PDMS-I}]_0 : [\text{AIBN}]_0$  equal to 100: 0.54: 0.46 at 80°C in dark. Figure 4-d presents the  $^1\text{H-NMR}$  of the reaction mixture after a polymerization conversion of 88.10% for bulk ITP of styrene. Weak signals corresponding to protons of terminal groups ( $-\text{C}_\text{H}(\text{Ph})-\text{I}$ , (HP)) are seen in 4.35-4.7 ppm. The conversion of styrene can be calculated by analysis of  $^1\text{H-NMR}$  of the reaction mixture in deuterated chloroform ( $\text{CDCl}_3$ ) via Eq. (1) except that  $I_{(\text{Ar-H}+1)}$  and  $I_{(3)}$  were used instead of  $I_{(\text{Ar-H}+a)}$  and  $I_{(c)}$ , respectively. Moreover,  $^1\text{H-NMR}$  analysis allowed us to assess the  $\overline{M}_n$  by integrating the reference peak of the two methyl groups ( $-\text{Si}(\text{CH}_3)_2-\text{O}-$ ) at about zero ppm ( $H_{\text{G}''}$ ) and comparing it to the aromatic group protons of the polymer at 6.14-7.57 ppm ( $H_{\text{Ar-H}}$ ) via Eq. (6) [29].

(6)

$$\overline{M}_{n,\text{PDMS-b-PSt}} = \left( \left[ \frac{6I_{(\text{Ar-H}+1)} - 36I_{(3)}}{5I_{(\text{G}''')}} \right] \times \overline{DP}_{n,\text{PDMS-I}} \times M_w \right) + \overline{M}_{n,\text{PDMS-I}}$$

where  $I_{(\text{Ar-H}+1)}$ ,  $I_{(3)}$  and  $I_{(\text{G}''')}$  indicate signal intensities of the phenyl rings (from PSt and styrene) and methine (from styrene), one of the methylene (from styrene) and  $-\text{Si}(\text{CH}_3)_2$  methyl (from PDMS) protons, respectively.  $\overline{DP}_{n,\text{PDMS-I}}$  (66) and  $\overline{M}_{n,\text{PDMS-I}}$  (5182 g mol $^{-1}$ ) indicate number of the  $-\text{Si}(\text{CH}_3)_2-\text{O}-$  groups and  $\overline{M}_n$  of the PDMS-I macrotransfer, respectively, which were estimated from the  $^1\text{H-NMR}$  (Figure 4) via Eqs. (4) and (5). The calculation results have been shown in Table 2. There is a good correlation between the  $\overline{M}_n$  values obtained from  $^1\text{H-NMR}$  spectra, SEC and that estimated theoretically, showing controlled characteristics of the reaction.

## CONCLUSION

Various methods were utilized to synthesize low to high molecular weight polystyrenes (PSts). Thermal bulk polymerization and conventional free-radical bulk and solution polymerizations were used to synthesize PSts with high and moderate molecular weights, in the ranges from 27290 to 300000 g mol $^{-1}$ , respectively. Reverse iodine transfer radical polymerization was used to synthesize PSt with low and controlled molecular weight (in the ranges from 4200 to 18100 g mol $^{-1}$ ). It was observed that RITP of styrene proceeds with controlled characteristics, so that products with predetermined molecular weight and a relatively narrow molecular weight distribution could be synthesized. Moreover,  $\omega$ -iodo poly(dimethylsiloxane) (PDMS-I) as a macrotransfer agent was used for iodine transfer radical polymerization (ITP) of styrene. PDMS-b-PSt diblock was verified by  $^1\text{H-NMR}$  and SEC analyses. Good agreement between the number average molecular weight calculated from  $^1\text{H-NMR}$  spectra, SEC and that calculated theoretically indicated the controlled characteristic of the reaction. From the results obtained, one can conclude that PSts with different but expectable molecular weights in the ranges from low to high molecular weights can be synthesized only using one polymerization method, i.e. radical polymerization, with different mechanisms.

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