Pergamon

Tetrahedron Letters, Vol. 38, No. 7, pp. 1133-1136, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(96)02461-6

Reactions of the "Stable" Nitroxide Radical TEMPO. Relevance to "Living" Free Radical Polymerizations and Autopolymerization of Styrene

Terrence J. Connolly and J. C. Scaiano*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Abstract: The stable nitroxide TEMPO is shown to react with styrene and polystyrene models under conditions typically used for polymerizations. These results show that the nitroxide is not inert at the elevated temperatures necessary to conduct polymerizations. The implications of hydrogen abstraction and olefin addition by the nitroxide are discussed, particularly as they apply to initiation, control of polydispersity and nitroxide mediated autopolymerization of styrene. © 1997, Elsevier Science Ltd. All rights reserved.

Although free radical polymerization typically results in polydisperse resins, recent advances have made it possible to prepare polymers with polydispersities well below the theoretical limit of 1.5[1]. Since the seminal report by Georges et al on TEMPO mediated "living" free radical polymerization of styrene[2], an increasing number of papers have appeared dealing with the synthesis of stoichiometric initiators[3-6], effects of additives[7-9], and the mechanism and kinetics of the reaction[10-15]. It has been proposed that the reaction occurs via an equilibrium between dormant and active chain carriers via reversible capping of the polystyrene chain by TEMPO, a stable free radical which is known to react with carbon-centered radicals at rates somewhat below the diffusion limit. The proposed mechanism of the reaction is shown in Scheme 1 where P_nT is the TEMPO capped dormant polymer, $P_n^{\bullet}$ is the active, growing polymer and $T^{\bullet}$ is TEMPO.

$$P_n^{\bullet} + T^{\bullet} \underset{k_L}{\overset{k_L}{\rightleftharpoons}} P_nT \qquad [1]$$

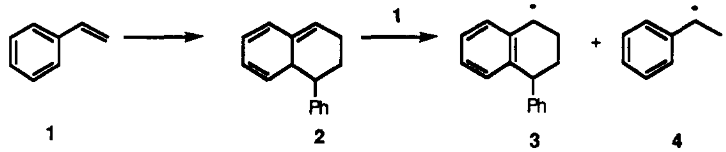
$$P_n^{\bullet} + \text{styrene} \xrightarrow{k_P} P_{n+1}^{\bullet} \qquad [2]$$

Scheme 1

The capping reaction (see eq. 1) is not reversible at room temperature, and polymerizations following the mechanism of Scheme 1 are typically carried out at temperatures around 125 °C, where k_{-L}, the rate constant for release of the growing polymer chain, is sufficiently large to activate the dormant polymer, P_nT.

It is generally accepted that the nitroxide radical, owing to its remarkable stability at room temperature, plays no other role in the reaction mechanism than to cap the living polymer. However, nitroxide radicals are known to behave as true radicals. The pioneering work of Haszeldine[16-18] has shown that bis(trifluoromethyl)-nitroxide will abstract hydrogen from a variety of substrates, including alkylbenzenes, and add to the double bond of substituted ethylenes. Ingold has provided kinetic parameters for a number of these reactions[19,20].

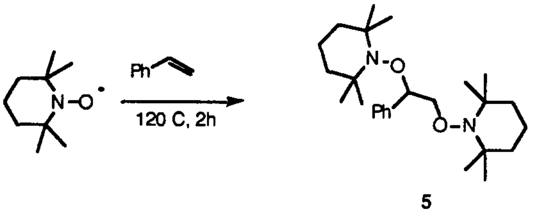
The Xerox team has published two papers on the autopolymerization of styrene in the presence of TEMPO[21,22]. Although their study focused mainly on the effect of added acid, they found that in the absence of additives, but in the presence of TEMPO, polymerization of styrene was possible. Although the polydispersities reported were not as low as those obtained when styrene was polymerized in the presence of TEMPO and benzoyl peroxide, the GPC traces did not show the high molecular weight tail indicative of true free radical polymerization. Since the polymerization did show some properties consistent with a "living" system, they concluded that the Mayo mechanism (Scheme 2) was operating, and that TEMPO merely controlled the growth of polystyrene initiated by **3** or **4** in a manner similar to the way it controls the reaction when initiated by benzoyl peroxide.



Scheme 2

Given the literature precedence for some nitroxides reacting with olefins, we decided to re-investigate the reactions leading to the autopolymerization of styrene in the presence of nitroxides to see if TEMPO could initiate polymerization. Initially, we set up two identical reactions: one which contained only freshly distilled styrene, the other containing, in addition to styrene, 5 mol % TEMPO. Heating these reactions at 120 °C for 18 hours resulted in the formation of polystyrene, isolated as a white solid after dissolution of the viscous oil in THF and precipitation with methanol. What was immediately obvious was the difference in yield of polystyrene. In the case of styrene alone, a yield of 45% was obtained, whereas the reaction conducted in the presence of TEMPO afforded an 89% yield of polymer.

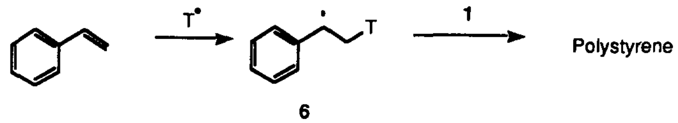
Encouraged by these results, we then heated an equimolar mixture of TEMPO and styrene at 120 °C for 2 hours. Chromatography of the resulting dark residue on silica gel afforded the di-TEMPO adduct **5**, isolated as a pale yellow oil, in yields ranging from 20-40%.



[3]

The assignment of **5** was based on the ^{1}H- and ^{13}C-NMR, key of which was the ABX pattern in the ^{1}H-NMR spectrum resulting from what were originally the olefinic protons of styrene. Heating **5** in the presence of distilled styrene under the previously described conditions also resulted in polymer formation in a yield of 70%, indicating that **5** is also a stoichiometric initiator. Adduct **5** resembled the Hawker initiator both in structure and reactivity[3]. In this case, TEMPO acts as both the initiator and the trap, whereas in Hawker's case, the terminal end is derived from benzoyl peroxide.

Under our conditions we could not find evidence to support the formation of **3** or **4**. This seems to indicate that the autopolymerization of styrene in the presence of TEMPO does not follow the Mayo mechanism, but may follow the mechanism outlined in Scheme 3, where the active chain is created via addition of TEMPO to the terminal end of styrene, followed by propagation and step-wise chain growth from **6**.

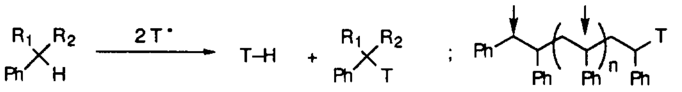


Scheme 3

Repeating reaction [3] in the presence of 1 equivalent of benzoic acid also led to the formation of adduct **5**, however the yield was lowered to 9%. Replacing benzoic acid with camphor sulfonic acid completely inhibited the reaction; no evidence could be found that supported the formation of **5**. The reactions between styrene and TEMPO, both in the absence and presence of benzoic acid, are typically red in color, presumably due to the presence of the nitroxide. However, when the reaction was conducted in the presence of camphor sulfonic acid (CSA), the reaction mixture turned black, and remained black throughout the course of the reaction. The suppressed yields in the presence of acid additives and the inability to recover any TEMPO after the reaction was complete presumably reflect that the TEMPO reacts with acid. This lowering of the concentration of TEMPO results in less addition product. This may also account for the decreased polydispersities reported by Georges for the autopolymerized styrene. The decrease in TEMPO concentration due to reaction with acid would result in fewer chains being initiated by TEMPO addition to styrene.

Changing the substrate from styrene to β-methylstyrene and exposure to the same reaction conditions resulted in the recovery of starting material. This failure of TEMPO to add to β-methylstyrene supports the radical addition mechanism proposed above, since it is well known that β-methylstyrene will not polymerize via a radical mechanism.

Since Haszeldine reported that bis(trifluoromethyl)nitroxide abstracted hydrogen from toluene at room temperature, we were intrigued by the possibility of TEMPO having the same reactivity at elevated temperatures. When equal amounts of TEMPO, styrene and ethylbenzene, a polymer-chain model, were heated at 120 °C for 2 hours, only **5** was formed, indicating that hydrogen transfer was not competitive with radical addition to the double bond. We then found that heating TEMPO in ethylbenzene at 120 °C for 2 hours did not result in any hydrogen abstraction. However, heating TEMPO in the presence of toluene, ethylbenzene or cumene for 12 hours, resulted in the formation of adducts formed via initial hydrogen abstraction, and subsequent trapping of the benzylic radical by another equivalent of TEMPO. When equimolar amounts of toluene and ethylbenzene were used, a 1:1 mixture of adducts was formed. When statistically corrected, this shows a *slight* preference for abstraction of a hydrogen from ethylbenzene. After this work was completed, we discovered that Opeida has recently reported on the hydrogen abstraction of methylbenzenes by TEMPO,[23] although he based his results on ESR results, and not by isolating the products.



R_1=H, Me; R_2=H,Me

Scheme 4

Shown in Scheme 4 is the generic reaction between TEMPO and toluene, ethylbenzene or cumene. Shown beside the reaction is polystyrene. Knowing now that TEMPO does abstract hydrogen efficiently from benzylic positions, and given the large number of hydrogens in a polystyrene chain that are similar to those in ethylbenzene and cumene, it would seem that hydrogen abstraction from the polymer and subsequent polymer growth from the newly created active center may contribute to polydispersity.

In summary, we have reported on two reactions of TEMPO that may be of relevance to those working in the field of TEMPO mediated "living" free radical polymerizations. We have shown that TEMPO does efficiently add to styrene and readily abstracts benzylic hydrogens. We have also provided evidence showing that TEMPO mediated autopolymerization of styrene need not follow the Mayo mechanism, but can proceed via initial addition of TEMPO to the terminal end of styrene followed by polymerization initiated by the benzylic radical. Recently developed kinetic models[10-14] should include the possible role of TEMPO as an initiator if they are to account fully for the reaction mechanism.

Acknowledgments

This work has been supported by the Natural Sciences and Engineering Research Council of Canada and was carried out while JCS was the recipient of a Killam Fellowship awarded by the Canada Council.

References

(1) Odian, G. *Principles of Polymerization;* 3rd ed.; John Wiley & Sons: New York, 1991, pp 293-296.

(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.

(3) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185.

(4) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* **1996**, *29*, 5245.

(5) Li, I.; Howell, B. A.; Ellaboudy, A.; Kastl, P. E.; Priddy, D. B. *ACS Polymer Prepr.* **1995**, *36*, 469.

(6) Connolly, T. J.; Baldovi, M. V.; Mohtat, N.; Scaiano, J. C. *Tetrahedron Lett.* **1996**, *37*, 4919.

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

(8) Baldoví, M. V.; Mohtat, N.; Scaiano, J. C. *Macromolecules* **1996**, *29*, 5497.

(9) Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Brousmiche, D.; Georges, M. K. *Macromolecules* **1995**, *28*, 8453.

(10) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316.

(11) Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 4391.

(12) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 2746.

(13) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 3324.

(14) Mardare, D.; Shigemoto, T.; Matyjaszewski, K. *ACS Polymer Prepr.* **1994**, *35*, 557.

(15) Hawker, C. J.; Barcley, G. G.; Dao, J. *J. Am. Chem. Soc.* **1996**, *118*, 11467.

(16) Banks, R. E.; Haszeldine, R. N.; Stevenson, M. J. *J. Chem. Soc. (C)* **1966**, 901.

(17) Banks, R. E.; Choudhury, D. R.; Haszeldine, R. N. *J.C.S. Perkin I* **1973**, 1092.

(18) Banks, R. E.; Birchall, J. M.; Brown, A. K.; Haszeldine, R. N.; Moss, F. *J.C.S. Perkin I* **1975**, 2033.

(19) Doba, T.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 3958.

(20) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 3094.

(21) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *ACS Polymer Prepr* **1994**, *35*, 870.

(22) Georges, M. K.; Kee, R. A.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. K. *J. Phys. Org. Chem.* **1995**, *8*, 301.

(23) Opeida, I. A.; Matvienko, A. G.; Ostrovskaya, O. Z. *Kinet. Catal.* **1995**, *36*, 441.

(*Received in USA* 27 *September* 1996; *revised* 11 *December* 1996; *accepted* 12 *December* 1996)