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LETTERS

The thermolysis and photochemistry of hybrid initiators for 'living' free radical polymerization

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Abstract

A new initiator potentially capable of both thermal and photochemical initiation of 'living' free radical polymerization (LFRP) has been prepared. Both of these reaction pathways have been examined and identified in terms of their products. The thermal reaction is highly dependent on the reaction conditions and displays competitive radical and ionic reactivity. In the presence of a proton source, the ionic pathway is highly favored. Photochemical activation leads predominantly to Norrish type I cleavage where the photoproducts further react by α-cleavage resulting in the formation of benzaldehyde.

Since the seminal work by Georges[1] reporting the preparation of low polydispersity (PD) polystyrene using radical conditions and the pioneering work by Moad and Rizzardo,[2,3] there has been considerable growth and discovery in this field. Several groups have reported on the successful application of unimolecular initiators such as the benzyloxystyrene based initiators (**1**) popularized by Hawker,[4] and the benzylic type initiators (**2a**–**b**) reported by us[5–8] and others.[9–11] The incorporation of the nitroxide moiety into the initiator is key (vide infra) to controlling the PD and rendering the polymer capable of living growth. Here we report on the dual radical and ionic pathways available for the thermal decomposition of the new benzoin based initiator **3**. The photochemistry of this initiator is also examined.

The general reaction mechanism of LFRP is outlined in Scheme 1. The key to the process of controlled polymerization is the weak C–O bond between the benzylic carbon and the nitroxide. At slightly elevated temperatures required for polymerization, this bond is labile and reversibly generates the chain carrier. The build up of nitroxide during the reaction makes the back reaction, or generation of the dormant polymer, a more favorable reaction without the use of scavengers to control the nitroxide concentration. Furthermore, the control over the polymerization arises from the fact that the propagating and reversible termination by TEMPO are the only steps available as the cross coupling between two nitroxides is not

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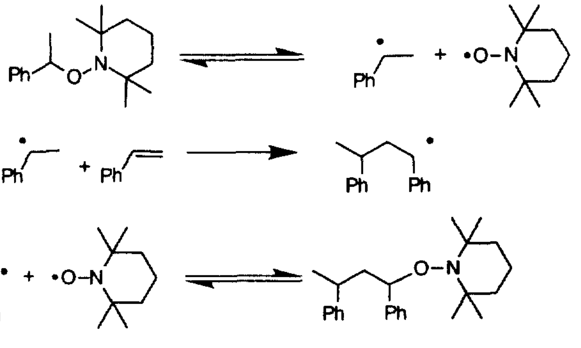
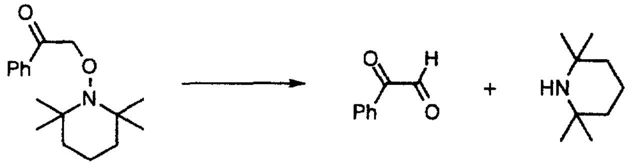
involved.[12] The suppression of fast reactions in the presence of a persistent radical was modeled by Fisher a number of years ago and has recently been experimentally verified.[9,13,14]



Scheme 1. General mechanism of LFRP

The homolytic scission of C–O bonds of *O*-alkyl alkoxyamines as shown in Scheme 1 is not an exclusive reaction. In fact, Barton and Hunter have reported[15] that the thermolysis of compounds containing a nitroxide α to the carbonyl group provides 1,2-dicarbonyl products, as shown in Scheme 2, presumably via an ionic mechanism.

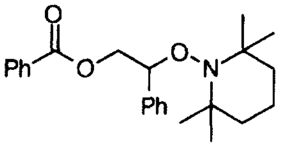


Scheme 2. Thermal decomposition products determined by Barton

In connection with our studies on thermal[6] and photochemical[5,16] initiators, we examined the chemistry of **3**[17] exposed to both these reaction conditions. The benzoin framework of **3** contains an adjacent carbonyl-nitroxide moiety similar to Barton and Hunter's study. In addition, **3** also contains a benzylic-TEMPO arrangement analogous to the initiators in Fig. 1. The benzoin framework of **3** contains the merger of the Barton strategy and the conventional LFRP initiator all in one with both decomposition pathways available. The thermolysis and photolysis of **3** are discussed.

1. Thermal chemistry of 3

According to the reactions shown in Schemes 1 and 2, two reaction mechanisms are available to **3** as previously discussed. Deoxybenzoin (**4**) arises from homolytic cleavage giving a carbon centered



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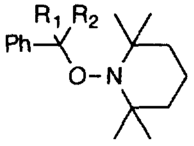
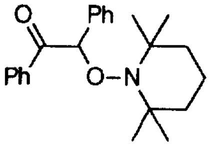


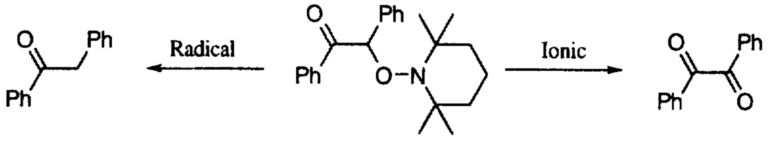
2a : $R_1=R_2=H$
2b : $R_1=CH_3$; $R_2=H$



3

Figure 1.

radical followed by hydrogen abstraction. An ionic pathway results in the rupture of the N–O bond, and ultimately the formation of benzil (**5**) (Scheme 3). Preliminary thermal decomposition studies of **3** were done in a sealed tube in the absence of oxygen or any other reagent. Qualitative product studies showed the formation to be predominately **4** and **5** with minor radical cross coupling. The significant formation of these products shows a competition between radical and ionic pathways. The same experiment was repeated in the presence of camphorsulfonic acid (CSA) and a different ratio of decomposition products was obtained being predominately **5** and only trace amounts of **4**. The substantial change in product distribution is indicative of a major change in reaction path. Therefore, experimental conditions were modified to influence the decomposition route and verify our hypothesis.

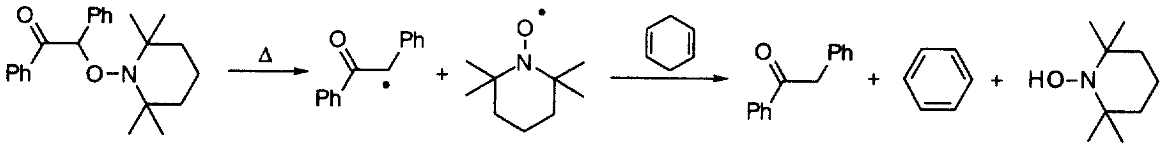


4 **5**

Scheme 3. Thermal decomposition pathways of **3**

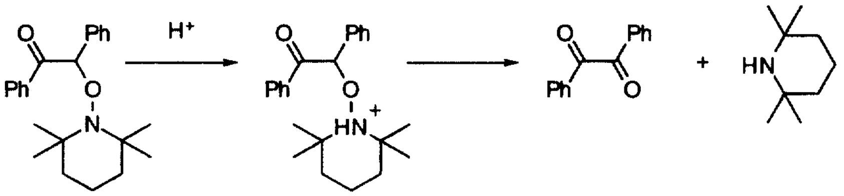
A typical experimental procedure for the thermal investigation consisted of refluxing **3** in decalin (bp 189°C) overnight in the presence of one of the two following reagents: two equivalents of freshly distilled 1,4-cyclohexadiene (CHD) or 10 mole percent amount of *p*-toluene-sulfonic acid (*p*TsOH). These were added prior to refluxing followed by deaeration of the solution with nitrogen for 20 minutes. Refluxing in an inert solvent such as acetonitrile had no effect as its boiling point is most likely too low for the energy required to induce C–O or N–O bond cleavage.[6] An aliquot of the reaction mixture was analyzed by reverse phase analytical HPLC and the products were identified by their retention times and absorption spectra compared to subsequently injected authentic samples. The HPLC response factors of the products were also calibrated against authentic samples.

Refluxing **3** under an inert atmosphere leads to simple homolytic C–O cleavage to give the persistent nitroxide (TEMPO) and carbon centered radicals. The lifetimes of these radicals are sufficiently long and can further undergo hydrogen abstraction as seen in Scheme 4. The hydrogen abstraction reaction from a good hydrogen donor such as CHD[18] leads to deoxybenzoin (**4**) as a major product. In sufficiently high concentrations of CHD, the hydrogen abstraction reaction will be kinetically favored over the back reaction with the nitroxide since both of these are bimolecular reactions;[11,19] in any event, the latter has no chemical consequences as far as products are concerned, and is due to the Fischer–Ingold persistent free radical effect.[9,13] The formation of **4** was observed in a ratio of 2.9:1 over **5** after thermal decomposition of **3** in the presence of CHD. This follows the conventional radical decomposition pathway shown in Scheme 4.



Scheme 4. Thermal induced decomposition of **3** in the presence of CHD

Substituting the organic acid, *p*TsOH, for CHD followed by the same thermal parameters gave an inverted product ratio of 1:3.5 for **4**:**5**. This indicates suppression of the radical route in favor of the ionic pathway according to Scheme 5. We note that in the absence of CHD the radical route may involve extensive radical cross termination to form the starting material. The protonation of the nitroxide nitrogen of **3** is the governing step and subsequently biases the system towards ionic decomposition. Hoffman-type elimination of the amine moiety results in the generation of benzil. The presence of deoxybenzoin suggests that a minor radical mode arising from neutral **3** is still present. This occurs as only a catalytic amount of *p*TsOH was used. Repeating the thermolysis in the presence of one equivalent of *p*TsOH resulted in only a small amount of deoxybenzoin being detected, hence a complete switch to ionic chemistry.

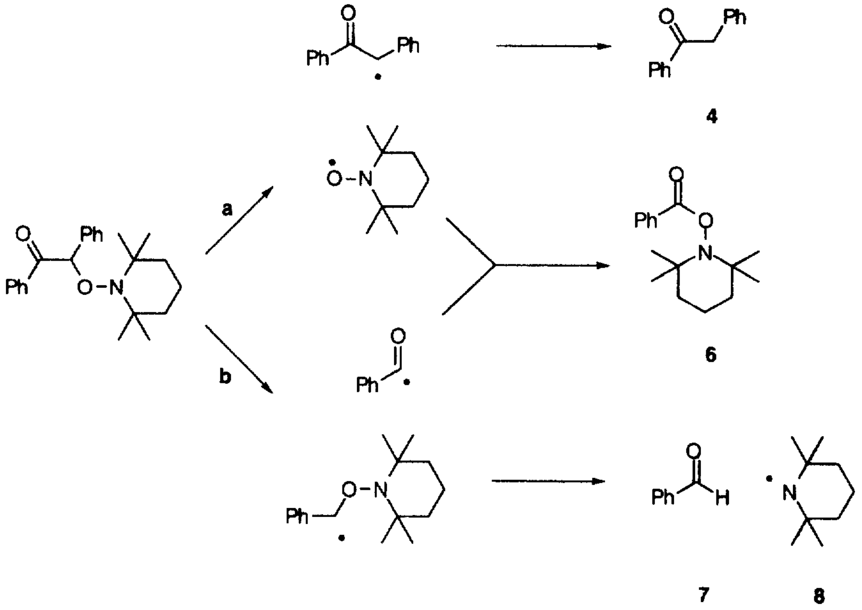


Scheme 5. Ionic pathway for the thermal decomposition of **3**

2. Photochemistry of 3

Due to the competitive thermal reaction pathways and the inability to suppress benzil forming reactions, the use of **3** as an initiator for TEMPO mediated thermal 'living' polymerization is limited. Given our interest in designing photochemical initiators for TEMPO controlled polymerization,[16] we believed that **3** may be a suitable photoinitiator for polymerization.

Irradiation of a solution of **3** in deaerated acetonitrile at 300 nm led to a complex mixture of products and were isolated by column chromatography. These were subsequently identified by NMR and compared to authentic samples. All of the identified products are shown in Scheme 6.



Scheme 6. Product distribution arising from the photodecomposition of **3**

The formation of deoxybenzoin indicates C–O bond cleavage (pathway **a**) does occur, leading to the deoxybenzoin radical, which can abstract hydrogen from the solvent.[20] The former bond cleavage process was confirmed in a crossover experiment in which compound **3** was irradiated in the presence of 4-hydroxy-TEMPO and led to an exchange of the TEMPO moieties. Products **7** and **8** arise via the known Norrish Type I cleavage (pathway **b**),[21] while trapping of the acyl radical by TEMPO generated from the first pathway leads to compound **6**. Once again, a crossover experiment with 4-hydroxy-TEMPO led to trapping of the acyl radical. Fragmentation of the other part of the radical pair from the Type I reaction leads to benzaldehyde, and presumably, the nitrogen centered radical that can further undergo hydrogen abstraction. This pathway is reminiscent of the reaction manifold observed in the reaction of diphenylcarbene and TEMPO.[22] Interestingly, this Norrish Type I cleavage was also observed in the solid state, as noted by the benzaldehyde peak in the NMR spectrum and, more qualitatively, by the smell of benzaldehyde present following irradiation. Unfortunately, the conversions in the solid state were quite low and do not allow for a complete study of the photodecomposition of **3**. This low conversion may be due to quenching of the excited state by the generated TEMPO or nitrogen centered piperidine radicals as both are known to quench ketone and aromatic triplets.[23]

3. Conclusion

Thermolysis of an *O*-alkylated nitroxide with moieties that favor both radical and ionic cleavage leads to products resulting from both pathways. Although the radical pathway is favored under standard conditions, addition of a proton source results in a switch to the ionic pathway. Photolysis results in products that appear to be formed via two competitive radical pathways. The product resulting from Norrish Type I cleavage fragment further reacts and leads to benzaldehyde and a piperidine radical similar to the reaction of carbenes with a nitroxide.

Acknowledgements

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17. Typical synthesis involves dissolving deoxybenzoin (1 equiv.) with Tempo oxonium salt (1.1 equiv.) in acetonitrile with a catalytic amount of *p*TsOH and stirring at room temperature until complete by TLC. Pour solution onto water and extract with dichloromethane followed by column chromatography (20:1, ethylacetate:hexanes) to give a white solid in 85% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.78–1.55 (18H, m); 5.97 (1H, s); 7.21–7.38 (3H, m); 7.42–7.49 (5H, m); 8.04 (2H, d). ^{13}C (300 MHz, $CDCl_3$) δ 16.9; 20.2; 20.3; 33.3; 33.5; 40.2; 59.8; 59.9; 93.1; 127.2; 127.5; 128.3; 129.4; 132.8; 135.2; 137.8; 198.3. EI (m/z, %) 351 (0.9), 285 (8.3), 268 (15.9), 195 (16.8), 167 (39.7), 156 (92.9), 141 (37.5), 105 (100), 91 (39.4), 77 (93.2), 56 (87.5), 41 (71.2).

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