Pergamon

PII: S0040-4020(97)00959-9

*Tetrahedron*, Vol. 53, No. 45, pp. 15225-15236, 1997

0040-4020/97 $17.00 + 0.00

# Development of a New Class of Rate-Accelerating Additives for Nitroxide-Mediated 'Living' Free Radical Polymerization

Eva Malmström, Robert D. Miller, and Craig J. Hawker*

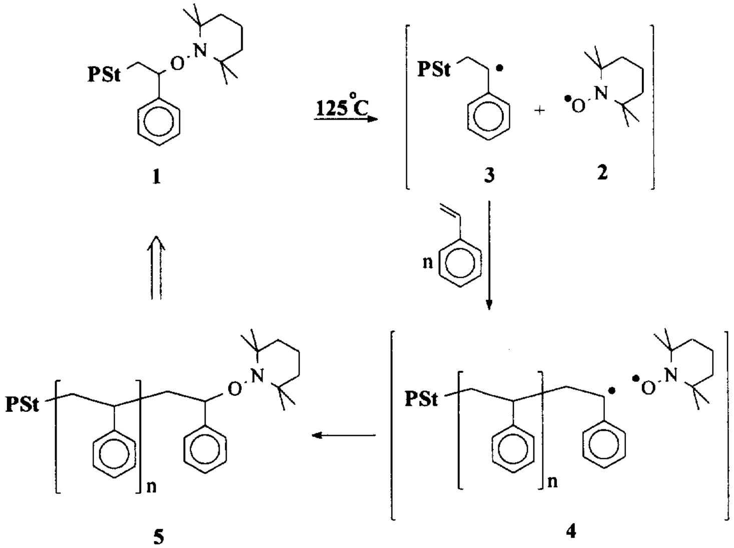
*Center for Polymeric Interfaces and Macromolecular Assemblies*
*IBM Almaden Research Center*
*650 Harry Road, San Jose, California 95120-6099*

***Abstract:*** Acylating agents have been identified as a new class of rate accelerating additives for nitroxide-mediated 'living' free radical polymerization. It is found that addition of 1 weight percent of acetic anhydride results in a significant decrease in the reaction time, 48 to 4 hours. This decrease in reaction time leads to greater control over the polymerization process with low polydispersity materials being obtained up to 150 000 a.m.u. A possible explanation for this effect is acylation of the alkoxyamine nitrogen leading to an increase in the lability of the C-ON bond.

## Introduction

The control of macromolecular structure has recently become an important facet of polymer science from both an academic and industrial viewpoint.[1] This interest is driven by the desire to prepare advanced materials with new and/or improved physical and mechanical properties combined with the realization that control of macromolecular architecture can lead to these property improvements. Until recently, synthetically demanding techniques, such as anionic,[2] cationic[3] or group-transfer polymerization[4] were the only available tools to accurately control structural features such as polydispersity, molecular weight, chain ends, and macromolecular architecture. While these techniques are successful, they are limited by their complexity, rigorous synthetic demands, as well as incompatibility with many functional groups/monomer units. To overcome these difficulties a range of new polymerization techniques based on 'living' free radical procedures have been developed in recent years.[5] Interestingly, many of these 'living' free radical techniques have their basis in modern synthetic organic and free radical chemistry.

Of the 'living' free radical techniques developed, the procedures mediated by stable nitroxide free radicals, such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), have attracted considerable interest.[6] The pioneering contributions to the development of nitroxide-mediated "living" free radical polymerization can be traced to the initial work of Moad and Rizzardo[7] and the subsequent refinement by Georges.[8] The fundamental observation of these groups was that under certain conditions, the free radical polymerization of styrene proceeds with little, or no termination to give narrow polydispersity polymers and can therefore be considered as pseudo-living in nature. Following these initial results, it has been shown that the 'living' nature of the nitroxide-mediated process is a direct result of the formation of a thermally labile alkoxyamine C-ON bond between the mediating nitroxide free radical and the propagating radical chain end. This results in a dormant, or inactive, intermediate, **1**, which is homolytically unstable and undergoes thermal fragmentation to give the stable nitroxide, **2**, and the polymeric radical, **3**. Significantly, the nitroxide free radical, **2**, does not initiate the growth of any extra polymer chains but it does react at near diffusion controlled rates with carbon centered free radicals. Therefore the polymeric radical, **3**, can undergo chain extension with a limited number of monomer units to yield a similar polymeric radical, **4**, in which the degree of polymerization has increased.



**Scheme 1**

Recombination of **4** with the mediating nitroxide radical then gives a chain extended dormant or inactive species, **5**, which is essentially the same as **1**. The cycle of homolysis-monomer addition-recombination can then be repeated to give well defined macromolecules (Scheme 1). It is the presence of a substantial amount of dormant chain ends in the polymerization mixture which is believed to be responsible for the 'living' nature of this unique procedure and the observed low polydispersities.[9]

The original initiating systems for "living" free radical polymerization were bimolecular systems where a traditional radical initiator, such as benzoylperoxide (BPO), was used together with a stable nitroxide free radical.[10] While successful, such a system does not readily allow control over structural features such as molecular weight, chain ends, or macromolecular architectures. To address this shortcoming the concept of unimolecular initiators, where a preformed alkoxyamine adduct comprising both a dormant initiating group and nitroxide in a 1:1 stoichiometry, was introduced.[11] Using a variety of mono- and multi-functional unimolecular initiators, the scope of nitroxide mediated 'living' free radical polymerization has been extended to produce narrow polydispersity materials with controlled molecular weights,[12] chain ends,[13] and chain architectures.[14] Also well-defined random[15] and block[16] copolymers can easily be prepared from a variety of monomers. The chemical stability of these alkoxyamine initiators under a variety of reaction conditions permits the introduction and manipulation of numerous functional groups. These functionalized initiators can then be used to prepare novel polymeric materials which are vital for probing a range of problems in material science.[17]

One of the major drawbacks of nitroxide-mediated "living" free radical procedures is the long reaction times and elevated temperatures that are required for these reactions to reach completion.[18] Typically, 'living' free radical polymerizations are carried out by heating a bulk mixture of the initiator and monomer at 120-130°C for 36-72 hours. Unfortunately, at these temperatures it has been shown that the autopolymerization of styrene based monomers can be a significant problem leading to loss of the 'living' character of the polymerization process and an inability to reach high molecular weights (ca. 200 000).[19] From an industrial point of view, reaction times of the order of 36-72 hours are also not economically attractive. A definite need for the development of simple rate accelerating additives therefore exists. Ideally these additives should lead to significant rate enhancements, giving reaction times of hours not days, provide the same high level of control over molecular weight and polydispersity, be compatible with a wide range of functional groups, and be easily removed. To this end, Georges[20] demonstrated that the rate of the TEMPO-mediated polymerization of styrene using benzoyl peroxide as an initiator can be increased by the addition of camphor sulfonic acid to the reaction mixture. In this case, although the polymerization reached ca. 90% completion in approximately six hours, the polydispersity was observed to increase with increasing amounts of camphor sulfonic acid (CSA).

This increase in polydispersity, coupled with the reactivity of many functional groups with strong acids, such as CSA, prompted us to investigate other rate accelerating additives for nitroxide mediated 'living' free radical polymerizations. In this report, the development of a new class of additives for 'living' free radical polymerizations is described.

## Experimental Section

Infrared spectra were recorded on a Nicolet spectrometer as thin films on NaCl. Nuclear Magnetic Resonance spectra were recorded on a Bruker AM 300 FT-NMR spectrometer using deuterated chloroform as solvent and the solvent signal as reference. Analytical TLC was performed on commercial Merck plates coated with silica gel $GF_{254}$ (0.25 mm thick). Silica gel for flash chromatography was Merck Kieselgel 60 (230-400 mesh). Size Exclusion Chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer with THF as the carrier solvent. Four 5 micron Waters columns (300 x 7.7 mm) connected in series in order of increasing pore size (100Å, 1000Å, $10^5$Å, and $10^6$Å) were used and calibration was performed using linear polystyrene standards. All chemicals were obtained from Aldrich and used as received. The synthesis of the unimolecular initiator, **6**, is described elsewhere.[23]

**N-benzoate succinimide 7.** To a solution of benzoyl chloride (5.00 g, 35.6 mmol) and N-hydroxysuccinimide (4.50 g, 39.0 mmol) in 70 ml dichloromethane was added a solution of triethylamine (4.00 g, 39.5 mmol) and 4-dimethylaminopyridine (0.43 g, 3.5 mmol) in dichloromethane (15 ml) dropwise. The reaction mixture was stirred for 45 minutes. The residue was extracted twice with water, dried with $MgSO_4$ and evaporated to dryness. The crude product was purified by flash chromatography eluting first with dichloromethane and gradually increasing to diethylether/dichloromethane (1:9) to give the product, **7**, as white crystals (6.72 g, 86%), m.p. 138-140°C. $^1H$ NMR ($CDCl_3$) $\delta$ 2.88 (s, 4H, C$H_2$), 7.45-7.52 (m, 2H, Ar*H*), and 7.63-7.69 (m, 1H, Ar*H*), 8.09-8.13 (m, 2H, Ar*H*): $^{13}C$ NMR ($CDCl_3$) $\delta$ 25.69, 125.15, 128.87, 130.56, 134.93, 161.88, and 169.24.

**N-Acetoxy succinimide 8.** A solution of N-hydroxy succinimide (5.00 g, 43.5 mmol), triethylamine (4.40 g, 43.5 mmol), and 4-dimethylaminopyridine (0.48 g, 3.9 mmol) in dichloromethane (70 ml) was cooled on an ice/water-bath. Acetyl chloride (3.10 g, 39.5 mmol) was added dropwise. After 4 hours the residue was extracted twice with water, dried with $MgSO_4$ and evaporated to dryness. The crude product was purified with flash chromatography eluting with dichloromethane, gradually increasing to diethylether/dichloromethane (1:5) to give the product, **8**, as white crystals (5.31 g, 85%), m.p. 131-134°C. $^1H$ NMR ($CDCl_3$) $\delta$ 2.31 (s, 3H, C$H_3$) and 2.81 (s, 4H, C$H_2$): $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.57, 25.57, 165.59, and 169.13.

**N-Acetoxy phthalimide 9.** A solution of N-hydroxyphthalimide (5.00 g, 30.7 mmol), triethylamine (3.10 g, 30.7 mmol), and 4-dimethylaminopyridine (0.34 g, 2.8 mmol) in dichloromethane (70 ml) was cooled on an ice/water-bath. Acetyl chloride (2.20 g, 39.5 mmol) was added dropwise. After 3 hours the residue was extracted several times with water, dried with $MgSO_4$ and evaporated to dryness. The crude product was purified with flash chromatography eluting with dichloromethane increasing to diethylether/dichloromethane (1:6) to give the product, **9**, as white crystals (4.50 g, 78%), m.p. 189-191°C. $^1H$ NMR ($CDCl_3$) $\delta$ 2.38 (s, 3H, C$H_3$) and 7.75-7.88 (m, 4H, Ar*H*): $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.61, 123.97, 128.85, 134.79, 161.87, and 166.56.

**N-Benzyloxy succinimide 10.** A solution of N-hydroxysuccinimide (5.00 g, 43.4 mmol), benzyl chloride (4.04 g, 47.9 mmol), potassium carbonate (6.00 g, 43.4 mmol) and 18-crown-6-ether (0.57 g, 2.16 mmol) in acetone (100 ml) was heated at reflux for 16 h, cooled and evaporated to dryness. The residue was partitioned between water and dichloromethane. The organic phase was dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with dichloromethane to give the product, **10**, as white crystals (5.62 g, 62 %), m.p. 139-141°C. $^1H$ NMR ($CDCl_3$) $\delta$ 2.62 (s, 4H, C$H_2$), 5.09 (s, 2H, C$H_2$), and 7.30-7.49 (m, 5H, Ar*H*): $^{13}C$ NMR ($CDCl_3$) $\delta$ 25.41, 78.60, 128.55, 129.42, 129.89, 133.31, and 171.14.

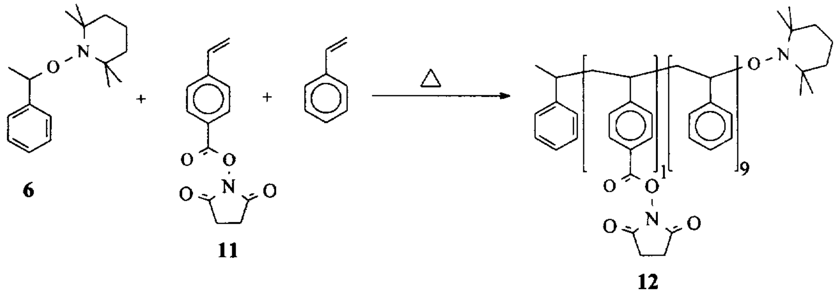
### General Procedure for Polymerization Reactions

To a round-bottom flask were added the initiator, **6**, (261 mg, 1.0 mmol), styrene (10.4 g, 100 mmol for conversion studies) and the required amount of additive. The polymerization mixture was then heated at 125°C under argon for 6 hours with samples being withdrawn at intervals. Molecular weights and polydispersities were measured by size exclusion chromatography after the excess styrene was removed by evaporation; no precipitation or fractionation techniques were employed. For determination of the extent of conversion, the samples were transferred directly from the polymerization mixture to an NMR tube and dissolved in $CDCl_3$. The relative percentages of polystyrene and styrene monomer were determined by integration of the relevant peaks.

For the molecular weight studies the crude polymerization mixture was precipitated into a mixture of acetone/isopropanol to remove the low molecular weight tail.

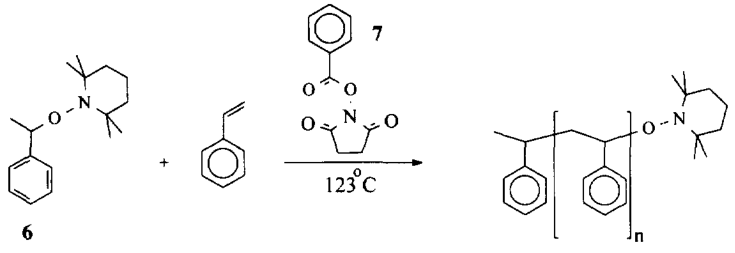
## Result and discussion

As part of our continuing studies[21] into the synthesis of complex macromolecular architectures by 'living' free radical procedures, the preparation of reactive linear polymers containing active ester functional groups was explored in detail.[22] Interestingly, when a 9:1 mixture of styrene and the p-vinyl benzoic acid derivative, **11**, were polymerized under typical living free radical conditions using **6** as an initiator, the polymerization reached completion within 6 hours (Scheme 2). This is in direct contrast to the polymerization of styrene with **6** which required 36 to 48 hours. The low polydispersity and accurately controlled molecular weights obtained for the active ester substituted polymer, **12**, coupled with similar observations for other active ester containing monomer units prompted a more thorough investigation into the cause of this dramatically increased rate of polymerization.



Scheme 2

In an effort to see whether the active ester group was the source of this rate enhancement, a number of small molecule active ester derivatives were prepared using standard chemistry. Varying amounts of these additives were then added to the polymerization of styrene initiated by **1** under standard conditions. For example, the 'living' free radical polymerization of 100 equivalents of styrene, **1**, and 10 equivalents of N-benzoate succinimide, **7**, was conducted at 125 °C under argon (Scheme 3).



**Scheme 3**

Samples were withdrawn from the reaction mixture at regular intervals and the extent of conversion determined using $^1$H-NMR and the molecular weights and polydispersities obtained by SEC. Significantly, the addition of **7** was found to have a dramatic rate-accelerating effect on the polymerization with a conversion of 80% being obtained after only 5 hours (Figure 1).

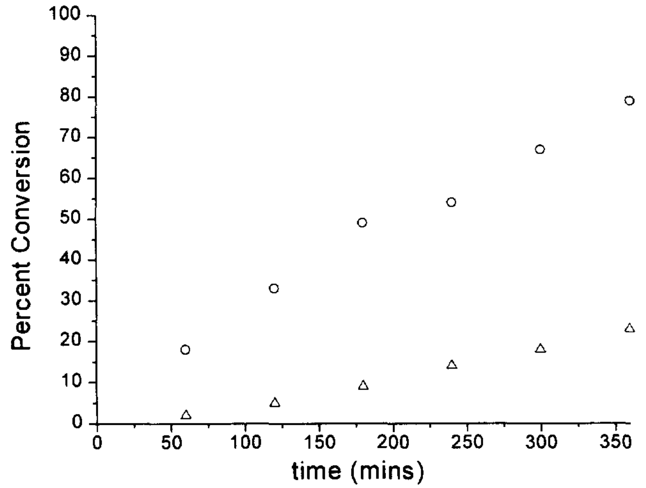
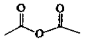
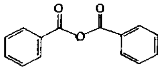
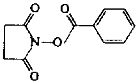
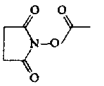
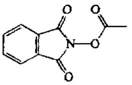
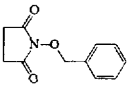
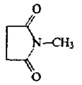
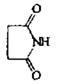
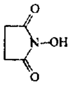
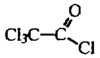
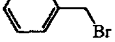


**Figure 1.** Percentage conversion as a function of time for the polymerization of styrene with **6** using (a) no additive (△) and (b) 10 weight percent of **7** (⊙).

The polymerization was also shown to proceed in a living fashion and shows a linear relationship between molecular weight, $M_n$, and percent conversion (Figure 2). The polydispersity for the crude reaction mixture was low (1.1-1.2) during the course of the polymerization which is similar to the results obtained in the absence of additive and demonstrates that the accelerating group does not need to be attached directly to the monomer unit.

**Table 1.** Effect of additive on nitroxide mediated 'living' free radical polymerization

| No. | Additive | Effect |
|---|---|---|
| **16** |  | + |
| **17** |  | + |
| **7** |  | + |
| **8** |  | + |
| **9** |  | + |
| **10** |  | - |
| **13** |  | - |
| **14** |  | - |
| **15** |  | - |
| **18** |  $Cl_3C-C(=O)Cl$ | + |
| **19** |  | - |
| **20** | $Me_2SO_4$ | + |

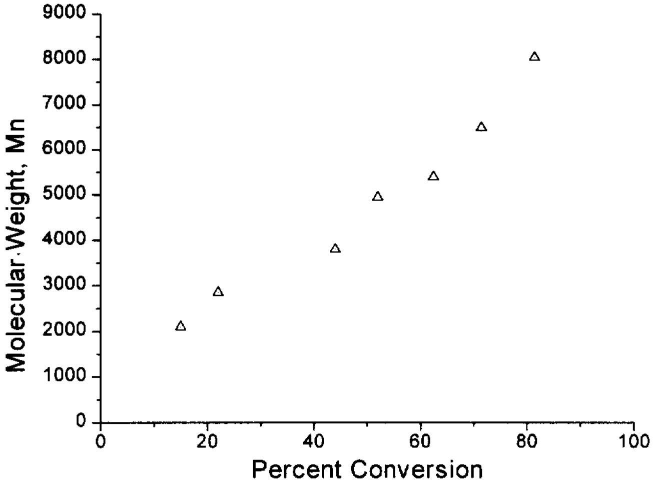


**Figure 2.** Evolution of molecular weight, $M_n$, with the percentage conversion for the polymerization of styrene at 123°C initiated by **6** using 10 wt% of **7** as an additive.

In an effort to determine the general features required for this accelerating effect, a range of possible small molecule additives was examined. In each case, 10 weight percent of additive was added to a 100:1 mixture of styrene and unimolecular initiator, **1**. As shown in table 1, only a subset of the additives provided a significant accelerating effect. Variation from the original active ester structure, **7**, included the removal of the acyl group to give the benzyloxy succinimide derivative, **10**. In this case, all activity was lost. Similar effects were observed for other simple succinimde derivatives, **13-15**. In fact, only in the case of other active ester derivatives, **8** and **9**, was an accelerating effect observed. Building on this observation, it was then found that simple anhydrides such as acetic anhydride, **16**, and benzoic anhydride, **17**, resulted in a similar accelerating effect. Other acylating reagents, such as the acid chloride, **18**, were also active.

Since acetic anhydride is a cheap, readily available reagent and is simple to remove due to its volatility, it was selected as the additive of choice for all further studies. The question of additive concentration and its effect on rate acceleration was then studied in a series of experiments where the acetic anhydride was varied from 0.1, 1, 2, 5, 10, to 20 % by weight of styrene. In all cases, the molar ratio of styrene to initiator, **6**, was 100:1 so the above experiments correlate with a molar ratio of additive to initiator of 0.1, 1.0, 2.0, 5.1, 10.2, and 20.4 respectively. As shown in figure 3, no further acceleration was observed on the addition of excess additive above a molar ratio of 1.0 , although a decrease in the molar ratio from 1.0 to 0.1 resulted in a pronounced decrease in the rate of acceleration was observed.

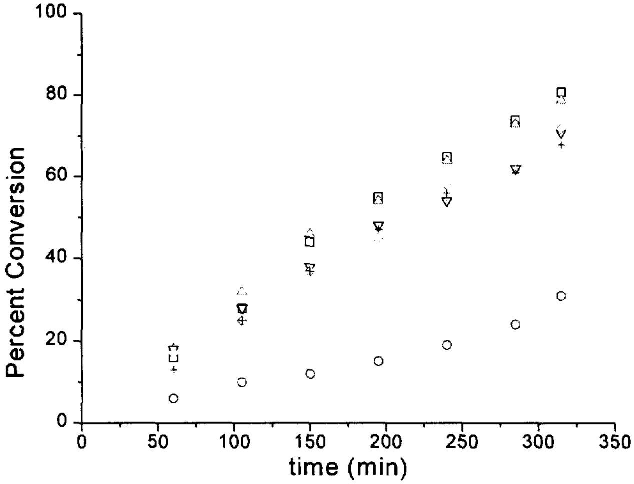


**Figure 3.** Percent conversion as a function of time for the polymerization of styrene with **6** using (a) 0.1 equivalents of $Ac_2O$ (⊙); (b) 1.0 equivalents of $Ac_2O$ (□); (c) 2.0 equivalents of $Ac_2O$ (△); (d) 5.1 equivalents of $Ac_2O$ (▽); (e) 10.2 equivalents of $Ac_2O$ (◇); and (f) 20.4 equivalents of $Ac_2O$ (+).

It was also interesting to note that increasing amounts of acetic anhydride did not increase the polydispersities of the crude polystyrene, a result which is in contrast to the effect of camphor sulfonic acid where increasing amounts of CSA led to higher polydispersities.[20]

A consequence of using additives to accelerate nitroxide mediated 'living' free radical polymerizations is that the influence of autopolymerization is lower due to the shorter reaction times. This may open up the possibility of preparing very high molecular weight polymers using this technique while maintaining control over molecular weight and polydispersity. Previously, it has been shown that the unimolecular initiator, **6**, offers excellent control over molecular weight and polydispersity for molecular weight up to 40 000 a.m.u.[23] For molecular weights in excess of 100 000 a.m.u., significant loss of control and polydispersities in excess of 1.50 are typically observed. To further probe the effect of acylating agents on nitroxide mediated 'living' free radical polymerization, the synthesis of a series of high molecular weight polystyrenes was conducted as outlined in Table 2. The agreement between theoretical[24] and experimental molecular weight is excellent for molecular weights up to 150 000 with polydispersities being less than 1.30. In this case, loss of control is only observed for molecular weights in excess of 200 000 which indicates that the acetic anhydride additive not only increases the rate of reaction, but also gives better control at higher molecular weights, a result which is fully consistent with decreased influence of autopolymerization.

**Table 2.** Molecular weight ($M_n$) and Polydispersity for the Purified Polymers Obtained from the Polymerization of Styrene in Presence of the Unimolecular Initiator, **6**, and Acetic Anhydride (1% by weight relative to styrene) at 125 °C under argon for 5 hours.

| Theor $M_n$[a] | $M_r$[b] | PD |
|---|---|---|
| 9 300 | 8 500 | 1.12 |
| 47 000 | 43 500 | 1.16 |
| 70 500 | 67 000 | 1.23 |
| 94 000 | 87 500 | 1.29 |
| 140 500 | 132 000 | 1.34 |
| 187 500 | 162 000 | 1.33 |
| 281 000 | 199 500 | 1.48 |
| 468 000 | 235 000 | 1.56 |

a) Theoretical Molecular Weights

b) Experimentally Determined Polystyrene equivalent weights

The presence of a dormant alkoxyamine functionality at the chain end of macromolecules prepared by 'living' free radical procedures has been exploited by a number of workers in the preparation of block copolymers.[16] Therefore a question of major importance is whether the addition of additives such as acetic anhydride leads to loss of the alkoxyamine group. To probe this, the polymerization of 40 equivalents of styrene with **6** in the presence of 2.5 equivalents of acetic anhydride was conducted under standard conditions. Significantly, the $^1$H NMR spectrum of the purified polymer did not indicate any degradation and the molecular weight, as determined by GPC ($M_n$ = 3 400, PD. = 1.09) and NMR ($M_n$ = 3 500) agreed well, both with each other, and with the theoretical value of 3 700. This feature indicates that approximately every polymer chain has a single alkoxyamine chain end.

A possible explanation for the observed rate acceleration of acylating agents is that the lone electron pair on the alkoxyamine nitrogen is undergoing a reversible acylation reaction (Figure 4). The coordination of this acyl group to the nitrogen atom induces a partial positive charge resulting in a polarization of the N-O bond towards the nitrogen. This weakens the C-O bond and further promotes the thermal dissociation of the C-O bond which increases the polymerization rate. Alternatively, the acylating agents may be reacting with free nitroxide, or its reduced hydroxyamine derivative, thereby decreasing the overall nitroxide concentration.

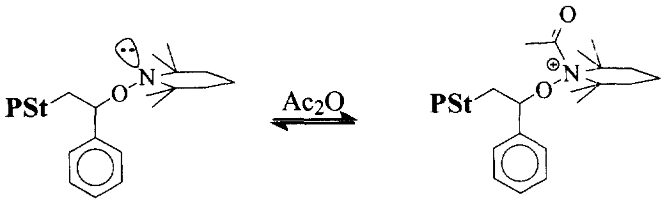


**Figure 4.** Proposed acylation of alkoxyamine end group leading to increased reactivity.

In an effort to investigate this feature, a series of polymerizations were performed with a second series of small molecule additives that may also interact with the nitrogen lone pair, alkylating agents. Under the same conditions as before, it was observed that benzyl bromide produced only a weak rate acceleration while the effect was very pronounced for the stronger alkylating agent, dimethyl sulfate. In the latter case, the polymerization reached completion within 4 hours, however the polydispersities were observed to be higher than those obtained for the acylating agents, 1.5-1.6 compared with 1.1-1.2.

In conclusion, it has been demonstrated that nitroxide mediated 'living' free radical polymerization is dramatically accelerated by the addition of small amounts of an acylating agent. A variety of acylating species, ranging from active esters to simple anhydrides such as acetic anhydride, were found to be effective. The addition of only one equivalent of acetic anhydride decreases the polymerization time from 48 to 5 hours. This dramatic reduction in polymerization times resulted in increased control over the polymerization process. Accurate control of molecular weights could now be obtained up to 150 000 a.m.u while maintaining polydispersities less than 1.30. The application of these novel rate enhancing additives to the polymerization of reactive polymers and other monomer systems, such as acrylates, is currently under study.

**Acknowledgments:** *This research was made possible by the National Science Foundation under Grant No. DMR-9400354 which supports the Center for Polymeric Interfaces and Macromolecular Assemblies and by the IBM Corporation. Fellowship support (EM) from the Hans Werthen Foundation and the Fulbright Commission is also gratefully acknowledged.*

## References

(1) Webster, O. W. *Science* **1994**, *251*, 887; Fréchet, J.M.J. *Science* **1994**, *263*, 1710.

(2) Quirk, R. P.; Lynch, T. *Macromolecules* **1993**, *26*, 1206.

(3) Fukui, H.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 7315.

(4) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473.

(5) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909; Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316; Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901; Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614; Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721; Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970; Wayland, B.B.; Poszmik, G.; Mukerjee, S.L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943; Granel, C.; DuBois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576; Hammouch, S. O.; Catala, J.M. *Macromol. Rapid Commun.* **1996**, *17*, 149; Li, I.Q.; Howell, B.A.; Koster, R.A.; Priddy, D.B. *Macromolecules* **1996**, *29*, 8554.

(6) Hawker, C. J. *Trends in Polymer Science* **1996**, *4*, 183; Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323; Hammouch, S. O.; Catala, J. M. *Macromol. Rapid Commun.*, **1996**, *17*, 683; Kazmaier, P. M.; Moffat, K. A.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; *Macromolecules* **1995**, *28*, 1841; Connolly, T.J.Baldovi, M.V.; Mohtat, N.; Scaiano, J.C. *Tet. Letts.*, **1996**, *37*, 4919.

(7) Solomon, D.H.; Rizzardo, E.; Cacioli, P., U.S. Patent 4,581,429, March 27, 1985.

(7) Solomon, D.H.; Rizzardo, E.; Cacioli, P., U.S. Patent 4,581,429, March 27, 1985.

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

(9) Moad, G.; Solomon, D.H. *The Chemistry of Free Radical Polymerization*, Elsevier Science, 167, **1995**.

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

(11) Hawker, C.J. *J. Am. Chem. Soc.* **1994,** *116*, 11314.

(12) Hawker, C.J.; Hedrick, J.L. *Macromolecules*, **1995**, *28*, 2993; Catala, J.M.; Bubel, F.; Hammouch, S.O. *Macromolecules* **1995**, *28*, 8441.

(13) Frank, B.; Gast, A.P.; Russell, T.P.; Brown, H.R.; Hawker, C.J. *Macromolecules* **1996**, *29*, 6531.

(14) Hawker, C.J. *Angew Chem. Int. Ed. Engl.*, **1995**, *34*, 1456; Leduc, M.R.; Hawker, C.J.; Dao, J.; Fréchet, J.M.J. *J. Am. Chem. Soc.* **1996,** *118*, 11111; Matyjaszewski, K.; Shigemoto, T.; Fréchet, J.M.J.; Leduc, M.R. *Macromolecules*, **1996**, *29*, 4167.

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

(16) Fukuda, T.; Terauchi, T.; Goto, A.; Ysujii, Y.; Miyamoto, T. *Macromolecules*, **29**, 3050, 1996; Li, I.Q.; Howell, B.A.; Dineen, M.T.; Priddy, D.B. *Polym. Prep.*, **38**, 762, 1997.

(17) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. J. *Science* **1997**, 275, 1458; Kulasekere, R.; Kaiser, H.; Ankner, J. F.; Russell, T. P.; Brown, H. R.; Hawker, C. J.; Mayes, A. M. *Macromolecules* **1996**, *29*, 5493; Kulasekere, R.; Kaiser, H.; Ankner, J. F.; Russell, T. P.; Brown, H. R.; Hawker, C. J.; Mayes, A. M. *Physica B* **1996**, *221*, 306.

(18) Connally, T. J.; Scaiano, J. C. *Tet. Letts.*, **1997**, *38*, 1133; Mardare, D.; Matyjaszewski, K. *Polym. Prep.*, **1994**, *35(1)*, 778; Gaynor S.; Greszta, D.; Mardare, D.; Teodorescu, M.; Matyjaszewski, K *J. Macro. Sci., Pure Appl. Chem.*, **1994**, *A31*, 1561.

(19) Matyjaszewski, K.; Gaynor S.; Greszta, D.; Mardare, D.; Shigemoto, T. *Macromol. Symp.*, **1995**, *98*, 73; Georges, M.K., Kee R. A., Veregin, R.P.N.; Hamer, G.K., Kazmaier, P.M. *J. Phys. Org. Chem.* **1995**, *8*, 301; Devonport, W.; Michalak, L.; Malmstrom, E.; Mate, M.; Kurdi, B.; Hawker, C.J.; Sinta, R.; Barclay, G.G. *Macromolecules*, **30**, 1929, 1997.

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

(21) Hawker, C.J.; Mecerreyes, D.; Elce, E.; Dao, J.; Hedrick, J.L.; Barakat, I.; Dubois, P.; Jerome, R.; Volksen, W. *Macromol. Chem. Phys.*, **1997**, *198*, 155; Hawker, C.J.; Fréchet, J.M.J.; Grubbs, R.B.; Dao J. *J. Am. Chem. Soc.* **1995,** *117*, 10763.

(22) Desai, A.; Malmstrom, E.; Devonport, W.; Mate, M.; Hawker, C.J. *Polym. Mat. Sci. Eng.*, **76**, 152, 1997.

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

(24) Theoretical molecular weights are calculated by assuming that one alkoxyamine initiating group leads to a single polymer chain, the degree of polymerization of which is governed by the ratio of styrene to initiator. The polymerizations are run to 90% conversion.

(*Received* 25 *April* 1997; *revised* 24 *June* 1997; *accepted* 1 *August* 1997)