# Synthesis of Poly(styrene)-*b*-poly(dimethylsiloxane)-*b*-poly(styrene) Triblock Copolymers by Iodine Transfer Polymerization in Miniemulsion

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ABSTRACT: The first synthesis of poly(styrene)-*b*-poly(dimethylsiloxane)-*b*-poly(styrene) triblock copolymer in miniemulsion has been achieved by controlled/living radical polymerization of styrene using a modified hydroxypropyl terminated poly(dimethylsiloxane) as a transfer agent for iodine transfer polymerization. First an α,ω-hydroxypropyl poly(dimethylsiloxane) was modified by esterification with 2-bromopropionic acid. The second step consisted in a nucleophilic substitution of bromine by iodine through the reaction with sodium iodide in acetone. Then, miniemulsion polymerization of styrene was performed in the presence of sodium dodecyl sulfate as surfactant, 2,2′-azobis(isobutyronitrile) as radical initiator, and the α,ω-diiodopoly(dimethylsiloxane) as both the hydrophobe and the macrotransfer agent. Stable white latexes were obtained with a good correlation between theoretical and experimental molecular weights. Considering the process and the polymerization type, rather low polydispersity indexes (around 1.7) were reached. A kinetic study showed an increase of the molecular weight with conversion. Last, a chain extension led to a shift of the molecular weight distribution giving evidence for the living character of the triblock copolymers.

## Introduction

Copolymers of polystyrene (PS) and poly(dimethylsiloxane) (PDMS) have been widely studied during recent years. These copolymers associate the unique properties of silicone with those of polystyrene. The exceptional properties of silicone include high stability toward heat and UV radiation, very low glass transition temperature, low surface energy and good gas permeability.[1] Moreover polysiloxanes are lipophilic. By association of these two polymers, new properties are obtained. PDMS and PS are incompatible, and therefore, phase separation and nanostructuration are observed.[2−4] Chen[5,6] studied the composition and the structure of the surface of PS-*b*-PDMS films after casting with different solvents. Fukumine[7] studied the micellization behavior of diblock copolymers in solution. Materials obtained after the micellization of PS−PDMS diblock copolymers were studied by Ma et al.[8] The association between these two polymers also opens the way to various applications. For instance, Ndoni et al.[9,10] studied the lubricating effect of thin styrene/dimethylsiloxane block copolymers films. The compatibilizing ability of PS−PDMS block copolymers in blends of PS and PDMS was observed by Chuai,[11,12] Maric,[13] and Selby[14] through morphology and surface segregation studies. Canelas and co-workers[15,16] took advantage of the solubility of PDMS in $scCO_2$ to use PS-*b*-PDMS as steric stabilizers for dispersion polymerization in $scCO_2$. Finally, Hoxmeier and the Shell Oil Company[17,18] used triblock copolymers PS-*b*-PDMS-*b*-PS in monomers such as D3 (hexamethylcyclotrisiloxane) or D4 (octamethylcyclotetrasiloxane) to form organogels.

To synthesize these copolymers, various polymerization techniques have been used. Among them, living anionic polymerization has been the most widely studied.[3,19−25] The macroinitiator technique has also been widely used. For instance, PDMS−PS block copolymers have been synthesized by atom transfer radical polymerization using a PDMS macroinitiator.[26−29] Other techniques include cationic polymerization,[3] thermal polymeric iniferters,[30,31] hydrosilylation between α,ω-dihydrogenopoly(dimethylsiloxane) and α,ω-divinylsilylated polystyrene,[32] nitroxide-mediated polymerization from an alkoxyamine[23,33] and the use of macroazoinitiator having siloxane units.[34]

In this work, we prepared PS-*b*-PDMS-*b*-PS copolymers by living radical polymerization in aqueous miniemulsion. Living radical polymerization (LRP)[35,36] includes a group of radical polymerization techniques which provide simple and robust routes to the synthesis of well-defined polymers and the fabrication of novel functional materials.[37−45] The general principle of the methods reported so far relies on a reversible activation−deactivation process between dormant chains (or capped chains) and active chains (or propagating radicals). Among the most efficient LRP methods (nitroxide-mediated polymerization,[39] atom transfer radical polymerization,[38,46−48] reversible addition−fragmentation chain transfer polymerization,[49] and iodine transfer polymerization (ITP)[50−52]), ITP polymerization is very attractive, and this work focuses on this method.

The mechanism of ITP with alkyl iodide is shown in Scheme 1. Unlike in step 4, the exchange process described in step 6 is thermodynamically neutral (i.e., degenerative transfer: $k_{ex} = k_{-ex}$, $K = 1$), because the propagating chains and the iodine-capped chains have the same structure on both sides of the reversible reaction. ITP has been successfully applied to the polymerization of styrene,[50,53,54] acrylates,[50,55,56] vinyl acetate,[57] butadiene,[58,59] fluorinated monomers (tetrafluoroethylene,[60,61] vinylidene fluoride,[60−64] hexafluoropropene[60−64]) and chlorinated monomers (vinyl chloride,[65,66] vinylidene chloride.[67,68]). Most studies of iodine transfer polymerization of styrene were realized in bulk. In few studies, some workers carried out ITP of styrene

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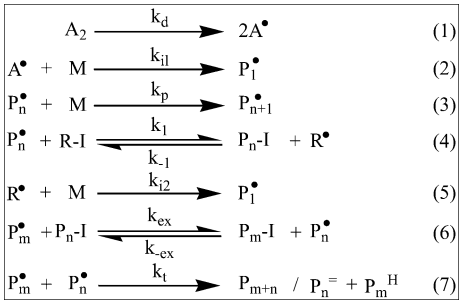
**Scheme 1. Reactions in Degenerative Transfer Polymerization with Alkyl Iodides**




in emulsion[69] and miniemulsion.[69−71] In this work we studied the ITP of styrene to make PS-*b*-PDMS-*b*-PS triblock copolymers in miniemulsion. To our knowledge, this is the first time that ITP and miniemulsion techniques are used to synthesize the title triblock copolymer. An α,*ω*-diiodo PDMS was first synthesized and then used as a macrotransfer agent in the miniemulsion radical polymerization of styrene.

## Experimental Section

**Materials.** The hydroxypropyl-terminated poly(dimethylsiloxane) RHODORSIL 1647 V60 (RHODIA) was used as received. Prior to use, this product was characterized by SEC and $^1$H NMR. The SEC shows a shoulder around 300 g mol$^{-1}$ corresponding to residual octamethylcyclotetrasiloxane (D4). The number-average molecular weight obtained by SEC ($M_{n,SEC}$) is around $M_{n,SEC}$ = 970 g mol$^{-1}$ (number-average degree of polymerization, $DP_{n,SEC}$ = 10.7) and the polydispersity index (PDI = $M_w/M_n$) is around 1.6. The $^1$H NMR detailed later gives a $DP_{n,NMR}$ = 12.5 corresponding to a molecular weight of $M_{n,H-NMR}$ = 1100 g mol$^{-1}$. The molecular weight given by $^1$H NMR is slightly higher than the one given by SEC because of the presence of D4. In our work, the molecular weight given by SEC was chosen as the molecular weight of reference. 2-Bromopropionic acid (ACROS, 99%), sodium iodide (SDS, 99%), sodium hydroxide (SDS), magnesium sulfate (VWR), acetone, toluene (Carlo Erba) and chloroform (SDS) were used without purification. For the esterification, methanesulfonic acid (Avocado, 70 wt % in water) was used as catalyst without purification. Styrene (Acros, 99%) was purified by vacuum distillation before use. 2,2′-Azobis(isobutyronitrile) (AIBN, Fluka, 98%) was purified by recrystallization in methanol. Dodecyl sulfate sodium salt (SDS, Aldrich, 98%) and iodine (Aldrich, 99.8%) were used as received. Water was deionized by passing through columns packed with ion-exchange resins.

**General Procedure for the Synthesis of the α,*ω*-Dibromopoly(dimethylsiloxane) (1).** Typically, the silicon oil (10 g, $M_n \approx$ 970 g mol$^{-1}$, Rhodorsil 1647 V60, 10.3 mmol), 2-bromopropionic acid (3.9 g, $M$ = 152.98 g mol$^{-1}$, 25.5 mmol) and methanesulfonic acid (0.24 g, $M$ = 96 g mol$^{-1}$, 70 wt % in water, 1.8 mmol) were dissolved in chloroform (100 mL) in a round-bottom flask equipped with a reverse Dean−Stark system and a condenser. The reaction was stirred for 6 h at 80 °C. The resulting solution was extracted with a solution of sodium hydroxide (0.1 N, 100 mL). Then the organic solution was washed with water until the pH was neutral. After drying upon magnesium sulfate, chloroform was removed under reduced pressure. Conversion > 90%; mass yield = 90%. $^1$H NMR ($\delta$ in ppm, $CDCl_3$): 4.35, q, Br**C**H(CH$_3$)*C*(*O*)O−; 4.1, m, −C**H**$_2$−O−C(O)−; 1.8, d, C**H**$_3$−CHBr−; 1.67, m, −CH$_2$−C**H**$_2$−CH$_2$−; 0.54, m, −Si(CH$_3$)$_2$−C**H**$_2$−; 0.04, m, −Si(C**H**$_3$)$_2$−. Anal. Calcd: Br, 13.0%. Found: Br, 13.2%.

**General Procedure for the Synthesis of the α,*ω*-Diiodo poly(dimethylsiloxane) (2).**[72] Typically, the α,*ω*-dibromo poly(dimethylsiloxane) (**1**) (5 g, $M_{n,SEC}$ = 1275 g mol$^{-1}$, 3.9 mmol) and sodium iodide (5.2 g, $M$ = 150 g mol$^{-1}$, 34.7 mmol) were dissolved in acetone (150 mL). The flask was equipped with a condenser. The solution was heated at reflux during 6 h in the dark. Then, the flask was slowly cooled to room temperature. The treatment consisted in the solvent evaporation under vacuum, always in the dark. After addition of diethyl ether to dissolve the PDMS, the solution was filtered to remove the NaBr formed during the reaction and the excess of NaI. Then, diethyl ether was removed under reduced pressure. Conversion >90%, mass yield = 94%. $^1$H NMR ($\delta$ in ppm, $CDCl_3$): 4.45, q, I−C**H**(CH$_3$)−; 4.08, m, −C**H**$_2$−O−C(O)−; 1.93, d, (C**H**$_3$)CHI−; 1.67, m, −CH$_2$−C**H**$_2$−CH$_2$−; 0.54, m, −Si(C**H**$_3$)$_2$−CH$_2$−; 0.04, m, −Si(C**H**$_3$)$_2$−. Anal. Calcd: I, 19.4%. Found: I, 19.3%.

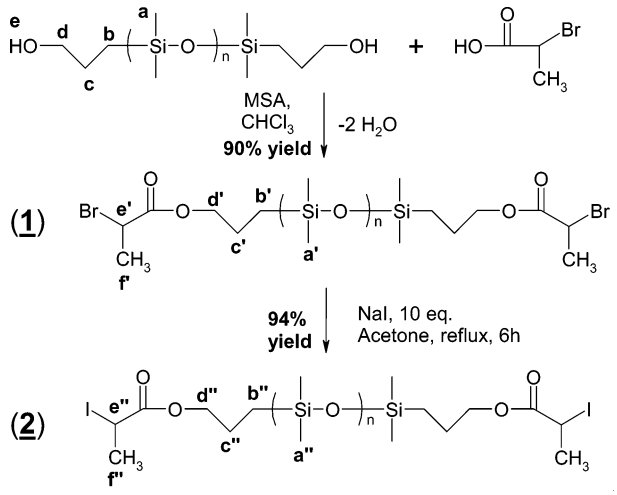
**General Procedure for Miniemulsion Polymerization.** [Styrene]/[AIBN]/[I−PDMS−I] = 68/0.19/1. Typically, water (70 g) was placed in a 250 mL glass reactor and thoroughly purged with argon bubbling for 30 min. A solution of SDS (400 mg, $M$ = 288.28 g mol$^{-1}$, 1.39 mmol) in water (10 g) was added in the reactor under argon flow, followed by a solution of AIBN (27 mg, $M$ = 164.2 g mol$^{-1}$, 0.16 mmol) and transfer agent (**2**, 1.14 g, $M_{n,SEC}$ = 1340 g mol$^{-1}$, 0.85 mmol) in styrene (6.06 g, $M$ = 104 g mol$^{-1}$, 58.2 mmol). The reaction medium was purged for 15 min with argon. Then the solution was miniemulsified by ultrasonication (Bioblock Scientific Vibra Cell 75043, 5 min, 8 kHz) under argon flow and the miniemulsion was purged for another 15 min with argon. The reactor was thermostated at 75 °C and the reaction proceeded for 5 h under argon atmosphere and magnetic stirring. Monomer conversion was determined by gravimetric analysis. Results: styrene conversion = 71%, $M_{n,th}$ = 6400 g mol$^{-1}$, $M_{n,NMR}$ = 8200 g mol$^{-1}$, $M_{n,SEC}$ = 7300 g mol$^{-1}$, PDI = 1.61, and particle diameter $D_p$ = 129 nm (monomodal).

**Chain Extension.** The seed latex prepared as above (71% monomer conversion) was used to resume the polymerization (chain extension). A solution of AIBN (0.0256 g, $M$ = 164.2 g mol$^{-1}$, 0.156 mmol) in styrene (5.00 g, $M$ = 104 g mol$^{-1}$, 48 mmol) was added to the seed latex (40.21 g) and the reaction medium was purged by argon bubbling during 30 min. The reaction proceeded in the dark under argon atmosphere with magnetic stirring during 5 h at $T$ = 75 °C. Results: styrene conversion = 38%, $M_{n,th}$ = 12 900 g mol$^{-1}$, $M_{n,NMR}$ = 14 500 g mol$^{-1}$, $M_{n,SEC}$ = 12 600 g mol$^{-1}$, PDI = 1.54, and particle diameter $D_p$ = 186 nm (monomodal).

**Styrene Polymerization by Reverse Iodine Transfer Polymerization (RITP).**[73−75] Styrene (6.00 g, $M$ = 104 g mol$^{-1}$, 57.7 mmol), toluene (7.50 g), AIBN (0.196 g, $M$ = 164.2 g mol$^{-1}$, 1.2 mmol) and iodine (0.152 g, $M$ = 254 g mol$^{-1}$, 0.6 mmol) were introduced in a Schlenk flask. After three freeze−thaw-pump cycles, the flask was heated at 75 °C in an oil bath. The polymerization was conducted in the dark under argon atmosphere with magnetic stirring. Conversion was determined by $^1$H NMR analysis on crude samples in $CDCl_3$ (conversion = 76%). Polystyrene was recovered by precipitation in methanol. Molecular weights were determined by size exclusion chromatography ($M_n$ after precipitation = 3700 g mol$^{-1}$, PDI = 1.20).

**Characterizations.** Size exclusion chromatography (SEC) was performed on dried samples dissolved in toluene, with a Spectra-Series P100 pump equipped with a Shodex Rise-61 refractometer detector and two 300 mm columns thermostated at 30 °C (columns mixed-D PL-gel 5 $\mu$m from Polymer Laboratories: $2 \times 10^2$ to $4 \times 10^5$ g mol$^{-1}$ molecular weight range). Toluene was used as eluent at a flow rate of 0.8 mL.min$^{-1}$. Calibration was performed with polystyrene standards from Polymer Laboratories. SEC analysis of PDMS in toluene gives a negative peak (because $n_{PDMS} < n_{Toluene}$) ($n_{PDMS}$ = 1.43; $n_{PS}$ = 1.591 and $n_{Toluene}$ = 1.496).[76,77] Therefore, the PDMS was analyzed using an inverse polarity to make the peak positive. Because of the values of d$n$/d$c$ and $n$ of PS and PDMS (d$n$/d$c$(PDMS) = −0.0938 mL·g$^{-1}$ at 25 °C at 546 nm[78] and d$n$/d$c$(PS) = 0.111 mL·g$^{-1}$ at 28 °C at 546 nm[79]), the triblock copolymers give a positive peak as soon as the weight fraction of PS in the triblock is higher than 46%. Thus, the detection of PS-poor triblock copolymers by the refractometer detector is less sensitive than that of PS-rich triblock copolymers. It means that the molecular weight distribution of such triblock copolymers given by SEC with this type of detector must be

**Scheme 2. Syntheses of α,ω-Dibromopoly(dimethylsiloxane) (1) from Rhodorsil 1647 V60 (MSA is Methanesulfonic Acid) and α,ω-Diiodopoly(dimethylsiloxane) (2) from (1)**




considered with caution, especially close to the critical composition indicated above (46 wt % PS). In this study, the weight fraction of PS was always higher than 46% (except possibly at very low styrene conversions).

$^1$H (250 MHz) and $^{13}$C (50.32 MHz) NMR analyses were performed in $CDCl_3$ on a Bruker Avance 250 MHz and a Bruker AC200. Particle size of the latex was determined with a Nanotrac 250 particle analyzer (Microtrac Inc.). pH measurements were performed with a Consort P500 apparatus from Bioblock Scientific. $^{13}$C NMR simulations were performed using ChemDraw Ultra 9.0 software.

## Results and Discussion

**Syntheses and Characterization of the Telechelic α,ω-Dibromopoly(dimethylsiloxane) (1) and the Telechelic α,ω-Diiodopoly(dimethylsiloxane) (2).** The azeotropic esterification in $CHCl_3$ catalyzed by methanesulfonic acid between the starting hydroxypropyl telechelic poly(dimethylsiloxane) RHODORSIL 1647 V60 ($M_n$ = 970 g mol$^{-1}$, PDI = 1.6) and 2-bromopropionic acid is quantitative (conversion >93%) and gives the expected product (**1**) in good yield (90%) (Scheme 2). The modification of **1** by reaction with sodium iodide[72] is quantitative (conversion > 96%) and gives the iodinated macrotransfer agent (**2**) in good yield (94%) (Scheme 2).

The $^1$H NMR spectrum of Rhodorsil 1647 V60 is not first-order (Figure 1). It shows three very different signals for each methylene groups −Si-**CH**$_2$−CH$_2$−**CH**$_2$−O which could be analyzed as a AA′MM′XX′ spin system (the signals of protons *b* and *c* are multiplets and the signal of proton *d* is a triplet) as demonstrated by Fruchier et al.[80] The mean number of siloxane units by NMR spectroscopy is $DP_{n,NMR}$ = 12.5 ($DP_{n,SEC}$ = 10.7) which gives a molecular weight of $M_{n,NMR}$ = 1100 g mol$^{-1}$. The $^1$H NMR spectra of the telechelic α,ω-dibromopoly(dimethylsiloxane) (**1**) and the telechelic α,ω-diiodopoly(dimethylsiloxane) (**2**) are also given in Figure 1. The signals of the protons *d*′ and *d*″ are not triplets because of the asymmetric carbon that carries the protons *e*′ and *e*″. Again, as for the starting material, the signals of the protons *b*′, *b*″ and *c*′, *c*″ are multiplets. The mean value of siloxane units by NMR spectroscopy for **1** is $DP_{n,NMR,(1)}$ = 10.6 which agrees well with the value given for the starting material Rhodorsil 1647 V60 ($DP_{n,SEC,Rhodorsil}$ = 10.7) and close to the $DP_{n,SEC,(1)}$ = 11.2 given by SEC. The elemental analysis of **1** gives 13.2% of bromine which is close to the theoretical percentage (12.97%) given by calculation using $M_{n,NMR(1)}$ = 1230 g mol$^{-1}$. The signals of the protons *e*″ and *f*″ are shifted because of the presence of the iodine atom. The mean value of siloxane units by NMR for **2** is $DP_{n,NMR,(2)}$ = 10.4 which is close to the $DP_{n,SEC,(2)}$ = 10.7. The percentage of iodine given by elemental analysis of **2** (19.3%) agrees well with the theoretical percentage (19.36%) given by calculation using $M_{n,NMR(2)}$ = 1310 g.mol$^{-1}$. As shown in Figure 1, $^1$H NMR spectroscopy allows to follow with precision both the esterification reaction and the bromine substitution.

**Synthesis of PS—PDMS—PS Triblock by ITP in Miniemulsion.** In miniemulsion polymerization, the monomer droplets are formed by ultrasonication of the initial monomer-in-water emulsion. To increase the stability of these monomer droplets and to avoid Ostwald ripening, a hydrophobic agent such as *n*-hexadecane is usually added.[81] In our study however this was not necessary because the PDMS macro transfer agent (**2**) plays the role of the hydrophobe. In our case, we have used rather low molecular weight PDMS ($M_{n,SEC,(2)}$ = 1340 g mol$^{-1}$). The use of a higher molecular weight PDMS should also be possible. Indeed, the PDMS will remain soluble in styrene even at high molecular weights ($\delta_{styrene}$ = 9.3 cal$^{1/2}$·cm$^{-3/2}$ and $\delta_{PDMS}$ = 7.3 cal$^{1/2}$·cm$^{-3/2}$).[76,82,83] However the efficiency of the hydrophobe against Ostwald ripening depends on its molar concentration, the latter being lower for high molecular weight PDMS (at a given weight fraction in styrene). Therefore, the efficiency of high molecular weight PDMS as hydrophobe would deserve attention. In the miniemulsion, the monomer, the transfer agent and the radical initiator are located in the monomer droplets and so the transportation of neither of these compounds across the aqueous phase is required.

An experiment was conducted at $T$ = 75 °C with [SDS] = 2 × cmc (cmc = critical micelle concentration, 2.6 g·L$^{-1}$) and the other concentrations were as follows: [styrene]/[AIBN]/[I−PDMS−I] = 68/0.19/1. After 5 h of reaction, the conversion in styrene was 71% and a stable white latex was obtained with a diameter particle size of 129 nm (monomodal particle size distribution). The SEC shows a clear shift toward higher molecular weights after the polymerization step and gives an experimental molecular weight of $M_{n,SEC}$ = 7300 g mol$^{-1}$ (PDI = 1.61) (Figure 2). This agrees well with the theoretical expected molecular weight, $M_{n,th}$ = 6400 g mol$^{-1}$ given by eq 1 assuming a complete consumption of the macrotransfer agent.

$$M_{n,theoretical} = M_{n,(2)} + \frac{m_{styrene}}{n_{(2)}} \times \alpha_{styrene} \qquad (1)$$

in which $M_{n,(2)}$ is the mean number-average molecular weight of **2**, $m_{styrene}$ is the mass of styrene, $n_{(2)}$ is the number of moles of **2**, and $a_{styrene}$ is the conversion of styrene. As mentioned in the Experimental Section, the tailing of the molecular weight distribution on the low molar mass side (non symmetrical distribution) for the triblock copolymers could be attributed to differences in d*n*/d*c* for PDMS (d*n*/d*c*(PDMS) = −0.0938 mL·g$^{-1}$ at 25 °C at 546 nm[78]) and PS (d*n*/d*c*(PS) = 0.111 mL·g$^{-1}$ at 28 °C at 546 nm[79]).

NMR analysis shows the complete disappearance of the signal corresponding to the iodinated chain ends of the PDMS macro transfer agent at 4.45 ppm and the appearance of the PS−I chain ends at 4.65 ppm (Figure 3).[54,84,85] This gives additional evidence for the formation of a triblock copolymer. NMR analysis permits to assess the number-average molecular weight by integrating the reference signal of the −C**H**$_2$−Si methylene groups next to the Si atom at 0.46 ppm ($I_{h'''}$) and comparing it to the integration of the aromatic protons of PS between 6 and 7.5 ppm ($I_{h'''}$) (eq

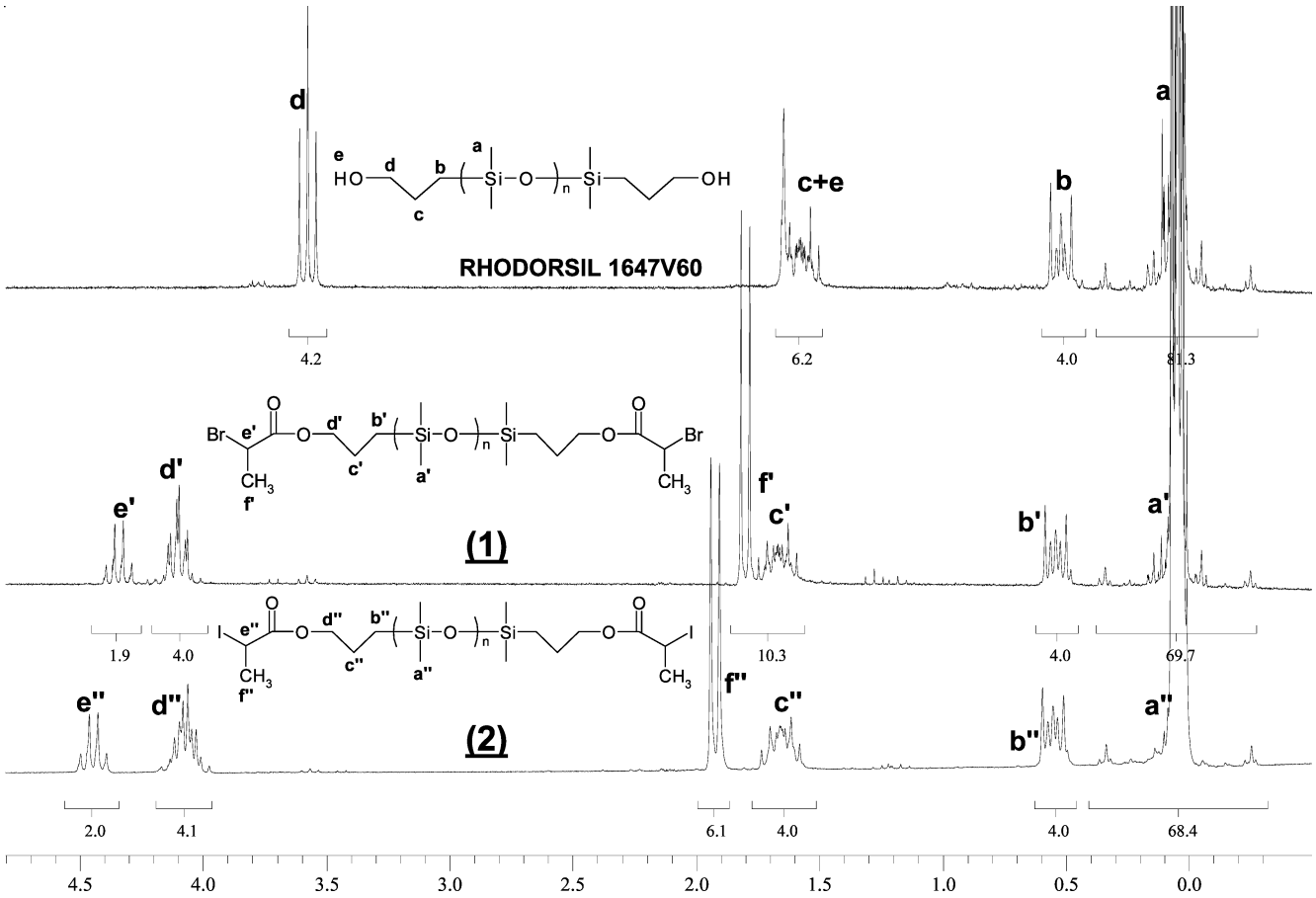



**Figure 1.** $^1$H NMR spectra of the starting Rhodorsil 1647 V60, the α,ω-dibromopoly(dimethylsiloxane) (**1**) and the α,ω-diiodopoly(dimethylsiloxane) (**2**) in $CDCl_3$: (Rhodorsil 1647 V60) $H_a$ (m, 0.04 ppm), $H_b$ (m, 0.52 ppm), $H_{c+e}$ (m, 1.57 ppm − 1.64 ppm), $H_d$ (t, 3.58 ppm); (**1**) $H_{a'}$ (m, 0.04 ppm), $H_{b'}$ (m, 0.54 ppm), $H_{c'}$ (m, 1.67 ppm), $H_{d'}$ (m, 4.1 ppm), $H_{e'}$ (q, 4.35 ppm), $H_{f'}$ (d, 1.8 ppm); (**2**) $H_{a''}$ (m, 0.04 ppm), $H_{b''}$ (m, 0.54 ppm), $H_{c''}$ (m, 1.67 ppm), $H_{d''}$ (m, 4.08 ppm), $H_{e''}$ (q, 4.45 ppm), $H_{f''}$ (d, 1.93 ppm).

2). Alternatively, the signal of the −C**H**Ph−I chain ends at 4.65 ppm ($I_{i'''}$) can be used (eq 3).

$$M_{n,NMR(b''')} = M_{n,(2)} + \frac{I_{h'''}/5}{I_{b'''}/4} \times M_{styrene} \quad (2)$$

$$M_{n,NMR(i''')} = M_{n,(2)} + \frac{I_{h'''}/5}{I_{i'''}/2} \times M_{styrene} \quad (3)$$

in which $M_{styrene}$ is the molecular weight of styrene.

These integrations give values of $M_{n,NMR(b''')} = 8200$ g mol$^{-1}$ and $M_{n,NMR(i''')} = 8600$ g mol$^{-1}$, respectively. These results are higher than both the theoretical molecular weight $M_{n,th} = 6400$ g mol$^{-1}$ and the molecular weight determined by SEC, $M_{n,SEC} = 7300$ g mol$^{-1}$. The difference between $M_{n,NMR}$ and $M_{n,SEC}$ could be due to the difficulty of integration of the low concentrated chain-end signals ($i'''$) and ($b'''$).

**Chain Extension.** To check the living character of the final copolymer latex prepared by miniemulsion polymerization, a PS−PDMS−PS latex was further used as a seed in emulsion polymerization of styrene. The seed latex had a monomer conversion of 71% before adding more styrene in one shot. The reaction was conducted at 75 °C with the following concentrations: [styrene]/[AIBN]/[PS−PDMS−PS] = 143/0.39/1. The results in Table 1 show that the molecular weight increases as theoretically expected while the polydispersity decreases slightly: $M_{n,SEC} = 12\,600$ g mol$^{-1}$, PDI = 1.54 ($M_{n,th} = M_{n,first\ block}$ + (mass of monomers) × conversion/ (moles of first block) = 12 900 g mol$^{-1}$ at 38% conversion) and $M_{n,NMR} = 14\,500$ g mol$^{-1}$. The final latex has a diameter particle size of 186 nm (monomodal particle size distribution). The number of particles

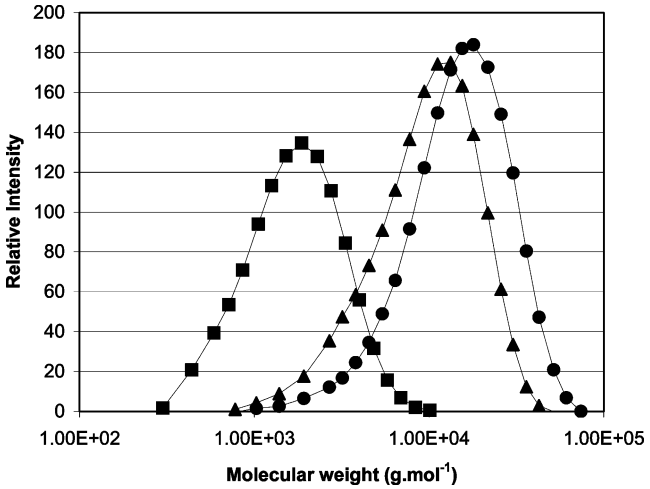



**Figure 2.** SEC (size exclusion chromatography) analyses: (■) α,ω-diiodo-PDMS (poly(dimethylsiloxane)) macrotransfer agent (**2**); (▲) PS-*b*-PDMS-*b*-PS (poly(styrene)-*b*-poly(dimethylsiloxane)-*b*-poly(styrene)) triblock copolymer prepared by iodine transfer polymerization (ITP) of styrene in miniemulsion ([styrene]/[2,2′-azobis(isobutyronitrile)]/[I−PDMS−I] = 68/0.19/1, [sodium dodecyl sulfate] = 2 × cmc, theoretical dry solid content at 100% conversion = 8.7%); (●) PS-*b*-PDMS-*b*-PS after chain extension by emulsion polymerization of styrene ([styrene]/[2,2′-azobis(isobutyronitrile)]/[PS-*b*-PDMS-*b*-PS] = 143/0.39/1, [sodium dodecyl sulfate] = 2 × cmc, theoretical dry solid content at 100% conversion = 18.8%).

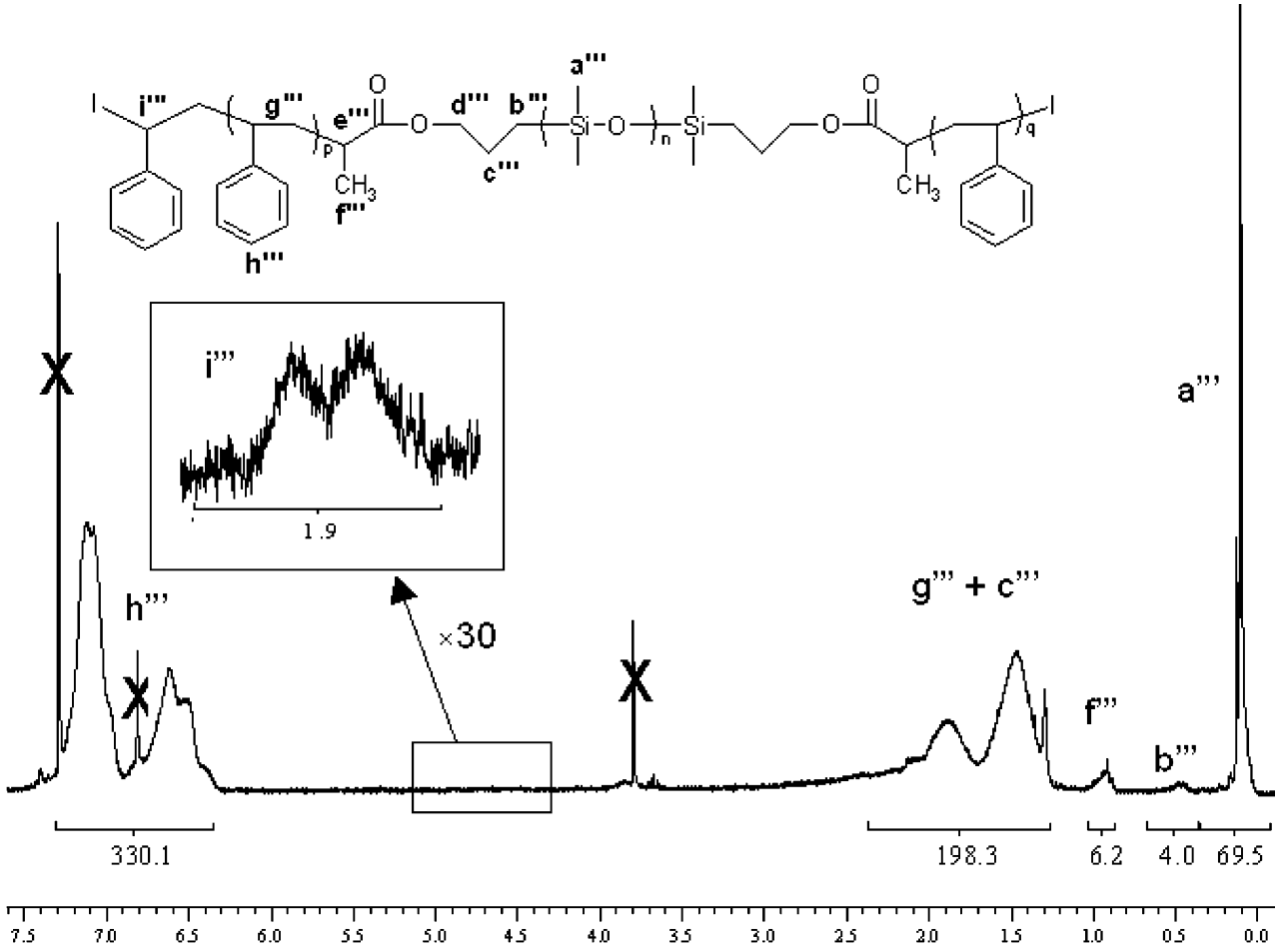



**Figure 3.** $^1$H NMR spectrum of the triblock copolymer PS-*b*-PDMS-*b*-PS (poly(styrene)-*b*-poly(dimethylsiloxane)-*b*-poly(styrene)) in $CDCl_3$: $H_{a'''}$ (m, 0.04 ppm), $H_{b'''}$ (0.46 ppm), $H_{f'''}$ (d, 0.91 ppm), $H_{c'''}$ and $H_{g'''}$ (m, 1.2−2.2 ppm), $H_{h'''}$ (m, 6.3−7.4 ppm), $H_{i'''}$ (m, 4.65 ppm). Other peaks: $CDCl_3$ (s, 7.26 ppm), 4-methoxyphenol: radical scavenger used to stop the polymerization reaction (s, 6.77 ppm and s, 3.75 ppm).

**Table 1. Characteristics of the PS-*b*-PDMS-*b*-PS (Poly(styrene)-*b*-poly(dimethylsiloxane)-*b*-poly(styrene)) Triblock Copolymers before and after Chain Extension[a]**

| run | type | time (h) | conversion (%) | pH | $M_{n,th}$[b] (g mol$^{-1}$) | $M_{n,NMR}$[c] (g mol$^{-1}$) | $M_{n,SEC}$[d] (g mol$^{-1}$) | $M_w/M_n$ | $D_p$[e] (nm) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | seed latex triblock PS−PDMS−PS copolymer | 5 | 71 | 2.23 | 6400 | 8200 | 7300 | 1.61 | 129 |
| 2 | chain extension of PS blocks | 5 | 38 | 2.18 | 12 900 | 14 500 | 12 600 | 1.54 | 186 |

[a] Chain extension of the PS blocks in emulsion at 75 °C: seed latex (miniemulsion), water (80 g), I−PDMS−I (1.14 g, 0.85 mmol), styrene (6.06 g, 58.3 mmol), AIBN (2,2′-azobis(isobutyronitrile), 0.027 g, 0.16 mmol), and SDS (0.4 g, 1.39 mmol). Chain extension: seed latex (40.2 g), styrene (5 g, 48 mmol), AIBN (0.026 g, 0.158 mmol). [b] Theoretical number-average molecular weight $M_{n,th} = M_{n,\text{transfer agent}} + m_{\text{styrene}} \times (\text{styrene conversion})/n_{\text{transfer agent}}$. [c] $M_{n,NMR} = M_{n,\text{transfer agent}} + (\int(C_6H_5)^{6.3-7.4\ \text{ppm}}/5) \times 104.15/(\int(\text{Si}-CH_2)^{0.46\ \text{ppm}}/4)$. [d] Measured by size exclusion chromatography in toluene, related to polystyrene calibration. [e] Particle diameter.

$N_p$ decreased from $8.0 \times 10^{13}$ to $6.9 \times 10^{13}$ particles per cm$^3$ during the seeded emulsion polymerization. This shows that no renucleation took place and that only a very limited destabilization and particle coagulation occurred. The copolymer latex was stable during several months and no flocculation was observed. A shift of the molecular weight distribution (MWD) toward higher molecular weights was observed (Figure 2). This shift combined with the narrowing of the PDI confirms that there is only a small fraction of dead chains.

**Kinetics of Miniemulsion Polymerization.** An experiment was conducted at $T = 75$ °C with [SDS] = 2 × cmc and the other concentrations were as follows: [styrene]/[AIBN]/[I−PDMS−I] = 177/0.27/1. The evolution of monomer conversion vs time indicates an inhibition period of about 20 min (Figure 4). This inhibition period might be due to the presence of some molecular iodine $I_2$ formed during the iodation step. Iodine is known to be a strong radical scavenger.[73,86−88] Once this small amount of iodine has reacted, the polymerization can begin.

The molecular weight increases with conversion (Figure 5). Because of the relatively low transfer constant of alkyl iodides in styrene polymerization, the molecular weight at low conversion is above the theoretical straight line. But with increasing conversion, the molecular weight approaches the targeted value. The polydispersity index increases to 1.88 at 75% conversion before decreasing to 1.73 at the final conversion of 93%. The apparent transfer constant $C_{tr,app}$ of **2** can be calculated by extrapolation at 0% conversion ($M_{n,0} = 7880$ g mol$^{-1}$ corresponding to $DP_{n,0} = (7880-1340)/104.15 = 62$ with $DP_{n,0} = [\text{styrene}]_0/([\mathbf{2}]_0 \times C_{tr,app})$ and $[\text{styrene}]_0/[\mathbf{2}]_0 = 177$). It gives approximately $C_{tr,app,(2)} = 2.8$. The transfer agent being difunctionnal, the transfer constant $C_{tr,(2)}$ for one chain end corresponds to $C_{tr,app,(2)}/2 = 1.4$. Since this value is higher than 1, it is

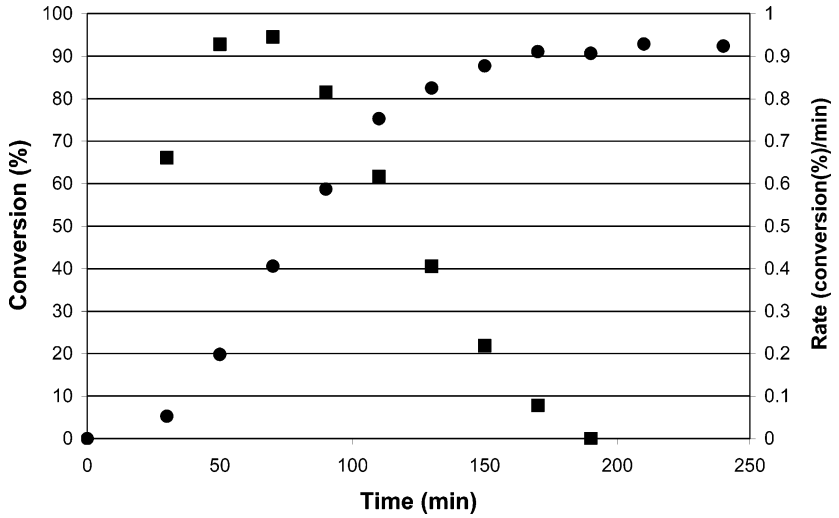



**Figure 4.** Conversion vs time (●) and rate of polymerization vs time (■) during the miniemulsion polymerization of styrene ($T$ = 75 °C, [sodium dodecyl sulfate] = 2 × cmc, [styrene]/[2,2′-azobis(isobutyronitrile)]/[I−PDMS−I] = 177/0.27/1, theoretical dry solid content at 100% conversion = 14%).

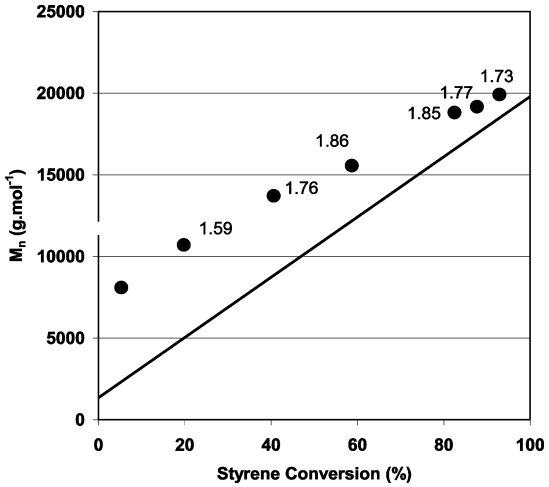



**Figure 5.** Molecular weight ($M_n$, ●) and polydispersity index (PDI, labels) vs conversion during the miniemulsion polymerization of styrene ($T$ = 75 °C, [sodium dodecyl sulfate] = 2 × cmc, [styrene]/[2,2′-azobis(isobutyronitrile)]/[I−PDMS−I] = 177/0.27/1, theoretical dry solid content at 100% conversion = 14%). The line stands for the ideal case given by $M_{n,theoretical} = M_{n,transfer\ agent} + m_{styrene} \times$(styrene conversion)/$n_{transfer\ agent}$.

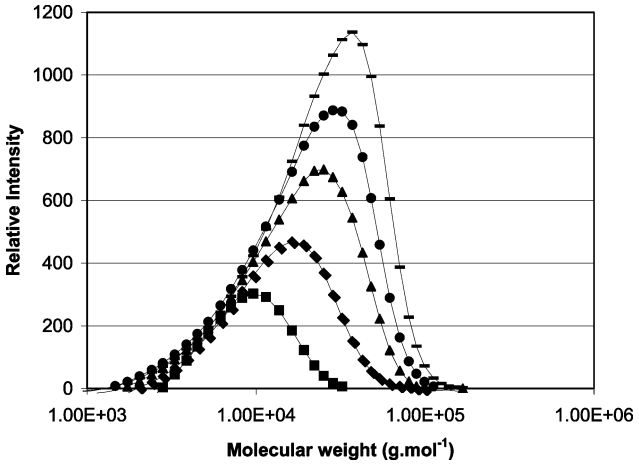



**Figure 6.** Evolution of the molecular weight distribution for the miniemulsion polymerization of styrene ($T$ = 75 °C, [sodium dodecyl sulfate] = 2 × cmc, [styrene]/[2,2′-azobis(isobutyronitrile)]/[I−PDMS−I] = 177/0.27/1, theoretical dry solid content at 100% conversion = 14%): (■) 30 min; (◆) 50 min; (▲) 70 min; (●) 90 min; (−) 150 min.

possible to achieve complete reinitiation of the second block. Last, the SEC chromatograms show a shift toward higher molecular weights as the conversion increases (Figure 6). Such a behavior is compatible with a living process through degenerative chain transfer.

**pH Evolution during the Polymerization.** Although the initial pH was neutral, we observed that the pH of the final copolymer latex was around 3. This was certainly due to the elimination of hydriodic acid HI during the polymerization step. So, the evolution of pH during the miniemulsion polymerization was followed ($T$ = 75 °C, [SDS] = 2 × cmc, [styrene]/[AIBN]/[I−PDMS−I] = 77/0.21/1) (Figure 7). The pH did not evolve during the ultrasonication step and remained nearly constant during the short inhibition period. It means that the iodinated chain ends of the PDMS are rather stable and are not prone to degradation by elimination of HI. But as soon as the polymerization begins and that some PS−I chain ends are formed, the pH decreases rather quickly and reaches a plateau at high monomer conversion. Therefore, it seems that the PS−I chain ends are more fragile and lead to elimination of HI. A calculation was done to determine the percentage of dead chain ends assuming that the pH drop is only due to the chain-end degradation and formation of HI. After 5 h of reaction the final pH is 2.57. This corresponds to $10^{-2.57} = 2.69 \times 10^{-3}$ mol L$^{-1}$ of formed HI ($2.69 \times 10^{-3}$ mol L$^{-1}$ × 0.16 $L$ = $4.31 \times 10^{-4}$ mol of HI). In comparison with the initial amount of iodinated chain ends ($2 \times 2.0174\ g_{PDMS\ transfer\ agent}$/1340 g mol$^{-1}$ = $3.011 \times 10^{-3}$ mol), it gives 14.3% of dead chain ends. Since each PDMS chain has two iodinated chain ends, there are only 0.143 × 0.143 = 2% of the PS-*b*-PDMS-*b*-PS triblock chains which have two dead chain ends. To limit chain-end degradation, it is better to stop the reaction as soon as possible once high conversion has been reached to avoid curing of the latex at high temperature for a long time.

Some model experiments were performed in order to gain a better understanding of the pH decrease. In the first model experiment, styrene was replaced by toluene (6 g) and all the other ingredients were kept the same: PDMS transfer agent (1.015 g, 0.76 mmol), AIBN (0.0296 g, 0.18 mmol), water (80 g), SDS (0.406 g, 1.41 mmol). The mixture was miniemulsified and heated during 5 h at 75 °C to study the pH evolution. pH diminished only slightly from 7.0 to 5.85. The pH drop

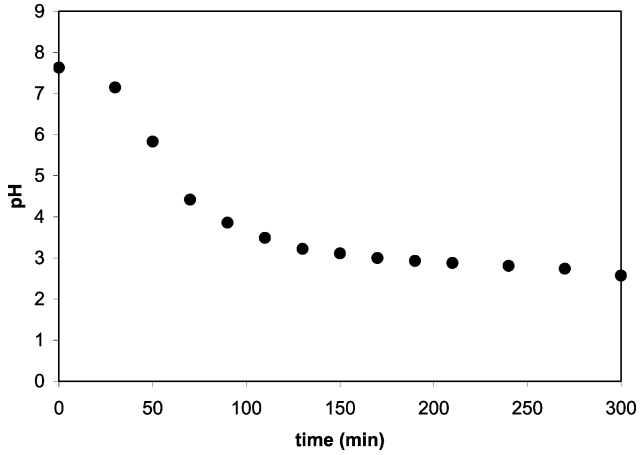
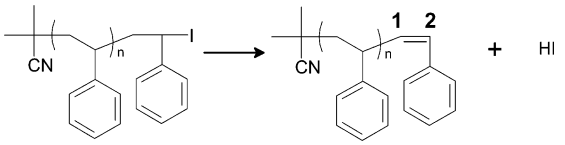



**Figure 7.** pH evolution vs time for the miniemulsion polymerization of styrene at $T = 75$ °C ([sodium dodecyl sulfate] = 2 × cmc, [styrene]/[2,2′-azobis(isobutyronitrile)]/[I−PDMS−I] = 77/0.21/1, theoretical dry solid content at 100% conversion = 7.9%).

**Scheme 3. Assumed Degradation Process of PS−I Chain Ends**

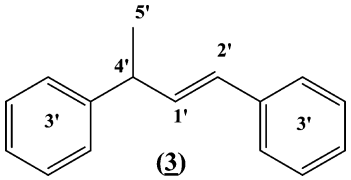



corresponds to the formation of $1.18 \times 10^{-7}$ mol of HI. This represents 0.008% of the iodinated chain ends of the PDMS macro transfer agent. Furthermore, NMR analysis showed no degradation of the PDMS chain transfer agent in these conditions. This experiment confirms that the iodinated chain ends $-CH(CH_3)-I$ of the PDMS macro transfer agent are stable and are not prone to degradation. One can suppose that the HI formation is probably due to the more labile PS−I chain ends formed during the polymerization step.

To prove this hypothesis, an iodine end-capped polystyrene was synthesized by RITP[73−75] in toluene. This PS−I chain transfer agent was miniemulsified by ultrasonication in the presence of toluene (PS−I transfer agent (1.78 g, $M_n = 3700$ g mol$^{-1}$, 0.48 mmol), toluene (3.9 g), water (8.28 g), SDS (0.036 g, 0.12 mmol)). After heating for 5 h at 75 °C, the pH had dropped from 7.0 to 2.50. pH drop corresponds to the formation of $2.6 \times 10^{-5}$ mol of $H^+$, corresponding to the degradation of 5.5% of the chain ends. This confirms that the iodinated PS−I chain ends are more fragile and undergo a faster degradation than the PDMS−I chain ends of the macrotransfer agent. It also explains why the pH only begins to drop when the polymerization has begun and some PS−I chain ends have been formed.

The chain-end degradation by HI elimination must produce terminal double bonds (hydrolysis of PS−I might also form PS−OH chain ends which can further react in acidic conditions to give indanyl terminations or terminal double bonds). Scheme 3 shows the assumed degradation process. We chose a model compound, 1,3-diphenyl-1-butene (**3**) (Scheme 4), to determine the approximative $^1$H chemical shifts of degraded poly(styrene) chain ends. The $^1$H NMR spectrum of **3** shows that chemical shifts of protons *1′* and *2′* are located between 6.33 and 6.46 ppm.[89] Therefore, the PS chain ends degradation cannot be observed by $^1$H NMR because the signals of the vinylic protons *1* and *2* are hidden by the aromatic signals of polystyrene. To support the assumed degradation process of the PS−I chain ends, the iodine end-capped polystyrene synthesized by RITP was characterized by $^{13}$C NMR (47 700 scans) after the pH study described above. A very thin band at 129.7 ppm can be attributed

**Scheme 4. Model Compound 1,3-Diphenyl-1-butene (3) ($^1$H NMR: 1.46 ppm (d, $J = 7$ Hz, 3H), 3.58−3.69 ppm (m, 1H), 6.33−6.46 ppm (m, 2H), 7.15−7.38 (m, 10H))**




to the $-\boldsymbol{C}H{=}CHPh$ marked *1* on the assumed chain-end degraded PS−I (Scheme 3). Another band at 28.5 ppm can be attributed to the nondegraded PS−I chain ends. Indeed, by simulating the $^{13}$C NMR spectra of the PS chain ends ($n = 2$) using the ChemDraw Ultra 9.0 software, the theoretical chemical shifts were 129.6 ppm for $-\boldsymbol{C}H{=}CHPh$ and 28.8 ppm for $-CH_2-\boldsymbol{C}H(Ph)-I$.

## Conclusion

Iodine transfer polymerization (ITP) of styrene in miniemulsion was achieved using an α,ω-diiodopoly(dimethylsiloxane) macrotransfer agent (**2**). The macrotransfer agent was synthesized in very good yield by esterification of a α,ω-dihydroxy precursor with 2-bromopropionic acid and then bromine substitution under the action of sodium iodide in acetone. The ultrasonication of an aqueous dispersion of **2** and AIBN in styrene in the presence of SDS gives a miniemulsion leading to a stable PS-*b*-PDMS-*b*-PS triblock copolymer latex after polymerization. Considering the method (ITP) and process (miniemulsion) of the polymerization, good polydispersity indexes are obtained (around 1.7). The kinetic study showed an increase of molecular weights with conversion and demonstrated the controlled character of the polymerization. The pH drop observed during the polymerization was assigned to the chain-end degradation by hydriodic acid elimination. This hypothesis was confirmed by $^{13}$C NMR spectroscopy. Degradation could be minimized by stopping the reaction as soon as possible once high conversion is reached. Indeed, the living character of the polymerization has been proved by a chain extension. Work is in progress in our laboratory to extend this process (living radical miniemulsion polymerization) to other monomers and compositions (particularly using PDMS of different chain lengths).

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