Controlled Radical Polymerization in the Presence of N-Oxyls

Susanne Brinkmann-Rengel,* Heinz-Friedrich Sutoris, Horst Weiß

BASF AG, 67056 Ludwigshafen, Germany

SUMMARY: Recent development in controlled radical polymerization has provided a tool to combine a relatively robust radical polymerization technique with structural control. This contribution focuses on stable free radical polymerization in the presence of nitroxides. The influence of 2,2,6,6-tetramethyl-piperidine-N-oxyl (TEMPO) and temperature on the copolymerization of styrene and acrylonitrile will be discussed. In the second part a new class of nitroxide stable free radicals will be presented that shows enhanced performance in styrene polymerizations.

Introduction

Industrial plastics can be divided into commodity, engineering and high performance plastics. Unlike the prediction made in 1975 performance plastics took less than 1% of the total market share in 1998. This trend indicates that the development of new polymers from new monomers is not crucial. Further development focuses mainly on property improvement of existing products. In this context the synthesis of defined materials from existing monomers has proven more and more important.

The design of defined materials includes molecular architecture, monomer selection, and introduction of functionality. Polymer molecules can be designed to linear, comb, star-shaped, dendritic, highly branched or network structures. If only one monomer is used the resulting polymers can be distinguished by molecular weight, polydispersity, or tacticity. If more than one monomer is applied versatility is further increased to statistical, alternating, tapered, block or graft copolymers. Last but not least functional groups can be incorporated into the polymer chain. Functional groups can be located at one or both chain ends or along the chain. Thus a variety of materials can be designed from existing components - provided a tool to control synthesis is available.

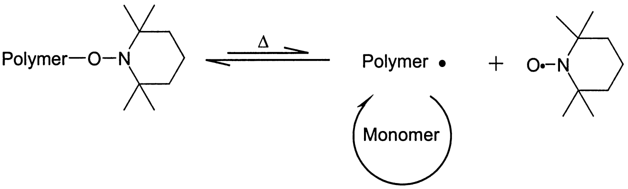
CCC 1022-1360/00/$ 17.50+.50/0

Radical polymerization is an important tool in polymer synthesis, because it tolerates a large number of functional groups and the polymerization process can easily be handled in large scales. Recently developed methods to control the polymerization are valuable as the versatility of radical polymerization can be combined with structural control. Several approaches to controlled radical polymerization (CRP) are reported in literature. The most important are stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT).[1-5] The advantages of the different methods are outlined elsewhere.[6] This contribution focuses on SFRP mediated by N-oxyl compounds.

Nitroxide mediated Stable Free-Radical Polymerization

The development of nitroxide-mediated polymerization was first performed by the groups of Solomon and Rizzardo and Georges.[7,8] A stable free radical is introduced into the polymerization medium and intervenes the polymerization process by establishing an equilibrium between growing polymer chains and stable free radical and polymer-N-oxyl adducts. The equilibrium is shifted towards the adducts which can be activated thermally. The concentration of growing polymer chains in the reaction medium is reduced. Biradical termination can be suppressed so that the growth of polymer chains can be well directed.

Scheme 1: Stable Free Radical Polymerization in the Presence of TEMPO.



Originally 2,2,6,6-tetra-methyl-piperidine-N-oxyl (TEMPO) was used as stable free radical. Due to the nature of the polymer-TEMPO bond polymerization is limited to reaction temperatures above 100 °C. Due to the reduced concentration of growing chains polymerization rate is reduced, too. Although termination reactions can be diminished, termination occurs eventually and free TEMPO accumulates in the reaction medium. Due to this persistent radical effect the polymerization slows down and finally stops.[9] Thus full conversion cannot be obtained and accessible molecular weights are limited. Only styrene and its derivatives or mixtures can be polymerized successfully.[10, 11]

Research of several groups aimed to overcome the problems outlined above. Work focused on the one hand on the investigation of kinetics and on comprehending the mechanism. [10, 12-16] Additives were introduced to speed up polymerization. [17-23] In another approach new stable free radicals were developed to enable polymerization at lower temperatures using a variety of monomers.[24-31] Calculations can be used to estimate the stability of N-alkoxyamine bonds.[32]

In this contribution two examples of our work will be briefly outlined. In the first part the influence of TEMPO on the copolymerization of styrene and acrylonitrile will be discussed. The second part focuses on a new class of controller molecules that shows enhanced polmerization performance in comparison to TEMPO.

Influence of TEMPO on Controlled Radical Copolymerization

Until recently only a few works dealt with controlled radical copolymerization.[33-42] We chose styrene and acrylonitrile as model system. The copolymerization of styrene and acrylonitrile was first studied in 1996 by Fukuda et al.[42] As his work focused on the preparation of poly(styrene)-*block*-poly(styrene-co-acrylonitrile) block copolymers, the copolymerization itself was not investigated in detail. In the mean time additional work was reported in literature.[43, 44] Although TEMPO acts as an inhibitor in acrylonitrile homopolymerization, SAN copolymers can be prepared by CRP. As pointed out above, the TEMPO-polymer bond can be activated thermally. The temperatures necessary for controlled radical polymerization are significantly higher than many examples of conventional radical polymerization reported in literature. The objective of our work was to investigate the influence of TEMPO and temperature on the copolymerization of styrene and acrylonitrile.[45, 46]

When molecular weights and polydispersities are compared, the differences between materials prepared in the presence or absence of TEMPO are obvious.

Whereas molecular weights above 300.000 g/mol and polydispersities around 2.0 are obtained when azeotropic mixtures of SAN are polymerized following a conventional procedure (FRP) using either thermal or dibenzoylperoxide initiation, molecular weights and polydispersities of samples prepared in the presence of TEMPO are significantly lower. Polydispersities range from 1.2 to 1.4 and molecular weights grow linearly as a function of conversion until conversions of about 60 % are reached. At higher conversion molecular weights level off to smaller values and polydispersity increases due to inevitable termination reactions. An induction period is observed when TEMPO is used as mediator.

Table 1: TEMPO-mediated Polymerization of Styrene and Acrylonitrile (75 : 25).

110 °C				120 °C			
Time [h]	Conversion [%]	Mn (GPC) [g/mol]	PDI	Time [h]	Conversion [%]	Mn (GPC) [g/mol]	PDI
1	2	--	--	1	1	--	--
2	3	7,300	1,26	2	4	8,631	1,33
5	33	33,000	1,38	4	39	36,580	1,36
8	50	44,600	1,39	8	65	51,210	1,43
16	65	55,100	1,40	16	> 90	56,610	1,62
40	85	58,800	1,53	-	-	-	-

To investigate the influence of TEMPO on copolymerization the acrylonitrile content of the monomer feed was varied over the whole composition range. Polymerizations were stopped below 5 percent conversion to rule out composition drift during polymerization. No major difference in the styrene content of polymers prepared by conventional or controlled radical polymerization was found.

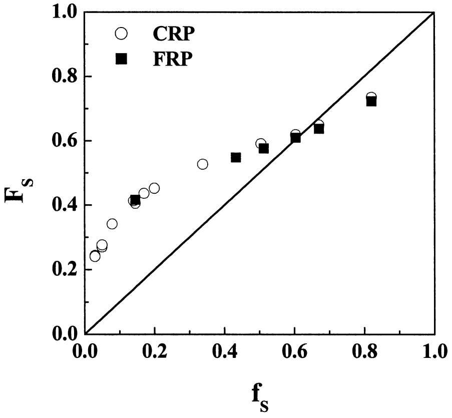


Figure 1: Copolymerization Diagram for Polymerizations carried out at 120 °C.

The copolymerization parameters were calculated using the method described by Kelen and Tüdös for temperatures ranging from 95 to 135 °C.[47] Taking the margin of errors into account no major difference between controlled and conventional radical polymerization is observed. The copolymerization parameters remain almost constant over the temperature range investigated. Nevertheless, it has to be noted that the temperature range for controlled radical copolymerization of styrene and acrylonitrile is limited: Below approx. 100 °C the polymerization is inhibited, above 135 °C control is lost using the controller concentration reported here.

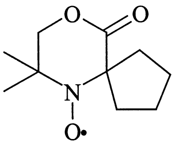
Table 2: Apparent Copolymerization Parameters.

	FRP		CRP	
T *[°C]*	r_{AN}	r_S	r_{AN}	r_S
97 ± 3	0.07	0.37	0.07	0.43
110 ± 3	0.07	0.41	0.08	0.45
122 ± 3	0.07	0.40	0.08	0.45
130 ± 3	0.07	0.41	0.09	0.53

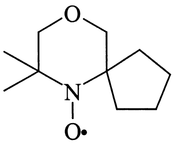
Although temperature dependence of copolymerization parameters derived from the terminal model is not observed, Ferrando and Longo recently reported evidence for temperature dependence of copolymerization parameters derived from the penultimate model, which result in a drift in sequence distribution with temperature.[48] The sequence distribution of polymers prepared at 120 °C was investigated and compared to the results obtained from Ferrando and Longo and to predictions from terminal and penultimate model calculated for the temperature investigated. The results obtained in our lab compare well with Ferrando and Longo, no difference between FRP and CRP is observed.[46] We additionally performed Monte-Carlo and PREDICI simulations, which will be reported elsewhere.[49]

New Nitroxides for Stable Free Radical Polymerization

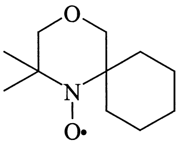
The development of new controllers is an important tool to overcome limitations of the TEMPO-mediated process. To influence the TEMPO-polymer bond bulky substituents are introduced into the vicinity of the nitrogen atom. Aditionally heteroatoms are incorporated into the controller molecule, as different electron withdrawing or donating groups could influence the TEMPO-polymer bond as well. Three N-oxyls of the morpholine and morpholone type were synthesized and evaluated in styrene polymerization.



1



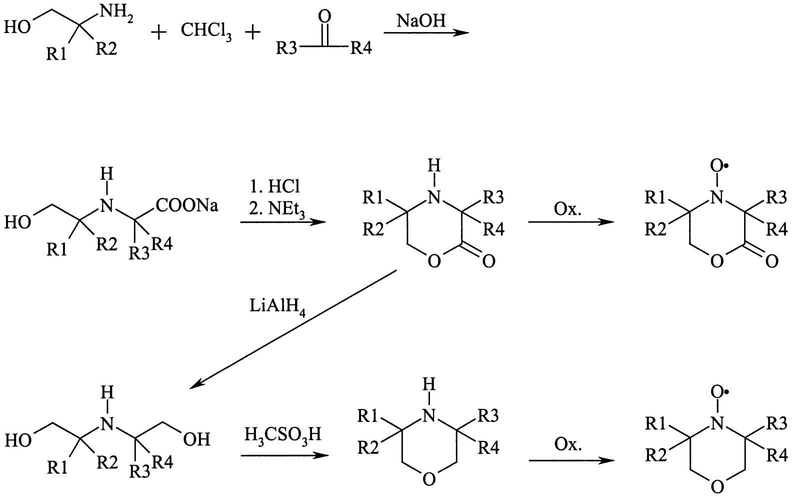
2



3

As shown in scheme 2, the synthesis of the controller molecules is accomplished following a route reported in literature for the synthesis of hindered amines.[50] The base induced reaction of aminopropanol, chloroform and a ketone yields a morpholone that can be directly oxidized to the N-oxyl. Alternatively, the morpholone is reduced, submitted to a ring-closing reaction followed by oxidation. The second route results in morpholine type N-oxyls.

Scheme 2: Synthesis of Morpholone- and Morpholine-N-Oxyls.



Nitroxides **1**, **2**, and **3** were used as mediators in styrene polymerizations performed at 125 °C in bulk. Using **1**, **2** and **3** higher conversions are obtained in shorter times. Using nitroxide **3** conversions larger 55 % can be obtained in two hours. Polymerizations performed in the presence of TEMPO yield 47 % conversion in five hours. No induction period is observed when **1**, **2**, or **3** is used as in the case of TEMPO. It is not immediately clear which structural feature in nitroxides **1**, **2**, or **3** reduces the induction period. Further investigations have to explore this aspect.

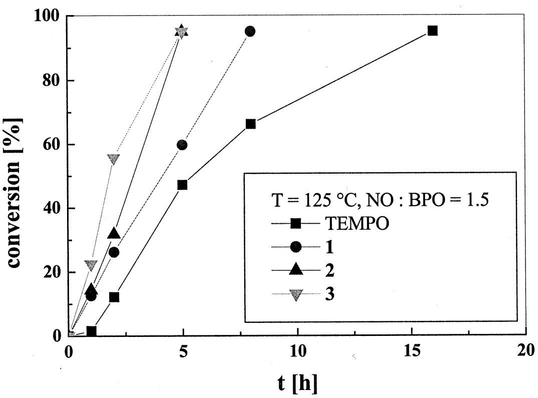


Figure 2: Evolution of Conversion as a Function of Reaction Time.

Polymers obtained in the presence of the new nitroxides show an almost linear dependence of molecular weight on conversion. Molecular weights observed compare well with results obtained from the TEMPO-mediated process.

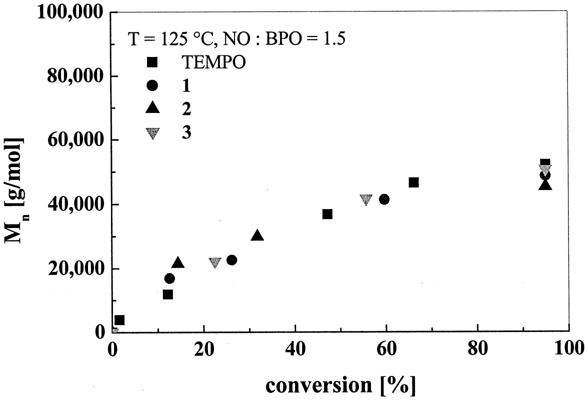


Figure 3: Molecular Weight as a Function of Conversion.

The evolution of polydispersity with conversion shows however, that accelerating polymerization results in larger polydispersities compared to TEMPO. Interestingly, polymers prepared in the presence of **3** that showed the fasted polymerization performed also best in terms of polydispersity.

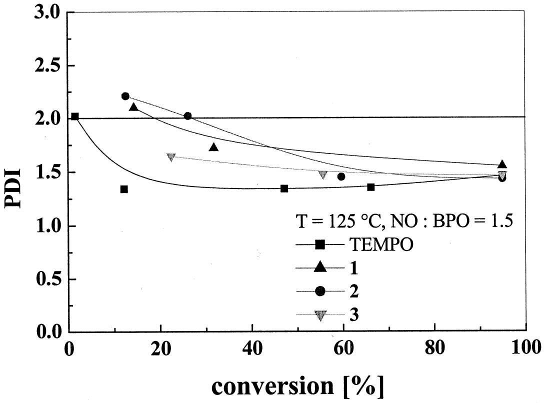


Figure 4: Polydispersity as a Function of Conversion.

The resulting polystyrene polymers can be used as macroinitiators in n-butyl acrylate polymerization. The polystyrene starting material prepared in the presence of **1** is dissolved in n-butyl acrylate and heated at 120 °C. After four hours 15 % conversion are observed. The number average molecular weight of the isolated polymer is shifted from 38,200 g/mol (PS-starting material) to 47,300 g/mol. The poly(n-butyl acrylate) content is estimated to be 22 % by ^{1}H NMR. Differential scanning calorimetry shows two glass transition temperatures at –46 and +98 °C, respectively. Recently Puts et al. outlined the advantages of nitroxides similar to **1** in acrylate polymerization.[51, 52] Improved performance from heteroatom containing nitroxides was recently published by Chong and co-workers.[29]

Conclusion

A variety of materials can be obtained from existing starting materials when the polymerization process can be controlled to yield defined materials. Through the combination of a robust radical polymerization technique tolerating many functional groups with enhanced structural control during polymerization, stable free radical polymerization is a valuable tool for the synthesis of defined materials.

The TEMPO molecule does not influence the copolymerization behavior of styrene and acrylonitrile in the temperature range investigated. Composition, copolymerization parameters and sequence distribution are within the margin of error compared to conventionally prepared polymers. Nevertheless, when materials prepared by conventional and controlled radical copolymerization are compared, differences may occur, which do not only result from differences in molecular weight and polydispersity. When copolymers are prepared via conventional radical polymerization and the azeotropic monomer composition is not used (and the composition drift is not compensated for by monomer feed) polymer chains with different composition among the polymer chains are obtained. In controlled radical polymerization however, the majority of chains is initiated at the same time resulting in polymers with a composition drift along the chains.

Bulky substituents and heteroatoms in the vicinity influence the stable free radical-polymer bond and thus the performance and outcome of polymerizations. This displays an important tool to overcome limitations of the TEMPO system.

Experimental

Monomers (styrene, acrylonitrile, n-butyl acrylonitrile), dibenzoylperoxide, and 2,2,6,6-tetra-methyl-piperidine-N-oxyl were used as supplied.

Polymerizations were performed in bulk using sealed glass ampoules protected by metal containers. The ratio of monomer to mediator to initiator was 1400 : 1.5 : 1 on a molar basis. Polymerizations were stopped by quenching to room temperature. The resulting polymers were precipitated into methanol, washed with methanol, and dried in vacuum.

Conversion was determined gravimetrically using a Mettler HR73 Moisture Analyzer. Molecular weights were determined by size exclusion chromatography using THF as eluent and polystyrene calibration. The acrylonitrile and butyl acrylate content was determined by NMR.

Acknowledgements

Support from D. Christie, Y. Durant is gratefully acknowledged. J. Malchus and Y. Cao are acknowledged for performing simulations. We thank K. Knoll, S. Lehmann, I. Hennig, W. Heckmann for analytics and N. Nießner, S. Haremza, B. Raether, and P. Barghoorn for helpful discussions.

References

1 M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer *TRIP* **2**, 66-72 (1994)
2 C. J. Hawker *Acc. Chem. Res.* **30**, 373-382 (1997)
3 T. E. Patten, K. Matyjaszewski *Adv. Mat.* **10**, 901-915 (1998)
4 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. Thang *Macromolecules* **31**, 5559-5562 (1998)
5 Y. K. Chong, T. P. T. Le, G. Moad, E. Rizzardo, S. H. Thang *Macromolecules* **32**, 2071-2074 (1999)
6 B. Raether *submitted to this journal*
7 US Patent 4,581,429, March 27,1985, D. H. Solomon, E. Rizzardo, P. Cacioli
8 M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer *Macromolecules* **26**, 2987-2988 (1993)
9 H. Fischer *Macromolecules* **30**, 5666-5672 (1997)

10 D. Greszta, K. Matyjaszewski *Macromolecules* **29**, 5239-5240 (1996)

11 D. Greszta, K. Matyjaszewski *Macromolecules* **29**, 7661-7670 (1996)

12 J. M. Catala, F. Bubel, S. O. Hammouch *Macromolecules* **28**, 8441-8443 (1995)

13 R. P. N. Veregin, P. G. Odell, L. M. Michalak, M. K. Georges *Macromolecules* **29**, 3346-3352 (1996)

14 K. Ohno, Y. Tsujii, T. Fukuda, *Macromolecules* **30**, 2503-2506 (1997)

15 A. Goto, T. Fukuda *Macromolecules* **30**, 5183-5186 (1997)

16 J. He, H. Zhang, J. Chen, Y. Yang *Macromolecules* **30**, 8010-8018 (1997)

17 M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, M. Saban *Macromolecules* **27**, 7228-7229 (1994)

18 P. G. Odell, R. O. N. Veregin, L. M. Michalak, D. Brousmiche, M. K. Georges *Macromolecules* **28**, 8453-8455 (1995)

19 R. P. N. Veregin, P. G. Odell, L. M. Michalak, M. K. Georges *Macromolecules* **29**, 4161-4163 (1996)

20 M. V. Baldovi, N. Mohtat, J. C. Scaiano *Macromolecules* **29**, 5497-5499 (1996)

21 D. Greszta, K. Matyjaszewski *J. Polym. Sci. A: Polym. Chem.* **35**, 1857-1861 (1997)

22 B. Keoshkerian, M. K. Georges, M. Qinlan, R. Veregin, B. Goodbrand *Macromolecules* **31**, 7559-7561 (1998)

23 H. Baethge, S. Butz, C.-H. Han, G. Schmidt-Naake *Angew. Makromol. Chem.* **267**, 52-56 (1999)

24 D. Benoit, S. Grimaldi, J. P. Finet, P. Tordo, M. Fontanille, Y. Gnanou *Polymer Preprints* **38 (1)**, 729-730 (1997)

25 R. D. Puts, D. Y. Sogah *Macromolecules* **29**, 3323-3325 (1996)

26 S. Butz, H. Baethge, G. Schmidt-Naake *Angew. Macromol. Chem.* **270**, 42-48 (1999)

27 Y. Miura, S. Mibae, H. Moto, N. Nakamura, B. Yamada *Polymer Bulletin* **42**, 17-24 (1999)

28 D. Benoit, V. Chaplinski, R. Braslau, C. J. Hawker *J. Am. Chem. Soc.* **121**, 3904-3920 (1999)

29 Y. K. Chong, F. Ercole, G. Moad, E. Rizzardo, S. H. Thang *Macromolecules* **32**, 6895-6903 (1999)

30 D. Benoit, E. Harth, P. Fox, R. M. Waymout, C. J. Hawker *Macromolecules* **33**, 363-370 (2000)

31 S. Grimaldi, J.-P. Finet, F. Le Moigne, A. Zeghdaoui, P. Tordo, D. Benoit, M. Fontanille, Y. Gnanou *Macromolecules* **33**, 1141-1147 (2000)

32 P. Marsal, M. Roche, P. Tordo, P. de Sainte Claire *J. Phys. Chem.* **103**, 2899-2905 (1999)

33 C. J. Hawker, E. Elce, J. Dao, W. Volksen, T. P. Russell, G. G. Barclay *Macromolecules* **29**, 2686-2688 (1996)

34 G. Schmidt-Naake, S. Butz *Macromol. Rapid Commun.* **17**, 661-665 (1996)

35 N. Ide, T. Fukuda Macromolecules 30, 4268-4271 (1997)

36 H. Baethge, S. Butz, G. Schmidt-Naake *Macromol. Rapid Commun.* **18**, 911-916 (1997)

37 S. Butz, H, Baethge, G. Schmidt-Naake *Macromol. Rapid Commun.* **18**, 1049-1055 (1997)

38 N. Ide, T. Fukuda *Macromolecules* **32**, 95-99 (1999)

39 H. Baethge, S. Butz, C. Han, G. Schmidt-Naake *Angew. Makromol. Chem.* **267**, 52-56 (1999)

40 E. Yoschida, Y. Takiguchi *Polymer J.* **31**, 429-434 (1999)

41 C. H. Han, M. Drache, G. Schmit-Naake *Angew. Makromol. Chem.* **264**, 73-81 (1999)

42 T. Fukuda, T. Terauchi, A. Goto, Y. Tsujii, T. Miyamoto *Macromolecules* **29**, 3050-3052 (1996)

43 M. Baumert, Diploma Thesis, Albert-Ludwig-Universität, Freiburg, Germany, 1996

44 M. Baumann, Diploma Thesis, Technische Universität Clausthal, Clausthal-Zellerfeld, Germany, 1997

45 S. Brinkmann-Rengel, J. Cao, N. Nießner *Polymer Preprints* **40 (2)**, 362-363 (1999)

46 S. Brinkmann-Rengel, N. Nießner *submitted to ACS Symp. Ser.*

47 T. Kelen, F. Tüdös *J. Macromol. Sci. – Chem.* **A9**, 1-27 (1975)

48 A. Ferrando, A. Longo *Polymer Preprints* **38 (1)**, 798-799 (1997)

49 Y. Cao, S. Brinkmann-Rengel, N. Nießner, Y. Yang *to be published*

50 J. T. Lai *Synthesis* **2**, 122-124 (1984)

51 EP 0 869 137

52 R. Puts, P. Nicholas, J. Milam, S. Tahilliani, W. Masler, N. Pourahmaday, *Polymer Preprints* **40 (2)**, 323-324 (1999)