

# Simplifying the Free-Radical Polymerization of Styrene: Microwave-Assisted High-Temperature Auto Polymerizations

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We have investigated the combination of the thermally auto-initiated free radical polymerization of styrene and precipitation polymerization in order to develop a fast and environmentally friendly approach to produce polystyrene. To achieve high reaction temperatures in a short period of time, microwave irradiation was utilized as the heating source. Styrene was used without any purification, e.g., without distillation or column filtration. Due to the auto-initiation of styrene at high temperatures no radical initiator was required. Different water- or ethanol-to-styrene ratios were heated far beyond their boiling points and at relatively high pressures for the auto-initiated polymerization of styrene. The obtained molecular weights could be controlled by the ethanol-to-styrene ratio in the case of ethanol as the solvent although the monomer conversions were rather low under the applied conditions. Moreover, the effect of a commercially available stable free nitroxide was investigated on the control over the polymerization. It has been observed that it is possible to control the molecular weight of the polymer by changing the ratio of styrene to free nitroxide (varied from 10:1 to 400:1) and moderate polydispersity indices (PDI = 1.3 to 1.9) could be obtained. Finally, the developed polymerization processes only require a simple purification step due to the precipitation of the polystyrene in the reaction solvent.

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## Introduction

Polystyrene is a commercially important amorphous thermoplastic because of its wide range of applications in, for example, packaging of food, household goods, construction, energy, and communications technology as well as thermal insulation for refrigerator liners. The popularity of polystyrene derives from the fact that it possesses many interesting properties, such as good processability, rigidity, transparency, low water absorption, and that it can be produced at low cost. Another key property is the excellent electrical insulation characteristics.<sup>[1–5]</sup>

The main production of polystyrene is conducted by bulk and suspension free-radical polymerization processes.<sup>[6,7]</sup> Polymerization at low temperatures (<100°C) requires the presence of chemical initiators. At higher temperatures (>100°C) styrene is able to auto-polymerize and, therefore, no initiator is required.<sup>[8,9]</sup> The thermally initiated polymerization can be controlled by temperature (0.1% h<sup>-1</sup> at 60°C, 2% h<sup>-1</sup> at 100°C, and 16% h<sup>-1</sup> at 130°C, respectively).<sup>[8]</sup> The main advantage of this thermal polymerization technique is the absence of an initiator. However, some of the disadvantages of the thermally initiated polymerization are the formation of low-molecular-weight oligomers and the difficulty to control the polymerization temperature.<sup>[10]</sup> It is possible to remove the undesired oligomers by dissolution and precipitation of the polymerization solution.

An alternative approach to produce polystyrene in a simple way is precipitation polymerization.<sup>[11–13]</sup> The advantage of this method is the absence of expensive and difficult to remove stabilisers in comparison to other heterogeneous polymerization techniques, such as emulsion and suspension polymerization. The precipitation polymerization starts as a homogenous solution and the desired polymer is precipitated during the polymerization, while unreacted monomer and possible oligomers stay in solution. In recent years, research has intensified using supercritical carbon dioxide as an environmentally friendly solvent.<sup>[11]</sup>

In this contribution, we have investigated the combination of the thermal and precipitation free radical polymerization of styrene in order to develop a fast and environmentally friendly approach to produce polystyrene. For this reason microwave heating was used to efficiently achieve elevated temperatures in short times. The use of a chemical initiator was not necessary because the radicals were initiated by heat. In addition, precipitation polymerization was used in order to simplify the overall process by combining polymerization and precipitation in one step, whereby only environmentally friendly solvents, such as water and ethanol, were utilized. In addition, the effect of the presence of a stable free nitroxide was examined in the thermally initiated polymerization of styrene in ethanol.

## Results and Discussion

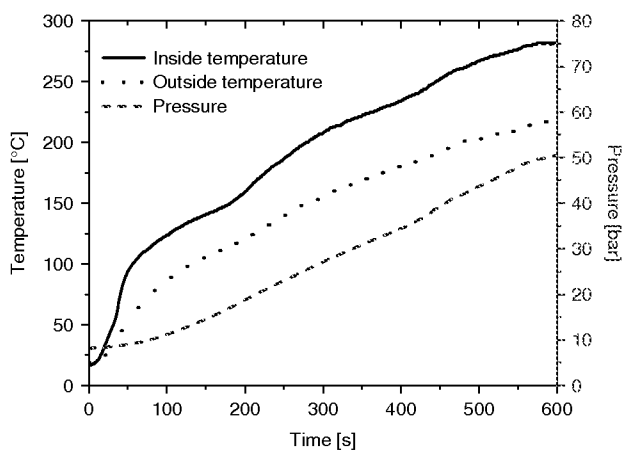
### Temperature-Initiated Polymerization of Styrene Under Near-Critical Water Conditions

The polarity and the hydrogen bonding of water are highly temperature dependent properties. Near-critical water (NCW) in the temperature range of 250 to 350°C is an environmentally benign solvent.<sup>[14–16]</sup> NCW has promising properties, e.g., a density and a dielectric constant similar to that of ambient acetone and a higher ionization constant than ambient water, which allows the simultaneous dissolution and reaction of organic and ionic species, as well as the swelling of polymers.<sup>[14,16]</sup> Furthermore, the increased ionization constant provides hydronium and hydroxide ions that are able to react as acidic or basic catalysts in chemical reactions.<sup>[16]</sup> In addition, purification of the reaction product becomes very easy because the product is precipitating at lower temperatures.<sup>[14,16]</sup>

This approach has already been successfully applied in organic chemistry<sup>[15]</sup> and we investigated its suitability for the free radical polymerization of styrene. Polystyrene has a high decomposition temperature (~310°C) and thus can be polymerized at temperatures up to 300°C. Furthermore, the polymerization of styrene is auto-initiating at high temperatures and no additional initiator is required.<sup>[9]</sup> The mechanism of the autopolymerization of styrene was first proposed by Mayo.<sup>[17]</sup> The polymerization starts with an initial [2+4] Diels–Alder reaction between two styrene molecules, which results in the non-aromatized Mayo adduct, which reacts further with another styrene molecule to form radicals.<sup>[9,17,18]</sup>

Although water and styrene are not miscible at ambient temperatures, at high temperatures the solubility parameters of water change, which might lead to dissolution of styrene in the water phase. To achieve temperatures up to 280°C, the Synthos 3000 microwave reactor from Anton Paar, equipped with quartz reaction vessels was used. This system allows reactions up to 300°C and 80 bar. A typical heating curve for the polymerization of styrene in water is shown in Fig. 1. The temperature and pressure inside a reference vessel was measured with a temperature/pressure sensor equipped with a gas thermometer, whereas the temperature of the vessel outside was measured by an IR sensor.

The fast heating of the reaction mixture (within 10 min to the preset value of 280°C) was achieved because of the good microwave absorption of water (dielectric constant: 80.4)<sup>[19]</sup> as



**Fig. 1.** Temperature and pressure profiles of the temperature-initiated polymerization of styrene in water.

a result of its polar structure. Styrene (dielectric constant: 2.4)<sup>[19]</sup> is apolar and, therefore, a poor microwave absorbing molecule and is heated indirectly by the water in this system. During the reaction a pressure of 50 bar is reached, which is due to heating above the boiling point of water. For the initial experiments a ratio of water to styrene of 10 to 1 was used and polystyrene with a number-average molecular weight ( $M_n$ ) of 25 790 Da and a polydispersity index (PDI) of 2.40 was obtained in moderate yields (31%). Before the polymerization, styrene was phase separated as a layer on top of the water phase, while the polystyrene was found to be on the bottom of the reaction vessel after the polymerization. To investigate the influence of the temperature on the thermally initiated polymerization of styrene, polymerization temperatures of 240, 200, 150, 120, and 90°C were investigated as well. At lower temperatures, e.g., 120 and 90°C, no polymer was obtained after 10 min and size exclusion chromatography (SEC) indicated that only very little auto-initiation has occurred. The obtained SEC traces were shifted to higher molecular weights with lower temperatures. Presumably, the radical concentration is relatively lower at lower reaction temperatures, which decreases the rate of termination reactions more than the rate of propagation. The relative intensity of the shoulders, which appear at higher elution volumes, increases with the polymerization temperature, which leads to broader molecular weight distributions. This indicates that the lifetime of the thermally initiated propagating chain is much lower at a higher temperature because of a higher concentration of the radicals. Therefore, lower  $M_n$  values were calculated with higher PDIs, as listed in Table 1. Surprisingly, the styrene conversion was not affected by the reaction temperature.

From these initial experiments it cannot be concluded whether the styrene and water were homogeneously mixed at elevated temperatures. To clarify this point, different solvent-to-monomer concentrations were applied under similar polymerization conditions. If styrene dissolves in water at high temperatures, lower molecular weights are expected for lower monomer concentrations as a result of reduced radical formation for more diluted reaction mixtures. In contrast, when styrene and water do not mix, all monomer concentrations should provide similar results because the polymerization would always take place in bulk styrene. Water-to-styrene ratios of 10 to 1, 10 to 2, 10 to 3, and 10 to 4, respectively, were used and the reaction temperature was set to 200°C. All experiments revealed similar molecular weights and molecular weight distributions (Table 2), although the monomer concentration was increasing. Therefore, it can be concluded that styrene is not soluble in water at high temperatures and that the polymerization behaves like a bulk polymerization.

Nevertheless, polystyrene with moderate molecular weights could be synthesised in short reaction times under microwave irradiation. The PDIs for a conventional free-radical

**Table 1.** Data of the thermally initiated polymerization of styrene after 10 min under microwave irradiation at different reaction temperatures (10:1 ratio of water to styrene)

Temperature [°C]	Conversion [%]	$M_n$ [g mol <sup>-1</sup> ]	Polydispersity index
280	31	25 790	2.40
240	31	28 900	2.27
200	32	36 670	1.93
150	31	45 980	1.82

polymerization can approach at best 2.0 and the values obtained in this contribution were found to be similar or slightly better for a system without any inertization.<sup>[20]</sup> The conversions increase with the amount of styrene due to a higher number of radicals formed at higher monomer concentrations.

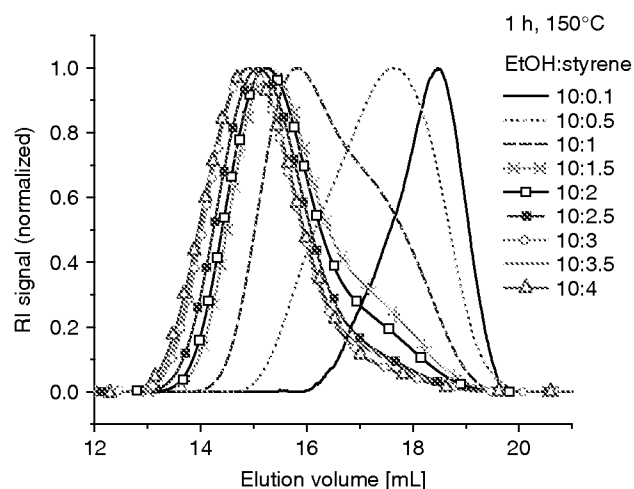
#### Temperature-Initiated Polymerization of Styrene in Ethanol

As described above, styrene was found to be insoluble in NCW. Therefore, the solvent was changed to ethanol, which is also known to be a 'green solvent'.<sup>[21]</sup> Styrene dissolves easily in ethanol to result in a homogeneous solution. However, the resulting polystyrene is not soluble in ethanol and precipitates from the polymerization solution to allow isolation by simple filtration. From the literature it is known that the thermal precipitation polymerization of styrene in ethanol at 150°C for 5 h results in polystyrene with a  $M_n$  of 47 000 Da and a PDI of 1.9.<sup>[22]</sup> Only low conversions (9%) were obtained, which were thought to be due to the ability of ethanol to induce transfer reactions. Nevertheless, we performed comparable experiments for 1 h in the Biotage microwave synthesizer at 150°C. Different ratios of ethanol to styrene were used (from 10:0.1 to 10:4) to investigate the influence of the monomer concentration on the molecular weight. The results of the SEC measurements are depicted in Fig. 2.

In general, the molecular weights shift to higher values with higher styrene concentrations. In particular, for the ethanol-to-styrene ratios from 10:0.1 to 10:3, a clear change in molecular weight is detected. The increase in molecular weight might be explained by the lower polarity of the styrene-ethanol mixture with higher styrene concentrations. The solubility of polystyrene is enhanced due to the lower polarity of the solvent mixture

**Table 2.** Data of the thermally initiated polymerization of styrene for different water-to-styrene ratios (200°C, 10 min)

Ratio H <sub>2</sub> O:styrene	Conversion [%]	$M_n$ [g mol <sup>-1</sup> ]	Polydispersity index
10:1	32	37 830	1.87
10:2	50	36 260	1.96
10:3	51	37 070	1.96
10:4	49	38 860	2.03



**Fig. 2.** SEC curves of the temperature-initiated precipitation polymerization of styrene for different ethanol-to-styrene ratios (150°C, 1 h).

and higher molecular weight polystyrene is precipitated. The obtained molecular weights, molecular weight distributions, and conversions are summarized in Table 3.

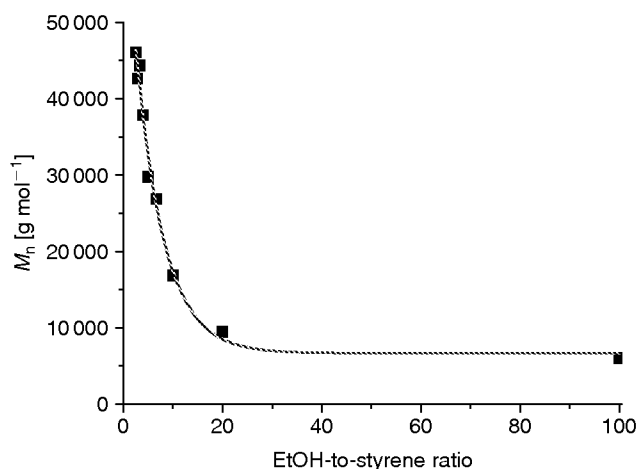
The molecular weight of the polystyrene varied between 6000 and 46 000 Da using different styrene concentrations and the PDIs were found to be in the range from 1.4 to 1.8 for a reaction time of 1 h; the obtained PDI values are relatively low for a free radical polymerization. Unfortunately, the conversions remained very low as described previously in the literature.<sup>[23]</sup> Longer reaction times did not increase the conversion, and the molecular weights were comparable. In addition, the precipitated polymer showed no clear phase separation, which might be correlated with the low conversions obtained. The  $M_n$  values as a function of the ethanol-to-styrene ratios are shown in Fig. 3.

The experimental data were fitted with an exponential decay function (1st order) to show a clear dependency of the molecular weight on the styrene-to-ethanol concentration. In principle, the required ethanol-to-styrene ratio for a desired molecular weight for the polymerization of styrene (1 h at 150°C) can be estimated from the observed plot.

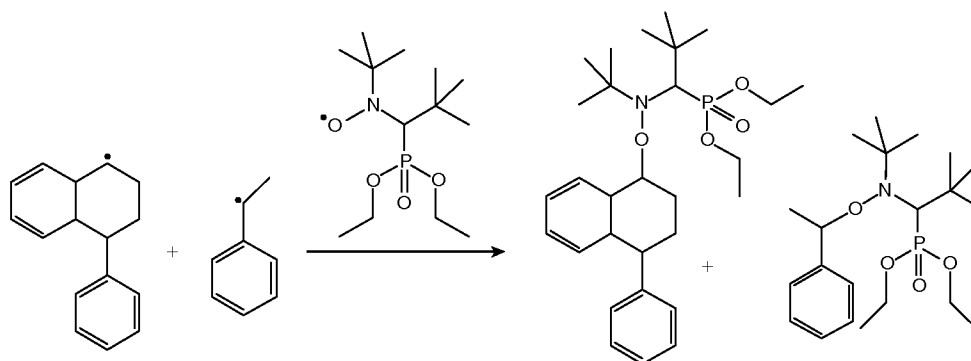
To improve the temperature-initiated polymerization of styrene in ethanol the stable free nitroxide *N,N*-*tert*-butyl-*N*-[1-diethylphosphono-2,2-dimethylpropyl] nitroxide (SG-1) was

**Table 3.** Data of the thermally initiated polymerization of styrene for different ethanol-to-styrene ratios at 150°C

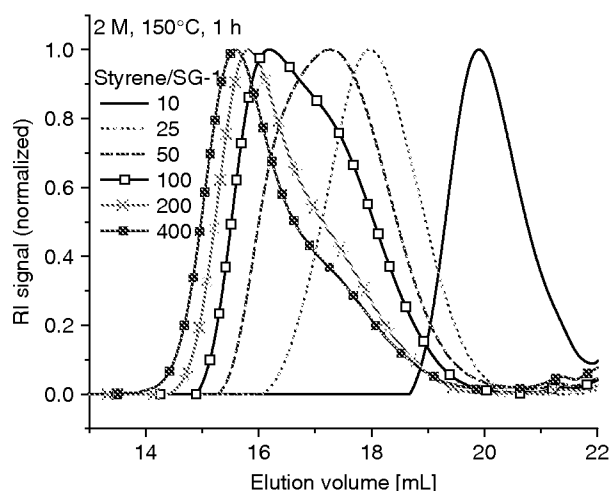
Ratio EtOH:styrene	Time [h]	Conversion [%]	$M_n$ [g mol <sup>-1</sup> ]	Polydispersity index
10:0.1	1	8	6020	1.40
10:0.5	1	13	9500	1.59
10:1	1	7	16 860	1.78
10:1	3	3	19 640	1.86
10:1	5	8	16 820	1.93
10:1.5	1	5	26 880	1.79
10:2	1	9	29 770	1.79
10:2.5	1	1	37 840	1.67
10:3	1	1	44 380	1.66
10:3.5	1	3	42 630	1.72
10:4	1	9	46 060	1.67



**Fig. 3.** Dependency of the  $M_n$  values on the ethanol-to-styrene ratio of the temperature-initiated polymerization of styrene for 1 h at 150°C. The data was fitted using an exponential curve fitting.



**Scheme 1.** Schematic representation of the general initiation step of the thermally initiated polymerization of styrene in the presence of SG-1.



**Fig. 4.** SEC curves of the thermally initiated precipitation polymerization of styrene for different SG-1 concentrations (2 M, 150°C, 1 h).

added to the polymerization system. From the literature it is known that the addition of free nitroxide, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), can improve the thermal polymerization at low temperatures (125°C) to result in narrow PDIs (~1.20 to 1.30).<sup>[18,23]</sup> At higher temperatures, e.g., 145°C, broader molecular weight distributions were obtained (PDI ~1.65). As a result of the TEMPO addition the molecular weight could be controlled during the thermal polymerization in bulk. However, an incubation period was observed depending on the amount of TEMPO. During the inhibition time, which can be several hours, no polymer is formed until the excess TEMPO is consumed. It was also reported that a high excess of TEMPO leads to the formation of a bis-TEMPO adduct, which is a poor initiating system for the thermal polymerization of styrene, and results in broad molecular weight distributions.<sup>[18]</sup>

In the current work, we have used SG-1 as a free nitroxide, because it has been reported to control the nitroxide-mediated polymerization of styrene in organic solvents rather well.<sup>[24–28]</sup> The addition of the free nitroxide leads to the formation of a new mediating system that consists of the radicals formed during the thermal initiation and SG-1 as depicted in Scheme 1.

Presumably, the excess SG-1 reacts with the auto-initiated radical centres and, thus, the reaction proceeds like a nitroxide-mediated polymerization. The radical concentration is relatively low in controlled radical polymerization techniques.<sup>[29,30]</sup>

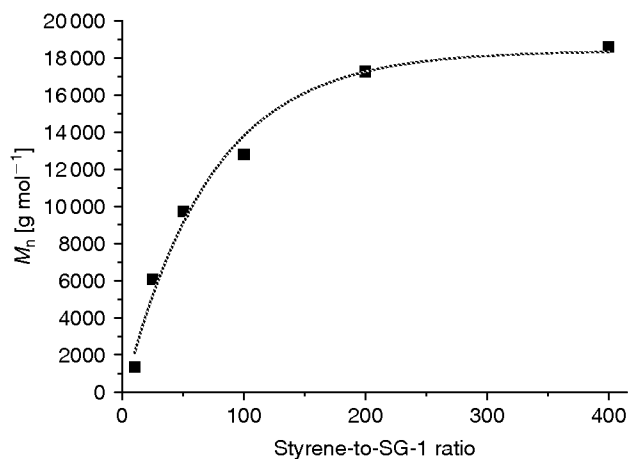
**Table 4.** Data of the thermally initiated polymerization of styrene with different styrene-to-SG-1 ratios and polymerization times at 150°C

Styrene/SG-1	Time [min]	Conversion [%]	$M_n$ [g mol <sup>-1</sup> ]	Polydispersity index
10	60	19	1330	1.32
25	60	53	6090	1.37
25	80	67	5620	1.39
25	100	69	5330	1.40
25	120	67	4850	1.35
50	60	56	9730	1.54
100	60	50	12 800	1.64
200	60	41	17 270	1.66
200	120	52	17 360	1.71
200	180	53	16 500	1.74
200	240	53	15 350	1.83
400	60	33	18 600	1.83

Therefore, the termination reactions are suppressed which leads to controlled molecular weights with low PDIs. The introduction of SG-1 as an end group also improved the precipitation behaviour of the polymer and led to a clear phase separation. Different concentrations of SG-1 were investigated, and varied from 400 to 10 (styrene to SG-1). For all polymerizations with SG-1, an ethanol-to-styrene ratio of 10 to 3 was used, which is equal to a monomer concentration of 2 M. The SEC traces for the polymerizations of styrene are shown in Fig. 4.

In general, the molecular weights shift more gradually with different SG-1 concentrations than with different styrene concentrations in ethanol in the absence of SG-1. In particular for high SG-1 concentrations the changes in molecular weight are more pronounced. The molecular weights, molecular weight distributions, and conversions are summarized in Table 4.

The molecular weights of polystyrene (from 1000 to 19 000 Da) were found to increase with decreasing styrene-to-SG-1 ratios. The PDI values varied between 1.32 and 1.83. In particular, for high SG-1 concentrations, the PDI values are similar to the ones obtained by the alkoxyamine-initiated nitroxide-mediated polymerization (PDI <1.5). For a styrene-to-SG-1 ratio of 25 and 200, different reaction times were tested and in all cases polymers with more or less comparable molecular weights (slight decrease with increasing reaction time) were obtained, which demonstrates that this is not a controlled radical polymerization, but that the relatively narrow molecular weight distributions might be due to precipitation during



**Fig. 5.** Dependency of the  $M_n$  values on the styrene-to-SG-1 ratio of the temperature-initiated polymerization of styrene for 1 h at 150°C. The data was fitted using an exponential curve fitting.

polymerization. Only a slight improvement in conversion was obtained for longer reaction times. In general, the conversions were much higher in comparison to the approach where only ethanol was used. Currently we have no explanation for the improved conversions when SG-1 is added to the polymerization mixture. The  $M_n$  values were plotted against the styrene-to-SG-1 ratios as shown in Fig. 5.

The experimental data were fitted to an exponential growth function (1st order). The plot illustrates the clear dependency of the molecular weight on the SG-1 concentration. In principle, the required SG-1 concentration to obtain polystyrene with a certain molecular weight can be calculated from this equation.

## Conclusions

In order to develop a fast and environmentally friendly approach to polymerize styrene, we combined two polymerization techniques: thermally initiated free radical polymerization and precipitation polymerization. The advantages of both polymerization techniques are the absence of a chemical initiator and the easy purification conditions (polymerization and precipitation in one step). Furthermore, microwave irradiation was used for fast heating and styrene was utilized without further purification to simplify the polymerization conditions.

Initial experiments were carried out using NCW (water in the temperature range of 250 to 350°C) as solvent, because the polarity and hydrogen-bonding of water are highly dependent on the temperature. The polymerization of styrene in NCW always led to polymers with comparable molecular weights, although different styrene concentrations were applied. Thus, we can conclude that styrene and polystyrene are not dissolved in high temperature water. However, moderate molecular weights (~38 000 Da) were obtained within a short time (only 10 min) with moderate yields (~31%).

Due to the insolubility of styrene in water, the solvent was changed to ethanol. In this case styrene was dissolved in the solvent and the polymer was precipitated during the polymerization. The molecular weight could be varied by changing the styrene-to-ethanol concentration. Unfortunately, monomer conversions were very low even after longer reaction times, which might be a result of transfer reactions.

The addition of SG-1 led to a polymerization system with moderate yields in only 1 h of reaction time. The molecular

weight could be varied by the amount of SG-1 and for high concentrations rather narrow PDIs for a free-radical polymerization could be observed. An additional precipitation step was not required.

For the styrene polymerizations in ethanol with and without SG-1, structure–property relationships were elucidated that allow a first prediction of the molecular weight when varying the styrene concentration or SG-1 amount.

## Experimental

### Materials

Styrene (Aldrich), ethanol (Biosolve, Ltd), and *N,N*-tert-butyl-*N*-[1-diethylphosphono-2,2-dimethylpropyl] nitroxide (SG-1 from Arkema) were used without further purification. Distilled water was utilized as solvent for the NCW experiments.

### Instruments

For the NCW experiments the microwave system Synthos 300 (Anton Paar) was used. In this multi-mode microwave system, the microwave power could be set in steps of 1 up to 1400 W. The temperature inside a reference vessel was measured by a gas thermometer and the outside temperature of all the vessels was obtained with an IR sensor at the bottom of the microwave cavity. A safety limit of 300°C was set for the inside and 280°C for the outside temperature. The maximum allowed pressure is 120 bar and the system was operated up to 80 bar.

For all other experiments that utilized ethanol as solvent, the microwave system Emrys Liberator (Biotage) was used. In this single-mode microwave system, a power of either 150 or 300 W can be chosen. The temperature was measured with an IR sensor, located at the side of the microwave cavity. The maximum temperature and pressure were 250°C and 20 bar, respectively.

Gas chromatography (GC) measurements were performed on an Interscience Trace GC instrument with a Trace Column RTX-5 connected to a PAL autosampler. For the injection of polymerization mixtures, a special Interscience liner with additional glass wool was used. SEC was performed on a Shimadzu SEC, equipped with a system controller SCL-10Avp, a LC-10AD pump, a RID-10A refractive index detector, a UV/vis detector DPD-10A, a PSS ETA-2010 differential viscometer, degasser DGU-14A, and a CTO-10A column oven and two PSS GRAM 10  $\mu$ m, 8  $\times$  300 mm, 1000/30 Å columns utilising DMA/LiCl (2.1 g L<sup>-1</sup>) as eluent (flow rate 1 mL min<sup>-1</sup>, column temperature 60°C). Polystyrene standards were used for calibration.

### Polymerization of Styrene

#### In Water

For the polymerization of styrene in pure water, 2 to 8 mL of styrene were added to 20 mL of distilled water in a 60 mL quartz vessel (Synthos 3000). The system was closed and polymerized for 10 min at 150 to 280°C under microwave irradiation. The obtained polymer was filtered off and dried overnight in a vacuum oven at 45°C. The conversions were determined gravimetrically and the molecular weight and molecular weight distributions were measured by SEC.

#### In Ethanol

For the polymerization of styrene in pure ethanol, 0.02 to 0.8 mL of styrene were added to 2 mL of ethanol in a microwave vessel (2 to 5 mL, Emrys Liberator). The system was closed

and purged with argon for 10 min. The reaction mixture was heated for 1 h at 150°C under microwave irradiation. Ethanol was removed from the reaction mixture and the obtained polymer was dried overnight in the vacuum oven at 45°C. The conversions were determined by GC measurements and the molecular weight and molecular weight distributions were measured by SEC.

#### *In Ethanol with SG-1*

For the polymerization of styrene in ethanol with SG-1 a stock solution of 7.33 mL of styrene in 24.67 mL of ethanol was prepared. A volume of 3 mL was transferred to a microwave vessel (2 to 5 mL, Emrys Liberator). To the stock solutions, 5.14 to 178.47 mg of SG-1 were added. The system was closed and purged with argon for 10 min. The reaction mixture was heated for 1 h at 150°C under microwave irradiation. Ethanol was removed from the reaction mixture by simply decanting and the obtained polymer was dried overnight in a vacuum oven at 45°C. The conversions were determined by GC measurements and the molecular weight and molecular weight distributions were measured by SEC.

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