

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236746897>

NMR Studies on the Mechanism of Reverse Iodine Transfer Polymerization of Styrene

ARTICLE *in* MACROMOLECULES · MARCH 2012

Impact Factor: 5.8 · DOI: 10.1021/ma3003888

CITATIONS

8

READS

24

3 AUTHORS, INCLUDING:



[Helen Pfukwa](#)

Stellenbosch University

13 PUBLICATIONS 34 CITATIONS

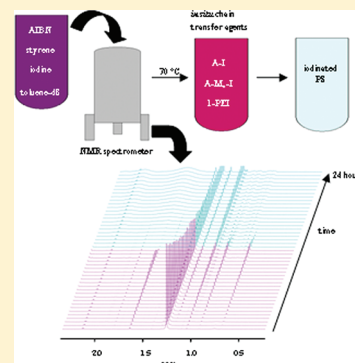
SEE PROFILE

NMR Studies on the Mechanism of Reverse Iodine Transfer Polymerization of Styrene

Trevor Wright, Helen Chirowodza, and Harald Pasch*

Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

ABSTRACT: The evolution of chain transfer agents (CTAs) was studied for the polymerization of styrene by reverse iodine transfer polymerization (RITP). CTAs are formed during an inhibition period where the radical initiator reacts with molecular iodine. These compounds were studied using *in situ* ^1H nuclear magnetic resonance (NMR) experiments. The molecular weight of polystyrene was evaluated with size exclusion chromatography (SEC) and ^1H NMR. Structural analysis of the resulting polymers was done using ^1H NMR spectroscopy and matrix-assisted laser desorption/ionization time-of-flight (MALDI–ToF) mass spectrometry. The inhibition period of styrene polymerized by RITP was much shorter than expected. This is due to the consumption of iodine in the reaction between styrene and iodine which reversibly forms 1,2-diiodoethylbenzene leading to the subsequent formation of 1-phenylethyl iodide (1-PEI). For the first time the formation of 1,2-diiodoethylbenzene as an intermediate structure in RITP of styrene has been proven experimentally. The active role of 1-PEI in the polymerization process is documented through the detection of phenylethyl end groups by MALDI–ToF and ^1H NMR.



INTRODUCTION

Reverse iodine transfer polymerization (RITP) is a technique where molecular iodine is reacted with initiator radicals to form alkyl iodide chain transfer agents (CTAs) *in situ*. The basic mechanism of RITP is shown in Scheme 1.^{1–3}

RITP is divided into two stages: (1) the inhibition period and (2) the polymerization period. Iodine is a strong inhibitor, and therefore, the inhibition period is ended only once all iodine has been consumed. Throughout the inhibition period, free radicals (A^\bullet) generated by the decomposing initiator (AIBN) react directly with iodine to form iodinated CTAs. The CTAs generated are A-I and $\text{A-M}_n\text{-I}$ ($n \geq 0$), where A is a radical from the initiator, M is a monomer unit, n is the average degree of polymerization, and I is the iodine atom. During the inhibition period, iodine can also react with the double bonds of a monomer molecule to form a 1,2-disubstituted olefin. The formation of these compounds is reversible and they tend to be very unstable in UV light.^{2,4,5}

The monomer conversion during the inhibition period is insignificant. Thereafter, however, the monomer is converted during the polymerization period, a process that is governed by a degenerative transfer mechanism.

Studies of styrene polymerization by RITP have been reported by Tonnar et al.³ and Shiman et al.⁶ It was observed that the mechanism for RITP of styrene differs significantly from that of acrylates and methacrylates. The experimental inhibition times reported were much shorter than the theoretical times. Although it was speculated that the short inhibition period is attributed to the formation of 1,2-diiodoethylbenzene (Scheme 2), which depletes free iodine,

no experimental proof has been reported in the literature of this compound being formed during the inhibition period of RITP. This side reaction does not, however, interfere with the formation of iodinated chain transfer agents, as it is reversible and iodine is liberated from the 1,2-diiodoethylbenzene throughout the polymerization.

The main objectives of this work were to prepare polystyrene by RITP in order to investigate the chemical structures of CTAs formed during the inhibition period. The formation of the CTAs was to be followed by ^1H NMR and the polymerization products were to be analyzed by SEC, NMR, and MALDI–ToF.

EXPERIMENTAL SECTION

Materials. Styrene (Sigma-Aldrich) was washed with 10% aqueous solution of sodium hydroxide and then washed with distilled, deionized water and dried with anhydrous magnesium sulfate. The monomer was then distilled under reduced pressure and stored at low temperatures. Toluene (Sigma-Aldrich 99%), deuterated toluene (C_7D_8 , Sigma-Aldrich 99%), deuterated benzene (C_6D_6 , Sigma-Aldrich 99%) and iodine (I_2 , ACROS Organics) were used as received. AIBN (Riedel de Haën) was recrystallized from methanol, dried under vacuum and stored at -5°C .

Polymerization of Styrene. In a typical homopolymerization reaction, styrene (1.00 g, 9.60×10^{-3} mol), toluene (1.25 g, 1.36×10^{-2} mol), AIBN (49.7 mg, 3.03×10^{-4} mol), iodine (45.3 mg, 1.78×10^{-4} mol) and a magnetic stirrer were added into a Schlenk flask and mixed by magnetic stirring. The mixture was then degassed by three successive freeze–pump–thaw cycles and then backfilled with argon.

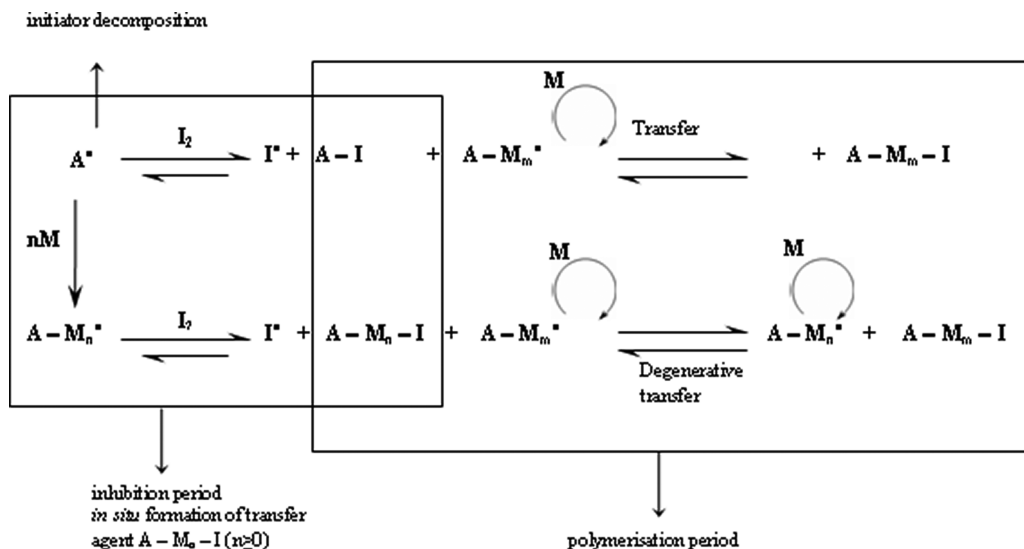
Received: February 27, 2012

Revised: March 8, 2012

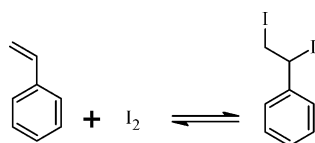
Published: March 20, 2012



Scheme 1. Basic Mechanism of RITP



Scheme 2. Reversible Formation of 1,2-Diiodoethylbenzene



The flask was then immersed in an oil bath that was preheated to 70 °C. The polymerization was carried out with magnetic stirring in the dark. After 24 h, the polymerization was halted by removing the flask from the oil bath and placing the flask in a container of ice. The polymer was dried in a vacuum oven overnight.

In situ ^1H NMR Monitoring of Styrene Polymerization.

Styrene polymerization was followed by *in situ* ^1H NMR at 70 °C in toluene- d_8 .

The sample NMR tube was inserted into the NMR spectrometer and a reference spectrum was acquired at 25 °C. The temperature of the NMR spectrometer was then equilibrated at 70 °C for 30 min before the NMR tube was reinserted into the spectrometer. The first spectrum was acquired 8–15 min after the sample was reinserted. Thereafter, spectra were obtained by taking 15 scans every 15 min for 23 h.

In a typical *in situ* ^1H NMR polymerization reaction, styrene (2.00 g, 19.2×10^{-3} mol), AIBN (99.5 mg, 6.06×10^{-4} mol), iodine (90.5 mg, 3.57×10^{-4} mol) were weighed carefully and mixed thoroughly in a glass vial. A portion of the mixture (0.25 mL) was introduced into a

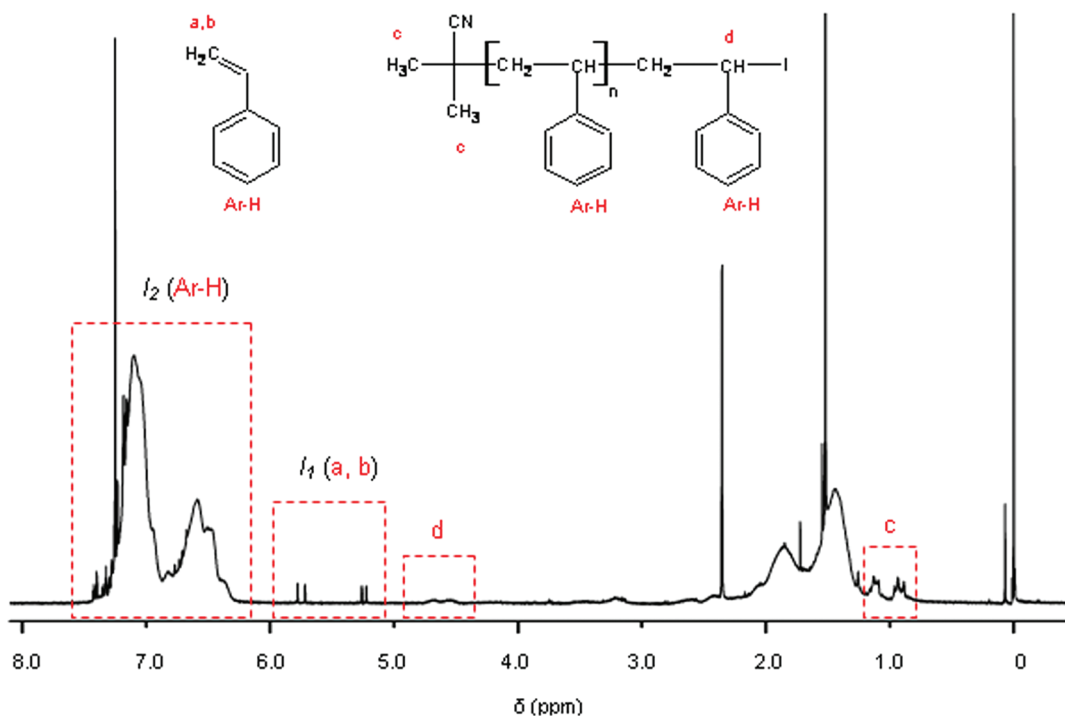


Figure 1. ^1H NMR spectrum in CDCl_3 of styrene polymerized by RITP at 70 °C ($[\text{styrene}] = 3.70 \text{ M}$, $[\text{toluene}] = 5.44 \text{ M}$, $[\text{AIBN}] = 0.12 \text{ M}$ and $[\text{I}_2] = 6.86 \times 10^{-2} \text{ M}$, conversion = 70%, $M_{n,\text{SEC}} = 2400 \text{ g}\cdot\text{mol}^{-1}$, $M_{n,\text{NMR}} = 2500 \text{ g}\cdot\text{mol}^{-1}$), showing the regions for the integrals I_1 and I_2 respectively.

Table 1. Results of Styrene Polymerization by RITP for 24 h at 70 °C^a

run	[AIBN]/[I ₂]	<i>M</i> _{n,target} (g/mol)	<i>t</i> _{inh,theory} (h) ^b	<i>t</i> _{inh,exp} (h)	convn (%) ^c	<i>M</i> _{n,theory} (g/mol) ^d	<i>M</i> _{n,SEC} (g/mol) ^e	PDI
1	1.5	8000	23	8	63	5100	4600	1.60
2	1.7	1500	14	8	62	900	700	1.53
3	1.7	3000	14	6	70	2150	2400	1.50
4	1.7	5500	14	5	68	3800	3600	1.58
5	1.7	8000	14	4	65	5250	4850	1.74
6	2.0	8000	9	4	72	5700	5300	1.76

^aPolymerization of styrene ([styrene] = 3.70 M) in toluene ([toluene] = 5.44 M) at 70 °C with AIBN and molecular iodine. ^bCalculated by $t_{inh,theory} = (-\ln((1-[iodine]_0)/f[initiator]_0))/k_d$ where $k_d = 3.71 \times 10^{-5} s^{-1}$ and $f = 0.7$. ^cDetermined by ¹H NMR in CDCl₃ by conversion = $(1 - (I_1/I_2)) \times 100$ where I_1 is the integral of the vinylic protons ($(\int CH_2=C)/2$) of styrene at 5.1 and 5.6 ppm, and I_2 is the integral of the aromatic protons ($(\int C_6H_5)/5$) of styrene and polystyrene. ^dCalculated by $M_{n,theory} = ((m_{styrene} \times conversion)/(2n_{iodine})) + M_{chain\ ends}$. ^eCalibrated using polystyrene standard.

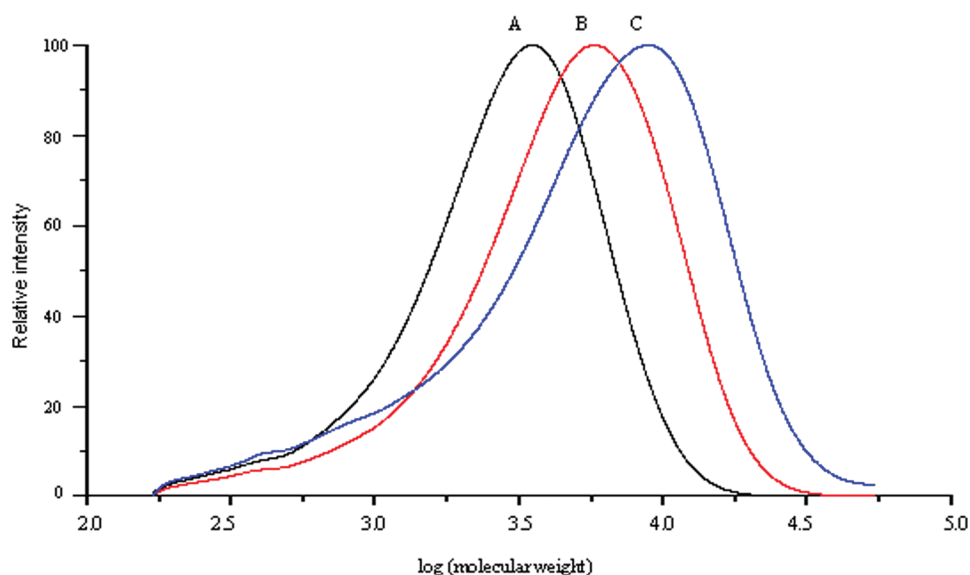


Figure 2. Molecular weight distributions from SEC (RI traces) of polymers prepared by RITP ([styrene] = 3.70 M, [toluene] = 5.44 M) for 24 h at 70 °C: (A) $M_{n,theory} = 3000 g \cdot mol^{-1}$, [AIBN] = 0.12 M and [I₂] = $6.86 \times 10^{-2} M$, conversion = 70%, $M_{n,SEC} = 2400 g \cdot mol^{-1}$, PDI = 1.50; (B) $M_{n,theory} = 5500 g \cdot mol^{-1}$, [AIBN] = $6.16 \times 10^{-2} M$ and [I₂] = $3.63 \times 10^{-2} M$, conversion = 68%, $M_{n,SEC} = 3600 g \cdot mol^{-1}$, PDI = 1.58; (C) $M_{n,theory} = 8000 g \cdot mol^{-1}$, [AIBN] = $4.19 \times 10^{-2} M$ and [I₂] = $2.46 \times 10^{-2} M$, conversion = 65%, $M_{n,SEC} = 4850 g \cdot mol^{-1}$, PDI = 1.74).

J Young NMR tube, followed by the addition of 0.25 mL of toluene-*d*₈. An internal reference of 20 μL of DMF was inserted into the J Young NMR tube. The sample in the NMR tube was degassed by three successive freeze–pump–thaw cycles and then filled with UHP argon gas.

Analyses. SEC was carried out using a SEC instrument equipped with a Waters 717plus autosampler, Waters 600E system controller and a Waters 610 fluid unit. For detection, a Waters 2414 differential refractometer was used. Two PLgel 5 μm Mixed-C columns and a PLgel 5 μm guard column were used. Polymer samples of 2 mg were dissolved in 2 mL of THF and the sample volume injected into the column was 100 μL, with the oven temperature kept at 30 °C. The eluent that was used was THF (HPLC grade, BHT stabilized) at a flow rate of 1 mL/min. Calibrations were done using narrow polystyrene standards with a molecular range of 800 to $2 \times 10^6 g \cdot mol^{-1}$. Data obtained from SEC were reported as polystyrene equivalents.

The ¹H NMR spectra were obtained on a Varian Unity INOVA 400 MHz spectrometer, with a pulse width of 3 μs (40°) and a 4 s acquisition time. The solvent used for crude polystyrene samples was deuterated chloroform (CDCl₃), with toluene-*d*₈ being used for online kinetic ¹H NMR experiments. All NMR spectra were processed using ACD Laboratories 10.0 ¹H NMR processor. The spectra were phased automatically, whereas baseline correction and integration were done manually. From the processed spectra it was possible to construct concentration profiles relative to an internal DMF reference.

MALDI–ToF analysis was performed using an AximaToF² spectrometer (Shimadzu Biotech) equipped with a nitrogen laser (337 nm). The instrument was operating at an accelerating potential of 20 kV. All analyses were carried out in the linear positive mode, with calibrations carried out using a 1450 Da poly(ethylene glycol) (PEG) standard. The mass accuracy of the instrument is ±2 Da. Samples were dissolved in dioxane with a concentration of 2 mg·mL^{−1}. The sample solutions were mixed with a 10 mg mL^{−1} solution of the matrix (dithranol/dioxane) in THF. The salt used to enhance ion formation was copper chloride (CuCl), with a concentration of 2 mg·mL^{−1}. The analyte-to-matrix ratio was 1:2. Here, 1 μL of the mixture was deposited on a stainless steel target, air-dried, and introduced into the spectrometer.

RESULTS AND DISCUSSION

The ¹H NMR peaks for AIBN, A–I and A–A were investigated for a solution of AIBN and iodine in deuterated benzene (C₆D₆) at 70 °C. The peak assignments were AIBN (δ = 1.15 ppm), A–I (δ = 1.54 ppm), and A–A (δ = 1.03 ppm), respectively. These assignments are in reasonable agreement with the chemical shifts observed by Lacroix-Desmazes et al.² but differ slightly due to NMR analysis operating temperature. The assignments made by Lacroix-Desmazes et al. were made after heating the reaction mixture at 70 °C and

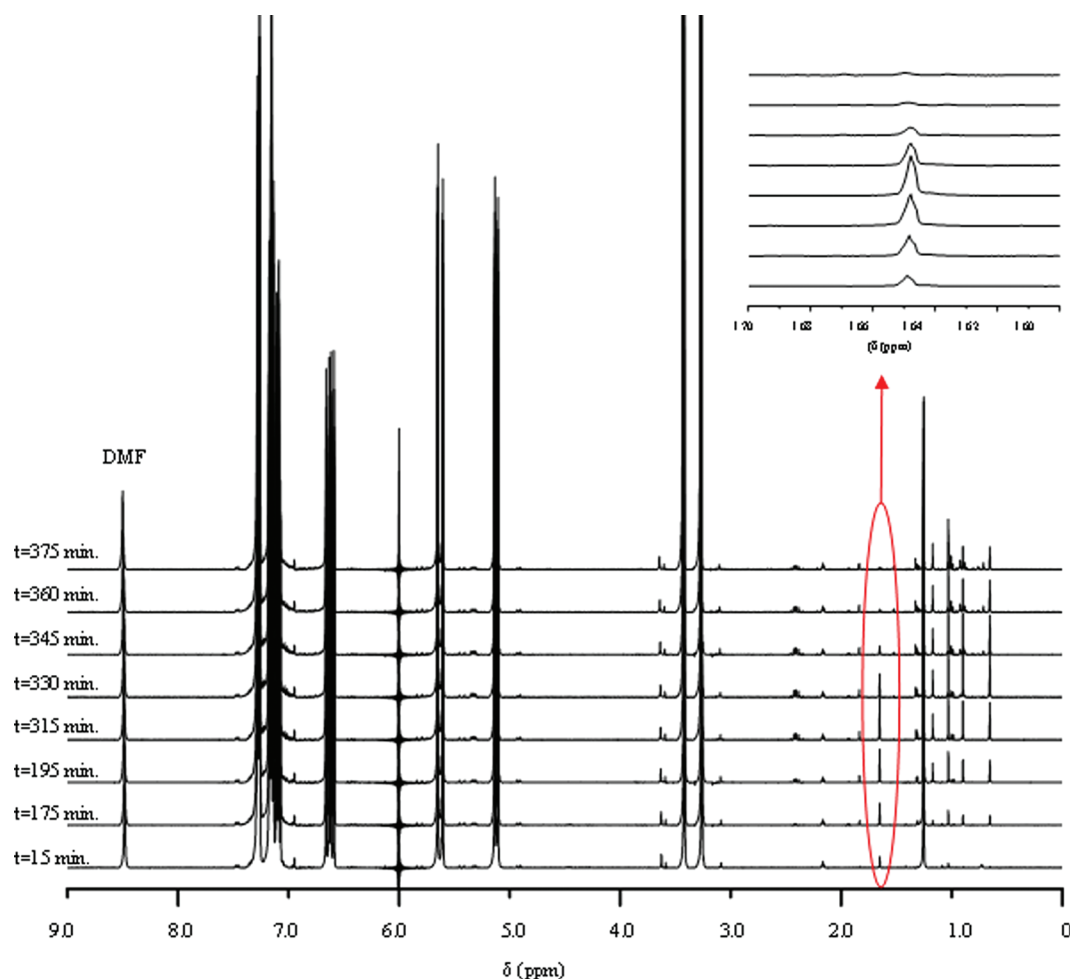


Figure 3. NMR spectrum of reaction medium during RITP of styrene in toluene- d_8 at 70 °C ($[\text{styrene}] = 4.27 \text{ M}$, $[\text{toluene-}d_8] = 4.82 \text{ M}$, $[\text{AIBN}] = 0.13 \text{ M}$ and $[\text{I}_2] = 7.91 \times 10^{-2} \text{ M}$), showing the formation and consumption of the A–I adduct during the inhibition period ($t_{\text{inh,exp}} \sim 360 \text{ min}$).

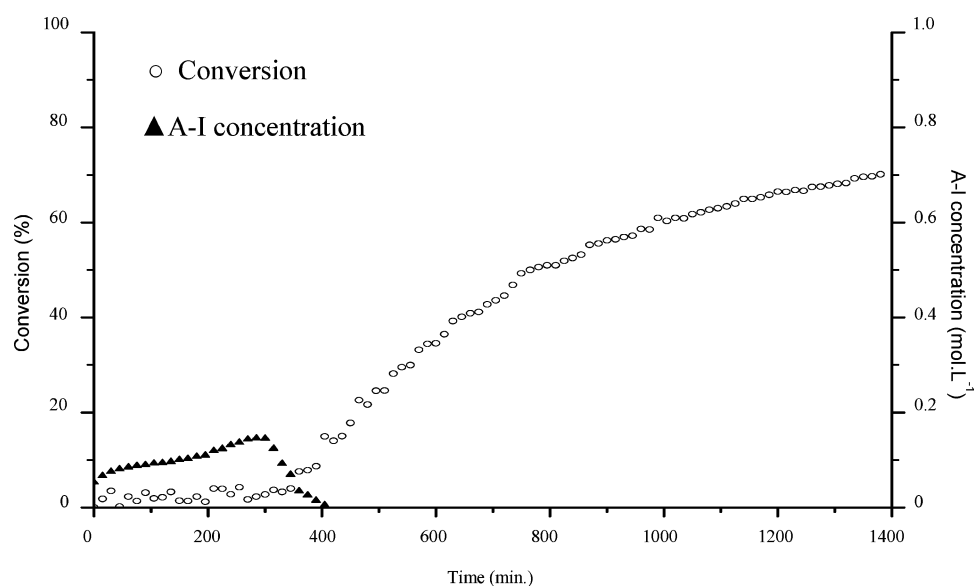
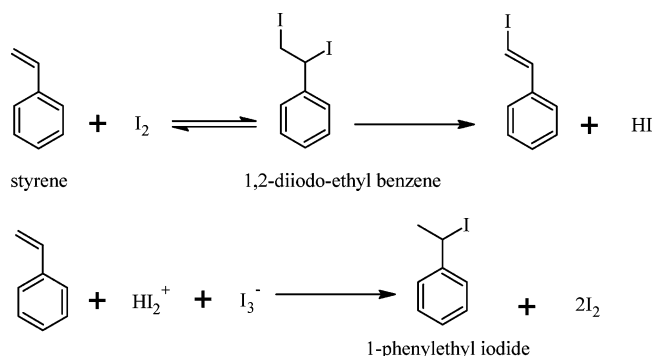


Figure 4. Evolution of styrene conversion and A–I adduct concentration ($t_{\text{inh,exp}} \sim 360 \text{ min}$) as a function of reaction time for the polymerization of styrene by RITP at 70 °C ($[\text{styrene}] = 4.27 \text{ M}$, $[\text{toluene-}d_8] = 4.82 \text{ M}$, $[\text{AIBN}] = 0.13 \text{ M}$, and $[\text{I}_2] = 7.91 \times 10^{-2} \text{ M}$).

the NMR spectrum measured at room temperature. The assignments made in our study were done with the NMR spectrum measured at 70 °C. The peak assignments change

slightly when styrene is added to the reaction mixture: AIBN ($\delta = 1.25 \text{ ppm}$), A–I ($\delta = 1.65 \text{ ppm}$), and A–A ($\delta = 0.90 \text{ ppm}$).

Scheme 3. General Mechanism for the Formation of 1,2-Diiodoethylbenzene and the Subsequent Formation of 1-Phenylethyl Iodide



A study of several alkyl iodides (with a general structure of R–I) used in styrene polymerization is reported in literature by Gaynor et al.⁷ Such alkyl iodides include 1-phenylethyl iodide (1-PEI), iodoform, and iodoacetonitrile. The radical formed by the loss of the iodine atom from such CTAs is stabilized by the R group, either by inductive or resonance effects.

In our study, polystyrene was synthesized by RITP at 70 °C, where various $[AIBN]/[I_2]$ ratios were used and molecular weights from 1500–8000 g·mol⁻¹ were targeted. The molecular weights and polydispersities of the samples were determined by SEC. The monomer conversion of styrene was determined by ¹H NMR analysis of the crude polystyrene samples in deuterated chloroform (CDCl₃). Using ¹H NMR, the monomer conversion was determined with eq 1

$$\text{conversion} = \left(1 - \frac{I_1}{I_2}\right) \times 100 \quad (1)$$

where I_1 is the integral of the vinylic protons ($(\int \text{CH}_2=\text{C})/2$) of styrene at 5.1 and 5.6 ppm, and I_2 is the integral of the aromatic protons ($(\int \text{C}_6\text{H}_5)/5$) of styrene and the resulting polystyrene (Figure 1).⁸ From the conversion the theoretical molecular weight ($M_{n,\text{theory}}$) was calculated using eq 2

$$M_{n,\text{theory}} = \frac{(m_{\text{styrene}} \times \text{conversion})}{(2 \times n_{\text{iodine}})} + M_{\text{chain ends}} \quad (2)$$

where m_{styrene} is the mass of styrene, n_{iodine} is the number of moles of molecular iodine, and $M_{\text{chain ends}}$ is the combined molecular weight of the cyanoisopropyl and iodine chain ends (195 g·mol⁻¹).^{1–3} The results for styrene polymerized by RITP at 70 °C for 24 h are shown in Table 1.

The conversion is not particularly high and is usually in the region of 65%. This may be explained by the low concentration

of AIBN near the end of polymerization. This means that there are insufficient numbers of initiator radicals to consume the iodine that is liberated from 1,2-diiodoethylbenzene.³ The monomer conversion also increases with increasing initiator to iodine ratio. The M_n values calculated from conversion are in reasonable agreement with the values obtained from SEC (Table 1). Figure 2 shows the refractive index (RI) detector traces of runs 3–5 (Table 1).

The distributions are unimodal with some low molecular weight tailing and a shift toward higher molecular weights as would be expected with increasing targeted molecular weights. The PDI values of the polystyrene samples are in an acceptable range (1.5–1.7) for polymers synthesized by an iodine mediated system.^{7,9} The relatively low PDI values obtained for the RITP of styrene may be attributed to the formation of 1-PEI during the inhibition period, since this transfer agent has been reported to give rise to low PDI values for degenerative transfer mediated polymerization of styrene.⁷ In addition to this, the polymerization of styrene is quite slow, which leads to low PDI values.¹⁰

Kinetic experiments followed by ¹H NMR were run to investigate the mechanism of RITP of styrene by examining the monomer conversion as well as the inhibition period and the evolution of chain transfer agents therein. The results in Table 1 show the experimental inhibition times ($t_{\text{inh,exp}}$) as well as the theoretical inhibition times ($t_{\text{inh,theory}}$) for the various experiments. The $t_{\text{inh,theory}}$ was calculated using eq 3

$$t_{\text{inh,theory}} = \left(-\ln \frac{1 - [\text{iodine}]_0}{f[\text{initiator}]_0} \right) / k_d \quad (3)$$

where $[\text{iodine}]_0$ is the initial concentration of molecular iodine in the reaction medium, f is the initiator efficiency with a value of 0.7,^{1,11} $[\text{initiator}]_0$ is the initial concentration of initiator (AIBN), and k_d is its dissociation constant.

During the inhibition period, the initiator decomposes to form radicals that react with molecular iodine to generate CTAs. The end of the inhibition period is marked visually by the change of color of the mixture from brown to colorless. This change in color is due to the complete consumption of iodine. According to the RITP mechanism (Scheme 1), CTAs are formed and consumed during the inhibition period, which is composed of two stages. In the first stage, iodine is consumed to form the A–I adduct, while in the second stage, the A–I adduct is consumed to form oligomers.¹ The decrease in A–I adduct concentration is indicative that the A–I adduct forms oligomers, and polymerization commences once all the A–I adduct has been consumed. The evolution of the A–I adduct over time is shown in Figure 3.

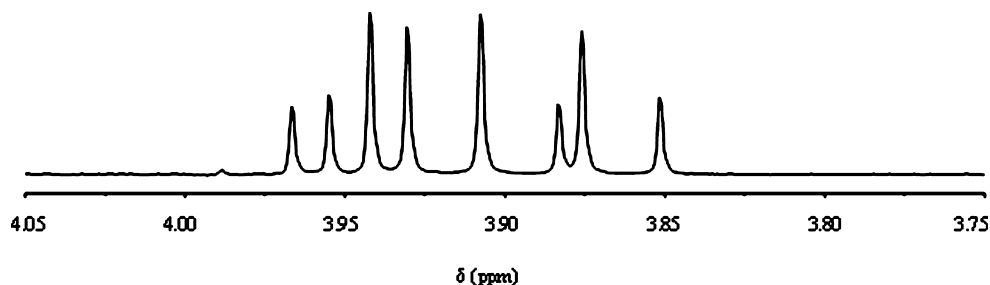


Figure 5. Enlarged portions of the ¹H NMR spectrum of 1,2-diiodoethylbenzene formed from a mixture of styrene and iodine in CDCl₃, showing the peaks for aromatic protons of 1,2-diiodoethylbenzene.

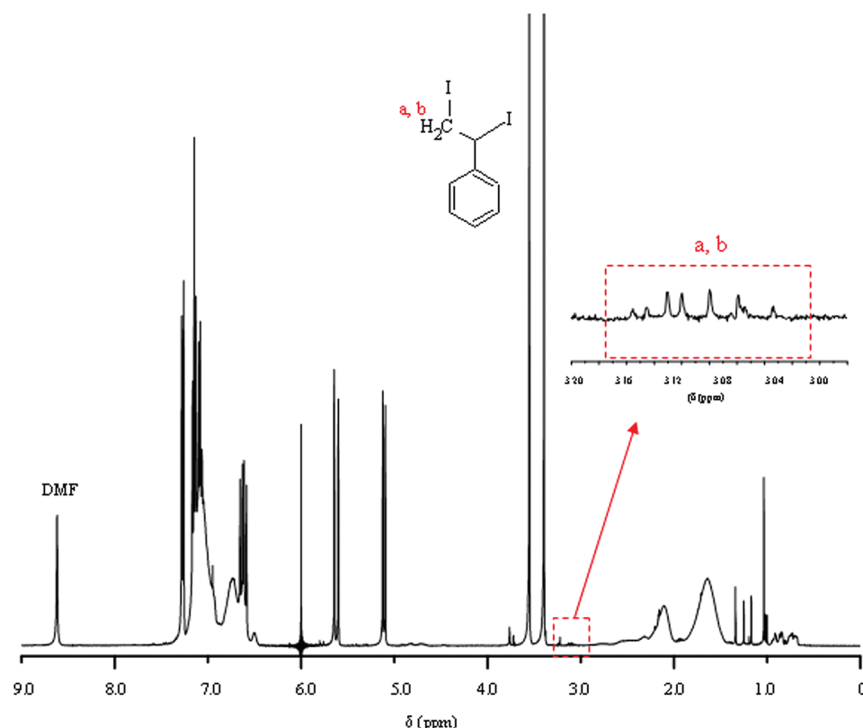


Figure 6. ^1H NMR spectrum of styrene polymerized by RITP in toluene- d_8 at 70 $^\circ\text{C}$ ($[\text{styrene}] = 3.70\text{ M}$, $[\text{toluene}] = 5.44\text{ M}$, $[\text{AIBN}] = 0.12\text{ M}$ and $[\text{I}_2] = 6.86 \times 10^{-2}\text{ M}$, conversion = 70%, $M_{n,\text{SEC}} = 2400\text{ g}\cdot\text{mol}^{-1}$, PDI = 1.50), showing the peaks for aliphatic protons of 1,2-diiodoethylbenzene.

The theoretical inhibition time for acrylates and methacrylates is dependent on the temperature and the ratio of initiator to molecular iodine, while being independent of the targeted molecular weight.^{1–3} However, for styrene polymerized by RITP, $t_{\text{inh,exp}}$ is dependent on the targeted molecular weight.³ From Table 1 it is evident that $t_{\text{inh,exp}}$ is much shorter than that of $t_{\text{inh,theory}}$. It can also be seen that $t_{\text{inh,exp}}$ decreases with increasing targeted molecular weight.

The inhibition period can be seen clearly by a conversion versus time profile, as shown in Figure 4. The plot shows that the A–I adduct concentration increases over time to a maximum and then decreases. Upon complete consumption of the A–I adduct, one can see the onset of polymerization. Throughout the polymerization period, the monomer is being converted, yet, toward the higher end of monomer conversion (>50%) there is a downward curvature ($t \sim 700\text{ min}$). This may indicate a reduction in the rate of polymerization. The half-life ($t_{1/2}$) of AIBN at 70 $^\circ\text{C}$ is about 5 h and the reason for this decrease in the rate of polymerization may be due to the low concentration of AIBN at the end of polymerization. This implies that there are insufficient initiator radicals to consume the iodine that is liberated from 1,2-diiodoethylbenzene, hence the limited monomer conversion.³

The shorter experimental inhibition time compared to the theoretical can be explained by the complex chemistry between iodine and styrene.^{4,5} The most notable reactions between iodine and styrene are as follows: (1) cationic polymerization of styrene by iodine, (2) reversible formation of 1,2-diiodoethylbenzene, and (3) formation of a charge transfer complex. Tonnar et al.³ suggested that the inhibition time for styrene polymerized by RITP is shortened due to the formation of 1,2-diiodoethylbenzene although this has never been proven experimentally (Scheme 3). When styrene and iodine are reacted

with one another, a colorless compound is formed. This colorless compound is 1,2-diiodoethylbenzene. Subsequently, hydrogen iodide is generated and an equilibrium reaction with free iodine gives I_3^- and HI_2^+ respectively. The cation (HI_2^+) is added to the monomer to generate 1-PEI, a commonly used chain transfer agent in ITP.^{8,12}

In order to identify 1,2-diiodoethylbenzene in RITP, the ^1H NMR spectrum of a mixture of styrene and iodine in CDCl_3 (Figure 5) was studied. The proton signals for 1,2-diiodoethylbenzene in this mixture were observed around 3.85–3.97 ppm. The peculiar multiplicity of the CH_2 group is explained as follows; the CH group of 1,2-diiodoethylbenzene is an asymmetric center and thus the CH_2 protons are not in the same chemical environment. The CH_2 protons couple with one another resulting in two doublets. They also couple with the CH proton and the number of signals is doubled, resulting in a total number of eight signals. When an RITP experiment is run at 70 $^\circ\text{C}$ using AIBN, iodine and styrene in toluene- d_8 , the peak positions are shifted to 3.04–3.16 ppm (Figure 6). Still, the same multiplicity is observed confirming that 1,2-diiodoethylbenzene is formed in the course of the styrene polymerization.

Comparable to 1,2-diiodoethylbenzene is the compound 2-iodo-1-phenylethanol, whose proton signals are observed at 3.25–3.45.^{13,14} The presence of 1,2-diiodoethylbenzene in the reaction medium suggests that there should also be 1-PEI (Scheme 3). It is assumed that 1-PEI is a chain transfer agent in RITP of styrene. Therefore, kinetic ^1H NMR spectra were examined in order to identify the proton signals of 1-PEI, as well as the subsequent phenylethyl end group protons that could transpire. Figure 7 is a ^1H NMR spectrum of styrene polymerized by RITP at 70 $^\circ\text{C}$, showing the proton signals for the methyl protons of 1-PEI and those of the phenylethyl end

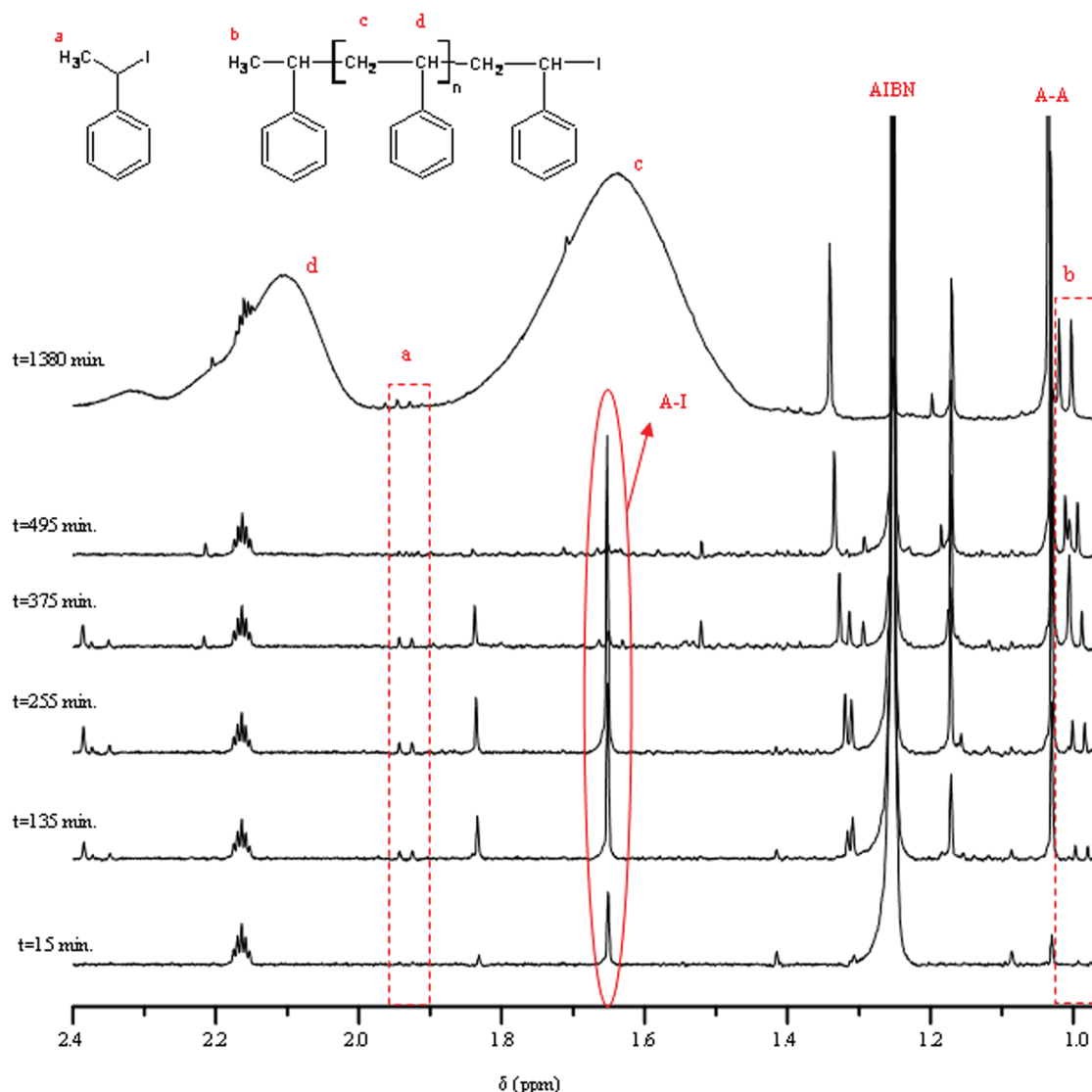


Figure 7. An enlarged portion (0.95–2.05 ppm) of the ^1H NMR spectrum in toluene- d_8 of styrene polymerized by RITP at 70 $^\circ\text{C}$ [styrene] = 4.27 M, [$\text{toluene-}d_8$] = 4.82 M, [AIBN] = 0.13 M and [I_2] = 7.91×10^{-2} M), showing the signals for the methyl protons of 1-PEI at 1.94 ppm and for the polymer phenylethyl end group at 0.97 ppm.

group of the polymer. The methyl proton signals in ^1H NMR were observed at 1.94 ppm, in reasonable agreement with Gaynor et al.⁷ who observed a doublet at 2.2 ppm after isolating 1-PEI. The phenylethyl end group proton signals of the polymer were observed at 0.97 ppm, which is in good agreement with the peak assignments observed by Goto et al.¹⁵

1-PEI could possibly originate from the autoinitiation of styrene, which entails the formation of the Diels–Alder dimer 1-phenyl-1,2,3,4-tetrahydronaphthalene, followed by the transfer of a hydrogen atom to form a phenylethyl and 1-phenyltetralyl radical.^{16–18} However, the ^1H NMR spectra for styrene polymerized by RITP showed no proton signals for the 1-phenyltetralyl radical. The use of MALDI–ToF to characterize polystyrene synthesized by various CRP methods has been reported in literature.¹⁹ MALDI–ToF analysis, run in linear mode, was used to substantiate the structures identified from ^1H NMR spectra of polystyrene synthesized by RITP. An enlarged portion of a typical MALDI–ToF

spectrum is shown in Figure 8. From the spectrum, several populations were identified and shown in Scheme 4 and Figure 8, respectively.

The terminating ends of these structures would be expected to be iodinated. However, during MALDI–ToF analysis the terminating end is fragmented by the cation of the salt. Also, the C–I bond in PS synthesized by RITP is weak and can fragment easily. Therefore, the expected iodine terminated PS was observed in the 1-H NMR spectra, whereas unsaturated structures are observed in MALDI–ToF.³

The major population of polystyrene oligomers is separated by a mass increment of 104 Da, corresponding to the monomer repeat unit. The structures identified in MALDI–ToF are listed in Table 2 with their respective predicted masses. The major population, which appears, e.g., at 2008.59 Da (Table 2), is the structure $\text{A-M}_{m-1}-\text{CH}=\text{C}(\text{Ph})\text{H}$ (Scheme 4). A 1-H NMR chemical shift for the unsaturated chain end would be expected at around 6.4–6.6 ppm. However, since the signal was not observed in ^1H NMR, the structure is assumed to form during

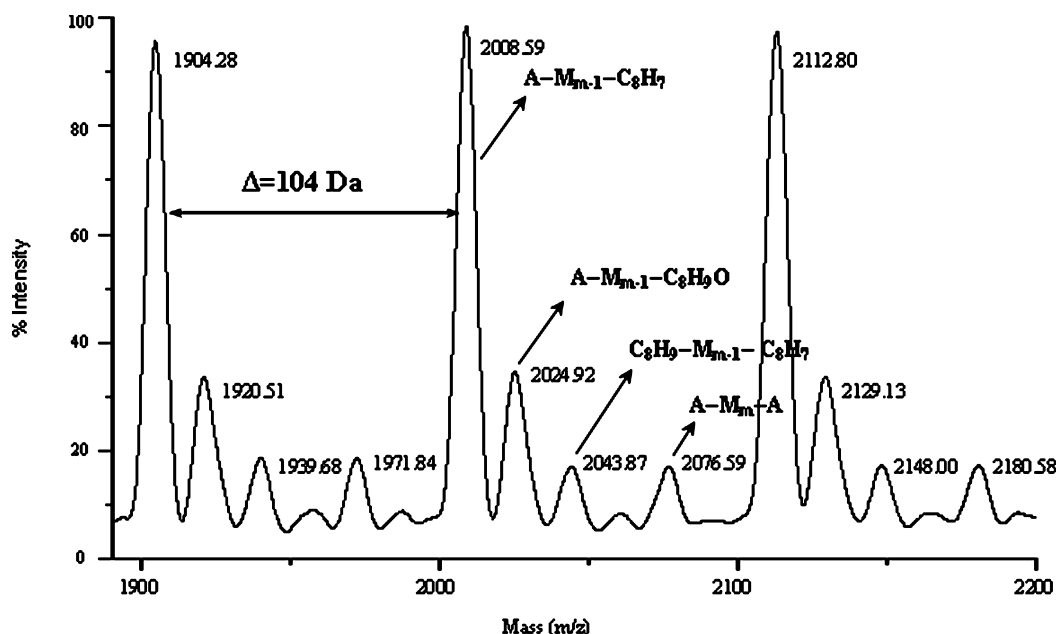


Figure 8. Enlarged portion of the MALDI–ToF spectrum (linear mode) of PS synthesized by RITP at 70 °C for 24 h ([styrene] = 3.70 M, [toluene] = 5.44 M, [AIBN] = 0.12 M and $[I_2] = 6.86 \times 10^{-2}$ M, conversion = 70%, $M_{n,SEC} = 2400$ g·mol^{−1}, $M_{n,NMR} = 2500$ g·mol^{−1}).

Scheme 4. Structures Identified from the MALDI–ToF Analysis of Polystyrene Synthesised by RITP at 70 °C

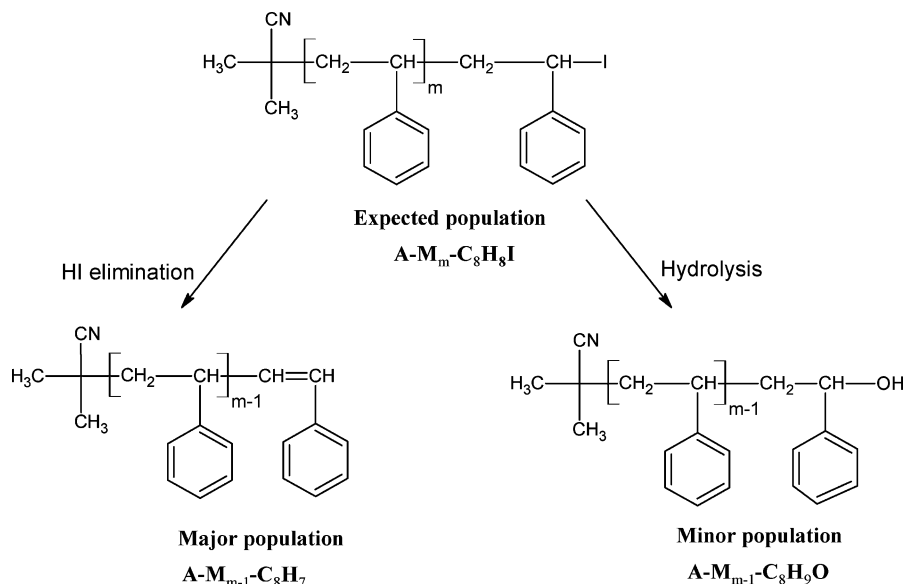


Table 2. Peak Assignments for MALDI–ToF Analysis (Linear Mode) of Styrene Polymerized by RITP for 24 h at 70 °C in Toluene

structure	<i>m</i>	experimental mass (<i>m/z</i>) ^a	theoretical mass (<i>m/z</i>) ^b
A–M _{<i>m</i>–1} –C ₈ H ₇ , –HI (Cu ⁺)	17	2008.59	2005.10
A–M _{<i>m</i>–1} –C ₈ H ₉ O, –HI (Cu ⁺)	17	2024.92	2023.11
C ₈ H ₉ –M _{<i>m</i>–1} –C ₈ H ₇ , –HI (Cu ⁺)	17	2043.87	2042.12
A–M _{<i>m</i>} –A (Cu ⁺)	18	2076.59	2074.16

MALDI–ToF analysis where HI is eliminated from A–M_{*m*}–I due to Cu⁺. The unsaturated population has been observed for the RITP³ of styrene as well as for metal–catalyzed CRP of styrene.²⁰

A minor population (Scheme 4) is observed at 2024.92 Da. A signal for the hydroxyl end group of this population is not

observed in ¹H NMR, and therefore might form due to hydrolysis of the halogen end group during MALDI ToF analysis.

A second minor population is observed at 2043.87 Da (Table 2 and Figure 9). 1,2-diiodoethylbenzene generates 1-PEI, a good transfer agent for CRP. The minor population contains a phenylethyl end group (C₈H₉–M_{*m*–1}–C₈H₇), which originates from the reaction between styrene and the alkyl iodide chain transfer agent.^{7,15} As was the case with the major population, this structure forms during MALDI–ToF analysis due to the elimination of HI. Another third minor population, appearing at 2076.59 Da, is that of a direct initiation and termination reaction (combination of the initiator and styrene) to form the structure A–M_{*m*}–A. These structures have been reported for iodine mediated polymerization.^{7,8,15,21}

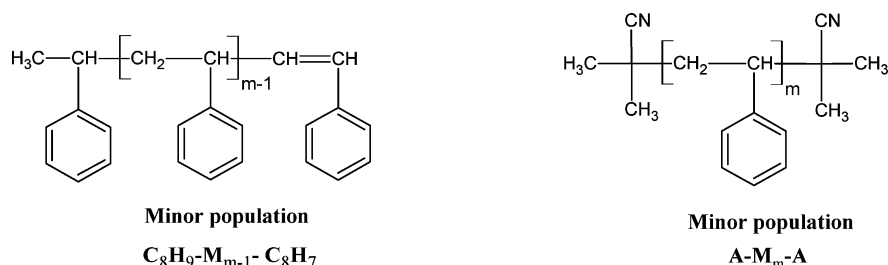


Figure 9. Structures identified in MALDI–ToF analysis for the minor populations that do not derive from the A–M_m–I population.

CONCLUSIONS

The mechanism of styrene polymerization by RITP is significantly different to that of acrylates and methacrylates.^{1,2} The inhibition period is the feature of its mechanism that makes it so different. Throughout the inhibition period, iodine reacts with initiator radicals to form chain transfer agents (A–I and A–M_n–I adducts). Iodine not only reacts with the initiator, but also reacts with styrene to form 1,2-diiodoethylbenzene. The inhibition period is significantly reduced due this side reaction. For RITP, this compound has not been reported. We found evidence of 1,2-diiodoethylbenzene in ¹H NMR, which consequently reacted with styrene to form a chain transfer agent, 1-PEI. This compound, commonly used in degenerative transfer mediated polymerization,⁷ has not been identified in literature for RITP. The evolution of 1-PEI was followed by *in situ* ¹H NMR and the resulting polymer structure containing phenylethyl end group was confirmed by MALDI–ToF analysis. Although iodine is liberated from 1,2-diiodoethylbenzene throughout the polymerization period of RITP, the monomer conversion is often limited (~65%) due to the shortage of initiator radicals toward the end of polymerization.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hpasch@sun.ac.za.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Mpact Company (South Africa) is acknowledged for funding this research. Lebohang Hlalele is acknowledged for his assistance and advice regarding *in situ* ¹H NMR. Karsten Rode (Deutsches Kunststoff-Institut) is acknowledged for performing the MALDI–ToF analysis.

REFERENCES

- (1) Boyer, C.; Lacroix-Desmazes, P.; Robin, J.-J.; Boutevin, B. *Macromolecules* **2006**, *39*, 4044–4053.
- (2) Lacroix-Desmazes, P.; Severac, R.; Boutevin, B. *Macromolecules* **2005**, *38*, 6299–6309.
- (3) Tonnar, J.; Severac, R.; Lacroix-Desmazes, P.; Boutevin, B. *Polym. Prepr.* **2008**, *49*, 68–69.
- (4) Fraenkel, G.; Bartlett, P. D. *J. Am. Chem. Soc.* **1959**, *81*, 5582–5590.
- (5) Trifan, D. S.; Bartlett, P. D. *J. Am. Chem. Soc.* **1959**, *81*, 5573–5581.
- (6) Shiman, D. I.; Kostyuk, S. V.; Gaponik, L. V.; Kaputskii, F. N. *Russ. J. Appl. Chem.* **2010**, *83*, 2028–2034.
- (7) Gaynor, S. G.; Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 8051–8056.
- (8) Valade, D.; Boyer, C.; Ameduri, B.; Boutevin, B. *Macromolecules* **2006**, *39*, 8639–8651.
- (9) David, G.; Boyer, C.; Tonnar, J.; Ameduri, B.; Lacroix-Desmazes, P.; Boutevin, B. *Chem. Rev.* **2006**, *106*, 3936–3962.
- (10) Matyjaszewski, K. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 769–776.
- (11) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1984**, *17*, 1094–1099.
- (12) Maschio, G.; Cerrai, P.; Giusti, R. *Polym. Bull.* **1982**, *8*, 147–153.
- (13) Cerritelli, S.; Chiarini, M.; Cerichelli, G.; Capone, M.; Marsili, M. *Eur. J. Org. Chem.* **2004**, *3*, 623–630.
- (14) Kotsuki, H.; Shimanouchi, T.; Ohshima, R.; Fujiwara, S. *Tetrahedron* **1998**, *54*, 2709–2722.
- (15) Goto, A.; Ohno, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 2809–2814.
- (16) Matyjaszewski, K. *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000; pp 122–123.
- (17) Pryor, W. A.; Coco, J. H. *Macromolecules* **1970**, *3*, 500–508.
- (18) Zammit, M. D.; Davis, T. P.; Haddleton, D. M.; Suddaby, K. G. *Macromolecules* **1997**, *30*, 1915–1920.
- (19) Ladaviere, C.; Lacroix-Desmazes, P.; Delolme, F. *Macromolecules* **2009**, *42*, 70–84.
- (20) Nonaka, H.; Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 2083–2088.
- (21) Lansalot, M.; Farcet, C.; Charleux, B.; Vairon, J.-P. *Macromolecules* **1999**, *32*, 7354–7360.