# First report of nitroxide mediated polymerization in an ionic liquid

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## Summary

Nitroxide-mediated free radical polymerizations (NMP) of styrene (St) and methyl methacrylate (MMA) were carried out in a room temperature ionic liquid: 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]$PF_6$). A bimolecular initiation system, benzoyl peroxide (BPO) along with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and a unimolecular initiation system, 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane ($\alpha$-hydrido alkoxyamine, TMPPAH)) were employed. Contrary to the results obtained for atom transfer radical polymerization (ATRP) and reversible addition-fragmentation radical transfer polymerization (RAFT) in the same ionic liquid, the molecular weights obtained in NMP were lower with broader polydispersities for a wide range of initiator ratios and temperatures due to the non-living nature of polymerization.

## Introduction

The study of radical polymerization has witnessed a renaissance because of the discovery of controlled/"living" polymerization processes in the past decade (Scheme 1). Many major advances have occurred in nitroxide-mediated (NMP) polymerization [1-3], transition metal mediated polymerization [4,5] and reversible addition-fragmentation chain transfer (RAFT) polymerization [6,7]. NMP is the oldest of these new methods and it has a similar mechanism to the use of iniferters (*ini*tiator-trans*fer* agent-*ter*minator), which is arguably the first attempt to develop a true living free radical polymerization reported about 20 years ago [8]. The principle of NMP is summarized in Scheme 1. The key to the success of this approach is that the concentration of the reactive chain ends is reduced to an extremely low level by reversible termination of the growing polymeric chain. The low overall concentration of the propagating chain end will minimize undesired side reactions, such as irreversible termination reactions through combination or disproportionation. Thus control over the entire polymerization process is achieved since all the chains should be initiated only from the desired initiating species and propagation should proceed in

a controlled fashion. Georges and coworkers obtained low polydispersity polystyrene by bulk polymerization of styrene in the presence of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and benzoyl peroxide (BPO) at 130°C [9]. While successful in yielding low polydispersity products of predictable molecular weight, the poorly defined nature and unknown concentration of the initiating species in t his process resulted in less tan ideal control of the polymerizations. Thus Hawker and coworkers developed universal initiators for nitroxide-mediated living free radical polymerizations [10]. Some of these initiators can excercise better control over the polymerization of various monomers.
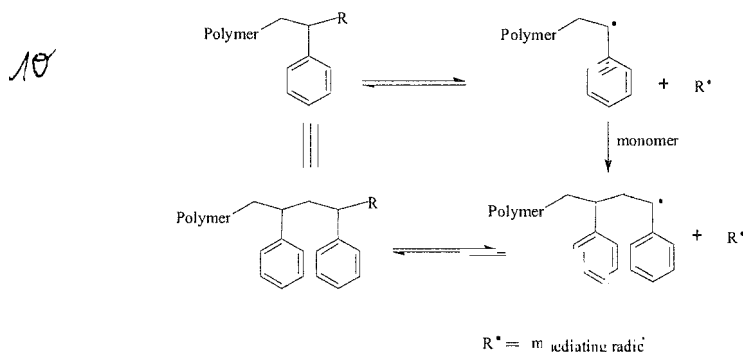


**Scheme 1.** Controlled polymerization of styrene with mediating radical

Over the past several years, room temperature ionic liquids (RTILs) have stimulated much interest among the chemistry community for their potential as green "designer solvents" and several excellent reviews are available recently [11-13]. RTILs not only show potential for use in separations and as electrolytes, but they are also promising solvents for chemical syntheses and particularly for catalysis. The use of RTILs as a polymerization medium has also recently attracted considerable interest. Conventional or controlled radical polymerization of styrene, methyl methacrylate (MMA), and acrylates has been carried out in various RTILs [14-19]. Haddleton *et al.* [14] reported the first example of transition-metal mediated living-radical polymerization of MMA in an RTIL. Rate of polymerization was enhanced compared to other polar/coordinating solvents. The removal of the residual catalysts was facilitated by the unique properties of the ionic liquid. The reversible addition--fragmentation chain transfer polymerization of acrylates, methacrylates, and styrene has also been reported in room temperature ionic liquids [19]. Acrylate and methacrylate polymerizations show a living character and lead to well-defined polymers, with narrow polydispersity (<1.3); in the case of styrene, the insolubility of the polymer in the ionic liquids stops the polymerization at an early stage.
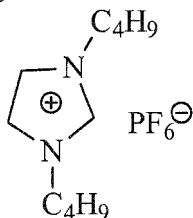


**Scheme 2.** Structure of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]$PF_6$)

In this work, the nitroxide TEMPO and a universal alkoxyamine initiator developed in Hawker's group were used to mediate free radical polymerizations of styrene and MMA which were carried out in 1-butyl-3-methylimidazolium hexafluorophosphophate ([bmim]PF$_6$, Scheme 2) under various conditions. Since we have previously noted enhanced rates of conventional radical polymerization in RTILs [15], it was our hope that the use of RTILs in NMP might enhance polymerization rates and allow the use of reduced polymerization temperatures (slow polymerizations and high temperatures are two of the factors limiting practical implementation of NMPs).

**Experimental**

*Materials*

Styrene (Aldrich, 99%) and MMA (Aldrich, 99%) were distilled to remove inhibitors and stored in calibrated ampoules. [Bmim]PF$_6$ (provided by Sachem Inc.) was washed with pure water five times and vacuum-dried ($10^{-6}$ torr) for over 24 hours. Benzene (Fisher, ≥ 99%) and dichlorobenzene (DCB, Fisher, ≥ 99%) were distilled from freshly crushed calcium hydride. BPO (Aldrich, 97%) was recrystallized from chloroform or acetone. TEMPO was purchased from Aldrich and used as received. 2,2,5-Trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane was generously provided to us by Dr. Craig Hawker of IBM Almaden Research Laboratory and was used as received.

*Instruments*

Size exclusion chromatography (SEC) was used to measure molecular weights and molecular weight distributions, $M_w/M_n$, of organo-soluble polymer samples with respect to polystyrene standards (Pressure Chemical Co.). The SEC experiments were carried out at 30 °C using a Polymer Laboratories Knauer 501 HPLC pump and Knauer 2301 RI detector. Two PSS (Polymer Standard Service) columns were used (one 100Å and one linear). The flow rate of the mobile phase (tetrahydrofuran) was 1 mL/min.

*Polymerization*

All polymerizations were done under high vacuum to ensure that the systems were oxygen free. After charging desired amounts of initiator (BPO), TEMPO and solvent ([bmim]PF$_6$) into a round bottom flask with a constriction, the system was degassed for 2 hr and a pre-determined quantity of monomer (styrene) was distilled into the reactor. The flask was removed from the vacuum line by heat-sealing at a constriction and kept in a pre-heated water bath. The polymerization was allowed to continue for the desired time and stopped by precipitation into methanol. In the case of copolymerization, the first block was made by the same procedure described above, but the polymerization time was shorter (< 4 hr). After taking about 5 mL of solution for sampling, the unreacted monomer was pumped away. Then a pre-determined quantity of the second monomer (such as MMA) was distilled in the system, and the reaction continued for the desired time. The MMA and styrene polymers were isolated

gravimetrically, methanol was used to remove residual RTIL, and the pure polymers were dried under vacuum.

## Results and Discussion

Control experiments on nitroxide-mediated radical polymerization of styrene via TEMPO-BPO bimolecular initiation system were first tried to make sure proper synthesis technique was employed throughout this work. The characterization data are summarized in Table 1, where it can be seen that our results are very close to the literature values generated under the same conditions [20].

**Table 1.** Molecular weight and polydispersity data for the nitroxide-mediated radical polymerization of styrene as a function of the TEMPO:BPO ratio in this work and in the literature.[a]

| This work | | | | In literature | | | |
|---|---|---|---|---|---|---|---|
| Entry | TEMPO:BPO | $M_n$ (g mol$^{-1}$)[b] | PDI[b] | Entry | TEMPO:BPO | $M_n$ (g mol$^{-1}$)[b] | PDI[b] |
| 1 | 1.12:1 | 13,800 | 1.26 | 1 | 1.10:1 | 15,200 | 1.29 |
| 2 | 1.00:1 | 17,500 | 1.23 | 2 | 1.00:1 | 16,500 | 1.35 |
| 3 | 0.81:1 | 19,300 | 1.29 | 3 | 0.81:1 | 19,200 | 1.38 |
| 4 | 0.70:1 | 17,200 | 1.48 | 4 | 0.70:1 | 20,100 | 1.45 |
| 5 | 0.50:1 | 21,700 | 1.58 | 5 | 0.48:1 | 21,000 | 1.60 |

[a] All reactions were carried out in bulk at 135°C for 5 hours with varied TEMPO:BPO ratios, BPO:styrene=10mg:1g; [b] From SEC-RI
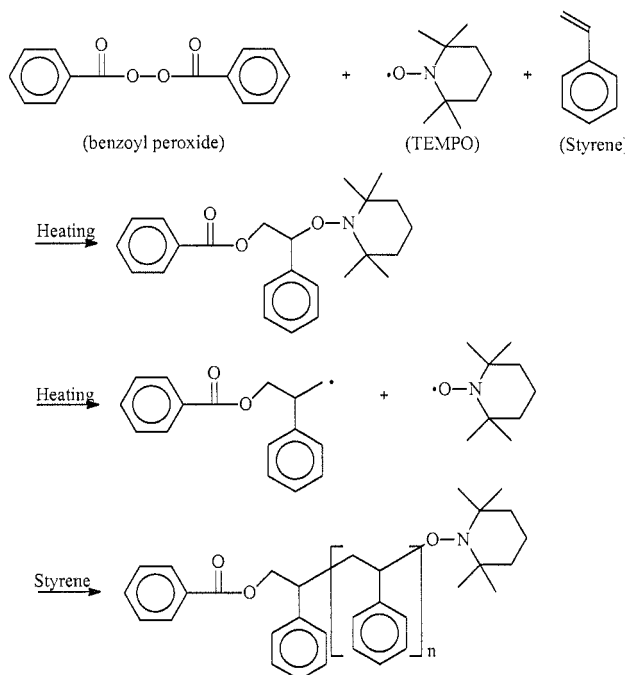


**Scheme 3.** Bi-molecular initiation system (BPO+TEMPO) for nitroxide-mediated radical polymerization

The polymerization of styrene, mediated by TEMPO was carried out in bulk, [bmim]PF$_6$ and dichlorobenzene and the results are listed in Table 2 (Scheme 3).

**Table 2.** Polymerization characteristics (conversion, molecular weight and polydispersity) for the polymerization of styrene mediated by TEMPO in bulk and in various solvents [a]

| Entry | Monomer | Solvent | T(°C)/ t (hrs) | Conv. (%)[b] | M$_n$ (g mol$^{-1}$)[a] | PDI[c] |
|-------|---------|---------|----------------|--------------|-------------------------|--------|
| 1 | styrene | [bmim]PF$_6$ | 115/68 | | No polymer | |
| 2 | styrene | [bmim]PF$_6$ | 125/40 | 1.9 | 1,640 | 1.23 |
| 3 | styrene | DCB | 130/44 | 16.4 | 3,250 | 1.25 |
| 4 | styrene | [bmim]PF$_6$ | 130/63 | 21.0 | 4,260 | 1.60 |
| 5 | styrene | [bmim]PF$_6$ | 135/25 | 16.9 | 1,070 | 2.69 |
| 6[d] | styrene | bulk | 123/69 | 90.0 | 7,800 | 1.27 |

[a] Solvent: 20 ml; monomer: 0.02mol; BPO: 0.165 mmol; [b] Measured gravimetrically; [c] From SEC-RI; [d] Data from reference 1

**Table 3.** Polymerization characteristics (conversion, molecular weight and polydispersity) for the polymerization of styrene by BPO/TEMPO in [bmim]PF$_6$ using various additives [a]

| Entry | Additive [b] | [Additive]/ [monomer] | Conv. (%)[c] | M$_n$ (g mol$^{-1}$)[d] | PDI[d] |
|-------|--------------|------------------------|--------------|-------------------------|--------|
| 1 | AA | 1.0:1.0 | 15.9 | 1,200 | 1.56 |
| 2 | AA | 2.6:1.0 | 23.6 | 1,100 | 5.07 |
| 3 | AA | 3.2:1.0 | 41.8 | 1,200 | 2.13 |
| 4 | AA | 10.8:1.0 | 16.9 | 18,400 | 2.66 |
| 5 | CSA | 1.0:1.0 | 24.1 | 700 | 2.71 |
| 6 | CSA | 2.1:1.0 | 18.7 | 1,250 | 1.61 |

[a] Solvent: 10 ml; monomer: 0.01mol; BPO: 0.0412 mmol; BPO/TEMPO=1.00/1.34; 135C/24hrs; [b] AA: Acetic Anhydride; CSA: 10-camphorsulfonic acid; [c] Measured gravimetrically; [d] From SEC-RI

From Table 1 we can see that under all reaction conditions, the polymerization of styrene using BPO/TEMPO in [bmim]PF$_6$ produced some polystyrene. However, the conversion and molecular weight of the resulting polymers were much lower than those obtained from the bulk under similar reaction conditions. Polydispersities were generally much higher than expected. One possible explanation is that [bmim]PF$_6$ interfered with the TEMPO mediated radical equilibrium. The polymerization results for styrene in DCB were not as good as those in bulk and the reason is probably that DCB can act as a radical chain transfer agent. Georges *et al.* [21] also reported that certain additives can accelerate the BPO/TEMPO initiating reactions of styrene, and we thus employed some of these agents. However, the effect in [bmim]PF$_6$ was very limited as seen in Table 3.

End-group analysis revealed similar structures for polymers made by the different methods but with the ratio of capping agent moiety (TEMPO) to initiator moiety (benzoyl) higher in [bmim]PF$_6$ than that in bulk (Figure 1). This was expected since there were more chains initiated thermally in this ionic liquids. There were no new peaks in $^{31}$P NMR reflecting degradation of [bmim]PF$_6$ when BPO, TEMPO and [bmim]PF$_6$ were heated together for long time at 135 °C. At 65 °C, TEMPO and [bmim]PF$_6$ can coexist in the reaction system but there was some slow degradation of TEMPO in this ionic liquid [22]. The color of the reaction system turned darker after heating, this was also an indication of degradation of TEMPO. $^{31}$P NMR technique

observed no residual anion ($PF_6^-$) in the polymer made in IL.

**Table 4.** Polymerization characteristics (conversion, molecular weight and polydispersity) for the polymerization of styrene and MMA by TMPPAH in [bmim]$PF_6$[a]

| Entry | Monomer | T(°C)/ t (hrs) | Conv. (%)[e] | $M_n$ (g mol$^{-1}$)[d] | PDI[d] |
|-------|---------|---------|---------|---------|--------|
| 1 | Styrene | 125/4 | 42.1 | 2,500 | 1.75 |
| 2 | Styrene | 130/14 | 27.8 | 2,100 | 1.47 |
| 3 | Styrene | 85/12 | 2.6 | 2,400 | 1.49 |
| 4 | MMA | 125/4 | 41.2 | 28,800 | 3.11 |

[a] Solvent: 10 ml; monomer: 0.06 mol; TMPPAH: 0.3 mmol; BPO/TEMPO=1.00/1.34; 135C/24hrs; [b]AA: Acetic Anhydride; CSA: 10-camphorsulfonic acid; [c] Measured gravimetrically; [d] From SEC-RI
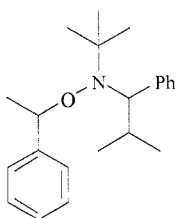
**Scheme 4.** Structure of 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TMPPAH)
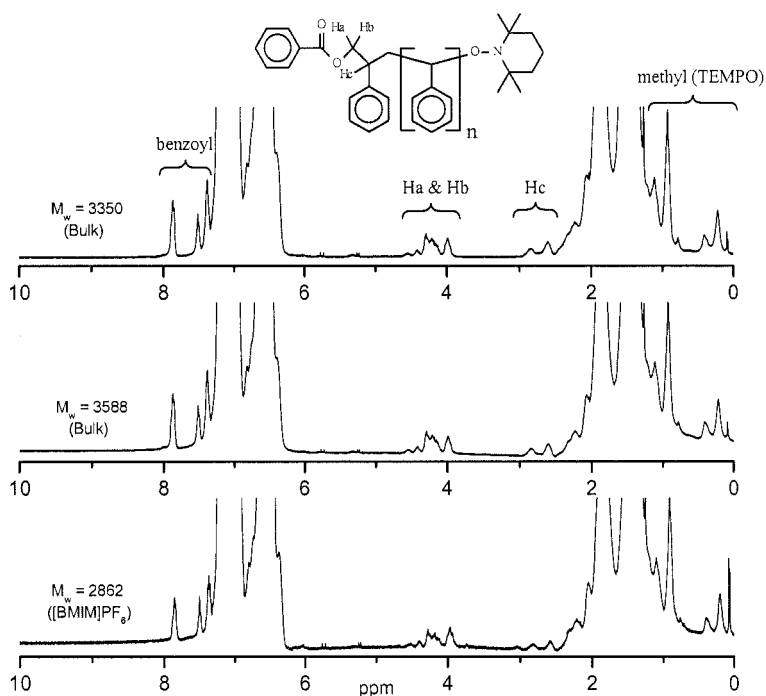


**Figure 1.** $^1$H NMR end-group analysis of NMP polymerized styrene in [BMIM]$PF_6$ and in bulk.

Even though BPO/TEMPO displays many of the fundamental aspects of living character in the polymerization of styrene, these are not true living systems. While the concentration and reactivity of radicals at the propagating chain end have been significantly reduced, termination is still not negligible. Hawker and coworkers developed various unimolecular initiators, which can better control polymerization [10]. We thus used 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TMPPAH, Scheme 4) as a universal initiator and the results are listed in Table 4. Our results were not as good as those obtained by Hawker *et al.* in bulk [10] but were better than those from the BPO/TEMPO system in that higher yields of polymer were obtained. It is possible that the difusion of the bulky mediating radical in the ionic liquids is not as same as in common organic solvents or in bulk. When the labile C-O bond is broken at elevated temperature, the ability of the mediating radical to diffuse away from propagating chain end could be hindered by the RTIL, causing recombination before another monomer can add to the chain end. Kinetically, free diffusion to or out of reaction cage should be a facile process [23]. This may also contribute to the observed difference.

With both initiation systems, attempts to make block copolymer by one-pot polymerization through sequential addition of monomers failed and only homopolymer was formed, reflecting the presence of dead chain ends after the formation of the first block. Note that residual first monomer was removed by vacuum prior to adding the second monomer; this strategy was previously used successfully to prepare block copolymers in ca. 50% yields by sequential polymerization of styrene and MMA in [bmim]$PF_6$ using conventional benzoyl peroxide initiation [24].

**Conclusions**

The polymerization of styrene and MMA using BPO/TEMPO and 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TMPPAH) as initiators in various solvents was studied. The overall results are not as good as those obtained in bulk with regards to rate of polymerization, molecular weight control, and polydispersity. Thus, our preliminary results fail to indicate kinetic or mechanistic advantages to conducting nitroxide-mediated polymerizations in RTILs. These results are surprising since prior work on conventional free radical polymerization in RTILs indicated large increases in rate of polymerization and molecular weight [15,25], so we had anticipated that RTILs could serve as "accelerants or promoters" in these polymerizations. The possible causes for the observed non-living "nitroxide-mediated" polymerization nature were the slow degradation of TEMPO in [bmim]$PF_6$ at high temperature and difficulty in diffussion of the mediating radicals away from the chain ends. Propagating chains were either initiated by the free radicals generated from BPO or thermally initiated, and the concentration of reactivated chain ends was very low ($\approx$0). In the case of styrene polymerization, the produced polymers were not soluble in [bmim]$PF_6$. Thus, the heterogeneous reaction system, difficulty in diffusion and slow degradation of TEMPO in [bmim]$PF_6$ all contributed to slow propagation rates and broad polydispersity of the synthesized polymers. Attempts to produce block copolymers by sequential addition of monomers failed under conditions used successfully for block copolymer formation in a RTIL using conventional free radical polymerization [24]. This also suggests that nitroxide mediated polymerization in the presence of [bmim]$PF_6$ does not proceed by a living polymerization mechanism.

# References

1.  Georges MK, Veregin RPN, Kazmaier PM, Hamer GK (1993) Macromolecules 26: 2987
2.  Hawker CJ, Bosman AW, Harth E (2001) Chem Rev 101: 3661
3.  Hawker CJ (1997) Acc Chem Res 30: 373
4.  (a) Wang JS, Matyjaszewski K (1995) J Am Chem Soc 117: 5614 (b) Xia J, Matyjaszewski K (2001) Chem Rev 101: 2921
5.  (a) Kato M, Kamigaito M, Sawamoto M (1995) Macromolecules 28: 1721 (b) Kamigaito M, Ando T, Sawamoto M (2001) Chem Rev 101: 3689
6.  Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, Mayadunne TA, Meijs GF, Moad CL, Moad G, Rizzardo E, Thang SH (1998) Macromolecules 31: 5559
7.  Vana P, Quinn JF, Davis TP, Barner-Konwollik C (2002) Australia J Chem 55: 425
8.  Otsu T, Yoshida M (1982) Makromol Chem Rapid Commun 3: 132
9.  Georges MK, Veregin RPN, Kazmaier PM, Hamer GK (1993) Macromolecules 26:2987
10. (a) Hawker CJ (1994) J. Am. Chem. Soc. 116:11185 (b) Benoit D, Chaplinski V, Braslau R, Hawker CJ (1999) J Am Chem Soc 121: 3904
11. Welton T (1999) Chem Rev 99:2071
12. Holbrey JD, Seddon KR (1999) Clean Products and Processes 1: 223
13. Wasserscheid P, Keim W (2000) Angew Chem, Int Ed 39:3772
14. Carmichael J, Haddleton DM, Bon SAF, Seddon KR (2000) Chem Commun 1237
15. Hong K, Zhang H, Mays JW, Visser A, Brazel C, Holbrey JD, Reichert WM, Rogers RD (2002) Chem Commun 1368
16. Sarbu T, Matyjaszewski K (2001) Macromol Chem Phys 202: 3379
17. Noda A, Watanabe M (2000) Electrochim Acta. 45: 1265
18. Zhao YL, Zhang JM, Jiang J, Chen CF, and Xi F (2002) J Polym Sci Part A Polym Chem 40: 3360
19. Perrier S, Davis TP, Carmichael AJ, Haddleton DM (2002) Chem Commun 2226
20. MacLeod PJ, Veregin RPN, Odell PG, Georges MK (1997) Macromolecules 30: 2207
21. Odell PG, Veregin RPN, Michalak LM, Brousmiche D, Georges MK (1995) Macromolecules 28: 8453
22. Ansari IA, Gree R (2002) Org. Lett. 4(9): 1507
23. Hawker CJ, Barclay GG, Dao JJ (1996) J Am Chem Soc 118: 11467
24. Zhang H, Hong K, Mays JW (2002) Macromolecules 35: 5738
25. (a) Harrison S, MacKenzie SR, Haddleton DM (2002) Chem Commun 2850 (b) Harrison S, MacKenzie SR, Haddleton DM (2002) Polym Preprints 43(2): 883