

High conversion study of “living” radical polymerization of styrene using DSC

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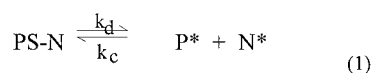
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SUMMARY: The influence of temperature on nitroxide-controlled living radical polymerization of styrene was examined. It has been established that only in a temperature range of 110 °C to 150 °C nitroxides are able to control radical polymerization. At temperatures above 160 °C the reaction was of rather a free radical character. The results were similar for all the various nitroxides used as capping agents: TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl), 4-hydroxy-TEMPO, 4-oxo-TEMPO and 4-acetamido-TEMPO. Differences were found only in the induction times of polymerization and were probably due to side reactions with the initiator (benzoyl peroxide). Living radical polymerization can be best controlled with these nitroxides at temperatures between 120 °C and 140 °C.

ZUSAMMENFASSUNG: Der Temperatureinfluß auf die N-Oxyl-kontrollierte radikalische Polymerisation von Styrol wurde untersucht. Nur in einem Temperaturbereich von 110 °C bis 150 °C sind N-Oxyle in der Lage, die radikalische Polymerisation zu kontrollieren. Bei Temperaturen ≥ 160 °C geht die Reaktion mehr und mehr in eine normale radikalische Polymerisation über. Es wurden 2,2,6,6-Tetramethylpiperidin-N-oxyl (TEMPO), 4-Hydroxy-TEMPO, 4-Oxo-TEMPO und 4-Acetamido-TEMPO untersucht. Unterschiede wurden nur in den Induktionszeiten und auch nur bei Reaktionen mit Radikalstarter (Benzoylperoxid) gefunden. Die beste Kontrolle der radikalischen Polymerisation findet zwischen 120 °C und 140 °C statt.

Introduction

The current techniques of applying stable nitroxyl radicals (N*) to control free-radical polymerization can be regarded as an ideal synthetic route to produce polymers with a well-defined, narrow polydispersity index. It combines the simplicity of the technically important radical polymerization with some advantages of the living polymerization. In recent years, great interest has been devoted to this “living” radical polymerization. The key step in keeping the radical polymerization in the living state is the reversible cleavage of the polystyrene-nitroxyl adduct (PS-N) as shown in Eq. (1).



$$K = \frac{k_d}{k_c} \quad (2)$$

The equilibrium between the dormant (PS-N) and growing species, P*, is described by the equilibrium constant K which is around $10^{-11} \text{ mol L}^{-1}$. The rate of propagation of styrene is independent of the adduct concentration but closely dependent on the thermal initiation, which is necessary to compensate for the radical loss during polymerization².

Experimental studies of high conversion and high temperature reactions are not common. This paper deals with

DSC studies of living radical polymerization of styrene at different temperatures. The DSC is used simultaneously as thermoanalytical instrument and as “reactor” allowing for the simple investigation of polymerization at high temperatures and with high conversion.

Experimental

Materials

Styrene (Aldrich) was distilled under reduced pressure. Benzoyl peroxide (BPO, Merck) was purified by recrystallization from chloroform/methanol. 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO, Fluka), 4-hydroxy-TEMPO (OH-TEMPO, Aldrich), 4-oxo-TEMPO (Hüls) and 4-acetamido-TEMPO (Hüls) were used without further purification. Molecular weight distributions and molecular weights were estimated by gel permeation chromatography (GPC) using Waters 150CV GPC/viscosimeter equipped with Styragel HT3, HT4, HT5 columns. The GPC measurements were performed with tetrahydrofuran as eluent; polystyrene standards were used for calibration.

The PS-N-oxyl adducts (macroinitiator) were synthesized in batch-reactors as described in³; PS-TEMPO: $M_n = 5400 \text{ g mol}^{-1}$, polydispersity $P_d = 1.19$; PS-4-oxo-TEMPO: $M_n = 4200 \text{ g mol}^{-1}$, $P_d = 1.28$; PS-4-acetamido-TEMPO: $M_n = 7800$, $P_d = 1.33$.

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Differential scanning calorimetry

The bulk isothermal polymerizations were investigated in steel-pans (120 μL) using a DSC 25 (Mettler-Toledo Star). Samples of 50 μL solution were placed into the DSC at 50 $^{\circ}\text{C}$ and heated up quickly to the desired temperature.

The polymerization samples with BPO and nitroxides were stored at 95 $^{\circ}\text{C}$ for 1 h before being heated to the desired reaction temperature. All reactions were performed until conversion was complete.

Results and discussion

In order to understand the temperature dependence of nitroxide-controlled polymerization, three kinds of systems were examined:

- bulk polymerization of styrene with BPO as radical initiator and N^* ($\text{BPO}/\text{N}^* = 1/1.3$);
- bulk autopolymerization of styrene with 3 mmol L^{-1} N^* ;
- bulk polymerization of styrene with 3 mmol L^{-1} PS-N.

Induction period

To ensure that all the radical initiator was consumed before the “living” polymerization began, a pre-polymerization step was performed. After heating the monomers to the reaction temperature, the system shows an induction period where no polymerization takes place. During this period the initial excess of N^* is reduced by thermal initiation of styrene.

Controlled radical polymerization performed with BPO and nitroxyl radicals (N^*) shows an induction period which is strongly dependent on temperature and nitroxide concentration. Fig. 1 shows the differences between the used nitroxides.

4-Oxo-TEMPO has nearly no induction time in contrast with other nitroxides. For a clearer understanding, experiments were carried out without radical initiator BPO (styrene with 3 mmol L^{-1} N^*). This nitroxide-controlled autopolymerization reveals no differences between the nitroxyl radicals, indicating that any variations in induction time originate from side reactions of 4-oxo-TEMPO with BPO or independent decomposition reactions of 4-oxo-TEMPO (Scheme 1). This concurs with the results of the polymerizations of PS-N in styrene where no differences between the various nitroxyl radicals were found (Fig. 2). If it is assumed that for polymerization with only PS-N adducts (macroinitiators) there is no excess of N^* , there is still an induction period observed at lower temperatures. It is, however, significantly shorter than for the experiment carried out with free N^* .

It is believed that secondary reactions of BPO with 4-oxo-TEMPO occur through hydrogen abstraction from

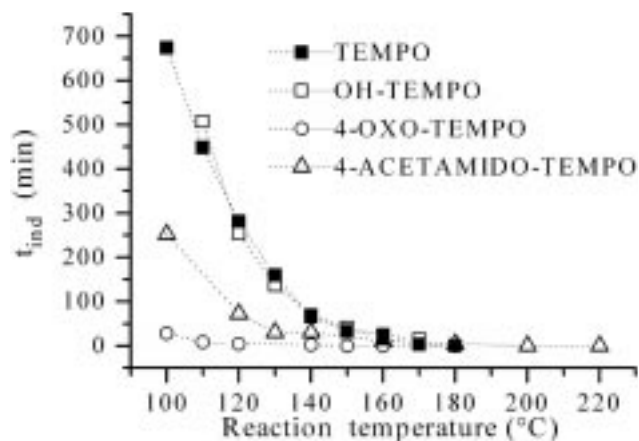


Fig. 1. Induction time of styrene polymerization with 0.02 mol L^{-1} BPO and 0.026 mol L^{-1} N^* .

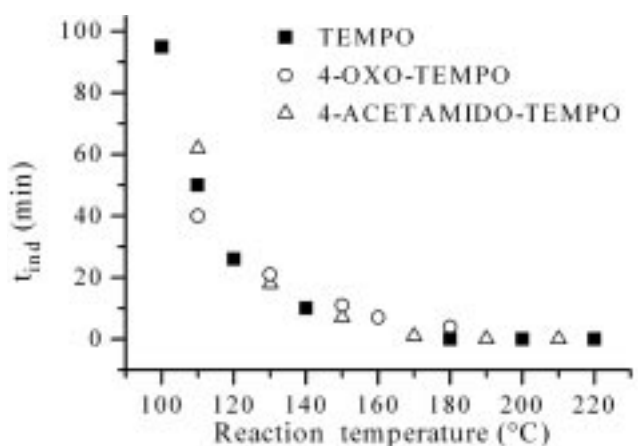
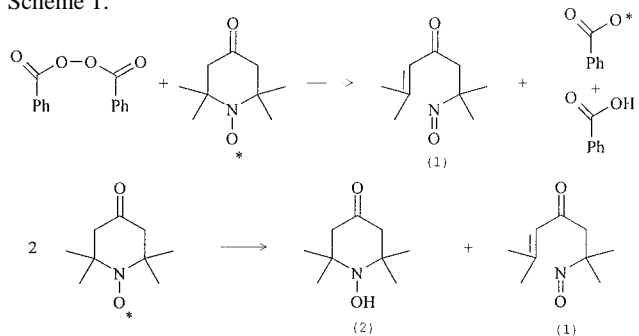


Fig. 2. Induction time of styrene polymerisation with 0.003 mol L^{-1} PS-N.

nitroxide by benzoyloxy radicals. This results in benzoic acid and an unsaturated nitroso compound **1**, which can undergo intramolecular “ene” reactions and produce hydroxylamine **2**⁴). The carbonyl group of 4-oxo-TEMPO activates hydrogen atoms in the 3 and 5 positions of the piperidine ring⁵), which results in a lower relative stability than the unsubstituted TEMPO (Scheme 1). The hydroxylamine **2** can also be formed by an independent decomposition reaction of nitroxides.

Scheme 1.



Temperature dependence of nitroxide-controlled styrene polymerization

In order to investigate the behavior of living radical polymerization within a wide temperature profile, the reactions were performed in the range of 100–220 °C. The resulting polymers were examined and compared according to their number-average molecular weights (M_n) and the polydispersity index (Pd). The results of 4-oxo-TEMPO are discussed separately (Fig. 3 and Fig. 4). They are used as an example for all examined nitroxides (Fig. 5 and Fig. 6), as a comparison of the examined nitroxides showed no remarkable differences.

For comparative purposes, the autopolymerization of styrene is carried out in the same temperature range. The M_n for thermal polymerization of styrene decreases with rising temperature due to the increased thermal initiation

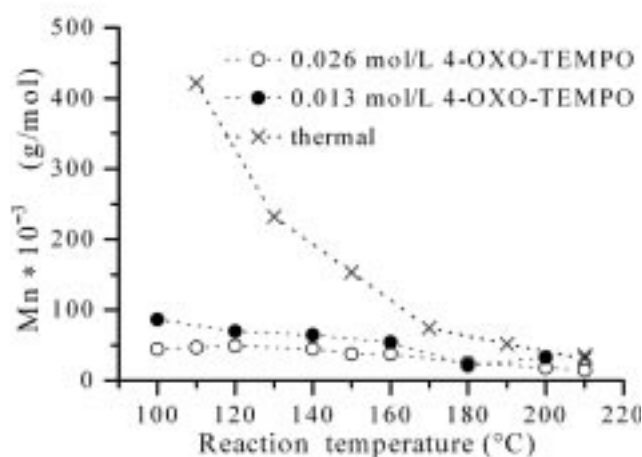


Fig. 3. M_n vs reaction temperature; styrene with BPO/4-oxo-TEMPO = 1:1.3 (mol/mol) and thermally produced polymer (100% conversion).

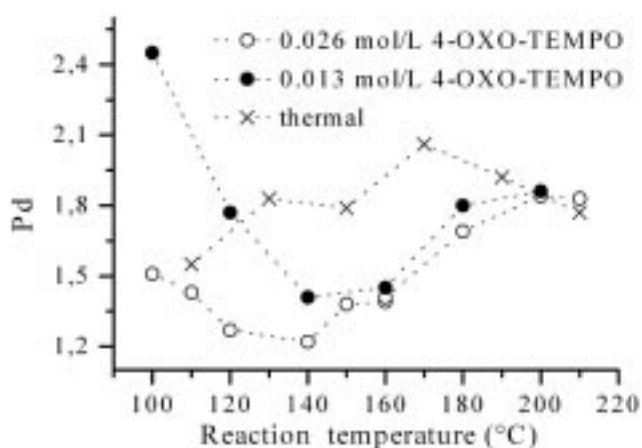


Fig. 4. Pd vs reaction temperature; styrene with BPO/4-oxo-TEMPO = 1:1.3 (mol/mol) and thermally produced polymer (100% conversion).

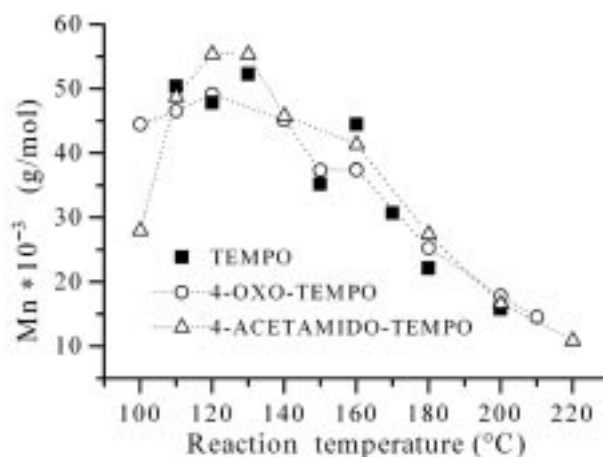


Fig. 5. M_n of styrene polymerization with 0.02 mol L⁻¹ BPO and 0.026 mol L⁻¹ N* (various nitroxides, 100% conversion).

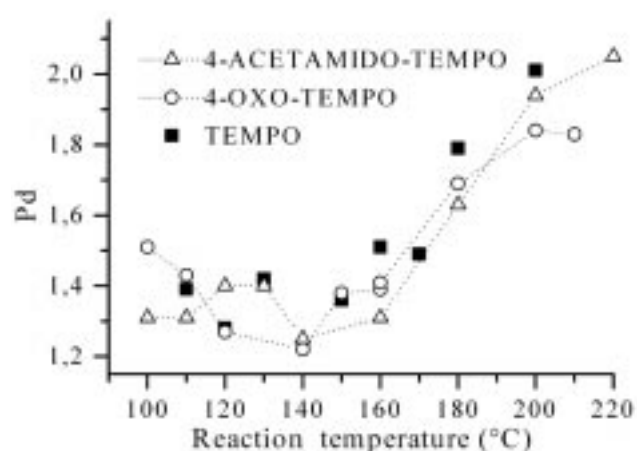


Fig. 6. Pd of styrene polymerization with 0.02 mol L⁻¹ BPO and 0.026 mol L⁻¹ N* (various nitroxides, 100% conversion).

(Fig. 3). For the nitroxide-controlled radical polymerization a different behavior can be expected.

It is assumed that every growing chain is capped with N*, so the molecular weight is strongly dependent on the nitroxide concentration. A lower N* concentration leads to a smaller molecular weight due to a lower concentration of growing chains. Fig. 3 shows the dependence of M_n upon N*-concentration and temperature.

In Fig. 5, M_n of styrene polymerization with various nitroxides versus reaction temperature is shown. From 100 °C to 120 °C, M_n increases for all nitroxide systems with rising temperature, caused by an increased reaction rate. At temperatures above 130 °C the increased thermal initiation also leads to a higher radical concentration. The nitroxides are not able to further control this as before. M_n decreases as in thermal polymerization and approaches its experimental values. Additionally, at these raised temperatures there is a significant decomposition of PS-N adducts⁶⁾ (as will be explained later). The polymerization assumes more and more a free radical charac-

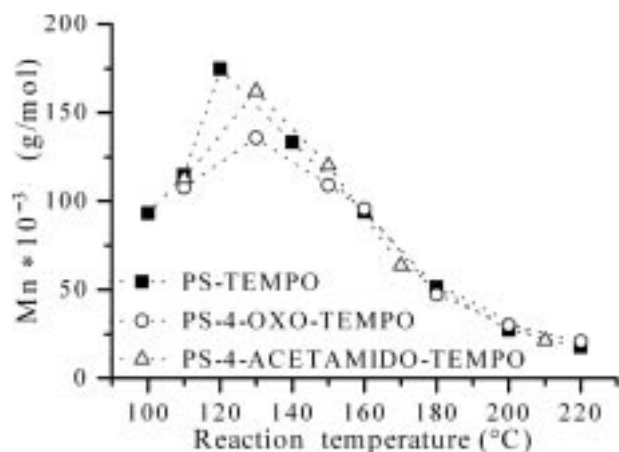


Fig. 7. M_n of styrene polymerization with 3 mmol L^{-1} PS-N as macroinitiator (various nitroxides, 100% conversion).

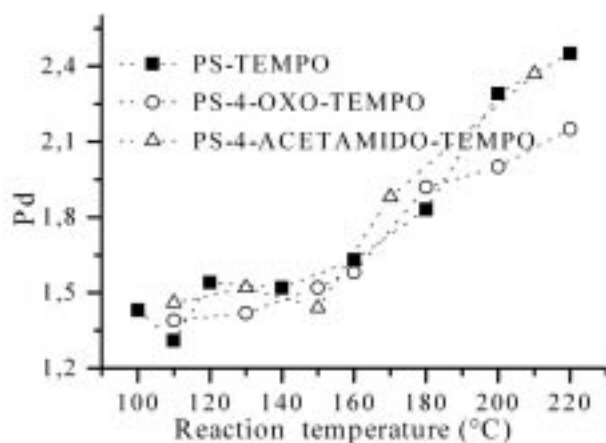


Fig. 8. Pd of styrene polymerization with 3 mmol L^{-1} PS-N as macroinitiator (various nitroxides, 100% conversion).

ter with increasing temperature (Fig. 6). The same results were obtained by polymerizing macroinitiators (PS-N) in styrene at this temperature (Fig. 7 and Fig. 8). For lower temperatures the M_n increased to a maximum limit at 120 $^{\circ}\text{C}$ or 130 $^{\circ}\text{C}$ and then decreased with increasing temperature due to the raised thermal initiation.

A minimum Pd is reached in the temperature range of 120–140 $^{\circ}\text{C}$ (Fig. 4). At lower N^* concentrations at 100 $^{\circ}\text{C}$, the high Pd is caused by simultaneous thermal and nitroxide-controlled polymerization which then leads to a bimodal molecular weight distribution (Fig. 9). These temperatures favor the dormant species (PS-N).

At temperatures above 160 $^{\circ}\text{C}$, the Pd exceeds the theoretical limit of Pd = 1.5 for conventional radical polymerization of styrene. If this broadening of Pd is only due to the increased thermal initiation, it should be possible to control the increased radical concentration with an adapted amount of N^* . Experiments with N^* concentrations up to 0.06 mol L^{-1} at temperatures from 160 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$ to control the accelerated autopolymerization

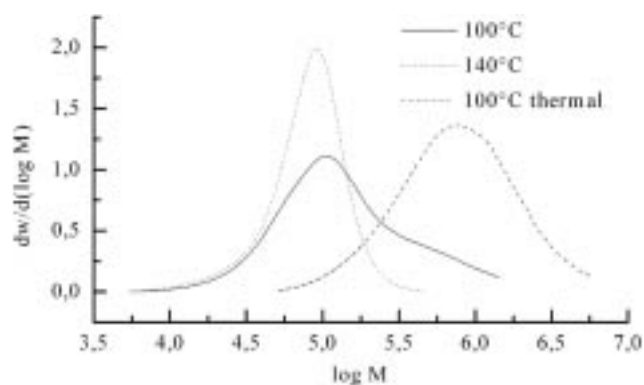


Fig. 9. Molecular weight distribution of styrene polymerization with 13 mmol L^{-1} 4-oxo-TEMPO ($\text{BPO}/N^* = 1:1.3$) at 100 $^{\circ}\text{C}$ and 140 $^{\circ}\text{C}$; the autopolymerization at 100 $^{\circ}\text{C}$ is shown for comparison.

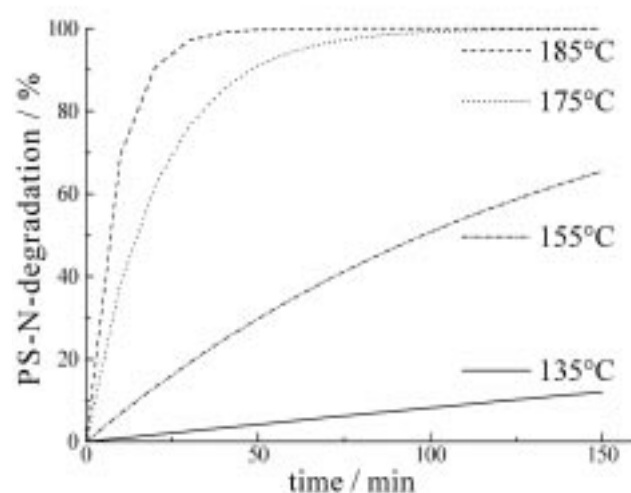
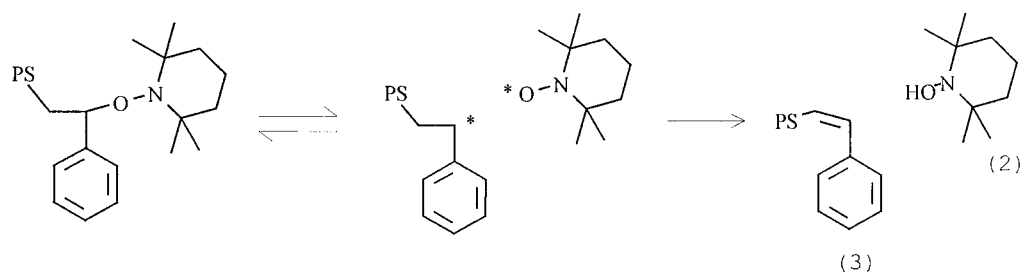


Fig. 10. PS-N decomposition at different temperatures calculated from the results of Fukuda et al.⁶

showed no decrease in the Pd. At these temperatures, a higher N^* concentration does not lead to a better control of free radical polymerization. Consequently, there must be side reactions. Fukuda et al. discussed decomposition of PS-N (Scheme 2), leading to dead-end polymers (**3**) and hydroxylamines⁶. Alongside the desired reversible dissociation of PS-N, upon β -proton abstraction the resulting radicals decompose. Fukuda et al. found a decomposition constant of $k_{\text{dec}} = 5.7 \cdot 10^{14} \text{ s}^{-1}$ and an activation energy of $E_A = 153 \text{ kJ mol}^{-1}$. In Fig. 10, the calculated decomposition of PS-N at different temperatures using these values is plotted to support our results. At 175 $^{\circ}\text{C}$, there is nearly 90% decomposition after 1 h. Chain control is not further possible. This limits the nitroxide-controlled radical polymerization to a temperature range of 110 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$.

Scheme 2.



Conclusion

The nitroxide-controlled styrene polymerization was examined over a wide temperature range for various nitroxides. Experiments were performed with and without a radical initiator (benzoyl peroxide) and with nitroxyl-terminated polystyrene macroinitiators PS-N. In conclusion, polymerization control is limited to a specific temperature range from 110°C to 150°C by thermal initiation, decomposition reaction of PS-N adducts and the nitroxides themselves. It is not affected by the concentration and type of capping agent.

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