

## Rate acceleration of N-oxy-mediated free radical random copolymerization of styrene and n-butyl methacrylate

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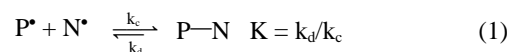
**SUMMARY:** The N-oxy-mediated free radical bulk copolymerization of styrene and n-butyl methacrylate was studied at 130 °C using dibenzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidine-N-oxy (TEMPO) as well as polystyrene-2,2,6,6-tetramethylpiperidine-N-oxy adducts (PS-TEMPO). The main focus was to describe a rate acceleration by additionally added radical initiator dicumyl peroxide (DCP), since the polymerization rates become rather slow with increasing butyl methacrylate content. The effects of DCP on the polymerization rates and the molar masses were studied and compared with the accelerating effects of camphersulfonic acid (CSA) and acetic anhydride (Ac<sub>2</sub>O). It was demonstrated that for an equimolar composition of the monomers, DCP allows a significant rate acceleration up to a factor of 9, depending on the polymerization conditions, without causing any appreciable increase in the polydispersity of the copolymers. In comparison with not accelerated copolymerizations, even the relative portion of dead chains can be reduced. The accelerating effects of CSA (factor 4) and Ac<sub>2</sub>O (factor 2) are distinctly smaller.

**ZUSAMMENFASSUNG:** Die N-Oxy-kontrollierte radikalische Substanz-Copolymerisation von Styrol und n-Butylmethacrylat bei 130 °C wurde untersucht, wobei die Bruttopolymerisationsgeschwindigkeit im Zentrum des Interesses stand. Als Initiierungs-/Terminierungssysteme wurden hierbei sowohl Kombinationen von Dibenzoylperoxid (BPO) und 2,2,6,6-Tetramethylpiperidin-N-oxy (TEMPO) als auch Polystyrol-TEMPO-Addukte verwendet. Um der drastischen Abnahme der Bruttopolymerisationsgeschwindigkeit mit zunehmender Butylmethacrylat-Konzentration im Reaktionsansatz entgegenzuwirken, wurde Dicumylperoxid (DCP) als zusätzlicher Initiator zur Reaktionsbeschleunigung verwendet. Der Einfluß des DCP auf die Polymerisationsgeschwindigkeit und die Molmassenentwicklung der synthetisierten Co- und Blockcopolymeren wurde untersucht und mit den literaturbekannten Beschleunigungseffekten von Camphersulfonsäure (CSA) und Essigsäureanhydrid (Ac<sub>2</sub>O) verglichen. Es konnte gezeigt werden, daß DCP eine signifikante Steigerung der Polymerisationsgeschwindigkeit bewirkt, ohne eine nennenswerte Verbreiterung der Molmassenverteilung hervorzurufen. Abhängig von den Reaktionsbedingungen ist für eine äquimolare Monomerzusammensetzung eine Steigerung der Reaktionsgeschwindigkeit bis zum Faktor 9 realisierbar. Im Vergleich zu nicht beschleunigten Copolymerisationen ist zusätzlich eine Reduzierung des Anteils an irreversibel abgebrochenen Polymerketten möglich. Die Beschleunigungseffekte von CSA (Faktor 4) und Ac<sub>2</sub>O (Faktor 2) sind deutlich geringer als die von DCP.

### Introduction

The control of the macromolecular architecture has recently become an important facet of polymer science. Due to the facile reaction conditions and the large number of monomers that can be homo- and copolymerized radically, much interest has been focused on the development in controlled/"living" free radical polymerization. The N-oxy-mediated free radical polymerization process<sup>1–7)</sup> is among the approaches most extensively studied. The key to its success is the reversible deactivation of the growing polymer radicals (P<sup>\*</sup>) by free stable N-oxy radicals (N<sup>\*</sup>), establishing the equilibrium shown in Eq. (1), where k<sub>c</sub> and k<sub>d</sub> are the rate constants of combination and dissociation, respectively. Irreversible bimolecular termination reactions were significantly reduced and polymerizations

behave in a pseudo-living fashion resulting in controlled molar masses and narrow molar mass distribution of the polymers.



However, long reaction times and a restricted number of polymerizable monomers limit the usefulness of this new polymerization process. These disadvantages are associated with the knowledge about the important function of the thermal self-initiation of the monomer, which is mainly responsible for providing a sufficient amount of radicals to compensate radical losses due to irreversible termination reactions and thus preventing an excessive accumulation of free N-oxy<sup>8–12)</sup>. In the case of a copoly-

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merization, a drastic decrease of the polymerization rate with increasing content of the non-self-initiating monomer could be expected. Actually, the copolymerization of butyl methacrylate (BuMA) with styrene (S) becomes rather slow at a high BuMA content and proceeds in a pseudo-living fashion only at lower BuMA concentrations, since the lengthening of the reaction time is additionally associated with an increasing occurrence of chain breaking reactions.

In this report, an approach for a more versatile use of the N-oxyl-mediated free radical polymerization is demonstrated with the main focus on the rate enhancement of controlled co- and block-copolymerizations of styrene and butyl methacrylate. The intention is the simulation of the missing self-initiation by using small amounts of a free radical initiator with a long half-time at reaction temperature<sup>13–18</sup>. To prevent losing control of the reaction, it will be essential that the amount of additionally produced radicals should be in the same range or only a few times higher than the number of radicals normally produced by thermal self-initiation in an N-oxyl-mediated styrene homopolymerization. The results of this acceleration concept are compared with the accelerating effects of the rate-enhancing additives camphersulfonic acid<sup>19–21</sup> (CSA) and acetic anhydride<sup>22</sup> (Ac<sub>2</sub>O).

## Experimental part

### Materials and characterization

Styrene (S, BASF) and butyl methacrylate (BuMA, Röhm) were distilled under reduced pressure. Benzoyl peroxide (BPO, Merck) and the synthesized polystyrene-2,2,6,6-tetramethylpiperidine-N-oxyl adducts (PS-TEMPO) (see below) were purified by precipitation from trichloromethane/methanol and from toluene/methanol, respectively. 2,2,6,6-Tetramethylpiperidine-N-oxyl (TEMPO, Fluka), dicumyl peroxide (DCP, Fluka), Ac<sub>2</sub>O (Aldrich), and CSA (Aldrich) were used as received.

The brutto polymerization rates ( $v_{br}$ ) were calculated from conversions below 15%. Conversions were determined gravimetrically.

Molar masses and molar mass distributions were estimated by size exclusion chromatography (SEC) using a Knauer gel chromatograph equipped with Macherey-Nagel columns 103–5 and 104–5 in series. Measurements were carried out with tetrahydrofuran as eluent and polystyrene standards were used for calibration.

### Polymerizations

All polymerizations were performed in bulk and carried out in batch reactors under gentle nitrogen purge and with stirring throughout the reaction. The polymers were recovered as precipitants from an excess of methanol, purified, and dried up to weight constancy.

For the synthesis of the PS-TEMPO-adduct, the reactor was charged with 8.73 mol L<sup>-1</sup> S and 39 mmol L<sup>-1</sup> TEMPO. After 30 min under gentle nitrogen purge, 30 mmol L<sup>-1</sup> BPO was added and the reaction mixture was preheated for 1 h at 95 °C to ensure complete BPO decomposition. Subsequently, the temperature was quickly increased to 135 °C to start the polymerization (time zero). After 445 min, the product was removed. SEC detected a  $M_n$  value of 13000 g mol<sup>-1</sup> and a polydispersity ( $M_w/M_n$ ) of 1.10. The TEMPO group at the chain end was apparent in the <sup>1</sup>H NMR spectrum and could be verified by a chain extension reaction.

The copolymerizations were performed at 130 °C either with BPO/TEMPO or with PS-TEMPO adducts (leading to poly(S)-*block*-poly(S-*co*-BuMA) block copolymers). The concentrations were 10 mmol L<sup>-1</sup> BPO and 13 mmol L<sup>-1</sup> TEMPO or 4 mmol L<sup>-1</sup> PS-TEMPO adduct. Using the BPO/TEMPO system, the polymerizations were carried out in the same way like the synthesis of the PS-TEMPO adduct (see above). The acceleration additives DCP (1–7 mmol L<sup>-1</sup>), Ac<sub>2</sub>O (13 mmol L<sup>-1</sup>), and CSA (5 mmol L<sup>-1</sup>) were added after the 95 °C period. Utilizing the PS-TEMPO adduct, the reaction was subsequently started after 30 min under gentle nitrogen purge. The rate accelerating additives (DCP, 0.5–4 mmol L<sup>-1</sup>) were applied before heating.

## Results and discussion

Before discussing the accelerating effects, we will first enter into the particularities of the unmodified N-oxyl-mediated S/BuMA copolymerization. Fig. 1 presents the time-vs.-conversion plots (Fig. 1, B) and the evolution of polydispersity ( $M_w/M_n$ ) as function of the conversion (Fig. 1, A) for a series of N-oxyl-mediated S/BuMA copolymerizations, with a stepwise variation of the molar ratios of the monomers. Due to the lack of continuously thermally self-initiated radicals, the polymerizations show, in contradiction to conventional free radical copolymerizations, a drastic decrease in rate with increasing BuMA contents. A lengthening of the induction period before the start of the polymerizations can also be clearly observed. For example, the variation of the S/BuMA monomer composition from a molar ratio of 9:1 to 4:6 reduces the brutto polymerization rate by a factor of four and lengthens the induction period from 20 min to nearly 120 min.

This decrease in rate is correlated with a loss in reaction control, exemplarily demonstrated by the broadening of the polydispersity in Fig. 2(A). The increase of polymerization time obviously promotes side reactions like thermal decomposition of the polymer-TEMPO adducts<sup>23</sup>. Additionally, due to the  $\alpha$ -methyl substituent of BuMA, a hydrogen atom transfer from the  $\alpha$ -methyl substituent of the BuMA chain end (P<sup>•</sup>) to the TEMPO radical takes place (Scheme 1), giving rise to polymers with olefinic end groups (P=) which could be verified by means of <sup>1</sup>H NMR ( $\underline{\text{CH}}_2=\text{C}$ ,  $\delta = 5.45$  and 6.2 ppm).

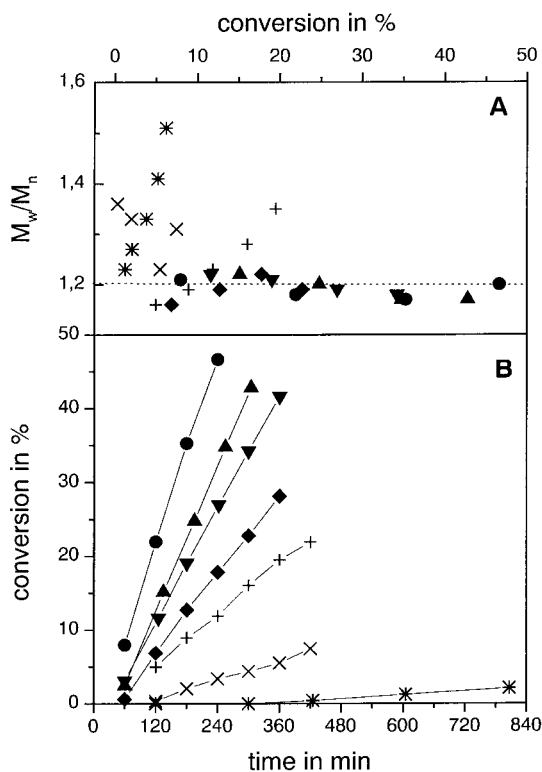
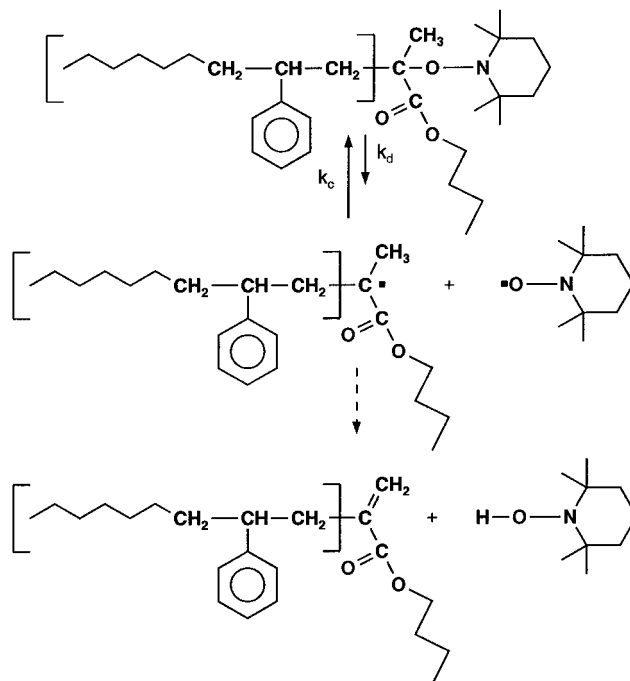


Fig. 1. Plots of conversion vs.  $M_w/M_n$  (part A) and conversion vs. reaction time (part B) for TEMPO-mediated S/BuMA copolymerizations with different molar monomer ratios performed with BPO/TEMPO at 130 °C. The molar S/BuMA ratios are 9:1 (●), 8:2 (▲), 7:3 (▼), 6:4 (◆), 5:5 (+), 4:6 (×), and 3:7 (\*).

According to recent literature<sup>18,24</sup> we additionally assume that the formed hydroxylamine (NH) reacts with a new macroradical ( $P^*$ ) through a further hydrogen transfer to give terminally saturated (dead) polymer (PH) and

Scheme 1: Reversible capping of a BuMA chain end with TEMPO and the irreversible chain termination by a hydrogen atom transfer leading to hydroxylamine and polymers with olefinic end groups (typical side reaction for monomers with  $\alpha$ -methyl substituent, like methyl<sup>1,25</sup> or butyl methacrylate).



reformed free N-oxyl ( $N^*$ ) (Eq. (2) and (3)). Thus, the hydroxylamine acts as a kind of retarder on the polymerization rate. It is evident that all of these side reactions lead to a further decrease in rate.

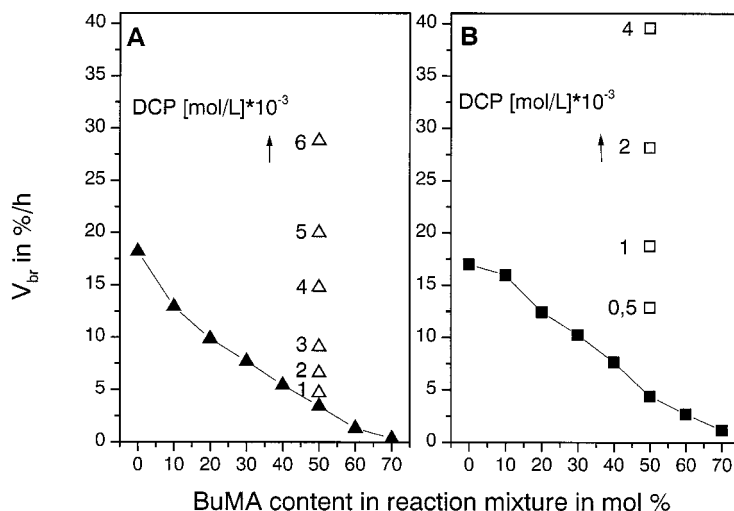
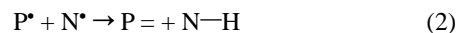


Fig. 2. Plots of  $v_{br}$  vs. BuMA content in the reaction mixture for TEMPO-mediated S/BuMA copolymerizations at 130 °C. The solid symbols illustrate non-accelerated copolymerizations. The open symbols demonstrate  $v_{br}$  values of accelerated copolymerizations; part A: copolymerizations performed with BPO/TEMPO, part B: copolymerizations performed with PS-TEMPO adduct.

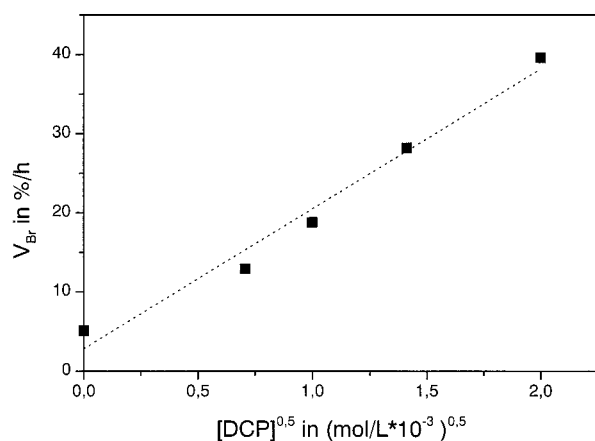


Fig. 3. Plot of  $v_{br}$  vs.  $[DCP]^{1/2}$  for TEMPO-mediated S/BuMA copolymerizations performed with an equimolar ratio of the monomers and PS-TEMPO adduct at 130 °C.

For equimolar monomer compositions in the reaction mixture, the effect of DCP on the brutto polymerization rates ( $v_{br}$ ) is presented in Fig. 2 using either BPO/TEMPO (A) or PS-TEMPO adducts (B). For each, small amounts of DCP lead to a significant rate acceleration. For the BPO/TEMPO system,  $v_{br}$  increases with increasing DCP concentrations up to 6 mmol L<sup>-1</sup> by a factor of 9. An even greater effect could be observed in case the PS-TEMPO adduct is used. A DCP concentration of 4 mmol L<sup>-1</sup> already gives rise to an increase in rate up to the factor of 8, resulting in a brutto polymerization rate of 40% h<sup>-1</sup>.

The differences between the BPO/TEMPO system and the PS-TEMPO-mediated copolymerizations may be found, on the one hand, in a higher concentration of free N-oxyl and on the other hand in an approximately 3 times higher number of growing chains while using the BPO/TEMPO system. Therefore, according to Eq. (2) and (3), an increased occurrence of side reactions can be suggested causing a decrease in rate relative to the PS-TEMPO system. A simple theoretical correlation between the DCP concentration and  $v_{br}$  is quite problematic for BPO/TEMPO systems, since the kinetic description is also complicated by effects of the by-products produced by reactions of the N-oxyl with the BPO<sup>26)</sup> (especially in the initial stage of the polymerization) and accelerating effects of the thermal initiation<sup>27)</sup>. In the case of the PS-TEMPO-mediated copolymerization an almost linear correlation between  $v_{br}$  and the square root of the DCP concentration is found (Fig. 3).

This result is in very good agreement with the kinetic description of PS-TEMPO-mediated S homopolymerizations by Fukuda et al.<sup>11)</sup>, assuming a linear relationship between  $v_{br}$  and the square root of rate of initiation ( $v_{ini}$ ), usually due to the thermal self-initiation of the monomer.

The controlled character of the rate-accelerated copolymerizations is clearly demonstrated in Fig. 4 by rate-enhanced S/BuMA copolymerizations performed with

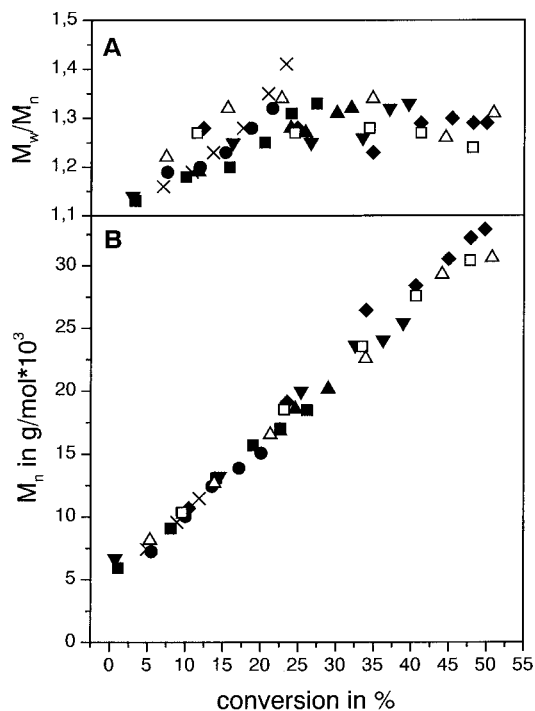


Fig. 4. Plots of conversion vs.  $M_w/M_n$  (part A) and conversion vs.  $M_n$  (part B) for TEMPO-mediated S/BuMA copolymerizations (equimolar monomer ratios) accelerated with different concentrations of DCP and performed with BPO/TEMPO at 130 °C. DCP concentrations ( $\times$ ) 0, ( $\bullet$ ) 1, ( $\blacksquare$ ) 2, ( $\blacktriangle$ ) 3, ( $\blacktriangledown$ ) 4, ( $\blacklozenge$ ) 5, ( $\square$ ) 6, and ( $\triangle$ ) 7 mmol L<sup>-1</sup>.

BPO/TEMPO at an equimolar monomer ratio. As presupposed for a controlled polymerization process, the molar masses increase almost linearly with monomer conversion, within experimental error. The obtained molar mass-vs.-conversion curves are nearly identical, demonstrating that the added DCP concentrations do not cause an appreciable increase in the total number of chains. This can on the one hand be contributed to the quite small DCP concentrations, and on the other hand to the fact that the net increase in the total number of the chains would only be half of the new initiated polymer chains, if one assumes a steady-state kinetic (number of new initiated chains is equal to the terminated ones) and that the macroradicals are terminated predominantly by combination with each other.

Also illustrated in Fig. 4, the polydispersities of the obtained copolymers are small according to the controlled polymerization mechanism, generally of less than  $M_w/M_n = 1.4$ , but could be as low as  $M_w/M_n = 1.2$ . A comparison of the polydispersities of the accelerated copolymerizations with those performed without DCP even shows smaller  $M_w/M_n$  values for the enhanced ones, especially for conversions above 15%.

In contrast to this, the use of PS-TEMPO adducts (Fig. 5, A) results in a broadening of the molar mass distribution with increased DCP concentrations and one may

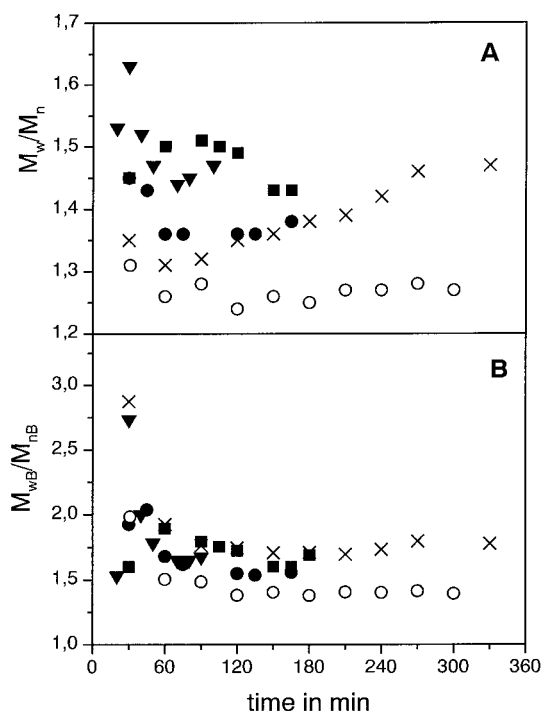


Fig. 5. Plots of reaction time vs.  $M_w/M_n$  (part A) and reaction time vs.  $M_{wB}/M_{nB}$  (part B, data calculated according to Eq. (4)) for TEMPO-mediated S/BuMA copolymerizations (equimolar monomer ratios) accelerated with different concentrations of DCP and performed with PS-TEMPO at 130 °C. DCP concentrations are (x) 0, (o) 0.5, (●) 1, (■) 2, and (▼) 4 mmol L<sup>-1</sup>.

suggest, at first glance, a loss of reaction control with increasing  $v_{br}$ . However, this assumption is not correct. In this case, the discussion of the molar mass distribution requires a separate consideration of both block sequences. Since side reactions are neglected, the  $M_w/M_n$  value of the resulting poly(S)-block-poly(S-co-BuMA) diblock copolymer can be given according to Tanaka et al.<sup>28)</sup> by means of Eq. (4), where index A stands for the polystyrene sequence and index B for the poly(S-co-BuMA) block sequence, respectively. The weight fraction of the sub-chains is given by  $x$ ,  $Y$  represents the heterogeneity parameter expressed by  $Y_i = (M_{wi}/M_{ni}) - 1$  with  $i = A$  or  $i = B$ .

$$M_w/M_n = 1 + x_A^2 Y_A + x_B^2 Y_B \quad (4)$$

Thus, using Eq. (4), the SEC results of the PS-TEMPO adduct and of the resulting diblock copolymers allow a calculation of the polydispersity of the copolymer sequence ( $M_{wB}/M_{nB}$ ). The results are shown in Fig. 5(B). The effect of the rate acceleration on the  $M_{wB}/M_{nB}$  of the copolymer sequence is significantly smaller as assumed first from Fig. 5(A). Obviously, the main differences regarding the polydispersity of the complete diblock copolymer could be contributed to differences in the chain length of the copolymer sequence relative to the polystyrene sub-chain. If the polydispersities of the copolymer sequences are compared with each other, the accelerated copolymerizations also show smaller  $M_w/M_n$  values than the non-enhanced ones.

Independent of the use of BPO/TEMPO or PS-TEMPO adducts, the increase in the polymerization rate obviously leads to a decrease of the relative portion of the side reactions discussed above because of the shorter reaction time. Moreover, the portion of irreversibly terminated polymer chains can be assumed qualitatively via the following chain extension experiment. Starting materials are poly(S-co-BuMA)-TEMPO adducts synthesized with and without DCP. They were taken at same monomer conversion and possess almost identical  $M_w$  values. Both copolymers were polymerized with styrene under the same reaction conditions and the finally obtained block copolymer products were taken at nearly the same conversion. The experiments and the SEC data are given in Tab. 1. The SEC curves are shown in Fig. 6.

It is obvious that the product resulting from the poly(S-co-BuMA)-TEMPO adduct synthesized using DCP has lower  $M_n$  and  $M_w$  values and a narrower molar mass distribution, demonstrated by the smaller polydispersity and the SEC traces that show a weaker tailing in the low-molecular-weight region. All this reflects a better reaction control and a greater amount of growing chains, which consequently demonstrates a less number of irreversibly terminated chains, regarding the starting copolymer synthesized with DCP.

To compare the rate acceleration obtained by DCP with the rate enhancement using organic acids or acylating agents, we also performed TEMPO-mediated S/BuMA copolymerizations in the presence of camphersulfonic acid (CSA) and acetic anhydride (Ac<sub>2</sub>O).

Tab. 1. Chain extension experiment: description of the experiment and SEC data of the starting and of the resulting products.

	Temperature (°C)	Time (min)	DCP (mmol L <sup>-1</sup> )	Conversion (%)	$M_n$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	$M_w/M_n$
Starting copolymer a	130	75	5	23.5	19 100	24 500	1.28
Starting copolymer b	130	420	0	21.9	16 500	23 200	1.41
Product c from a <sup>a)</sup>	115	300	0	29.8	54 100	73 100	1.35
Product d from b <sup>a)</sup>	115	300	0	30.1	57 000	134 700	1.82

<sup>a)</sup> [4 mmol L<sup>-1</sup>].

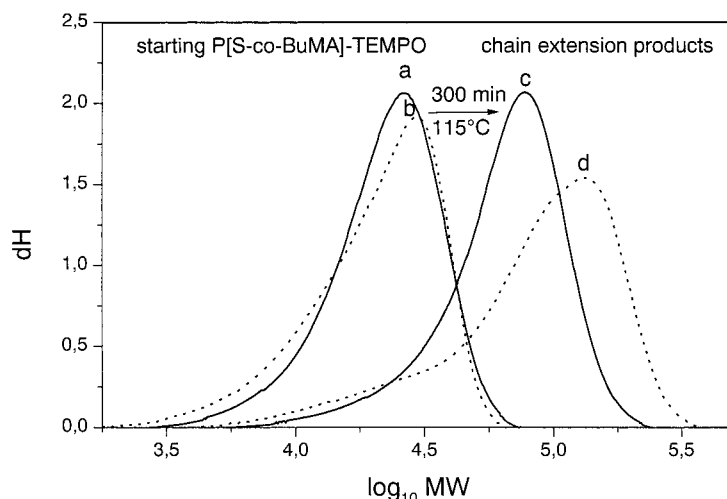


Fig. 6. SEC curves of the starting copolymers (a and b) and the resulting block copolymers (c and d) of the chain extension experiment described in the text and Tab. 1. The starting poly(S-co-BuMA)-TEMPO adduct a was synthesized with DCP, while material b was obtained without any acceleration (distinct longer reaction time). The chain extension product c is the product of starting material a, and the product d is obtained using product b.

For both additives, significant rate accelerations of N-oxyl-mediated styrene polymerizations were observed. In the case of CSA, Georges et al.<sup>19,20</sup> reported a decrease of the TEMPO concentration, already at the beginning of the polymerization, leading to an additional decrease in the length of the induction period. A direct reaction of the additive with TEMPO is assumed. Baldovi et al.<sup>21</sup> also found a decrease in the rate of combination ( $k_c$ ) between the N-oxyl and the growing macroradical. The complete mechanism of the rate enhancement is still unknown. Since for the application of CSA a distinct broadening of polydispersity was noticed, we used a relative small CSA concentration of 5 mmol L<sup>-1</sup> in order to find a compromise between the positive effect of rate acceleration and the negative broadening of the molar mass distribution.

In the case of Ac<sub>2</sub>O, Malmström et al.<sup>22</sup> give a reversible acylation reaction of the lone electron pair on the alkoxyamine nitrogen as a possible explanation of the rate enhancement, which should weaken the C—O bond and may promote its thermal decomposition. Alternatively, a reaction of the additive with free N-oxyl is discussed<sup>22</sup>. Since the maximum polymerization rate is reported for equimolar Ac<sub>2</sub>O/TEMPO ratios, the copolymerization was performed using equal Ac<sub>2</sub>O and TEMPO concentrations.

Fig. 7 demonstrates the evolution of  $M_n$  (Fig. 7, B) and the polydispersity (Fig. 7, A) as function of monomer conversion using CSA, Ac<sub>2</sub>O, or respectively DCP as additive. The results of a non-accelerated copolymerization are given, too. For all additives the copolymerizations proceed in a controlled manner. In analogy to DCP, the polydispersities operating with CSA or Ac<sub>2</sub>O are ranging from about  $M_w/M_n = 1.4$  to  $M_w/M_n = 1.2$  and are smaller than the ones of the non-accelerated copolymerization, especially at higher conversions.

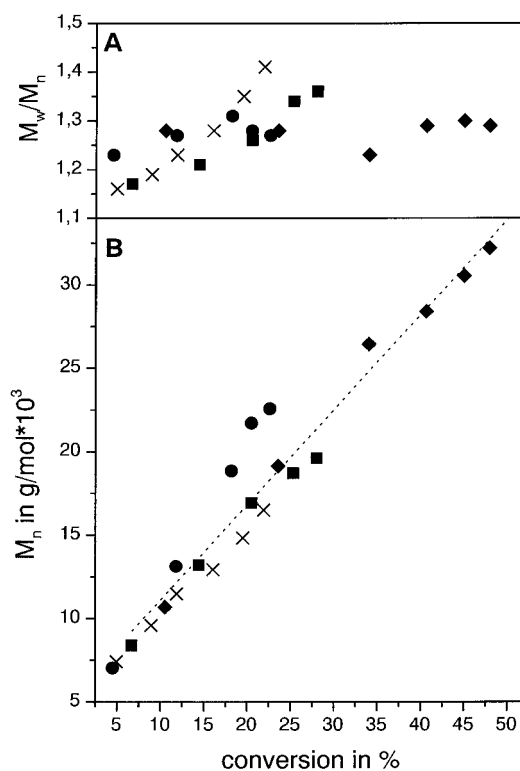


Fig. 7. Plots of conversion vs.  $M_w/M_n$  (A) and conversion vs.  $M_n$  (B) for TEMPO-mediated S/BuMA copolymerizations (equimolar monomer ratios) accelerated with DCP (◆) 5 mmol L<sup>-1</sup>, CSA (●) 5 mmol L<sup>-1</sup> and Ac<sub>2</sub>O (■) 13 mmol L<sup>-1</sup> in comparison to a non-accelerated S/BuMA copolymerization (×). All polymerizations were performed with BPO/TEMPO at 130 °C.

Nevertheless, the rate acceleration of Ac<sub>2</sub>O and CSA is distinct smaller than the acceleration by using DCP. As it is shown in Tab. 2, the application of Ac<sub>2</sub>O realizes a dou-

Tab. 2.  $v_{br}$  as function of the acceleration additive for a TEMPO-mediated S/BuMA copolymerization with an equimolar ratio of the monomers, performed with BPO/TEMPO at 130 °C.

Additive	Additive concentration (mmol L <sup>-1</sup> )	$v_{br}$ (% h <sup>-1</sup> )
No additive	–	3.5
Ac <sub>2</sub> O	13	7.2
CSA	5	14.5
DCP	5	20.0
DCP	6	28.8

bling and the utilization of CSA a fourfold increase of  $v_{br}$ , while DCP leads to a rate increase of up to the factor of almost 6 for 5 mmol L<sup>-1</sup> DCP or even up to 9 for 6 mmol L<sup>-1</sup> DCP. A further distinct rate increase using Ac<sub>2</sub>O should not be possible, as explained by the results of Malmström et al.<sup>22</sup>. In the case of CSA a further increase in rate would be correlated with a noticeable broadening of the molar mass distribution.

To draw a conclusion, the utilization of an additional initiator with a long half-time like DCP seems to be the most effective method for a rate acceleration of an N-oxyl-mediated S/BuMA copolymerization process without causing visible negative effects regarding the reaction control. In comparison with non-accelerated S/BuMA copolymerizations, the relative portion of dead chains can even be reduced. In general, this method should offer a more versatile use of N-oxyl-mediated free radical polymerization processes by making the polymerizations less dependent from the self initiation of the polymerized monomers, as very recently also shown by Fukuda et al.<sup>18</sup> as well as Baethge et al.<sup>17</sup>

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