

Optimization of the Nitroxide-Mediated Radical Polymerization Conditions for Styrene and *tert*-Butyl Acrylate in an Automated Parallel Synthesizer

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ABSTRACT: Automated parallel synthesizers provide fast and comparable screening of different polymerization parameters under similar conditions. In addition, these robotic systems eliminate handling errors, which may affect the results of a kinetic experiment more than the effect of an important parameter. The polymerization temperature and *N,N*-*tert*-butyl-*N*-[1'-diethylphosphono-2,2'-dimethylpropyl]nitroxide concentration were optimized for the homopolymerization of both styrene and *tert*-butyl acrylate to improve the control over the polymerization while reasonable polymerization rates were retained. Subsequently, polystyrene and poly(*tert*-butyl acrylate) macroinitiators were synthesized according to the knowledge obtained from the screening results. These macroinitiators were used for the preparation of block copolymers consisting of styrene and *tert*-butyl acrylate. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 6202–6213, 2006

Keywords: automated synthesizer; block copolymers; gel permeation chromatography (GPC); high-throughput experimentation; nitroxide-mediated polymerization; styrene; synthesis; *tert*-butyl acrylate

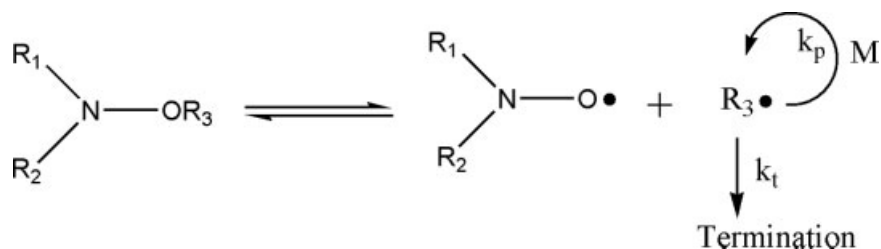
INTRODUCTION

The rapid development of controlled/living radical polymerization (CRP) techniques such as atom transfer radical polymerization (ATRP),^{1,2} nitroxide-mediated radical polymerization (NMP),^{3,4} and reversible addition–fragmentation chain transfer polymerization (RAFT)^{5,6} has allowed the straightforward synthesis of well-defined polymers and copolymers with desired compositions, architectures, and functionalities. All these CRP methods are based on a fast and reversible dy-

namic equilibrium between the dormant species and active species, as shown in Scheme 1 for NMP. The equilibrium constants, which are very low in these systems, keep the concentration of active species very low.⁷ As a result, termination and transfer reactions are minimized, and a CRP can be achieved under the appropriate polymerization conditions. However, this also involves relatively long polymerization times. According to mechanistic features, both NMP and ATRP are controlled by the persistent radical effect,^{8,9} whereas RAFT is based on a chain-transfer mechanism. ATRP and RAFT have some advantages over NMP, including better control for the synthesis of block copolymers and a wider range of monomers. Besides this, the controlling agents, such as metals or dithio compounds, that are used in ATRP and RAFT limit their industrial applica-

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Scheme 1. Schematic presentation of the nitroxide-mediated polymerization process.

tions. In contrast, there is no need to use metal- or sulfur-containing controlling agents for NMP; therefore, NMP has attracted a lot of attention for its environmentally benign radical chemistry.¹⁰

Kinetic investigations of NMP of different kinds of monomers have been reported by various groups.^{11–17} They synthesized libraries of nitroxide compounds to explore their effect on the NMP of styrene or acrylates.¹⁸ Besides this, they used different polymerization temperatures for the polymerization of many kinds of monomers with selected nitroxide compounds.¹⁹ Some research groups have investigated the effect of an excess of free nitroxide on the polymerization kinetics of styrene and acrylates as well.²⁰ However, these studies mainly focused on a few temperatures, and none of them investigated the effect of free nitroxide in a series for the homopolymerization of both styrene and *tert*-butyl acrylate. These separate investigations applying different conditions make a direct comparison very difficult.

In this contribution, our interest is to investigate the effects of both the reaction temperature (90–130 °C) and the amount of free nitroxide (0–10 mol % with respect to the initiator) on the rate of polymerization and on the control over the molecular weight distribution of the NMP of styrene and *tert*-butyl acrylate under very similar conditions. Therefore, we used an automated parallel synthesizer, which is a powerful tool that screens the effects of different parameters on the polymerization by conducting a large number of reactions under the same conditions and minimizing the handling errors. Previous reports have demonstrated that automated synthesizers²¹ provide fast and reliable screening possibilities and are well suited for investigations of various polymerization systems (e.g., ATRP,^{22,23} RAFT,²⁴ NMP,²⁵ anionic polymerization,²⁶ and cationic ring-opening polymerization (CROP²⁷) and a range of important polymerization parameters (temperature, reaction time, pressure, and amounts of ingredients) under similar conditions.

The automated parallel synthetic approach in this study was applied to optimize the NMP of styrene and *tert*-butyl acrylate with respect to the polymerization rate and control over the molecular weight distribution by the use of a Chemspeed SLT106 AcceleratorTM automated parallel synthesizer. The identified optimal temperatures and free nitroxide concentrations were applied for the synthesis of well-defined polymers as macroinitiators and also block copolymers even on larger scales.

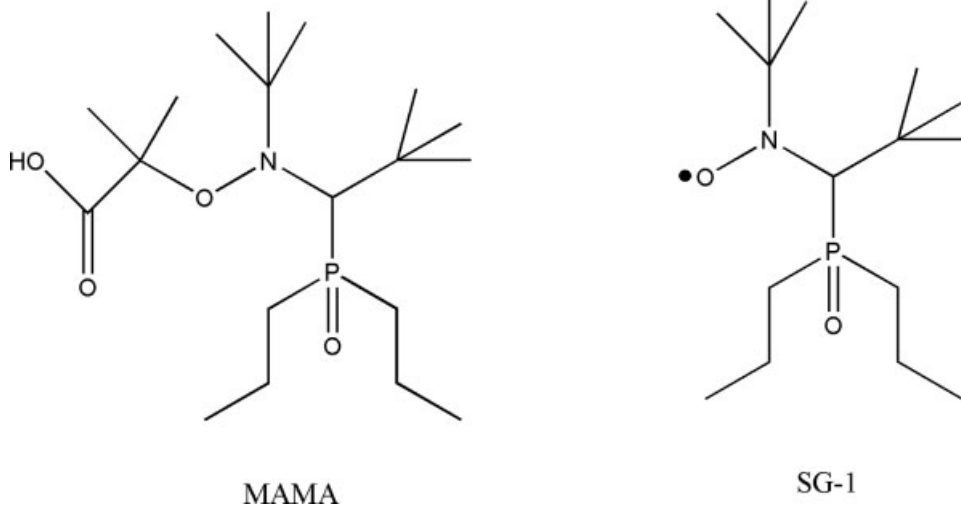
EXPERIMENTAL

Materials

Styrene, *tert*-butyl acrylate, and anisole were bought from Aldrich and purified over a neutral alumina oxide column before use. Chloroform and methanol were obtained from Biosolve, Ltd., and were used without further purification. MAMA, as an *N,N*-*tert*-butyl-*N*-[1'-diethylphosphono-2,2'-dimethylpropyl]nitroxide (SG-1)-based alkoxyamine initiator, and SG-1 as a free nitroxide (Scheme 2) were purchased from Arkema and used as received.

Instruments

The reactions were carried out in a Chemspeed SLT106 AcceleratorTM automated synthesizer. This synthesizer was equipped with a four-needle head, a solid dosing unit, a double-jacket heater reaction block, and an individual heater reactor block. The individually heater reactor block consisted of 16 parallel 13-mL reactors that all had a ceramic heating mantle, which could be individually heated from the ambient temperature to 230 ± 1 °C. The double-jacket heater block was connected to a Huber Unistat Tango (–40 to 145 ± 1 °C) to provide the heating. All reaction vessels were equipped with cold-finger reflux condensers that could be cooled or heated from –5 to 50 °C.



Scheme 2. Schematic presentation of (1) MAMA and (2) SG-1.

An inert atmosphere was maintained by the application of a 1.1-bar argon flow over the reactors and a 1.5-bar argon flow through the hood of the automated synthesizer.

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. Gel permeation chromatography (GPC) was measured on a Shimadzu system equipped with an SCL-10A system controller, an LC-10AD pump, an RID-10A refractive-index detector, and a PLgel 5-mm mixed-D column with a chloroform/triethylamine/isopropyl alcohol (94:4:2) mixture as the eluent at a flow rate of 1 mL/min and a column temperature of 50 °C. The molecular weights were calculated against polystyrene standards (from 3420 Da to 246 kDa).

General Procedure for Parallel Polymerizations

The hood covering the synthesizer was flushed with argon for 60 min. During this time, the stock solutions were bubbled with argon inside the hood. Afterwards, the reaction vessels were heated to 140 °C, and a 50-mbar vacuum was applied for 3 min. Subsequently, the vessels were filled with argon for 2 min. This procedure was repeated five times to obtain an inert atmosphere before the solutions were transferred to the reaction vessels. Determined amounts of liquids from different stock solutions were transferred to the

vessels with the liquid handling system. The total volume of each reaction was 4 mL with a monomer concentration of 2 M. The reaction vessels were vortexed for 10 min at 20 °C before zero-time samples were withdrawn. Sampling was performed with the four-needle head, which provided the possibility of transferring four samples from four different reaction vessels at the same time. Samples with a volume of 150 μ L were transferred to 2-mL vials, and afterwards, 1.5 mL of a chloroform/triethylamine/isopropyl alcohol (94:4:2) mixture was added to prepare samples that were ready to be analyzed by GC and GPC. After the first sampling step, the reaction vessels were heated to the desired temperatures, and samples were transferred at different times during the polymerization. After the reactions were completed, the reactors were cooled to 20 °C, and 2 mL of chloroform was added to each reactor. The reactors were vortexed for 15 min, and the aliquots were transferred to 8-mL vials.

Typical Procedure for the Optimization of the Polymerization Temperature

Two different stock solutions were prepared for styrene and *tert*-butyl acrylate. The stock solution for the polymerization of styrene was prepared by the addition of styrene (7.33 mL, 64.0 mmol), MAMA (244.0 mg, 0.64 mmol), and anisole (24.66 mL) together. The structures of the alkoxyamine initiator and free-nitroxide compound (SG-1) used in this study are depicted in Scheme 2. The volume of 4 mL was transferred from the stock solution to

seven reaction vessels to investigate the effect of temperature. The reaction vessels were heated to different temperatures (90, 100, 110, 115, 120, 125, and 130 °C) during the polymerization of styrene. The second stock solution was prepared by the addition of *tert*-butyl acrylate (5.81 mL, 40 mmol), MAMA (153.0 mg, 0.4 mmol), and anisole (14.19 mL) together. The volume of 4 mL was transferred from the second stock solution to four reaction vessels. These reaction vessels were heated to 90, 100, 120, and 130 °C during the polymerization of *tert*-butyl acrylate. The reaction vessels were vortexed for 10 min at 20 °C after the liquid transfers from stock solutions to vessels were complete. The first samples of the reactions (150 μ L) were transferred to 2-mL vials, and 1.5 mL of the chloroform mixture was added to each of them. After this first sampling, the reactors were heated to the desired temperatures. The reaction vessels were continuously vortexed at 600 rpm during the polymerization, with the reflux condensers set to -5 °C. During this time, samples were placed automatically in 2-mL vials at different times. All vials were characterized by GC and GPC after all the polymerizations were completed.

Typical Procedure for the Optimization of the Free Nitroxide Concentration

Five different stock solutions were prepared to investigate the effect of the free nitroxide concentration for styrene and *tert*-butyl acrylate. The first three stock solution vials contained anisole (8.48 mL), styrene (7.33 mL, 64.0 mmol), or *tert*-butyl acrylate (9.29 mL, 64.0 mmol). MAMA (512.6 mg, 1.28 mmol) and SG-1 (17.8 mg, 0.06 mmol) were dissolved or diluted in anisole (20 mL and 14 mL) for the preparation of the fourth and fifth stock solutions, respectively. Styrene or *tert*-butyl acrylate, MAMA, SG-1, and anisole were added to the vessels with different SG-1 ratios (1, 2, 4, 5, 6, 8, and 10 mol % of the initiator). The reaction vessels were vortexed for 10 min at 20 °C after liquid transfers from stock solutions to vessels were completed. The first samples of the reactions (150 μ L) were transferred to 2-mL vials, and 1.5 mL of a chloroform mixture was added. Subsequently, the reaction vessels were heated to 110 °C for the polymerization of both monomers. The reaction vessels were continuously vortexed at 600 rpm during polymerization, with the reflux condensers set to -5 °C. The samples were placed automatically in 2-mL

vials at different times. Subsequently, all samples were characterized by GC and GPC measurements.

Typical Procedure for the Synthesis of the Macroinitiators

Polystyrene macroinitiators with 50, 78, and 120 repeating units were synthesized on large scales according to the results obtained from the optimization reactions. Schlenk tubes were charged with styrene (15.0 mL, 131.0 mmol), anisole (3 mL), and different amounts of MAMA (0.996 g, 2.61 mmol; 0.600 g, 1.57 mmol; and 0.500 g, 1.31 mmol) weighed in flasks. The resulting mixtures were bubbled with argon for 30 min and placed into an oil bath at 120 °C. The reactions were stopped after 5.5, 6, and 6.5 h, and the formed polymers were precipitated into methanol after cooling to room temperature. A fine, white powder was obtained after drying in the vacuum oven (40 °C) overnight. The conversions were determined gravimetrically, and the number-average molecular weights were measured by GPC. The gravimetric yields were 70, 67, and 70% with number-average molecular weights of 5200, 8200, and 12,500 g/mol and polydispersity indices (polydispersity indices) of 1.08, 1.13, and 1.11 for polystyrene macroinitiators with repeating units of 50, 78, and 120, respectively.

A poly(*tert*-butyl acrylate) macroinitiator with 65 repeating units was synthesized on a large scale by the addition of *tert*-butyl acrylate (10 mL, 68.9 mmol), SG-1 (0.012 g, 0.041 mmol), MAMA (0.263 g, 0.689 mmol), and anisole (10 mL). The polymerization mixture was bubbled with argon for 30 min and immersed into an oil bath at 110 °C. After 12 h of polymerization, the mixture was precipitated into a water/methanol (50:50) mixture to remove the residual monomer. The precipitate was dried in a vacuum oven at 40 °C overnight. The gravimetric yield was calculated to be 50%, and the number-average molecular weight was found to be 8300 g/mol with a polydispersity index of 1.25 by GPC measurements.

Typical Procedure for the Synthesis of Polystyrene-*b*-(*tert*-butyl acrylate) and Poly(*tert*-butyl acrylate)-*b*-(styrene) Block Copolymers

A set of experiments was performed with a automated parallel synthesizer to investigate the kinetics of polystyrene-*b*-(*tert*-butyl acrylate) block copolymerizations initiated with different polysty-

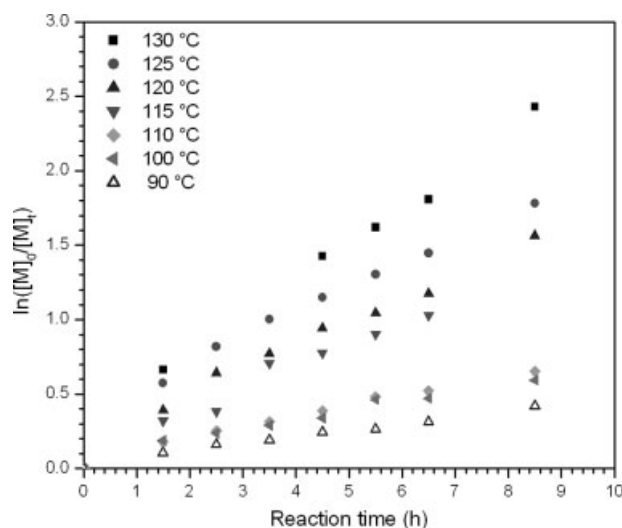


Figure 1. $\ln([M]_0/[M])$ versus time for the polymerization of styrene in anisole at different temperatures ($[\text{Styrene}] = 2 \text{ M}$, $[\text{MAMA}] = 0.02 \text{ M}$).

rene macroinitiators. Three different polystyrene macroinitiators with repeating units of 50, 78, and 120 were dissolved in anisole. In addition, *tert*-butyl acrylate and an SG-1 stock solution in anisole were prepared, and all solutions were bubbled with argon for 60 min. Three different molar ratios of *tert*-butyl acrylate to macroinitiators were added to vessels: 50:1, 100:1, and 150:1. Additionally, 6% SG-1 with respect to the initiator was added to all vessels to improve the control over the *tert*-butyl acrylate polymerization. The reactions were carried out at 110 °C for 20 h, and samples were taken at different times.

A poly(*tert*-butyl acrylate)-*b*-(styrene) block copolymerization was also investigated in the automated synthesizer. A stock solution consisting of poly(*tert*-butyl acrylate) as a macroinitiator, styrene, and anisole was prepared and bubbled with argon for 60 min. The polymerization was conducted at 110 °C for 35 h, and samples were withdrawn at different times. The monomer conversions and number-average molecular weights for all samples were determined by GC and GPC.

RESULTS AND DISCUSSION

The objective of this investigation was the optimization of the reaction temperature and the amount of free nitroxide for the NMP of styrene and *tert*-butyl acrylate to obtain the desired molecular weights and at the same time achieve reasonable rates of polymerization. Moreover,

the optimized polymerization conditions should lead to the synthesis of homopolymers or block copolymers with narrow molecular weight distributions.

Automated parallel synthesizers are powerful tools that screen the effects of different parameters on polymerizations by conducting many reactions under identical conditions and minimizing the handling errors. Previously, controlled and living radical polymerization systems (ATRP, RAFT, NMP, cationic polymerization, and anionic polymerization) as well as emulsion polymerizations were conducted successfully by the use of automated parallel synthesizers.^{25,28–31} In this study, an automated parallel synthesizer platform was used extensively to investigate the NMP conditions.

NMP with various nitroxide compounds has been investigated in detail by different research groups.^{11–17,32–34} Fischer et al.³³ reported that derivatives of β -phosphonylated nitroxide compounds allowed them to perform polymerizations at higher rates than those that could be achieved with 2,2,6,6-tetramethylpiperidinyl-1-oxy derivatives by their high activation rates at low temperatures. Besides this, the alkoxyamine initiator used in this study bears a carboxylic acid functionality. This functionality can be used for postpolymerization modifications, whereas the nitroxide compound still provides the living feature on the other end of the polymer chain.

The optimization reactions were conducted in solution to prevent a high viscosity that would reduce the efficiency of automated sampling. Ani-

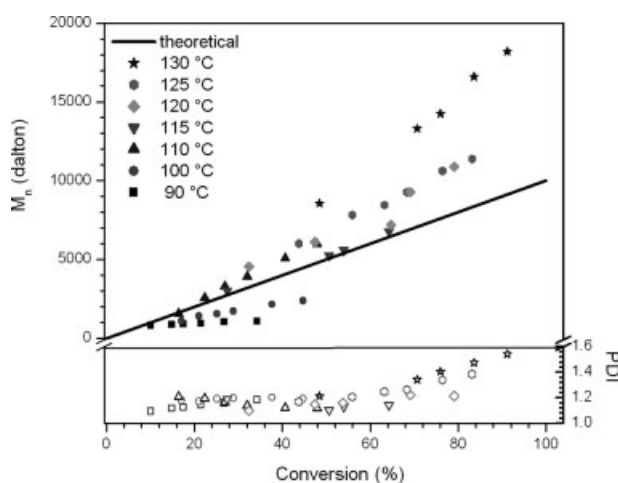


Figure 2. Number-average molecular weight (M_n) and polydispersity index (PDI) versus the conversion for the polymerization of styrene in anisole at different temperatures ($[\text{Styrene}] = 2 \text{ M}$, $[\text{MAMA}] = 0.02 \text{ M}$).

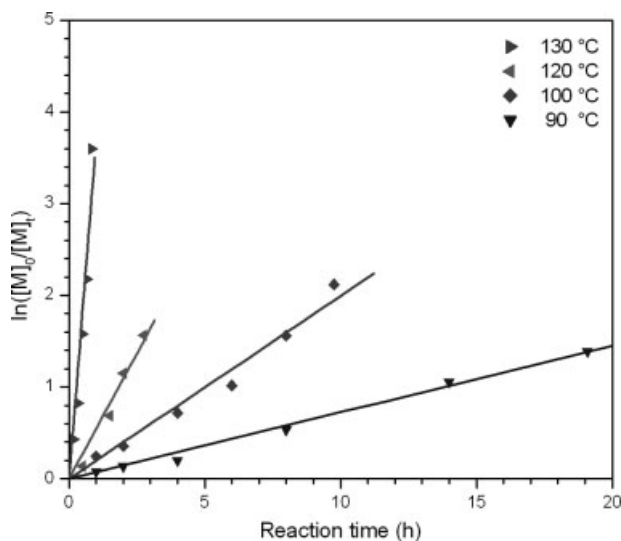


Figure 3. $\ln([M]_0/[M])$ versus time for the polymerization of *tert*-butyl acrylate in anisole at different temperatures ($[tert\text{-Butyl acrylate}] = 2 \text{ M}$, $[MAMA] = 0.02 \text{ M}$).

sole was used as a solvent because it has a high boiling point (154 °C) in comparison with toluene (111 °C). This enabled us to perform the polymerizations at higher temperatures. As a first step, the optimization of the reaction temperature for the NMP of styrene in anisole was performed to determine the most efficient polymerization temperature. A stock solution was prepared with a monomer concentration of 2 M in anisole and a monomer-to-initiator ratio of 100. Then, 4 mL of this stock solution was transferred to seven dif-

ferent reactors. The individual ceramic heating mantles of the vessels were set to 90, 100, 110, 115, 120, 125, and 130 °C, and samples were taken at different times. All samples were characterized with GC and GPC to determine the conversion of the monomer, molecular weight, and molecular weight distribution, respectively. As shown in Figure 1, higher polymerization rates were achieved for styrene with the elevated reaction temperatures, as expected. The semilogarithmic first-order kinetic plots for the polymerizations of styrene at different reaction temperatures revealed linear first-order behavior for all polymerization temperatures. A large increase in the rate of polymerization was observed for styrene between 110 and 115 °C. The reason for this may be the autoinitiation of styrene, which is becoming more evident at elevated temperatures. The molecular weights were generally close to the theoretical line with polydispersity indices below 1.3 at moderate reaction temperatures. The experimental molecular weights that were lower than the theoretical values for the polymerizations at 90 and 100 °C were most likely due to a slower initial polymerization rate that resulted in a broader molecular weight distribution and thus also resulted in lower molecular weights. It is obvious that increasing the reaction temperature will increase the rate of polymerization. However, this increase in the rate of polymerization should be provided without a loss of control over the polymerization. Figure 2 shows that in the case of a polymerization temperature

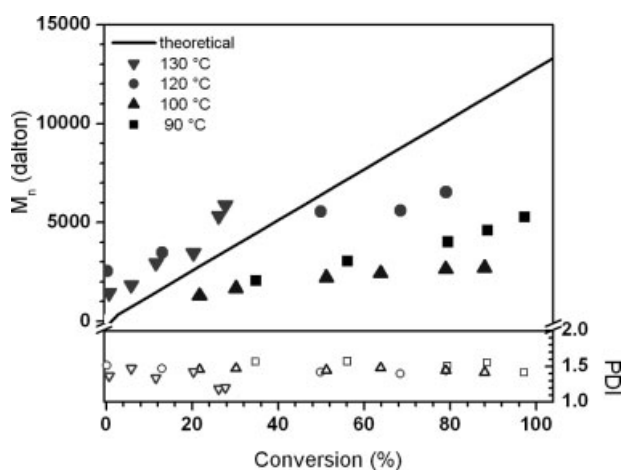


Figure 4. Number-average molecular weight (M_n) and polydispersity index (PDI) versus the conversion for the polymerization of *tert*-butyl acrylate in anisole at different temperatures ($[tert\text{-Butyl acrylate}] = 2 \text{ M}$, $[MAMA] = 0.02 \text{ M}$).

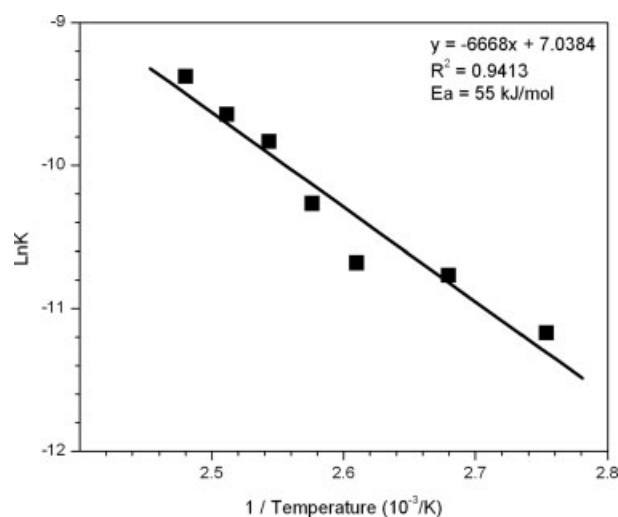


Figure 5. $\ln K$ versus the reciprocal of the temperature ($1/T$) for the NMP of styrene (Arrhenius plot; E_a = activation energy).

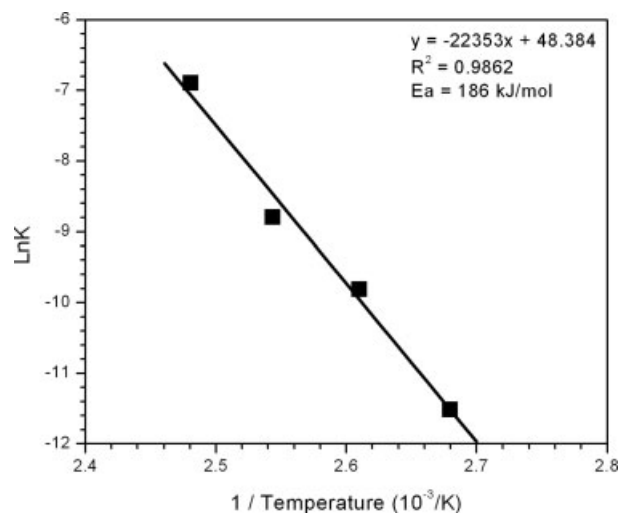


Figure 6. $\ln K$ versus the reciprocal of the temperature ($1/T$) for the NMP of *tert*-butyl acrylate (Arrhenius plot; E_a = activation energy).

of 130 °C, the molecular weights were above the theoretical line, and the polydispersity indices were above 1.4. This deviation from the theoretical line shows a loss of control over the polymerization of styrene initiated by MAMA at 130 °C. This loss of control is most likely due to a combination of increased termination reactions and autoinitiation of styrene.

A second set of reactions was conducted to optimize the polymerization temperature of *tert*-butyl acrylate at 2 M in anisole with a monomer-to-initiator ratio of 100. Four different reaction

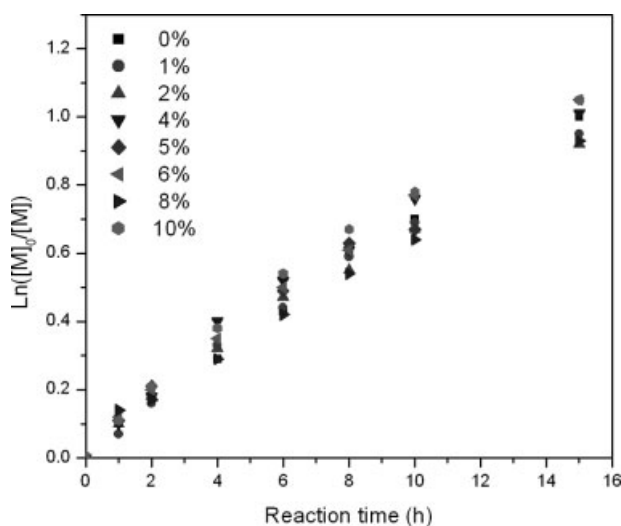


Figure 7. $\ln([M]_0/[M])$ versus time for the polymerization of styrene in anisole at different free nitroxide concentrations ($[Styrene] = 2\text{ M}$, $[MAMA] = 0.02\text{ M}$).

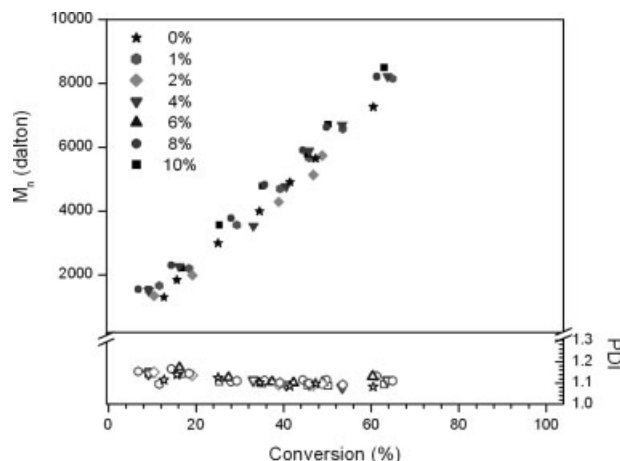


Figure 8. Number-average molecular weight (M_n) and polydispersity index (PDI) versus the conversion for the polymerization of styrene in anisole at various free nitroxide ratios ($[Styrene] = 2\text{ M}$, $[MAMA] = 0.02\text{ M}$).

temperatures (90, 100, 120, and 130 °C) were examined as described previously. The kinetic data for the homopolymerization of *tert*-butyl acrylate are shown as a $\ln([M]_0/[M])$ –time plot in Figure 3 (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration). Faster polymerization rates were observed for the polymerization of *tert*-butyl acrylate at elevated temperatures. Similarly to the homopolymerization of styrene, the values for *tert*-butyl acrylate exhibited linear first-order behavior for all investigated temperatures. To calculate the

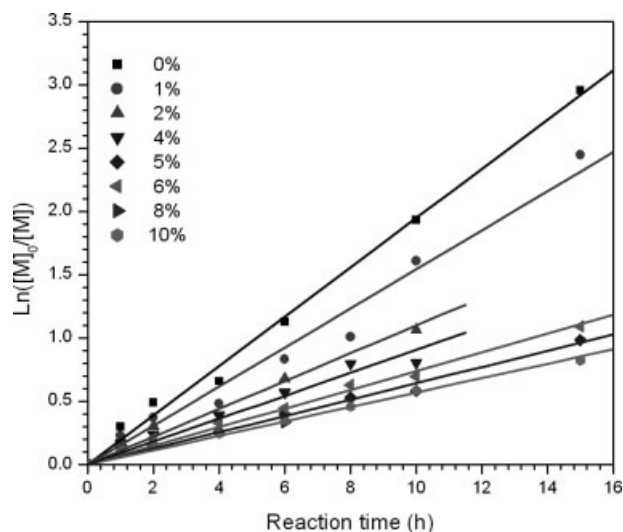


Figure 9. $\ln([M]_0/[M])$ versus time for the polymerization of *tert*-butyl acrylate in anisole at different free nitroxide concentrations ($[Styrene] = 2\text{ M}$, $[MAMA] = 0.02\text{ M}$).

Table 1. Polymerization of *tert*-Butyl Acrylate in Anisole at Different Ratios of Free Nitroxide^a

| Run | Initiator/SG-1 | Time (h) | Conversion (%) | $M_{n,theo}$ (g/mol) | $M_{n,GPC}$ (g/mol) | PDI (M_w/M_n) | k_{app} ($10^{-5} s^{-1}$) |
|-----|----------------|----------|----------------|----------------------|---------------------|-------------------|--------------------------------|
| 1 | 1:0.00 | 15 | 95 | 12,200 | 7,800 | 1.53 | 5.41 |
| 2 | 1:0.01 | 15 | 91 | 11,700 | 7,200 | 1.59 | 4.28 |
| 3 | 1:0.02 | 10 | 65 | 8,300 | 7,600 | 1.39 | 3.05 |
| 4 | 1:0.04 | 10 | 55 | 7,100 | 7,600 | 1.35 | 2.51 |
| 5 | 1:0.05 | 15 | 63 | 8,100 | 7,200 | 1.30 | 1.78 |
| 6 | 1:0.06 | 15 | 66 | 8,500 | 7,300 | 1.31 | 2.05 |
| 7 | 1:0.08 | 6 | 28 | 3,600 | 6,500 | 1.24 | 1.65 |
| 8 | 1:0.10 | 15 | 56 | 7,200 | 6,700 | 1.24 | 1.58 |

^a k_{app} = apparent propagation rate; M_n = number-average molecular weight; $M_{n,GPC}$ = GPC-determined number-average molecular weight; $M_{n,theo}$ = theoretical number-average molecular weight; M_w = weight-average molecular weight; PDI = polydispersity index.

number-average molecular weights of poly(*tert*-butyl acrylate), polystyrene standards for the GPC calibration were preferred to poly(methyl methacrylate) standards on the basis of previous findings.³⁵ Nevertheless, the calculated molecular weights were not close to the theoretical line, and this was an indication of chain-transfer reactions. In this case, hydrogen abstraction from the end of the polymer chain might be the favored chain-transfer reaction, resulting in a loss of control over the polydispersity index, as depicted in Figure 4.

On the basis of the temperature optimization, Arrhenius plots were drawn for the NMP of styrene and *tert*-butyl acrylate to calculate the activation energies, which are shown in Figures 5 and 6, respectively. The apparent propagation rates were calculated from the slopes of plots of $\ln([M]_0/[M]_t)$ versus time (s^{-1}). It was assumed that the ratio of dormant and active species, that is, the concentration of propagating species, was constant at all temperatures. The apparent propagation rate at 120 °C was 0.54×10^{-4} for the NMP of styrene and 1.52×10^{-4} for the NMP of *tert*-butyl acrylate. The activation energies for the NMP of styrene and *tert*-butyl acrylate were 55 and 186 kJ/mol with regression coefficients of 0.9667 and 0.9862, respectively. Gnanou et al.³⁶ reported the activation energies for the bulk polymerization of styrene and *tert*-butyl acrylate with macroinitiators, that is, polystyrene₃₅/SG-1 and poly(*tert*-butyl acrylate)₃₅/SG-1, as 121 and 130 kJ/mol, respectively.³⁶ Although it is obvious that the activation energy values reported by Gnanou et al. are different from the ones reported here, we do not know the exact reason for this discrepancy. A possible explanation for this observation might be the use of

different polymerization media, namely, bulk versus anisole.

In the next step, the effect of the free nitroxide concentration on the polymerization of styrene in anisole was investigated at 110 °C. It was reported by Studer et al.³⁷ that the conversion of the monomer is independent of the alkoxyamine concentration for the NMP bulk polymerization of styrene. In contrast, Yin et al.³⁸ reported that the addition of free nitroxide to the bulk polymerization medium of styrene improves the control over the molecular weight distribution, by which lower polymerization rates were observed. Therefore, we investigated the effect of free nitroxide on the NMP of both styrene and *tert*-butyl acrylate in anisole. Eight different ratios of free nitro-

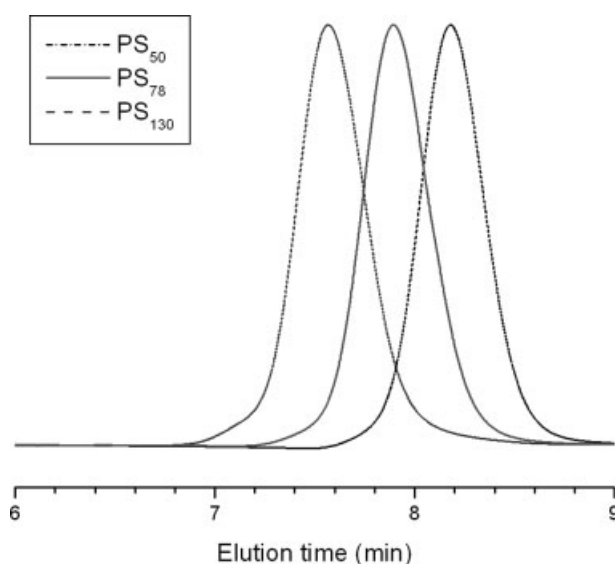
**Figure 10.** GPC traces of the polystyrene macroinitiators.

Table 2. Polymerization of Polystyrene and Poly(*tert*-butyl acrylate) Macroinitiators Initiated by MAMA in Anisole^a

| Run | Monomer | Monomer/ Initiator | Additive (SG-1) | Time (h) | Conversion (%) | $M_{n,theo}$ (g/mol) | $M_{n,GPC}$ (g/mol) | PDI (M_w/M_n) |
|-----|-----------------------------|-----------------------|--------------------|-------------|-------------------|-------------------------|------------------------|----------------------|
| 1 | Styrene | 100:1 | — | 5.5 | 70 | 7,300 | 5,200 | 1.08 |
| 2 | Styrene | 120:1 | — | 6 | 67 | 8,400 | 8,200 | 1.13 |
| 3 | Styrene | 200:1 | — | 6.5 | 70 | 14,600 | 12,500 | 1.11 |
| 4 | <i>tert</i> -Butyl acrylate | 200:1 | 0.06 | 12 | 50 | 12,800 | 8,300 | 1.25 |

^a M_n = number-average molecular weight; $M_{n,GPC}$ = GPC-determined number-average molecular weight; $M_{n,theo}$ = theoretical number-average molecular weight; M_w = weight-average molecular weight; PDI = polydispersity index.

xide (SG-1), from 0 to 10 mol % (with respect to the amount of the initiator), were used for both monomers. As shown in Figure 7, no significant effect of the addition of free nitroxide was observed on the rate of polymerization of styrene. In addition, there was no difference detected between the number-average molecular weights of the samples, which exhibited a linear increase with increasing conversion, as shown in Figure 8.

However, in the case of the nitroxide mediated *tert*-butyl acrylate polymerization in anisole, a significant decrease in the polymerization rate was observed, and the control over the molecular weight distribution of poly(*tert*-butyl acrylate) was improved by the introduction of slight excess of free nitroxide. The semilogarithmic kinetic plot of the NMP of *tert*-butyl acrylate with different amounts of free nitroxide is shown in Figure 9. The molecular weights and polydispersity indices of end samples are summarized in Table 1. It can be concluded that the addition of a 5–6% excess of free nitroxide (with respect to the amount of the alkoxyamine initiator) to the polymerization medium of *tert*-butyl acrylate improves the control over the molecular weight distribution with reasonable polymerization times.

After the optimization of the reaction temperature and the amount of free nitroxide for the NMP of styrene and *tert*-butyl acrylate, polystyrene macroinitiators with three different repeating units and a poly(*tert*-butyl acrylate) macroinitiator were synthesized according to the insights into the polymerization kinetics that were obtained from parallel screening experiments. Polystyrene macroinitiators with narrow molecular weight distributions as low as 1.08 were synthesized in anisole at 110 °C without any additional free nitroxide. These macroinitiators were intended for further use in the synthesis of polystyrene-*b*-(*tert*-butyl acrylate) block copolymers. Subsequently, the macroinitiators were characterized

by GPC, and the traces are shown in Figure 10. In addition, a poly(*tert*-butyl acrylate) macroinitiator with 65 repeating units was synthesized in anisole with additional SG-1 (6%) at 110 °C and a reaction time of 12 h. The synthesis of these macroinitiators is described in further detail in the Experimental section, and the results are summarized in Table 2.

Moreover, polystyrene-*b*-(*tert*-butyl acrylate) block copolymers were synthesized in the automated synthesizer with different polystyrene macroinitiators and characterized by GC and GPC. An excess of SG-1 (6%) was added, and the reactions were carried out at 110 °C for 20 h; samples were taken at different times. The kinetic data for the block copolymerization are illustrated in Figure 11 as a semilogarithmic kinetic plot. The conversion of *tert*-butyl acrylate was limited when the polymerization was initiated with the polystyrene macroinitiator. A possi-

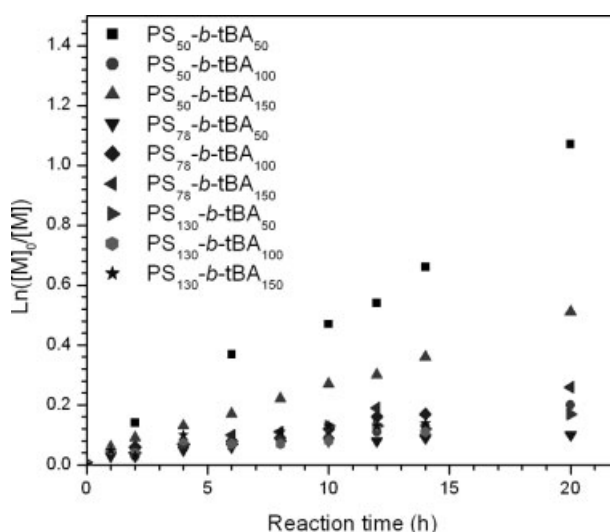
**Figure 11.** $\ln([M]_0/[M])$ versus time for the block copolymerization of *tert*-butyl acrylate in anisole initiated with polystyrene macroinitiators.

Table 3. Block Copolymerization of Polystyrene-*b*-(*tert*-butyl acrylate) at Different Macroinitiator-to-Monomer Ratios^a

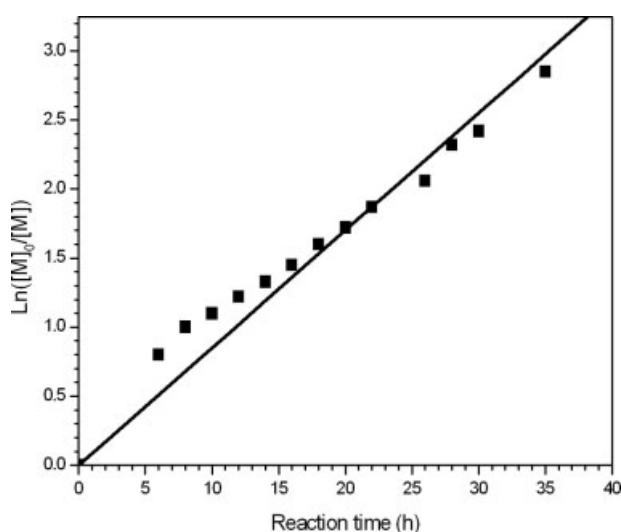
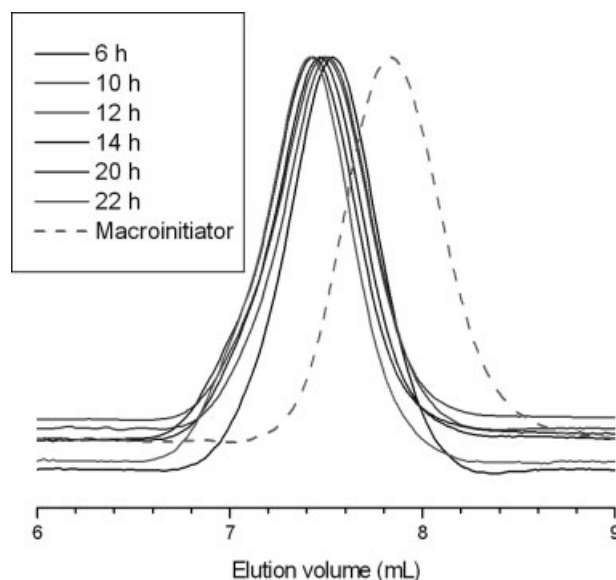
| Run | PS _n (n) | Initiator/ <i>tert</i> -Butyl Acrylate | Time (h) | Conversion (%) | $M_{n,theo}$ (g/mol) | $M_{n,GPC}$ (g/mol) | PDI (M_w/M_n) |
|-----|---------------------|--|----------|----------------|----------------------|---------------------|-------------------|
| 1 | 50 | 1:50 | 20 | 65 | 13,600 | 6,700 | 1.17 |
| 2 | 50 | 1:100 | 20 | 18 | 7,500 | 6,600 | 1.12 |
| 3 | 50 | 1:150 | 20 | 40 | 10,300 | 14,800 | 1.33 |
| 4 | 78 | 1:50 | 20 | 10 | 9,400 | 8,900 | 1.10 |
| 5 | 78 | 1:100 | 14 | 15 | 10,200 | 9,900 | 1.09 |
| 6 | 78 | 1:150 | 20 | 23 | 11,100 | 11,100 | 1.15 |
| 7 | 120 | 1:50 | 14 | 11 | 14,800 | 14,800 | 1.13 |
| 8 | 120 | 1:100 | 14 | 10 | 14,100 | 15,600 | 1.10 |
| 9 | 120 | 1:150 | 14 | 13 | 14,500 | 17,300 | 1.11 |

^a M_n = number-average molecular weight; $M_{n,GPC}$ = GPC-determined number-average molecular weight; $M_{n,theo}$ = theoretical number-average molecular weight; M_w = weight-average molecular weight; PDI = polydispersity index; PS_n (n) = degree of polymerization of the PS macroinitiator.

ble reason for this limitation may be hydrogen abstraction of the free nitroxide and subsequent coupling reactions. Nevertheless, polystyrene-*b*-(*tert*-butyl acrylate) block copolymers could be obtained with narrow molecular weight distributions. The data obtained from this screening are summarized in Table 3.

The poly(*tert*-butyl acrylate)-initiated block copolymerization of styrene was also investigated to synthesize block copolymers with lower polydispersity indices at higher monomer conversions. The reactions were carried out at a monomer concentration of 2 M and with 6% excess SG-1 at 110 °C for 35 h. The poly(*tert*-butyl acrylate) macroinitiator exhibited good initiation and

revealed a controlled polymerization of the second block, as shown in Figure 12. The poly(*tert*-butyl acrylate)-*b*-(styrene) block copolymers were synthesized with low polydispersity indices and good control over the polymerization. The experimental and theoretical molecular weights, polydispersity index, and conversion values were as follows: the GPC-determined number-average molecular weight was 18,600 g/mol, the theoretical number-average molecular weight was 17,100 g/mol, the polydispersity index was 1.20, and the conversion was 84%. GPC traces of the block copolymers at different polymerization times are shown in Figure 13.

**Figure 12.** $\ln([M]_0/[M])$ versus time for the block copolymerization of styrene in anisole initiated with poly(*tert*-butyl acrylate) macroinitiators.**Figure 13.** GPC traces of poly(*tert*-butyl acrylate)-*b*-(styrene) block copolymers at different reaction times.

CONCLUSIONS

The systematic kinetic screening of two important parameters for the NMP of styrene and *tert*-butyl acrylate, the polymerization temperature and the concentration of free nitroxide, was investigated with an automated parallel synthesizer platform. The Chemspeed AcceleratorTM provided fast, reliable, and comparable results for the optimization of the NMP conditions.

The polymerization temperature has the greatest effect on the rate of polymerization. Therefore, the optimization of the polymerization temperature of styrene and *tert*-butyl acrylate was conducted at seven and four different temperatures, respectively. Control over the polydispersity index was lost when the polymerization temperature was increased above 120 °C for the polymerization of both monomers. The optimum polymerization temperatures for the NMP of styrene and *tert*-butyl acrylate were determined to be 120 and 115 °C, respectively.

Moreover, the effect of introducing a slight excess of free nitroxide was investigated. For the case of styrene polymerization, no significant influence was observed on the polymerization rates and even on the molecular weight distributions. However, the polymerization rate of *tert*-butyl acrylate was reduced by the introduction of a slight excess of free nitroxide to the polymerization medium. It can be concluded that the addition of 5–6% free nitroxide with respect to the initiator improved the control over the polydispersity indices of the final polymers with reasonable reaction periods. According to the knowledge obtained from the optimization reactions, polystyrene and poly(*tert*-butyl acrylate) macroinitiators were synthesized with different chain lengths and narrow molecular weight distributions. Finally, polystyrene-*b*-(*tert*-butyl acrylate) and poly(*tert*-butyl acrylate)-*b*-(styrene) block copolymers were synthesized with narrow molecular weight distributions (polydispersity index < 1.2) in the automated synthesizer and also characterized by GC and GPC to determine the monomer conversions and molecular weights. In conclusion, the synthesis of block copolymers consisting of styrene and *tert*-butyl acrylate repeating units is more efficient and well controlled with poly(*tert*-butyl acrylate) macroinitiators in comparison with polystyrene macroinitiators.

These results demonstrate the possibility of a fast screening of important parameters in an automated synthesizer for NMP. The results will be

used in future work for the preparation of libraries of well-defined AB and ABC block copolymers with different monomer ratios. Moreover, micelle formation and pigment stabilization are possible applications following the hydrolysis of the *tert*-butyl acrylate block of the copolymers.

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